Capturing structure-property relationships of complex gels with physical and chemical crosslinking

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Capturing structure-property relationships of complex gels with physical and chemical crosslinking

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Gels are used in many applications ranging from bioengineering and pharmaceuticals to food technology and soft-robotics because of their tunable physical and mechanical properties. In many of these applications, the materials need to sustain large deformation. The microstructure of gels changes significantly at large strain values, causing a deviation in the stress responses from that at low strain. The desired mechanical responses of gels can be obtained by tuning their microstructure, therefore, the structure-property relationship for gels is required to be understood for their practical applications.

This dissertation discusses two types of gels, one consists of chemical crosslinking and hydrophobic associations, and the other gel only consists of physical crosslinking. The microstructure of these two gel systems is investigated and related to their mechanical responses. The gel system with chemical and physical crosslinking mimics properties of biomaterials like resilin. Resilin is a protein-elastomer that enables biological species for power amplified activities by taking benefits of specific responses of hydrophilic and hydrophobic segments. Inspired by the microstructure
and mechanical properties of resilin, a stretchable and resilient hydrogel was synthesized through a simple free radical polymerization technique. These gels retract from the stretched state to the original state with high speed over a short time, such behavior has not been frequently reported for synthetic hydrogels. This gel is also capable of performing a power-amplified activity like catapulting an object. In addition to retraction experiments, the mechanical properties of this gel were investigated in tensile and cyclic loading to determine their resilience. The hydrophobic polymer concentration affects the swelling behavior and mechanical responses such as stretchability and resilience.

The second gel system considered here is a physically assembled ABA triblock copolymer dissolved in a B-selective solvent. Here, two different triblock copolymers with different concentrations were utilized. The real-time microstructural change was captured using a RheoSAXS setup with a high flux X-ray beam. The real-time microstructure of these gels subjected to temperature, varying oscillatory strain amplitude, and during relaxation after step strain was captured. This dissertation advances the understanding of the structure-property relationship of microstructurally complex gels towards their potential practical applications.

Key words: chemical gels, physical gels, stretchability, resilience, scattering, structure-property relationship
DEDICATION

I dedicate this dissertation to my parents, who give me love, tenderness, caring, happiness, and support every second and the example to be courageous, passionate, and hardworking to reach the best. To my brothers, who teach me how to fight battles, from computer games to graphic design and mortal virus. To my sisters, who gave me the warmth of a mom when I was far from home and gave me the happiness of my hermosos, who teach me how to love and enjoy life. To my cousins, who made me feel always at home, even being kilometers away from home. To my love, because this would not be possible without him, all the love, patience, and stories kept me walking, and all the support and knowledge cleared my path.
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CHAPTER I
INTRODUCTION

Gels have gained significant research interest due to their tunable mechanical responses that can be obtained by tweaking their complex microstructure formed by chemical and physical crosslinking. A fundamental understanding linking the microstructure of gels and their physical properties is necessary for developing gels aimed towards practical applications. This dissertation investigates two types of gels, one with chemical and physical crosslinking, and another gel with only physical crosslinking. For the first gel, the study is focused on understanding and demonstrating physical properties like elastic modulus, stretchability, resilience, and retraction utilizing a variety of custom-built instruments and protocols. These properties were also related to the microstructure of gels. For the second gel, the study discusses the change in the transient micellar microstructure while the gel was subjected to thermal and mechanical loads.

1.1 Gels

Gels are defined as crosslinked polymeric networks swollen in a solvent [3, 38]. This solvent remains trapped within the gel network due to a good interaction with at least one component of the polymer network. Gels can be classified into many types based on the solvent, network complexity, and crosslinks. For example, based on the type of solvents such as water or an organic solvent, the gel can be classified into hydrogels or organogels. Similarly, based on the number of networks
present in the system, they can be classified as single network or double network gels. In this dissertation, the gels have been categorized based on the type of crosslinks forming the network as chemically crosslinked gels and physically crosslinked gels.

Chemically crosslinked gels or chemical gels are those in which the crosslinks are formed by covalent bonds [100, 24, 94, 13, 65]. The physically crosslinked gels or physical gels are those in which the polymer chains are connected by physical interactions, such as Van der Waals interactions, hydrogen bonds, or ionic interactions [100, 94, 65]. The low modulus, high stretchability, stimuli responses, tunable mechanical properties, and ease to synthesize make the gels attractive for many applications like in biomedical fields for bandages, contact lens, and prosthetics, and consumer products like gelatin deserts and shoe soles [100, 94, 22, 128, 69, 127].

1.1.1 Chemically Crosslinked Gels

In chemically crosslinked gels, the polymer chains are connected by covalent bonds. These gels are generally synthesized by a crosslinking of chains during polymerization or after polymerization. Thermal and free-radical polymerization are typical examples of crosslinking during polymerization while crosslinking after polymerization includes methods like photo and radiation crosslinking [38, 59]. Free-radical polymerization is used to synthesize single-component hydrogels like poly(acrylamide) and multicomponent hybrid hydrogels such as poly(ethylene glycol)dimethacrylate/gelatin methacrylate [24, 13, 62, 59, 65].

Most of these gels are synthesized in an aqueous solution using a crosslinker and are referred to as hydrogels. For example, polyacrylamide hydrogels are prepared by using standard free-radical polymerization with bisacrylamide as crosslinker. Another example of the free-radical
Chemically crosslinked gel indicating polymer chains, crosslinks, and mesh size length ($\xi$).

Polymerized gels is gelatin hydrogel crosslinked with bisvinylesulfonemethyle [48]. Here, $\text{-$NH}_2$ groups present in the gelatin polymer are utilized to crosslink with terminal $C = C$ groups in bisvinylesulfonemethyle to form $C - N$ links [48].

The gelation of chemical gels proceeds with the reaction and is often recognized by a plateau in their storage modulus in time oscillatory shear experiments, signifying the completion of the reaction [13]. The mesh size ($\xi$) formed by the polymers and crosslinkers (figure 1.1) is difficult to control due to the free-radical polymerization, resulting in a variation of the polymer mesh size over a range [62]. An inhomogeneous mesh size also causes a variation in the mechanical properties leading to moderate values of maximum stretchability, modulus, and fracture energy of the gel.

Chemical gels generally display low stretchability, high modulus, and high fracture energy.

The mechanical properties of chemical gels are often tuned by changing the monomer to crosslinker ratio, solvent, and composition of the polymers for the case where more than one
polymers forming the network. These hydrogels have been used in biomedical applications, however, due to the toxicity of some catalysts and the use of different components for the initiation and propagation of the reactions, most of these gels like poly(ethylene glycol acrylate) [18] require further purifications, such as chromatography, precipitation, or dialysis [65].

1.1.2 Physically Crosslinked Gels

In physically crosslinked gels, the polymer chains are crosslinked by solvophobic interactions, Van der Waals forces, hydrogen bonds, or electrostatic forces like ionic interactions [100, 94, 69, 37, 126, 149, 148]. In these types of gels, the parameters such as temperature, nature of the solvent, or pH determine the mechanical properties and microstructure.

This dissertation only focuses on physical gels formed by solvophobic interactions in which the gelation is triggered by the strong temperature-dependent solubility [126, 66, 106, 11, 149, 93, 82]. For the case of water as a solvent, these interactions are referred to as hydrophobic interactions. These gels consist of an ABA type of copolymer dissolved in either A or B block-selective solvent. The A- and B-blocks are generally incompatible to each other at room temperature and are connected through anionic polymerization.

If the solvent is A-blocks selective, a few of the B-blocks assemble together forming flower-like independent micelles. Pluronic gels are the most popular example of this kind of morphology. The polymer in these gels consist of poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) [PEO-PPO-PEO] dissolved in water [2]. The microstructure of these gels is called “core-corona" where the core is a PPO aggregate, and the solvated PEO-blocks form the corona. These micelles are connected through the inter-penetration of PEO chains among the micelles, helping to immobilize
Physically crosslinked gel in which the midblocks form bridges and the endblocks form aggregates.

the solvent [74]. For the gels where the solvent is B-blocks selective, the aggregation of the A-blocks is likely to occur (see figure 1.2). In this case, the A-blocks are generally assembled in aggregates, and the B-blocks are connecting the micelles [126, 66, 31, 32, 108, 11, 149, 148, 93, 82, 141].

ABA gels in B-selective solvents are attractive to many applications because of their tunable mechanical properties. By changing the A- or B-block lengths, solvent, temperature, concentration, and cooling rate, the gel microstructure, gelation temperature [81, 106, 148], modulus [66, 86, 99], relaxation time [30, 81, 149], maximum stretchability [33, 46], strain-stiffening [33, 46], creep failure [82, 83], and fracture energy [82, 83, 81, 108] can be tuned. Also, the addition of nanoparticles like graphene or homopolymer changes the mechanical responses significantly [149].
In addition, these gels are also used as a model to understand the effect of gel microstructure on their gel mechanical responses.

ABA gels in B-selective solvents are widely studied in the literature using various combinations of polymers and solvents. For example, poly(styrene)-poly(isoprene)-poly(styrene) [PS-PI-PS] polymer forms gels various PI-selective solvents like mineral oil, tetradecane, paraffinic oil, and squalane [130, 97, 126, 66, 95, 82, 83, 81]. In those gel systems, the substitution of PI-blocks by poly(ethylene/butylene) [PEB] or poly(ethylene/propylene) [PEP] blocks also form gels, however, PEP and PEB have better solubility than PI due to its hydrogenated state. Similarly, poly(methylmethacrylate)-poly(n-butylacrylate)-poly(methylmethacrylate) [PMMA-PnBA-PMMA] forms gel2 in 2-ethyl-1-hexanol or n-butanol (also called acrylic gels). Here PnBA blocks can also be substituted by poly(butadiene) (BD) or poly(tert-butyl acrylate) [144, 56].

Although these two acrylic gel systems are composed of different polymers, they display some similarities. For example, from low to relatively high concentrations, both systems display micellar microstructure that evolves to cylindrical and further to lamellar microstructure at higher polymer concentrations [66]. However, there are also some differences in the physical behavior of acrylic gels, such as strain-stiffening behavior at low concentrations. Interestingly, for other systems such as styrene endblock gels, stiffening responses are not reported for low concentrations of polymer [81].

1.2 Physical Characteristics of Gels

These gels are viscoelastic in nature. They exhibit the characteristics of solid materials such as tensile modulus, stretchability, and fracture toughness. Due to the presence of solvent and the
resultant viscous dissipation, these gels also display properties like stress relaxation, creep failure, and strain-rate dependent tensile modulus. The main characteristics required to understand the physical behavior of physical and chemical gels are presented below.

1.2.1 Gelation

The gelation is identified as a point where the polymer network becomes strong enough to bear the load. For the chemical gels, this point is identified in terms of reaction time and for physical gels, it is identified in the terms of temperature [13]. In chemical gels, the formation of the network occurs as the reaction proceeds triggering the gelation. As shown in figure 1.3 on the next page, the gelation in these gels is often recognized by a plateau in the storage modulus ($G'$) over time using time sweep or flow sweep experiments with low oscillation strain amplitude ($\gamma_{amp}$) and frequency ($\omega$) values. The loss modulus $G''$ also increases over time but not as steep as $G'$, signifying the energy loss through viscous dissipation as the network forms. A plateau in $G'$ value signifies the completion of the reaction. The gelation in these networks is tuned by changing the polymer to crosslinker concentration, pH and temperature of the environment, crosslinker type, and catalyst [13, 48, 26].

For a few chemical gels, the gelation time has shown to vary with applied frequency in time-sweep experiments. For these systems, Winter-Chambon criterion is generally applied to determine the gelation point [135, 17, 136]. In this method, $\tan(\delta)$ curves pertaining to different $\omega$-values are plotted as a function of time, and their crossover point is reported as the gelation time.

In physical ABA gels, the temperature triggers the gelation due to a change in solubility of A-blocks, when using a B-block selective solvent. Here, the gelation temperature is identified
Figure 1.3

Time sweep experiment for a chemical gel prepared by free radical copolymerization of acrylic acid, methacrylamide, and poly(propylene glycol) diacrylate. A plateau in $G'$ values, higher than $G''$ values, indicates the solid-like behavior of the gel.

by a crossover point of $G'$ and $G''$ in temperature sweep experiments [149, 148, 81]. Before the gelation point, the network behaves like a fluid, and after the gelation point, the material has a soft solid-like behavior. Essentially, the gelation temperature is not a fixed value and also depends on $\omega$. For example, figure 1.4 on the following page shows two frequency sweep experiments for a physical gel at different temperatures indicating a shift in the crossover frequencies. For their frequency-dependent gelation, Winter Chambon criterion is often implemented to identify the gelation point [113, 104, 141, 81].

This criterion identifies the gel point where $G' \approx G''$ and $G', G'' \sim \omega^k$. The first verification is probed by identifying a crossover point of $\omega$-dependent tan($\delta$) curves indicating that $G'$ and $G''$ are not dependent on $\omega$. The second verification requires a power law to fit the data, displaying the same exponent. This criterion is also shown to be applicable for some physical gels like
Figure 1.4

Frequency sweep experiment for an PS-PI-PS triblock copolymer gel (10 wt%) in mineral oil. Storage modulus ($G'$) and loss modulus ($G''$) of a physical gel as a function of oscillation frequency ($\omega$) at (A) 62°C and (B) 72°C.

PS-PEB-PS, however, other ABA gels like PS-PI-PS gels are shown not to fulfill either or both criteria, limiting the applicability of Winter Chambon criterion [104, 81].

The gelation of the chemically crosslinked gels is governed by the crosslinker to monomer ratio and temperature [13, 62, 24]. A higher temperature is shown to increase the reaction rate kinetics leading to a faster gelation while increasing the crosslinker to monomer ratio first decreases and then increases the half-gelation time, as shown for poly(acrylamide) gels [13]. For physically crosslinked gels, the gelation temperature depends on the length of A-blocks and B-blocks, polymer concentration, and type of solvent [106, 109, 148, 81]. Gels with longer A-blocks and B-blocks are shown to have higher gelation temperature because both contribute to a better connectivity of network [106]. Increasing the polymer concentration also increases the gelation temperature due to a high chain density contributing to the network formation and strength at high temperatures.
Similarly, a poorer solvent to A-blocks or a more favorable solvent to B-blocks facilitates the gelation mechanism at high temperatures [56, 148].

1.2.2 Viscoelasticity

The viscoelasticity is a property of the materials that have an elastic and a viscous response when they are subjected to deformation. Here, the “viscous” term identifies the loss in the energy stored by a material, and “elastic” term signifies the ability of a material to retain the applied energy in the form of strain energy [36]. A material, such as a rubber band, is considered to be elastic and responds immediately when deformation is applied to it. On the contrary, water is considered as a purely viscous system dissipating all the energy applied to it.

Gels are viscoelastic in nature. For chemically crosslinked gels, the elastic properties are contributed by the segments between the crosslinks [122, 101]. For the ABA gels, B-blocks bridging two aggregates bear the load. A higher density of load-bearing chains increases the modulus of the material, therefore, the elasticity is higher for the case of a high crosslinker to monomer ratio in chemical gels. Similarly, for the physical gel, a higher polymer concentration increases the elasticity, however, other factors like A- and B-block length, temperature, and solvent also affect the elastic modulus of the gel [106, 20, 19, 83].

The viscous dissipation in the chemical gel is predominantly caused by the defects of the microstructure and the polymer motion in the solvent [5]. In addition, the poroelasticity, i.e. solvent motion within the polymer mesh during the gel deformation, also plays a role [6, 88]. In ABA gels, the viscous dissipation takes a complex form due to the dynamic nature of bonds. At large time scales, the observation time is comparable to the bond lifetime, thus, the gels become
more viscous [95, 126, 141, 83]. Similar phenomena occur at temperatures near gelation, where A-blocks have sufficient energy to overcome the physical interaction resulting in a shorter bond lifetime [84, 82]. Such time and temperature-dependent viscous behavior are represented by the time-temperature superposition experiments, where frequency sweep experiments performed at different temperatures are superimposed to obtain a shifted frequency-dependent master curve [126, 95]. A crossover between storage and loss modulus signifies an inverse of the time scale below which the ABA gels behave like a fluid. In summary, in ABA gels, the elastic behavior is prominent at low time scales and low temperatures (for gels forming at lower temperatures) while the viscous behavior is significant at high time scales and high temperatures.

1.2.3 Microstructure

The microstructure of gels governs the mechanical properties. These polymeric chains in the network can take many conformations like aggregations, loops, bridges, and dangling chains.

For chemically crosslinked gels, the network is generally composed of a polymer mesh and is often characterized by techniques like small-angle X-ray scattering (SAXS) and small-angle neutron scattering (SANS) [76]. With an increase in the crosslinker to polymer ratio, the mesh size ($\xi$) becomes smaller [62]. Using the shear modulus $G'$, the mesh size can also be estimated as, $\xi = (k_B T / G')^{1/3}$, considering that the modulus originates from thermal fluctuations [32]. Here $k_B$ is Boltzmann’s constant and $T$ is the temperature in Kelvin.

In physical gels a minimum concentration has to be reached for the polymers to bear the load and form a gel. This minimum polymer concentration is called critical micelle concentration (CMC). A concentration below CMC is not expected to form a gel at any temperature [126]. When
the gel is analyzed by shear-rheometry at that critical concentration, the system forms a weak gel with a $G'$ modulus of 10-100 Pa that appears slightly higher than the $G''$.

Gel microstructure can be investigated using scattering experiments through which the polymer chains configuration, their aggregation, and characteristic distance can be obtained by the analysis of the form factor and structure factor from the collected scattering patterns [80, 66, 106, 148, 81]. From the scattering profiles, capturing $I(q)$ as a function of $q$ can be used to interpret different arrangements in the network, and fitting of mathematical models helps to validate a predicted structure. Generally, the polymer chains are represented by cylinders displaying $I \propto q^{-1}$, swollen chains displaying $I \propto q^{-5/3}$, and polymer mesh by mass fractal displaying $I \propto q^{-(2 \text{ to } 3)}$ [44, 148].

For physically assembled ABA gels in B-selective solvents at low polymer concentrations, the microstructure normally consists of flower-like micelles in which loops and dangling chains are formed, resulting in a viscous solution [126]. With an increase in concentration, the microstructure takes the form of loosely connected micelles due to the proximity of another ABA-chain facilitating the connection [106, 148]. With a further increase in concentration, the micelles connectivity increases due to the increase in aggregates number density, which increases the modulus of the gel [106]. The microstructure transforms to a cylindrical and then to a lamellar formation, as shown by experiments and simulations [66, 71]. In these gels, a cylindrical formation is expected at high polymer concentrations.

1.3 Characterization Techniques of Gels

The characterization of gels requires various techniques to obtain information about their microstructure and their chemical and mechanical properties. The testing methods used in this
dissertation include Fourier transform infrared spectroscopy (FTIR) and small-angle X-ray scattering (SAXS) that will provide information about the composition and structure of the system, respectively. The techniques used for the characterization of the mechanical properties include oscillatory shear measurements, tensile, cyclic loading, and retraction experiments.

1.3.1 Chemical Characterization: Fourier Transform Infrared Spectroscopy

The Fourier transform infrared spectroscopy (FTIR) is a method in which infrared light is focused on a sample through an interferometer and records the signal (interferogram). The output light of the sample is correlated with the sent wavelength and transformed into a spectrum [49]. Every spectrum has a value of absorption and emission of the wavelength, displaying an identifying value for each compound and providing information about the composition of the material [49].

There are two main methods to analyze samples, the transmission and the reflectance methods. The transmission method used for liquids, solids, or gases, performs the analysis by infrared radiation at specific wavelengths [115]. The reflectance method is used for liquids, solids, or gases, which were difficult to analyze by the transmittance method [115]. The reflectance technique performs the analysis with an attenuated total reflectance cell with single or multi-bounce, meaning the number of infrared beams that the sample surface reflects [115]. The analysis mainly focuses on the shifting of the spectrum peaks and the change in the area of the absorbed or transmitted wavelengths.

Other techniques like mass spectroscopy and NMR is also an analogous technique for the chemical characterization of materials [8, 90, 92, 140]. However, FTIR is used in gels as a relatively fast and simple method to analyze the chemical structure [117, 138, 139] and to detect
unreacted elements verifying the crosslinking and interactions of the network [4, 8, 39, 90, 140], or branching of polymers [117]. For example, in the synthesis of poly(acrylamide)/montmorillonite (PAAm/MMT) hydrogels, the formation of the network is indicated by the suppression of $\ce{OH}$ bands, present in MMT, also by the shifting of $\ce{N-H}$ bands and $\ce{NH_2}$ bending, present in PAAM, to lower wavenumber values in the hydrogel [39].

### 1.3.2 Microstructure: Small Angle X-Ray Scattering

Small-angle X-ray scattering (SAXS) is a technique to determine structures of macromolecules ranging from 1 to 100 nm [43]. The working principle lies in the scattering of electrons from the cloud of electrons present in the material. It provides information about the size, shape, and number of nano-scale to micro-scale particles in the system [43, 57]. In SAXS experiments, a sample is placed between the X-ray source and detector and the X-ray beam is incident on the sample. The scattered electrons are received by the detector [105], which registers the scattering angle and intensity of the radiation to create a two-dimensional pattern (see figure 1.5).
The 2D-pattern is often analyzed by a theoretical model or by simulations to gain insight about the microstructure of the material [61]. For the theoretical model, the data is reduced to one-dimensional scattering intensity \( I(q) \) as a function of scattering angle \( q \) by averaging over a sector and analyzed. The \( q \)-parameter is related to the scattered angle \( \theta \) by the relationship \( q = 4\pi \sin \theta / \Lambda \), where \( \Lambda \) is the wavelength of the incident beam. Smaller particles produce wider patterns, as they scatter the rays in higher angles, and bigger particles produce a narrower pattern (see figure 1.5 on the preceding page), therefore, the sample-to-detector distance is often varied based on the size of particles. The length scale \( L \) of the particles can be estimated by \( L = 2\pi / q \), when using \( q \)-values related to structure factor peaks [44]. Simulations are often used for cases where the structure is complex to be represented by simple models like for disordered proteins [50].

For chemically crosslinked gels, the reduced \( I(q) - q \) data generally represents a curve, which is further fitted with a theoretical model to gain insight about the mesh size [76]. For example, in poly(acrylamide) gels, it was shown that an increase in crosslinker to monomer ratio strongly increases the mesh size, however, the characteristic dimension of the heterogeneities was found to weakly decrease [24]. Similarly, the characterization of physically assembled gelatin gels using SAXS and scaling arguments revealed that the solvent quality changes from good to theta with an increase in polymer concentration [37].

For ABA triblock gels, SAXS is widely used to understand the effect of temperature, polymer concentration, and respective lengths of A- and B-blocks on their microstructure [106, 148, 83, 81]. For acrylic gels, SAXS experiments represent a featureless \( I(q) - q \) curve above the gelation temperature suggesting the absence of a network in the system. With a decrease in temperature,
the formation of aggregates leads to the evolution of inter-aggregate scattering peaks indicating the formation of a polymer network [106, 148]. At low polymer concentrations, an inter-aggregate peak can also be observed, however, the network is not connected and the aggregates are flower-like micelles [126]. At higher concentrations, the microstructure can evolve into a cylindrical and further to a lamellar, as shown for the PS-PEB-PS and PS-PI-PS gels [66].

While SAXS is a unique indirect measurement tool to identify the microstructure, its applicability is limited for a complex microstructure like biomolecules, therefore, a priori knowledge of the system is necessary. It is also difficult to characterize a microstructure if the size of two entities present in a material falls in the same range of length scale, or the same \( q \)-range. In these cases, the decomposition of data needs careful analysis.

These complex cases are generally addressed by contrast matching in small-angle neutron scattering experiments (SANS) [45]. In these experiments, as the neutrons interact directly with the nucleus, it is possible to differentiate atoms of hydrogen and deuterium, and a good contrast between solvent and chains can be captured. For example, this method was used to investigate pluronic hydrogels, where heavy water \( (D_2O) \) is used as a solvent, instead of water, to increase the contrast for poly(ethylene oxide) solvated chains. By using water, only poly(propylene) aggregates are identified, but a good contrast between solvent and solvated poly(ethylene oxide) chains is not obtained.

A similar technique is also used for acrylic gels, where SAXS is shown to capture the characteristics of PMMA-aggregates, but SANS experiments with deuterated butanol \( (C_4D_{10}) \) as solvent are able to capture the configuration of solvated PnBA-chains as well [148]. However, SAXS has an advantage over SANS through relatively shorter data collection time. SAXS is also preferred
over other microstructure characterization techniques like transmission electron (TEM) or scanning electron microscopy (SEM) due to the ease of sample preparation.

1.3.3 Mechanical Characterization

Gels are capable to sustain large deformations, but their stress responses often become non-linear with respect to strain as a consequence of a change in their microstructure. A single instrument is not sufficient to elucidate the mechanical properties of gels comprehensively. In this dissertation, a set of characterization techniques using commercial and custom-built setups have been used to investigate the mechanical performance of gels. Commercial instruments can have load measurement limits restricting the exploration of the gel’s mechanical properties over a wide range of applied load, therefore, using custom-built setups helped to have better control over the parameters and facilitated the testing of the gels.

1.3.3.1 Shear-rheology

The shear-rheometry experiments capture the stress responses of gels when subjected to shear deformation and can be classified into two types - flow and oscillatory. The setup utilized for these measurements is known as rheometer. In the flow experiments, a continuous deformation is applied to the sample to gain insight into viscosity as a function of time, temperature, or shear-rate. In stress-relaxation experiments, a step strain ($\gamma_{step}$) is rapidly applied to the gel and allowed to relax. During relaxation, the time-dependent shear modulus ($G(t)$) is recorded as a function of time ($t$), which is stress divided by the applied strain. The $G(t) - t$ data is further characterized based on different models to gain insight into the relaxation behavior of gels. In creep experiments, the constant stress is applied to the gel and the resultant strain is monitored over time.
Application of strain load to a gel sample in rheological experiments. A parallel plate geometry indicating the application of strain ($\gamma$) to a gel sample and the obtained sinusoidal graph of $\gamma$ as a function of time.

In the oscillatory experiments, the gel is sheared in a sinusoidal form of strain (applied wave) and frequency, and the stress responses (resultant wave) are measured, or vice versa. In these experiments a sinusoidal shear deformation ($\gamma$) of amplitude $\gamma_{amp}$ is applied to the sample, can be mathematically represented as $\gamma = \gamma_{amp} \sin(\omega t)$ (see figure 1.6). The stress response ($\sigma$) of the material also follows a sine wave with amplitude $\sigma_{amp}$ and phase-lag $\delta$, mathematically expressed as, $\sigma = \sigma_{amp} \sin(\omega t + \delta)$.

The stress response can be further rewritten as, $\sigma/\gamma_{amp} = G' \sin(\omega t) + G'' \cos(\omega t)$ [36]. Here, the $G'$ signifies the ability of the material to store the strain energy and can be related to the elasticity. The $G''$ represents the loss of energy over a loading cycle and can be related to the viscous dissipation. For a purely elastic material the response will be instantaneous, therefore,
Sinusoidal strain ($\gamma$) applied to a sample and corresponding stress response ($\sigma$) over time of pure elastic ($\delta=0$), viscoelastic ($0<\delta<\pi/2$), and pure viscous materials ($\delta=\pi/2$).

$\delta \rightarrow 0$, while for the purely viscous material, $\delta \rightarrow \pi/2$ indicating the complete dissipation of supplied energy. For viscoelastic materials $0<\delta<\pi/2$ (see figure 1.7).

The $G'$ and $G''$ are deduced from the decomposition of the resultant waves into different sine function series. For a linear elastic material, the resultant wave is often a pure sine wave or with a very low contribution of other harmonics [52]. For the case of non-linear responses, the resultant wave is contributed by more than one harmonic of Fourier decomposition. Alternatively, Chebyshev decomposition can also be applied to gain insight into the non-linear contribution to the modulus [34].

When using oscillatory measurements, the material can be tested by varying the frequency, amplitude, time, and temperature. In frequency sweep experiments, an oscillatory shear is applied using a fixed $\gamma_{amp}$ and temperature while varying the $\omega$ over a desired range, and the $G'$ and $G''$ are recorded. It relates the material response with different time scales and is often utilized to probe relaxation times.

In amplitude sweep experiments, an oscillatory shear is applied with fixed $\omega$ and temperature while varying $\gamma_{amp}$ over a range. It gives information about amplitude-dependent moduli, non-
linear characteristics like strain-hardening or strain-softening, ultimate stress, and point of failure [120].

In time sweep experiments, an oscillatory load with a constant temperature, $\gamma_{amp}$, and $\omega$ are applied to gather information about the behavior of the material over time. These experiments provide insight into the curing process, gelation in chemical and physical gels, and possible degradation of the material like solvent evaporation or decomposition [120, 47].

In temperature sweep experiments, an oscillatory shear load is applied with a fix $\gamma_{amp}$ and $\omega$ while varying the temperature over a range. These experiments serve to determine the gelation temperature and moduli of the gel at a particular temperature.

Although shear-rheology is the most popular tool for characterizing viscoelastic materials, such as gels, it suffers from the solvent evaporation and the limitation of torque limits of the rheometer, which further restricts the investigation over a narrow window of frequencies, amplitudes, and shear-rates. Also, samples with inhomogeneous surfaces and non-continuous bulk, like tissues, are difficult to analyze on this setup.

### 1.3.3.2 Tensile Experiments

The tensile experiments are a common method to relate the stress-strain dependence of materials. In these experiments, an uniaxial load is applied to a dogbone-shape sample (figure 1.8 on the next page). The sample is held on a setup with the clamped head. It is anticipated that the deformation in the sample will prominently occur in the gauge region with the sample stretch. A smooth converging curvature of the dogbone avoids stress concentration points. The nominal stress is generally measured as a function of applied strain. The strain is directly calculated by
normalizing the applied stretch with gauge region length. Tensile tests provide information about tensile modulus or Young’s modulus $(E)$, ultimate stress, break point, and non-linearity as large strain values can be applied (figure 1.8).

Although successful for polymers and metals, this technique has been less utilized for characterizing gels, in comparison to other testing methods like shear-rheology and dynamic mechanical analysis (DMA). This is primarily due to the low modulus of gels causing difficulty in supporting the gel on the setup, or clamping the dogbone head, that causes the sample to bulge, or the large deformation, that is not limited to the gauge region. To overcome these problems, researchers have utilized different protocols and custom-built setups.

Recently, PS-PEB-PS gels were tested in a custom-built setup where the sample was supported on shoulder-supporting pins rather than clamping [86]. For the strain measure, those samples were marked with lines and the distance between them was measured to obtain strain. Later, a similar setup was utilized to elucidate the effect of PI-block length, strain rate, and polymer
concentration on the tensile properties of PS-PI-PS gels [82, 83, 81]. It was demonstrated that a gel with entangled PI-blocks displays a strain-rate dependent modulus, especially at high strain values [82, 83, 81]. Although successful in relating the stress responses of gels to deformation at large strain values, a true strain could not be measured using this setup. To overcome this, a new approach was introduced where samples were marked with circles, which elongates to form ellipses. A ratio of the major- and minor-axes of the ellipses normalized by circle radius was used to estimate the strain and true stress values [9].

1.3.3.3 Cyclic Loading Experiments

Cyclic loading experiments are performed to characterize the energy loss in a material over a loading-unloading cycle (see figure 1.9 on the next page) in a tensile mode. In these experiments, a sample is stretched to a prescribed load (loading cycle) and return to the point where that load becomes zero (unloading cycle). The loading-unloading cycle is generally controlled by either applied stress or strain. A difference in area between the loading and the unloading cycle represents the energy loss. A resilient material generally represents a minimal energy loss.

Stress-controlled experiments are preferable for soft materials as the compression of the sample after zero stress is prevented and the sample is held to prevent slippage. Further, using stress-controlled cyclic loading, the residual strain over cycles can be quantified (\( \epsilon_{r,1} \) and \( \epsilon_{r,2} \) in figure 1.9 on the following page).

Utilizing cyclic loading experiments requires adequate extensibility and stiffness of the sample to be measured in tensile mode, which is mainly valid for elastomers [125]. And this is the primary reason for which the physically assembled gels are not generally tested for resilience. Double
Stress ($\sigma$) versus strain ($\varepsilon$) plot for the cyclic loading experiment of a gel sample. The $\sigma$-$\varepsilon$ plot indicates two loading and unloading curves along with the stress reached ($\sigma_1$, $\sigma_2$) and the residual strain ($\varepsilon_{r1}$, $\varepsilon_{r2}$) for each cycle.

Network gels are prominently tested on these setups evaluating the damage to the gel network. For example, for a double network clay/polyacrylamide hydrogel displays high resilience ($\approx 91\%$) in the second loading cycle when stretched up to 11 times while reaching $\approx 125$ kPa [151].

1.3.3.4 Retraction Experiments

The retraction experiments are used to measure the returning velocity and acceleration of materials after released from a stretched state. The retraction property quantifies how fast the energy stored in the material is released. A good retractable material must have a combination of high energy storage capacity, low energy loss, and fast deliverance.

These experiments consist of snapping a stretched string of material from the bottom and measuring the retraction velocity. As the elastic wave propagates through the material, the material unfurls generating a momentum that pulls the string upwards [125, 55]. The retraction velocity is
essentially dictated by the velocity of the stress wave in the material, however, the experimental retraction velocity of the material is generally lower.

In the literature, the retraction experiments are mainly focused on elastomers due to their utilization in the industry [40]. For example, rubber is mainly used in tire manufacturing. Recently, a theoretical framework was created to estimate the retraction velocity of pulse (stress wave propagation) and of the material as a function of applied stretch ratio and corresponding stress, displaying an agreement between experimental and theoretical values for natural rubber [125].

The stress-strain relationship used for the calculation of the velocities is generally obtained from the tensile experiments. Many gels have shown to exhibit high modulus, stretchability, and resilience, however, their retraction properties were not investigated.

A material capable to show high retraction is useful for power amplified activities like striking and hopping [54]. These experiments are generally performed on rubbers due to their ability to stretch and that do not break under creep loading. The retraction experiments on gels are rather challenging due to the long dimensions of a sample, high number of samples, and high probability of solvent evaporation.

1.4 Challenges of Gels

Nowadays, gels with chemical and physical crosslinking still have many challenges to be addressed. In this dissertation, some challenges related to the structure-property relationship of gels are discussed. Accordingly, the two gel systems considered here, one with chemical and physical crosslinking and another with only physical crosslinking, four chapters of this dissertation are dedicated to elucidate the challenges and approaches considered to address them.
For the gels with chemical and physical crosslinking, the challenges associated is the development and characterization of a resilin-like polymeric gel have been addressed. Resilin is a protein found in biological species that empowers them with quick actions like hopping and striking for survival. Although storing small elastic energy in tissues, these species deliver the energy in microseconds accounting for a high power amplified output. Numerous attempts were made in the literature to obtain such synthetic material [96, 121, 29, 25]. These developments were either limited by the complexity of their synthesis route or by the balance between the desired properties. An optimum balance between high stretchability, low hysteresis, and retractability is highly desired in a material to conduct power amplified activities. Also, there are no commercial instruments or standard protocols available to conduct the corresponding tests on gels. This dissertation demonstrates the development and characterization of such hydrogel.

For gels with only physical interactions, the challenges addressed in this dissertation are capturing and characterizing the transient behavior of triblock physically assembled gels. Physically assembled gels have been investigated in detail over the last decades to relate their gelation and mechanical properties with their microstructure [126, 66, 106, 148, 83, 81]. Most of those studies were based on dynamic mechanical testing and related to the gel microstructure at static conditions. The instantaneous microstructure dictates the mechanical property of the material, therefore, such extrapolation explains the small deformation responses but not completely the change in microstructure at large deformations. Also, the change in the microstructure at high strain was not directly captured. These investigations were limited by the availability of the right experimental tool and the stress relaxation tendency of physical gels. The investigation present in this dissertation overcomes both problems by utilizing a small-angle X-ray scattering (SAXS) setup
with a high-flux beam, directed orthogonal to the applied strain direction, equipped with shear-stage rheometer to capture the scattering pattern of gels subject to deformation, during gelation, and stress relaxation.

1.5 Organization of Thesis

This dissertation is divided into four chapters, in conjunction with the present introductory chapter. Chapter II focuses on the development of a hydrogel with physical and chemical crosslinks using a simple synthesis scheme. Using a combination of hydrophilic and hydrophobic crosslinks, a resilin-like gel capable to perform a power amplified activity was synthesized. The swelling behavior of this gel indicates a highly absorbing water capacity. This chapter also elucidates the protocols used on custom-built tools to measure the retraction velocity and acceleration of the gel, the stretchability in tensile mode, and the resilience using cyclic uniaxial loading. An optimum balance between high stretchability, low hysteresis, and retractability enables this gel to perform power-amplified activities. Through catapulting an object, the conversion of elastic strain energy to kinetic energy was also estimated.

Chapter III extends the second chapter to investigate the effect of hydrophobic polymer concentration in the gel system. Since low resilience and retractability are expected with decreasing concentration of hydrophobic polymer, the changes in the physical properties such as extensibility, ultimate stress, resilience, and swelling in water and in different concentrations of saline solutions were studied and compared. This chapter elaborates the role played by the hydrophobic aggregates in dictating the mechanical responses of the system and identifies the remarkable stability of these gels in saline environments.
Chapter IV is targeted to analyze the dynamic microstructure of gels with 10% and 20% weight fractions of poly(styrene)-poly(isoprene)-poly(styrene) [PS-PI-PS] copolymers in mineral oil subjected to temperature, strain, and during stress relaxation. The stress responses are also captured using a stress-controlled rheometer. The dynamic micellar microstructure is characterized and compared with the theoretical model. The gelation has been captured occurring over a wide temperature range. At large deformation, only a fraction of PS-aggregates connected by PI-chains participate in load bearing. The change of microstructure during stress relaxation is compared for different temperatures.

Chapter V discusses the change in microstructure of gels with poly(methyl methacrylate)-poly(n-butyl acrylate)-poly(methyl methacrylate) [PMMA-PnBA-PMMA] copolymer in 2-ethyl-1-hexanol as a function of temperature and strain. This chapter utilizes a comparison of high and low concentration of polymer gels for their microstructure and rheological response. The micellar microstructure of high polymer concentration gel (30 wt%) was characterized during gelation and applied deformation along with the rheological measurements. Using the anisotropic factor, the change in the microstructure during deformation is quantified. The results are further compared with low polymer volume fraction gels composed of three PMMA-PnBA-PMMA polymers of different PMMA- and PnBA-block lengths. A similar shear modulus but different microstructure of low polymer volume fraction gels demonstrate the importance of individual blocks in dictating the mechanical properties.

Chapter VI summarizes the conclusions from each chapter and attempts to provide the future directions towards a better understanding and engineering of the retractable hydrogel. Also, it
suggests further experiments that need to be performed to gain more insight into the microstructure of physically assembled gels.
CHAPTER II

ACHIEVING HIGH-SPEED RETRACTION IN STRETCHABLE HYDROGELS


2.1 Introduction

Elastomeric biopolymers such as resilin play a vital role in dictating the power amplification process [29, 89, 96, 116]. Biological species perform some remarkable activities necessary for locomotion, feeding, and defense [54]. Many of these activities include a power amplification mechanism in which a particular biological system rapidly releases stored-energy by achieving a very high velocity over a short period of time, resulting in high power output. Such power amplification allows insects such as locust to jump and Mantis shrimp to kill prey by its appendage strike [54, 91]. These elastic biopolymers display high and reversible stretchability with low energy dissipation—typically characterized as high resilience—and rapidly retract to their original dimensions after the removal of mechanical load [29, 42]. Specifically, resilin displays up to 300% stretchability and high resilience, as >90% of the applied energy stored during deformation is recovered [29, 96, 116]. Such remarkable properties of resilin have been attributed to a balanced
combination of entropic and enthalpic elasticity originated from the presence of hydrophilic (exon I) and hydrophobic (exon III) segments in resilin [29, 89, 96, 116].

A reasonably good understanding regarding the origin of elasticity in elastomeric biomaterials allows us to engineer materials mimicking some characteristics of those biomaterials. There are many potential applications, viz., in artificial muscles, prosthetic devices for assisting people with restricted mobility, energy harvesting, and enabling soft-robots for power amplification [55]. Since hydrogels are the natural choice of mimicking water containing biomaterials, there are numerous efforts in developing highly stretchable and resilient hydrogels [25, 117]. However, some of these hydrogels are based on recombinant proteins, therefore, obtaining a significant amount of such materials for practical applications is challenging [29, 121]. There also have been efforts to synthesize polymeric hydrogels with high stretchability and resilience, but many of the synthesis schemes require complex reaction routes that limit their large-scale applicability [25, 117]. Furthermore, although many of these systems display high stretchability, a significant energy dissipation during cyclic loading is observed [119, 39, 137]. None of these hydrogels have been tested for the retraction behavior from a stretched state, however, the dissipation observed in many gels likely to cause lower retraction velocity, which will defeat the very purpose of their applications for power amplification.

Here, we report a highly stretchable and resilient hydrogel that displays a very high retraction velocity gained over a short period of time, i.e., with high acceleration, after released from a stretched state. The hydrogels are synthesized through a simple reaction scheme involving free-radical copolymerization of acrylic acid (AAc), methacrylamide (MAM), and poly(propylene glycol) diacrylate [PPGDA] using potassium persulfate (KPS) as an initiator. To the best of our
knowledge, a hydrogel capable of achieving such high retraction velocity and acceleration has not been reported in the literature. Because of these attributes, these hydrogels have been demonstrated to catapult projectiles over a long-distance.

2.2 Experiment Details

2.2.1 Materials

To synthesize gels in this study, we have used poly(propylene glycol) diacrylate (PPGDA) with a molecular weight of 800 g mol\(^{-1}\), sodium dodecyl sulfate (SDS, 98.5%), acrylic acid (AAc, 99%), methacrylamide (MAM, 98%), and potassium persulfate (KPS, 99%). All these chemicals were obtained from Sigma Aldrich and used as received. Sodium chloride (NaCl, 99.9%) was purchased from Fisher Scientific and was used as received. For all experiments, deionized water of resistivity 18.2 m\(\Omega\) was used.

2.2.2 Hydrogel Synthesis

The gel samples were synthesized with different concentrations of monomers (AAc and MAM). The nomenclature used for the gels (17%--, 27%--, 37%-Gels) indicates the total concentration of the monomers (g mL\(^{-1}\)) used to synthesize the gels. First, an aqueous 0.8 M NaCl solution was prepared. 83 mL of saline solution was mixed with 7% (g ml\(^{-1}\)) of SDS, considering 100 mL as the volume basis. The solution was stirred using a magnetic stirrer at 220 rpm for approximately 30 min in a warm water bath maintained at 55 °C until a clear solution was observed. The desired amount of a monomer mixture was prepared separately by adding MAM into AAc, maintaining a weight ratio of 1:4, and considering 100 mL as a basis for the calculation. The monomer mixture was mixed for approximately 15 min at 220 rpm using a magnetic stirrer at room temperature
(22 °C). The clear solution of SDS in saline water was taken out from the warm water bath and mixed with 1% (g g⁻¹) of PPGDA using the monomer mixture weight as a reference. This solution was mixed for 5 min using a magnetic stirrer at 220 rpm. After mixing, the monomer mixture was added dropwise to this solution and stirred for additional 5 minutes to obtain a mixture of reactants. 0.2% (g g⁻¹) of KPS was prepared, considering the monomer mixture as a basis, added into 17 mL of saline solution, and stirred for 5 min. The KPS solution was added dropwise to the reactant mixture while stirring it at 220 rpm. The final transparent solution was poured in an airtight glass container and placed in a water bath at 75 °C for 2 h to obtain a translucent gel. The containers used to cast the gels were a 2 L bottle, 5 mL vials, and 5 mm diameter glass tubes. Once the gels formed, the heat source was turned off, and the water bath was allowed to cool down for the next 24 h before samples are used for further testing.

### 2.2.3 Swelling Experiments

For the swelling tests, small cubic samples (10×10×10 mm³) were weighed, dried in a vacuum oven (≈226 torr) for 72 h at room temperature, and weighed again to determine the water loss. The water content in the as-prepared gels was estimated as the change in the gel weight after drying with respect to the initial sample weight. Next, the samples were immersed in 50 mL of DI water for 24 h to swell. The swelling ratio (g g⁻¹) was obtained as a ratio of change in sample weight after swelling to the dry weight.

### 2.2.4 Tensile testing

All mechanical tests were performed at room temperature (22 °C). A custom-built setup was used for conducting the tensile experiments, and the details regarding the experimental setup and
data analysis protocol can be found in our previous publications [82, 83]. In these experiments, a
dogbone-shaped gel sample was prepared by cutting from the gel-sheet using a 3D-printed punch.
The dogbone sample had a gauge length of 4.2 mm, breadth of 4.2 mm, and an approximate
thickness of 9.5 mm. The dogbone sample was held by the four supporting pins fixed to the
top and bottom support blocks. A clamp was attached at the top and bottom blocks to avoid the
sample slippage. The sample was stretched by moving the top supporting block using a moving
stage (M414.3PD, Physik Instrumente). The sample was stretched at a stage velocity of 1 mm s\(^{-1}\)
(strain rate (\(\dot{\varepsilon}\)) of 0.048 s\(^{-1}\)) until the failure of gel occurred. The setup was controlled by a
custom-built program in NI LabVIEW framework. During the sample stretching, images were
taken using a monochrome camera (Grasshopper3, Point Grey Research Inc.) at \(\approx 16\) fps. Every
sample was marked with three lines (1,2,3) at the gauge region to calculate strain (\(\varepsilon\)) and
\(\dot{\varepsilon}\) by using a custom-built image-processing program in MATLAB. Here, \(\varepsilon\) represents the average of
the change in distance between lines 1-2, 2-3, and 1-3, normalized by their initial distances. The
corresponding stretch ratio, \(\lambda\), can be estimated as \(\varepsilon+1\). The force value corresponding to an
applied stretch is measured by the deflection of a cantilever with a known stiffness. Nominal stress
(\(\sigma\)) was estimated by dividing the measured force with the initial cross-sectional area of the gauge
region of the sample.

2.2.5 Cyclic loading and determining resilience

Cyclic loading experiments were also performed using the custom-built setup described above.
In these experiments, samples were stretched with the same strain rate (\(\dot{\varepsilon}\)) of 0.048 s\(^{-1}\) until those
experienced the prescribed nominal stress (\(\sigma\)). After the prescribed stress was attained, the samples
were unloaded with the same strain rate until the stress became zero. The applied strain and strain rates were determined from the images as described above in the tensile testing section.

2.2.6 Retraction experiments

For the retraction experiments, a gel string sample with a diameter of 4 mm and a length of 45 mm was clamped at both ends on the tensile testing setup. The sample was then stretched, and stretch ratios of $\lambda=3$, 4, 5, and 6 were considered. The sample was then marked with seven equidistant lines that were tracked during the retraction process, as described below. The string was cut with scissors adjacent to the bottom clamp and was allowed to retract. The retraction process was recorded using a high-speed camera (Miro M310, Phantom) at $\approx5000$ fps. The images were analyzed using a custom-developed image-processing program in MATLAB. The data was used from the time at which the string was snapped. While retracting, the string slacks as soon as it crosses its initial length. The data after slack-time were not used for analysis.

To calculate the velocity of each marked line, a fifth-order of Fourier series was used to fit the position ($f$) vs. time ($t$) data, which can be mathematically represented as $f(t) = a_0 + \sum_{i=1}^{5} a_i \cos(\omega t) + \sum_{i=1}^{5} b_i \sin(\omega t)$, where $a_0$, $a_i$s, $b_i$s, and $\omega$ are the fitting parameters. The resultant function was then differentiated to obtain the velocity. The differentiation of the above equation can be mathematically expressed as $\frac{df(t)}{dt} = \omega \left( -\sum_{i=1}^{5} a_i \sin(\omega t) + \sum_{i=1}^{5} b_i \cos(\omega t) \right)$. The expression was further differentiated to estimate the acceleration, which can be mathematically represented as $\frac{d^2 f(t)}{dt^2} = -\omega^2 \left( \sum_{i=1}^{5} a_i \cos(\omega t) + \sum_{i=1}^{5} b_i \sin(\omega t) \right)$. 

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2.3 Results and Discussion
2.3.1 Hydrogel synthesis

As displayed in figure 2.1 on page 44A, upon a chemical reaction, AAc and MAM form hydrophilic poly(acrylic acid) (PAAc) and poly(methacrylamide) (PMAM) chains. The hydrophobic PPGDA chains connect the PAAc and PMAM chains forming crosslinks. Figure 2.1 on page 44B represents a schematic of the proposed network structure of the gel. Note that PPGDA chains can also polymerize as a result of the free radical reaction, leading to a significant distribution in their molecular weight. Because of hydrophobicity, the PPG blocks collapse, and multiple of these blocks can associate in forming hydrophobic aggregates. The surfactant sodium dodecyl sulfate (SDS) in the sodium chloride (NaCl) reaction media promotes the formation of these hydrophobic aggregates [103]. The gels are opaque, indicating a phase-separated structure.

For the present study, we have considered 17%, 27%, and 37% (g mL$^{-1}$) total monomer (MAM and AAc) concentration while keeping a constant MAM to AAc weight ratio of 1:4. A fixed proportion of KPS (0.2% (g g$^{-1}$)) and PPGDA (1% (g g$^{-1}$)) with respect to the total monomer weight was used for each gel. These gels are referred to as 17%- , 27%- , and 37%-Gels throughout the article. The water content of the as-prepared 17%- , 27%- , and 37%-Gels has been determined as 80.87±0.88%, 67.64±0.15%, and 64.92±0.09%, respectively, by drying the gel samples in a vacuum oven for 72 h at room temperature (figure A.1 on page 146A-B and table A.1 on page 154). During gel formation, we have observed some level of syneresis likely related to the presence of hydrophobic monomers, therefore, the polymer concentrations in the gels were slightly higher than the monomer concentration used.
No significant additional swelling was observed when the as-prepared samples were stored in a 0.8 M aqueous NaCl solution. However, submerging the samples in water results in significant swelling. Specifically, the dried 17\%- , 27\%- , and 37\%- Gel samples immersed in water for 24 h can absorb water ≈87.85±14.92, 44.16±1.35, and 34.55±0.05 times of their dry weight, respectively (figure A.1 on page 146C and table A.1 on page 154). In this study, we have considered the as-prepared sample for further testing. However, significant swelling in water indicates the high stretchability of our gels. Also, as the samples are stable in NaCl solution, these samples can be used in a saline environment.

The structure of our gels can be compared with resilin, a disorderly protein that consists of both hydrophilic and hydrophobic segments [96]. At low strain, the resilin elasticity is governed by the entropic stretching of hydrophilic segments (exon I) [29, 89, 96, 116]. In contrast, the high-strain response is primarily governed by the stretching of hydrophobic segments (exon III) [29, 89, 96, 116]. The hydrophobic content dictates the water content in the gel, therefore, the modulus of the material. The power amplification mechanism in many biological systems can be attributed to the rapid retraction response of resilin from a stretched state. Such a response is not only dictated by the entropic spring-like response of hydrophilic chains but also by the behavior of hydrophobic stretched chains in an aqueous environment. In the stretched state, the hydrophobic segments in contact with water, an unfavorable solvent, rapidly return to their original collapsed condition once the strain is removed. However, the enthalpic penalty is not significant, therefore, resilin is highly resilient. For our gels, we expect to see similar mechanical responses of the hydrophilic and hydrophobic segments mimicking the mechanical properties of resilin.
2.3.2 Mechanical properties

The synthesized gels are highly compressible and resilient. As displayed in figure 2.1 on page 44C, a cylindrical sample with an initial height of 5 mm was compressed to 1 mm with a strain rate \( \dot{\varepsilon} \) of 0.2 s\(^{-1}\), and the sample quickly recovered to the original height with a negligible residual strain after the compressive strain was released. The sample has an ability to return to its original form even after undergoing a complex deformation (figure 2.1 on page 44D1-2). The sample can also bear a concentrated load without failing (figure 2.1 on page 44D3).

As the samples display excellent resilience behavior in compression mode, the stretchability and gel modulus have been determined using tensile testing at room temperature (22 °C) using a custom-built instrument developed in our research group [82, 83]. Figure 2.2 on page 45A shows nominal stress \( \sigma \) as a function of strain \( \varepsilon \) for 17%--, 27%--, and 37%-Gels obtained from these tensile experiments using a strain rate \( \dot{\varepsilon} \approx 0.048 \) s\(^{-1}\). The \( \sigma \) is calculated considering the initial cross-sectional area of the sample gauge region (see figure A.2 on page 147). To determine the strain values accurately, we have used an image analysis technique, where the distance between the lines drawn on the sample as a function of time was used to estimate \( \varepsilon \) and \( \dot{\varepsilon} \) (figure 2.2 on page 45B and figure A.2 on page 147) [82, 83]. This technique allows us to determine strain values more accurately in comparison to the traditional methods, where the displacement of the sample clamp or a stage is tracked to determine the strain values, possibly leading to an erroneous higher stretchability of the gel samples [86]. Our gel samples display a typical s-shaped response of elastomers [122, 119] and a high stretchability before failing, \( \varepsilon_f \) (figure 2.2 on page 45C). For example, the \( \varepsilon_f \) for the 17%-Gel is as high as \( \approx 8.6 \). Images of the stretched gels with three different polymer concentrations are displayed in figure A.3 on page 148A-C for comparison. In
addition, experiments were also performed at $\dot{\epsilon} \approx 0.48 \text{s}^{-1}$, however, no noticeable change in the $\sigma - \epsilon$ behavior was observed by increasing $\dot{\epsilon}$ an order of magnitude (figure A.3 on page 148D), indicating low energy dissipation in these gels. The $\sigma - \epsilon$ responses display higher initial slopes with increasing polymer concentration, indicating an increase in modulus. To determine the small-strain tensile modulus ($E$), the neo-Hookean model expressed as $\sigma = (E/3)((\epsilon + 1) - (\epsilon + 1)^{-2})$ for the uniaxial loading was fitted over the range of $0 \leq \epsilon \leq 0.35$ (figure A.4 on page 149) [122]. The estimated $E$ values are 15.1, 56.8, and 103.1 kPa for the 17%-Gel, 27%-Gel, and 37%-Gel respectively (figure 2.2 on page 45D). With the increase in monomer concentration, a higher modulus ($d\sigma/d\epsilon$) can be noticed, however, the $\epsilon_f$ value decreases with increasing monomer concentration. The difference between $\epsilon_f$ of 27%-Gel and 37%-Gel is not significant, similar to that observed in the swelling experiments. In determining the resilience behavior of these gels, cyclic loading tests were performed on three gel samples considered here. Although it is preferred to stretch the samples to a prescribed strain, real-time strain measurements from the images have been found to be difficult. Therefore, the samples were stretched to a prescribed stress value using strain rate, $\dot{\epsilon} \approx 0.048 \text{s}^{-1}$ and then unloaded to zero stress with the same $\dot{\epsilon}$. After completion of one loading cycle, the stress was continuously increased by 10 kPa for the next cycle until the sample failed, mostly at the $\epsilon_f$ values obtained from the tensile tests (figure 2.2 on page 45C). Results for the 37%-Gel for particular stress values are shown in figure 2.2 on page 45E-F. The loading and unloading cycles for all gels with 10 kPa step-increase are shown in figure A.5 on page 150, figure A.6 on page 151, and figure A.7 on page 152. The strain-recovery after unloading is almost complete, as the residual strain has been found to be negligible, especially at the high-stretch values and for higher monomer concentration. For example, the residual strain for all gel samples is $\approx 5.7\%$.
for the $\sigma=30$ kPa cycle, however, it reduces to 2% for 37%-Gel for the $\sigma=130$ kPa cycle. The actual strain recovery can be a little higher, particularly for a low applied stress, as we have a few percentages of measurement error in capturing the position of marked lines ($\approx 0.2$ mm error in measuring distances between the lines on the samples). The resilience behavior of these gels can be quantified as the ratio of energy recovered during the unloading cycle to the energy absorbed during the loading cycle. A remarkable resilience of $\approx 98\%$ is captured for the 37%-Gel (table A.2 on page 155). With a decrease in the monomer concentration, the resilience reduces to 90.3% for 27%-Gel and 88.6% for 17%-Gel. Overall, we have obtained less than 10% energy loss during a cycle, which is not very significant. The high resilience of our gels can mostly be attributed to the reversible stretching of hydrophilic chains. When subjected to a load, the stretching of hydrophilic chains between two crosslinks occurs, followed by the dissociation of hydrophobic aggregates and subsequent stretching of hydrophobic blocks, as the entropic penalty in chain stretching is lower than overcoming the hydrophobic association energy. Once the load is removed, in addition to the hydrophilic chains, the hydrophobic chains also retract quickly from the unfavorable aqueous environment to form aggregates again, leading to high resilience and almost full strain recovery. The low hysteresis loop also indicates that the enthalpic loss associated with dissociation and reformation of hydrophobic aggregates is not significant, similar to that observed in the resilin. Such a small loss can be attributed to the low molecular weight of hydrophobic PPG-chain, which experiences less intermolecular friction [117, 151]. The resilience values of the present gels are comparable to those obtained for recombinant resilin and elastin with the resilience of $\approx 97\%$ and 90%, respectively [29]. Recently, the hydrophobicity of polydimethylsiloxane in polyethylene glycol-water system was also exploited to synthesize a gel with high resilience ($\approx 98\%$) [25]. However,
the maximum stretchability ($\lambda_f \approx 4$) and tensile modulus ($E \approx 16$-34 kPa) of that gel system were significantly lower than that of our gel, in addition to the specialized synthesis scheme used there [25]. Polymer-clay nanocomposite hydrogels display ultra-low hysteresis at $\approx 50\%$ strain, however, it takes $\approx 60$ s to recover from $500\%$ strain [117]. In contrast, our gels recover instantaneously, even at high strain. The instantaneous recovery of the samples was further explored through the retraction experiments. Since we have maintained a constant monomer to crosslinker ratio, an increase in monomer concentration increases the crosslinking density leading to a higher gel modulus [122]. Strain-stiffening behavior observed in all three gels at high can be related to the finite-extensibility of the chains [31] as most likely, the hydrophobic aggregates dissociate, and the PPG chains are stretched. Strain-stiffening allows these gels to carry a concentrated load, as seen in figure 2.1 on page 44D3, despite not having a very high $E$.

### 2.3.3 Retractability of hydrogels

figure 2.3 on page 46 shows the results of retraction experiments performed on a 37%-Gel string using the stretch ratio ($\lambda = \epsilon + 1$) of 6. Here, the stretched string was snapped at the bottom clamp and then allowed to retract freely. The sample was marked with seven equidistant lines (figure 2.3 on page 46A1-A2) to track the position of lines with time as the sample retracted. The line positions were tracked from the release of the string until the time it slacked. The results presented here correspond to Line 1, which achieved the highest velocity and acceleration during the retraction. The position of Line 1 for all three gels are plotted as a function of time in figure 2.3 on page 46B for $\lambda=6$. After a few milliseconds (ms) of the sample release, the position of Line 1 deviates from the straight line (indicating static initial condition), and decreases linearly with
time, indicating a constant velocity. This curvature between the static position and the constantly decreasing line corresponds to the sample acceleration [125].

The line position with time was fitted with a fifth-order Fourier series, and the obtained function was then differentiated for estimating velocity and acceleration (figure 2.3 on page 46C-D and figure A.8 on page 153). Figure 2.3 on page 46E and F summarize the maximum velocity and acceleration for the \( \lambda \) values of 3-6. With the increase in monomer concentration, both velocity and acceleration increase suggesting that higher values can be obtained by further increasing the monomer concentration or partially drying the samples. The maximum velocity and acceleration for 37%-Gel and \( \lambda = 6 \) are \( \approx 16 \text{ m s}^{-1} \) and \( \approx 4 \times 10^3 \text{ m s}^{-2} \), respectively.

The retraction velocity values are comparable to the frog hopper jump (\( \approx 4.7 \text{ m s}^{-1} \)), and mantis shrimp appendage strike (\( \approx 30 \text{ m s}^{-1} \)) [54]. The acceleration is similar to the jump of a frog hopper (\( \approx 5.4 \times 10^3 \text{ m s}^{-2} \)) [54]. The retraction velocity of our gel is lower than that of dry, vulcanized natural rubber (\( \approx 125 \text{ m s}^{-1} \)) [125] but somewhat similar to the polyurethane elastomers (\( \approx 25 \text{ m s}^{-1} \)) [54]. To the best of our knowledge, this is the first demonstration of achieving such a high velocity and acceleration in hydrogels.

For the elastomer like rubber, the free retraction velocity can be theoretically calculated as,

\[
    u = \sqrt{\sigma(\lambda - 1)/\rho},
\]

which results from the propagation of retraction pulse through the material [125]. For the calculation of \( u \), we have used density, \( \rho \approx 1.05, 1.10, \) and \( 1.14 \text{ g mL}^{-1} \) for the 17%-., 27%-., and 37%-Gels, respectively. \( \sigma \) corresponding to a particular \( \lambda \) value was estimated from figure 2.2 on page 45A. The density of each gel was determined by measuring the mass of the as-prepared cubic-shaped sample and the volume occupied by that sample. Figure 2.3 on page 46E compares \( u \) as a function of \( \lambda \) with the experimentally obtained values of Line 1 for each gel.
Here, the predicted $u$ values are 1.1-1.7 times the experimentally obtained retraction velocity of Line 1 but are of the same order of magnitude. The equation used for estimating $u$ originates from the momentum balance; therefore, it does not account for any dissipation in the system. A small amount of dissipation related to the viscous drag the hydrophilic chain may experience during their motion in the solvent may have caused the deviation of the retraction velocity from $u$ [42]. This dissipation also likely lowers the acceleration values in our gels compared to that observed in some biological systems $\approx 10^5 \text{ m s}^{-2}$ [54].

2.3.4 Solid projectile launching by hydrogels

Since our gels have high stretchability and resilience, we have shown their applications for catapulting solid projectiles. As shown in figure 2.4 on page 47, by using a 37%-Gel string, we have been able to launch a solid projectile of 1.53 g to a distance ($L$) of $7.96 \pm 0.24$ m. The achieved projectile velocity was $15.93 \pm 0.63$ m s$^{-1}$, and 93% of the energy stored in the system during stretching was converted into kinetic energy. This was achieved for $\lambda \approx 6$, and different $L$ values can be obtained by considering different $\lambda$ values. Also, the sample can be reused multiple times. This further opens up novel applications of the gels reported here.

2.4 Conclusions

In conclusion, we report a novel hydrogel synthesized through a simple free-radical copolymerization scheme. By selecting an appropriate ratio of hydrophilic PAAc and PMAM chains and hydrophobic associations of PPGDA chains, highly stretchable ($\lambda \approx 8.6$) and resilient gels ($\approx 98\%$) with a negligible residual strain ($\approx 2\%$) have been obtained. After released from a stretched state, the gel samples achieve retraction velocity as high as $\approx 16$ m s$^{-1}$ and acceleration $\approx 4 \times 10^3$ m s$^{-2}$. These
properties resemble naturally occurring elastomeric biopolymers, like resilin. High resilience and stretchability can be utilized in many activities, such as catapulting a projectile or other power amplification systems. Because of a simple synthetic route, the hydrogel properties can be further tuned, and new applications can be envisioned.
Figure 2.1

Chemical structure and stretchability of hydrogel. (A) Reaction scheme for the hydrogel formation. (B) The three-dimensional structure of hydrogel, where hydrophobic aggregates (pink spheres) containing PPGDA molecules (blue chains) are connected by the hydrophilic PAAc and PMAM chains (green chains). Here, the green diamonds represent covalent bonds. (C) Compression of a 27%-Gel sample representing the undeformed state (C1), after compression (C2), and after removing the stress (C3). (D) Complex deformation of a gel string (37%-Gel) in an undeformed state (D1), forming a knot (D2), and supporting 100 g deadweight (D3).
Figure 2.2

Tensile testing and cyclic loading experiments. (A) Nominal stress ($\sigma$) as a function of strain ($\epsilon$) for 17-, 27-, and 37%-Gels. Results are an average of three runs with standard deviation. (B) Images of the 17%-Gel sample during a tensile experiment: (B1) initial condition ($\epsilon=0$), and (B2) before the failure of the gel, capturing high stretchability of the sample ($\epsilon=8.45$). (C) Failure stress ($\sigma_f$) and failure strain ($\epsilon_f$) for the three gels. The error bars represent the standard deviation. (D) Young’s modulus of the three gels obtained by fitting the neo-Hookean model to the experimental data up to $\epsilon \approx 0.35$. The error bars represent the standard deviation. (E) Results from cyclic loading experiments for 37%-Gel are plotted for the stress values $\sigma=10, 30, 90,$ and 130 kPa and shifted to zero $\epsilon$ for comparison. (F) Each cycle is shifted by 0, 4, 8, and 12 units, respectively, along the strain-axis for clarity.
Retraction of gel samples from a stretched-state. Image of a 37%-Gel string: (A1) at the stretched condition, $\lambda=6$ at $t=0$ ms., marked with 7 lines (Line 1-7), and (A2) fully retracted after $t\approx19$ ms. (B) Position, (C) velocity, and (D) acceleration of Line 1 as a function of time for all gels with $\lambda=6$. In (B) both the experimental data and the fitting of the Fourier series are shown. (E) Retraction velocity as a function of different $\lambda$ for all three gels. A comparison of the experimentally observed velocity of Line 1 with theoretically predicted retraction velocity ($u$) as a function of $\lambda$. (F) Maximum acceleration corresponding to Line 1 as a function of $\lambda$ for all three gels. The error bars represent the standard deviation.
Figure 2.4

Application of gels for launching projectile. Image and scheme of a projectile launching by using a 37%-Gel for stretch, $\lambda=6$. 
CHAPTER III

INVESTIGATING THE EFFECT OF HYDROPHOBIC POLYMER CONCENTRATION IN STRETCHABLE HYDROGELS

3.1 Introduction

Chapter II presents a highly stretchable hydrogel capable to perform power amplification. Such property was attributed to the balance between hydrophobic associations of poly(propylene glycol) diacrylate [PPGDA] and hydrophilic segments of poly(acrylic acid) [PAAc] and poly(methacrylamide) [PMAM] chains. Since the hydrophobic PPGDA associations have been hypothesized to be linked to the large deformation responses like low hysteresis and high retraction velocity, it is important to investigate the effect of PPGDA concentration on the mechanical properties of these gels. The present chapter mainly focuses on the role played by the PPGDA concentration on the thermal and stress responses of gels. The PPGDA concentration was varied sequentially in the gels as 0.1%, 0.3%, 1%, and 3% considering the monomer concentration as a basis. while the rest of the components were maintained the same. In the present work, we have elucidated how the PPGDA concentration affects the uniaxial stress response, hysteresis, and swelling behavior in solutions with different salt concentrations.
3.2 Experiment Details

3.2.1 Materials

For the synthesis of the gels, sodium dodecyl sulfate (SDS), acrylic acid (AAc), methacrylamide (MAM), potassium persulfate (KPS), and poly(propylene glycol) diacrylate (PPGDA) were purchased from Sigma Aldrich. The molecular weight of PPGDA was 800 g mol\(^{-1}\), and the purity of the reactants was 98.5, 99, 98, 99, and 99.9 for SDS, AAc, MAM, KPS, and NaCl, respectively. Sodium chloride (NaCl), purchased from Fisher Scientific, was dissolved in deionized water to prepare NaCl solutions at 0.8, 0.4, and 0.2 M. The deionized water used had a resistivity of 18.2 mΩ. All the reactants were used as received.

3.2.2 Hydrogels Synthesis

All the gels were prepared by fixing the content of monomers to 37 g per 100 mL of saline solution. The content of monomers only includes AAc and MAM at 4:1 weight by weight ratio. The saline solution was composed of NaCl at 0.8 M in deionized water. First, 7.00 g of SDS were added to 83 mL of saline solution and dissolved in a water bath at 55 °C for \(\approx\) 30 min until a clear solution was formed. In a separate container, the monomer mixture was prepared by adding 7.40 g of MAM in 28 mL of AAc at room temperature (RT, 22 °C) and stirred for 15 min. Separately, 0.07 g of KPS was mixed at RT with the rest 17 mL of saline solution and stirred for 5 min or until dissolved. Later, the SDS-solution was taken out of the water bath, and the desired amount of PPGDA was immediately added dropwise, stirring for \(\approx\) 5 min. Next, the monomer mixture was added dropwise to the latter solution and stirred for additional \(\approx\) 5 min. Next, the KPS solution was also added dropwise to the previous solution and stirred for \(\approx\) 5 min more. Immediately after, the final transparent solution was poured in an airtight 2 L bottle and placed at 75 °C for 2 h. After
that time, a gel sheet was formed, and the heat source was turned off to allow the water bath to cool for the next 24 h. All the mixing and dissolution processes were performed with different magnetic stirrers at 220 rpm. The amount of PPGDA added was 37, 110, 366, and 1099 µL for the 0.1%, 0.3%, 1%, and 3%-Gels, respectively. Note that the gels are named throughout this article according to their content of PPGDA (wt%) with respect to the monomers’ weight (37% w/v).

3.2.3 Swelling Experiments

For the swelling experiments, four small-size cubes of ≈10×10×10 mm³ were cut from 0.1%- and 0.3%-Gel sheets and weighed. All samples were placed in a vacuum oven (≈226 torr) at RT and dried for 120 h. Time after which the temperature was increased to ≈35°C and the gels were dried for additional 96 h. Four different beakers contained separately 50 mL of deionized water and three saline solutions at 0.2 M, 0.4 M, and 0.8 M of NaCl. Next, each gel sample was immersed for 4 days (96 h) in water or a saline solution. After that time, the water and solutions were changed and freshly prepared with the same composition after every 24 h, and the gels were immersed again for the next two days. The surface of the gels was gently dried when possible with soft tissues before any measurement. The weight gained by the gels was recorded, for one week, every 24 h. And the swelling capacity (wt%) was calculated as the ratio of change in sample weight after swelling to the dry weight of gel.

3.2.4 Shear-rheological Experiments

Shear-rheological experiments were performed on the samples using a hybrid TA Instruments Discovery HR2-Rheometer equipped with a Peltier plate. The geometry used for the experiments was a 25 mm diameter parallel plate and a custom-built solvent trap using Fomblin Y (purchased
from Sigma Aldrich and used as it is). In these tests, a solution sample was loaded at RT on the bottom plate of the rheometer and the gap was adjusted to 1 mm. Next, the Fomblin Y was used to form a bath contained in the solvent trap and covering both plates of the geometry and the sample to avoid evaporation of the solvent. The temperature was then increased to 75 °C to form the gel in situ. This in situ experiment was performed at a strain ($\varepsilon$) of 0.001 and oscillatory frequency ($\omega$) of 0.5 rad s$^{-1}$ for $\approx$15000 s. After forming the gel, frequency and temperature sweep experiments were performed on the same sample. The frequency sweep experiment was performed at $\varepsilon$=0.001 and at RT over an $\omega$-range of 0.1-100 rad s$^{-1}$. The temperature sweep experiment had first a cooling and then a heating cycle using $\varepsilon$=0.001 and $\omega$=0.5 rad s$^{-1}$. The cooling cycle was performed over a temperature range of 22-4 °C, and the heating cycle over a temperature of 4-90 °C with a step of 2 °C and a soak time of 90 s.

3.2.5 Tensile Experiments

A custom-built setup was used to perform the tensile tests on the gels. The setup included a moving stage (M414.3PD, Physik Instrumente), a position sensor, and a monochrome camera (Grasshopper3, Point Grey Research Inc.). All these components were synchronized and controlled by a custom-built NI LabVIEW program. For these experiments, dogbone-shaped samples were cut from the gel sheets with a 3D-printed mold. The dimensions of the dogbone sample gauge were 4.2×4.2×9.5 mm$^3$ for length, breadth, and thickness, respectively, as defined in our previous study, and marked with 3 lines for analysis [4]. The gel sample was held by supporting pins and clamps attached to the top and bottom bars of the stage to avoid slippage of samples. The moving stage displaces vertically upwards to stretch the gel. The camera recorded the experiment at 16 fps.
to track the displacement of the 3 marked lines in the gel to measure strain ($\epsilon$). The average change in the distance between lines, normalized by their initial distances, estimated $\epsilon$ and corresponding stretch ($\lambda = \epsilon + 1$) by using a custom-built image-processing program in MATLAB. The applied strain-rate ($\dot{\epsilon}$) was 0.048 and 0.48 s$^{-1}$. While stretching the gel, a position sensor measured the displacement of a cantilever, with known stiffness, to calculate stress. Here, the nominal stress ($\sigma$) is the result of dividing the measured force by the initial cross-sectional area of the sample gauge.

3.2.6 Cyclic Loading Experiments

The same custom-built setup used in the tensile experiments was used for the cyclic loading experiments. The dogbone sample was held in the same manner as it was in the tensile experiments. However, in these tests, the sample was loaded and stretched until reaching a determined $\sigma$, and then the gel was unloaded to reach zero stress. Multiple cycles of loading and unloading were performed in each gel with a step of 10 kPa, i.e. 10 kPa, 20 kPa, 30 kPa, and so on, until the gel failure. The $\dot{\epsilon}$ values used for loading and unloading were 0.048 and 0.48 s$^{-1}$. The gauge of the sample was marked with 3 lines to measure $\epsilon$ and $\lambda$ by using the monochrome camera at 16 fps. The stress was also estimated by the position sensor and cantilever bend from the response of the gel. A custom-built MATLAB program calculated the resilience and hysteresis by estimating the areas under the loading and unloading curves, and the residual strain (%) was estimated by the ratio of last $\epsilon$-value from unloading cycle to maximum $\epsilon$ reached in the cycle.
3.3 Results and Discussion
3.3.1 Hydrogels synthesis

The gels were synthesized through a simple reaction route, as mentioned in chapter II. The main network is formed by chemically crosslinked polymeric chains of hydrophilic AAc and MAM forming poly(acrylic acid) [PAAc] and poly(methacrylamide) [PMAM]. KPS is used as the initiator in the free radical reaction. The hydrophobic PPGDA chains, which are chemically bonded to both PAAc and PMAM, associate together to form aggregates. This arrangement of covalently bonded hydrophilic chains and physically associated aggregates forms a mesh, which traps the water within forming the gels. The gels obtained after the synthesis are opaque but change into translucent and transparent gels with an increase in PPGDA concentration. The images of the aspect change in gels are shown in the appendix as figure B.1 on page 158.

3.3.2 Mechanical properties

figure 3.1 on page 60A shows the in situ gelation of both 0.1%- and 0.3%-Gels subjected to oscillatory strain. At the beginning of the experiment, the liquid solutions do not display a clear trend of storage ($G'$) and loss ($G''$) modulus, most likely due to the applied torque that reaches the lower torque limit of the rheometer. However, from $\approx 10^3$ to $5 \times 10^3$ s both samples display an increase of moduli, signifying the development of the microstructure formation. At $\approx 12 \times 10^3$ s, both moduli reach a plateau due to the completion of gel formation. The inset image shows the opaque 0.1%-Gel surrounded by the Fomblin Y bath. This bath served as a solvent trap, expected to discourage water evaporation at high temperatures and over time. The gelation is also noticeable for the difference of an order of magnitude between $G'$ and $G''$, where $G'$ becomes at least one magnitude higher than the $G''$. For 0.1%- and 0.3%-Gels, the $G'$ values at the plateau region
are in the range of 200-300 kPa. A similar value of $G'$ plateau for these samples indicates that both gels behave in the same manner at low deformation. The time attained from both samples to complete the gelation was no significantly different indicating that structure formation follows the same mechanism.

In figure 3.1 on page 60C, the frequency sweep experiments are performed over a frequency ($\omega$) range of 0.1 to 100 rad s$^{-1}$ using an $\epsilon_{amp}$=0.001 at RT. These experiments show that both $G'$ and $G''$ of 0.1%- and 0.3%-Gels are weakly dependent on $\omega$. Temperature sweep experiments were also performed on 0.3%-Gel with a cooling and a heating cycle using an $\epsilon_{amp}$=0.001 and $\omega$=0.5 rad s$^{-1}$. First, a cooling cycle from RT to 4 °C was applied on the gel sample with the ramp rate of 2°C min$^{-1}$. Immediately after the cooling cycle, the heating cycle was applied on the gel increasing the $T$ from 4 to 80 °C. Here, both moduli slightly decrease with an increase in temperature.

From these heating and cooling cycles, it can be noticed that an increase in temperature decreases the $G'$ gradually, probably due to an increase in PAAc and PMAM chain mobility at higher temperatures. An increasing trend of $G''$ at lower temperatures can be attributed to the increase in solubility of PPGDA contributing to the viscous dissipation.

Tensile experiments were performed at RT on 0.1%-., 0.3%-, 1%-, and 3%-Gels at a strain-rate ($\dot{\epsilon}$) of 0.048 s$^{-1}$, as shown in figure 3.2 on page 61A with nominal stress ($\sigma$) plotted against strain ($\epsilon$). All the gels follows the same $\sigma$ − $\epsilon$ behavior representing a straight line of higher slope at low $\epsilon$-values followed by a curve of lower slope at high $\epsilon$-values. This curve maintains an increasing trend of $\sigma$ until reaching the ultimate failure stress. Lower PPGDA concentrations in the gel display higher stretchability. In particular, 0.1%-Gel reaches up to $\epsilon \approx 10.5$. However, higher
concentrations of PPGDA produce an increase in the ultimate stress and tensile modulus but reduce the stretchability. For instance, 3%-Gel reaches up to 83.6 kPa, but its maximum stretchability is $\varepsilon \approx 1.4$. Note that all gels display an S-shape $\sigma - \varepsilon$ curve—a typical characteristic of elastomers [122, 119].

Figure 3.2 on page 61B1 displays the image for 0.1%-Gel at zero-load ($\varepsilon = 0$) along with the unperturbed microstructure and B2 displays those at maximum elongation ($\varepsilon = 10.31$). Here, the blue diamonds represent the covalent bonds between AAc-MAM (light blue chains) and PPGDA (yellow chains), and the orange circles the PPGDA aggregates. We hypothesize that the small deformation stretches the hydrophilic chains while the large deformations dissociate the hydrophobic aggregates.

Figure 3.2 on page 61C displays the tensile modulus ($E$) of all gels estimated using low $\varepsilon$ values ($0 \leq \varepsilon < 0.3$) by fitting the $\sigma - \varepsilon$ curves with the neo-Hookean model for uniaxial loading. Higher PPGDA concentrations lead to an increase of $E$ as expected. The maximum $E$ value of $\approx 143.4$ kPa was reached by the 3%-Gel and the minimum value of $\approx 68.4$ kPa by the 0.1%-Gel. It appears that the low strain modulus is weakly affected by an increase in PPGDA concentration by 30 times. As discussed before, the low-strain response is essentially affected by the density of chemically crosslinked PAAc and PMAM chains, however, the inhomogeneity with respect to the mesh size as a result of the free-radical reaction may not have a significant contribution from the hydrophobic associations to the low-strain modulus.

Interestingly, the gels with a low PPGDA concentration show a prominent $\dot{\varepsilon}$-dependence of stress response. As observed in figure 3.2 on page 61D, 0.1%-Gel was studied at $\dot{\varepsilon} \approx 0.048$ and 0.48 s$^{-1}$. At low $\varepsilon$-values the gel presents an identical response for both $\dot{\varepsilon}$. However, a distinct behavior can be observed at high $\varepsilon$-values in which the gel displays higher $\sigma$ for a higher
A similar trend can be observed for 0.3%-Gel (figure B.2 on page 159). And as shown in chapter II, 1%-Gel does not display a shift with increasing $\dot{\varepsilon}$. Note that $\dot{\varepsilon}$-dependent response is a characteristic of viscoelastic materials and the pure elastic material is not expected to display a $\dot{\varepsilon}$-dependent modulus, therefore, it can be argued that the presence of fewer PPGDA associations, at low PPGDA concentrations, makes the gels more viscoelastic.

To estimate the resilience of gels, cyclic loading and unloading experiments have been performed in the stress-controlled mode with a step of 10 kPa. The results for 0.3%-Gel are shown in figure 3.2 on page 61E. In these experiments, $\dot{\varepsilon} \approx 0.048$ has been used for both loading and unloading of samples. Note that the loading-unloading cycles follows the stress-strain relationship obtained from the tensile experiments (figure 3.2 on page 61A) for the stress applied up to 40 kPa. With increasing stress, stiffening behavior at lower strain values was observed. The cycles for 0.1%- and 1%-Gel are also shown in figure B.3 on page 160. The highest resilience displayed by the 0.1%, 0.3%, and 1%-Gels are $\approx 65\%$, $93\%$, and $98\%$, respectively, corresponding to the maximum $\sigma$ sustained by the gel. The resilience of each gel decreases for lower $\sigma$. The maximum stress sustained by the gel, and corresponding residual strain and resilience for 0.1%, 0.3%, and 1%-Gels are indicated in table 3.1 on the following page. As observed, the residual strain at maximum stress for 0.1%, 0.3%, and 1%-Gels is $\approx 15\%$, $2\%$, and $2\%$, respectively (see table 3.1 on the next page). Note that higher resilience and lower residual strain are displayed by gels with higher PPGDA concentrations. Higher content of PPGDA increases the elastic response of gel due to its hydrophobic nature.

The swelling capacity of the gels was calculated with respect to the dry weight of gels. figure 3.3 on page 62A displays the swelling capacity of 0.1%- and 0.3%-Gels as a function of time. The
Table 3.1

Resilience of gels. Maximum stress, residual strain, and resilience values for 0.1%-Gel, 0.3%-Gel, and 1%-Gel corresponding to the highest stress cycle applied during cyclic-loading experiments.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Maximum stress [kPa]</th>
<th>Residual strain [%]</th>
<th>Resilience [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1%-Gel</td>
<td>40</td>
<td>14.5</td>
<td>64.9</td>
</tr>
<tr>
<td>0.3%-Gel</td>
<td>80</td>
<td>1.7</td>
<td>92.5</td>
</tr>
<tr>
<td>1%-Gel</td>
<td>130</td>
<td>2.1</td>
<td>97.7</td>
</tr>
</tbody>
</table>

Swelling capacity of dried gels displays a slight difference. Note that the initial water content of the gels was 56.3% for 0.1%-Gel and 58.8% for 0.3%-Gel. With the time elapse, the swelling capacity seems to reach a plateau, therefore, fresh water was used after 96 h to measure any further swelling of gels. A sudden increase in the water swelling capability of gels can be observed. After 144 hr of observation time, the swelling capacity in water of 0.1%- and 0.3%-Gels was ≈6000 and 12000%, respectively.

Figure 3.3 on page 62B represents the swelling capacity of 0.1%- and 0.3%-Gels in NaCl solution of 0.2 M, 0.4 M, and 0.8 M. With a lower salinity of the immersion solution, from 0.8 M to 0.4 M and 0.2 M, the swelling capacity gradually increases independently of the PPGDA concentration. Note that at NaCl 0.8 M, which is the same saline concentration used as a solvent for the synthesis of the gels, the swelling remains constant with time and does not significantly change, even with a fresh immersing solution. These experiments indicate that the swelling in these gels is driven by the migration of NaCl from the gel to the solution in which they are immersed. A lower NaCl concentration in the gels, resultant of greater migration of salt to the immersion solutions with higher water content, weakens the shielding of anionic AAc-chains. As a result, the
AAc-chains experience repulsion from each other and enable the network to accommodate more water increasing their swelling capability. Also, the PPGDA concentration increases the swelling capability of the gels. A future study of the effect of PPGDA molecular weight on the mechanical properties of these gels and the conformation of the network is required.

A visual analysis of swelling in different solutions can be made in figure 3.3 on page 62C-D for 0.1%- and 0.3%-Gels. The as-synthesized gels (figure 3.3 on page 62C1-D1) have an opaque color, which after drying for \(\approx 216\) h changes to a slight yellow (figure 3.3 on page 62C2-D2) and returns to an opaque color after swelling in saline solutions (figure 3.3 on page 62C3-D3). Note that the dried gels immersed in NaCl 0.8 M absorb less water than that present in the as-prepared gels. Particularly, the water content in as-synthesized gels was \(\approx 60\) wt\%, and during swelling they absorb \(\approx 50\) wt\% water while maintaining a yellowish color. However, when the gels are immersed in pure water, they turn into translucent gels in the first hours. Also, after 144 h, 0.3%-Gel turns into a transparent gel, but 0.1%-Gel still has some translucent portions (figure B.4 on page 161).

### 3.4 Conclusions

The present work elucidates the role played by PPGDA concentration on the mechanical responses of gels. A higher PPGDA concentration leads to a slight increase in low-strain modulus but a significant increase in high-strain modulus. The gel with a higher PPGDA concentration is found to have lower stretchability and high ultimate stress. The gel with lower PPGDA concentration displays \(\varepsilon\)-dependent stress responses indicating that the PPGDA increases the elasticity of the gel. This is elucidated through the cyclic loading-unloading responses where the gels with high PPGDA concentration display lower residual strain and higher resilience. The swelling capacity of the dried
gels in water is slightly affected by the PPGDA concentration, but the change in swelling capacity is not significant in saline solutions. Essentially, the swelling phenomenon in these gels is dictated by the NaCl migration from the bulk of the gel outwards to the immersion solution, resulting in a higher swelling of gels in pure water than in saline solutions.
Shear-rheological results of gels. (A) *In situ* gelation of samples displaying storage modulus ($G'$) and loss modulus ($G''$) as a function of time for 0.1%- and 0.3%-Gels using strain amplitude ($\gamma_{amp}$) of 0.001 and frequency oscillation ($\omega$) of 0.5 rad s$^{-1}$ at a temperature ($T$) of 75 °C. The inset image shows the 0.1%-Gel formed and the custom-built solvent trap geometry with the Fomblin Y bath. (B) Frequency sweep results for 0.1%- and 0.3%-Gels displaying $G'$ and $G''$ as a function of $\omega$ using $\gamma_{amp}$=0.001 at RT. (C) Temperature sweep results for 0.3%-Gel with cooling (22-4 °C) and heating (4-80 °C) cycles representing moduli as a function of temperature using $\gamma_{amp}$=0.001 and $\omega$=0.5 rad s$^{-1}$. 

Figure 3.1
Figure 3.2

Tensile and cyclic loading results. (A) PPGDA-concentration effect for the tensile experiment. The graph displays the nominal stress ($\sigma$) as a function of strain ($\varepsilon$) for 0.1%-Gel, 0.3%-Gel, 1%-Gel, and 3%-Gel. Images and microstructure scheme of the tensile experiment for 0.1%-Gel at (B1) $\varepsilon=0$ and at (B2) $\varepsilon=10.31$. (C) $\sigma - \varepsilon$ curves for 0.1%-Gel, 0.3%-Gel, 1%-Gel, and 3%-Gel fitted with the neo-Hookean model for uniaxial loading at low strain ($0 \leq \varepsilon < 0.3$). The respective tensile modulus ($E$) values for the gels have been estimated as $\approx 68.4$, $88.7$, $103.1$, and $143.4$ kPa. (D) Strain-rate ($\dot{\varepsilon}$) effect for 0.1%-Gel. The graph displays $\sigma - \varepsilon$ curves for $\dot{\varepsilon} \approx 0.048$ and $0.48$ s$^{-1}$. (E) Cyclic loading data for 0.3%-Gel. The graph shows the cyclic loading curves along with the tensile curve for comparison. In all graphs, the error bars, smaller than the symbols in some cases, represent the standard deviation.
Swelling capacity of gels in water and saline solutions. (A) Swelling capacity of 0.1%- and 0.3%-Gels in pure water as a function of time. (B) Swelling capacity of 0.1%- and 0.3%-Gels in NaCl solutions at 0.2 M, 0.4 M, and 0.8 M as a function of time. After 96 h, all the immersion fluids were changed for fresh ones and changed again after 24 h. Images of the (C) 0.1%-Gel and (D) 0.3%-Gel for the samples (-1) as-synthesized, (-2) after drying for 216 h, and (-3) after swelling for 24 h.
CHAPTER IV

CAPTURING THE TRANSIENT MICROSTRUCTURE OF A PHYSICALLY ASSEMBLED GEL SUBJECTED TO TEMPERATURE AND LARGE DEFORMATIONS

4.1 Introduction

ABA triblock copolymer gels in B-selective solvents are a class of gels that have garnered significant research interests over the last few decades [66, 126, 27, 106, 109, 82, 83, 81]. These gels have been investigated for their potential applications in various areas ranging from biomedical fields as wound dressing [75], protein carriers [16], and drug delivery [129, 147], to ballistics [86], microfluidic devices [118], and soft robotics [123, 4]. These gels are significantly different than chemically crosslinked gels [134, 4], and the underlying principle of gelation in these gels is the strong temperature-dependent solubility of the A-blocks (endblock) in the chosen solvent, in comparison to the very small change of solubility of the B-blocks (midblock) with temperature. At higher temperatures, both A- and B-blocks are soluble in the solvent, however, the A-block’s solubility becomes poor with the decrease of temperature. This causes the aggregation of a few A-blocks at low temperatures, forming physically associated crosslinks (aggregates) bridged by B-blocks. The B-blocks remain soluble in the solvent and act as load-bearing chains. This process leads to the formation of a physically assembled triblock copolymer gel. The gels investigated in this study consist of poly(styrene)-poly(isoprene)-poly(styrene) [PS-PI-PS] in mineral oil. Here, the PS-blocks form the aggregates, and these are connected by load-bearing bridges of PI-blocks
Due to the temperature-dependent solubility of A- and B-blocks, these gels are thermoreversible, and become a polymer solution (sol) at higher temperatures and a soft elastic solid (gel) at lower temperatures.

Previously, there has been a significant effort to understand the effect of polymer volume fraction (\(\phi\)) [106, 149, 83], temperature [106, 149], block lengths [10, 83, 20, 19, 86], endblock homopolymer addition [109], and solvent [148] on the physical properties of triblock copolymer gels, such as gelation behavior, critical gelation concentration, stress-relaxation, moduli, and rate-dependent responses. However, most of these properties were realized through macroscopic experimental observations, and the relationships between their mechanical properties and the microstructure are not well established.

Small-angle neutron/X-ray (SANS/SAXS) scattering has been used to understand the change in ABA gel microstructure while varying the \(\phi\) [66, 106], endblock and midblock lengths [106, 83], and temperature [106, 149], but mostly at the static condition. In those studies, structural information obtained from the scattering data at the static condition has been used to explain the gel responses subjected to mechanical deformation, leaving a gap between the theoretical understanding, prediction, and the experimental observations. For example, the characteristic time-scale for stress-relaxation in these gels determined from rheological experiments has been linked to the endblocks pullout from the aggregates and their reassociation with other aggregates [126, 56, 106, 31, 149, 95, 82, 83]. However, no information is available regarding the time scale associated with complete microstructure recovery. Therefore, real-time observation of the change in gel microstructure subjected to a mechanical deformation can provide further understanding.
regarding the microstructure-dependent mechanical properties of these gels, including structural reorganization during the relaxation process.

Such investigation requires real-time data collection using SAXS/SANS techniques while the gel is subjected to mechanical loading. However, these experiments possess two main challenges. The first challenge is the requirement of a fast data collection necessary to capture the microstructure at any particular stress or strain value. This can be overcome by using a high flux beam typical to a synchrotron. The second challenge is the availability of an instrument that allows the data collection along the appropriate plane. There are many reports in the literature to elucidate the real-time microstructural change during processing, and subjected to flow, mechanical loading, and magnetic field on polymers [85, 41, 133, 23, 14, 114, 145], complex fluids [77, 87], protein gels [111], and wormlike micelles [73, 72]. In these studies, interesting microstructure development such as shear-rate dependent orientation development has been reported. Such investigations for ABA gels are limited, as the previous investigations on acrylic gels formed by poly(methyl methacrylate)–poly(n-butyl acrylate)–poly(methyl methacrylate) [PMMA–PnBA–PMMA] in 2-ethyl-1-hexanol and n-butanol capture the microstructure only at the static condition [148, 108, 83].

For high modulus polymers and elastomers, it is possible to capture the real-time microstructural change as a function of uniaxial strain typically achieved in tensile testing [23, 132]. However, there are significant challenges to capture the real-time microstructure data during the tensile test of physically assembled gels. Particularly, because of their lower modulus, it is difficult to hold these samples in a tensile testing instrument. Also, the samples can undergo creep during the tests [82, 83]. Alternatively, the change in the gel microstructure subjected to mechanical deformation can be investigated in a shear-stage, where the scattering data collection is in the x-y
plane while the beam is in the z-direction. Here "x" represents the flow/stretch direction ($v$), "y" denotes velocity gradient ($\nabla v$), and "z" denotes the vorticity direction ($v \times \nabla v$). Using this setup, microstructural information in the stretch, or flow direction, and orthogonal to that, i.e., in the flow-gradient direction can be collected. This setup has been recently utilized to investigate the structural change in associative protein gels subjected to thermal load, oscillatory deformation, and during stress-relaxation [111]. Such a setup has also been utilized in our investigation.

The present work focuses on the real-time investigation of transient microstructural change in physically assembled gels as a function of temperature, oscillatory strain, and during stress-relaxation. We have explored such transient microstructural changes in 10 wt% and 20 wt% of PS-PI-PS triblock copolymer dissolved in mineral oil, referred to as 10%-Gel and 20%-Gel, respectively. The PI-block molecular weight is higher than its entanglement molecular weight ($\approx 6.4 \text{ kg/mol}$), leading to a slight entanglement of PI-blocks in 20%-Gel. We have used both the RheoSAXS and shear-rheology techniques in parallel to relate the microstructural change with the applied load since our RheoSAXS setup cannot measure the stress [14, 111]. The RheoSAXS data was collected in the x-y plane, which provided a unique insight regarding the gel microstructure, particularly during large amplitude oscillatory strain (LAOS), where the structure changes reversibly in a strain-cycle.

4.2 Experiment Details
4.2.1 Materials

Kraton D1164 is a poly(styrene)-poly(isoprene)-poly(styrene) [PS-PI-PS] triblock copolymer, kindly provided by Kraton Inc. Klearol white mineral oil (kindly provided by Sonneborn Inc.) was the solvent used for the gel preparation [82, 83, 81]. The number-average ($M_n$) and weight-
average ($M_w$) molecular weight of D1164 polymer are $\approx 112$ kg/mol and $\approx 125$ kg/mol, respectively, estimated based on the polystyrene standard \cite{82, 83, 81}. The polymer has 29 wt\% of PS and 71 wt\% of PI, as indicated by the manufacturer. The estimated $M_n$ of the PS-block is $\approx 16.2$ kg/mol, and that of the PI-block is $\approx 79.4$ kg/mol.

4.2.2 Sample preparation

The samples were prepared by adding the desired amount of D1164 polymer in white mineral oil and mixing at 120 °C by using a magnetic stirrer at 320 rpm. The polymer solutions were placed in a convective oven at 120 °C for 6 hrs, allowing the bubbles to escape, leading to clear solutions. Gels were obtained by cooling these solutions. We have considered two gels with 10 wt\% and 20 wt\% concentrations of D1164 polymer, corresponding to the polymer volume fractions ($\phi$) of 0.089 and 0.181 \cite{82, 83}, respectively. These gels are referred to as 10\%-Gel and 20\%-Gel throughout this article. Table C.1 on page 164 summarizes the polymer weight and volume fractions and the PS and PI weight fractions in each gel.

4.2.3 Shear-rheology experiments

For the shear-rheology experiments, the polymer solution was poured in a rectangular mold of 2 mm thickness and was allowed to cool for $\approx 30$ min through natural cooling, obtaining gel sheets. Square-shaped specimens (30 mm×30 mm) were cut from the gel sheets for individual rheology experiments. A TA Instruments Discovery HR-2 hybrid rheometer equipped with a Peltier plate was used. The experiments were conducted using a 25 mm parallel plate geometry with a gap of 1 mm. 240 grit adhesive-backed silicon carbide sandpaper (Allied High Tech Products Inc.) was attached to the top and bottom plates to avoid possible slippage of samples on the rheometer.
4.2.4 RheoSAXS experiments

The rheology experiments in conjunction with the small-angle X-ray scattering (RheoSAXS) experiments were conducted for the 10%- and 20%-Gels on the DND-CAT beamline of the Advanced Photon Source at Argonne National Lab (ANL, Chicago, IL). The source of X-ray had a wavelength of 0.7293 Å (energy=17 keV). A custom-built shear-stage equipped with an annular cone and plate geometry was used (figure 4.1) [14, 111]. The top geometry (cone) had a cone angle of 5°. The annular bottom plate had an inner diameter of 30 mm and an outer diameter of
50 mm. A 1 mm diameter pinhole (beam path) drilled through the bottom plate of the shear-stage at an angle of 2.5°, allowed the X-ray beam to pass through the sample (figure 4.1 on the previous page). This bottom plate was equipped with a thermocouple. The samples were loaded in the sol state at ≈80 °C and 100 °C for the 10%- and 20%-Gel, respectively. For the experiments at room temperature, the samples were cooled down to room temperature (≈27 °C) by blowing air on the samples for ≈30 minutes to ensure their thermal equilibrium. The shear-stage was then tilted by 2.5° from its horizontal axis to align the beam-path for capturing the scattering data at the flow-vorticity plane [14, 15, 111]. For the experiments where the scattering data were collected as a function of temperature, the samples were loaded in a liquid state and allowed to cool down before the stage was tilted. In these cases, the sample was allowed to cool naturally without blowing air onto the sample. However, for the experiments performed at higher temperatures than room temperature, like the stress-relaxation experiments at 40 °C, the samples were brought down to experimental temperature by blowing air. A minimum waiting time of 15 min was allowed at the experimental temperature to attain thermal and structural equilibrium. Unless there was a macroscopic fracture, the same sample was used for multiple rheology experiments. However, after each experiment, the samples were heated to the sol state to erase the strain history. If the sample fractured during the test, a fresh sample was loaded using the same procedure discussed above.

The scattering data were collected for 10%- and 20%-Gels in three sets of experiments viz. (1) temperature sweep without any applied strain as the gelation of the sample was taking place, (2) oscillatory shear experiments with strain amplitudes ($\gamma_{amp}$) of 0.1 and 1, using a frequency ($\omega$) of 1 rad/s at different temperatures, and (3) stress-relaxation experiments at different temperatures after the application of a step shear strain ($\gamma_{step}$) of 0.3. The two-dimensional (2D) scattering
patterns were collected using a CCD detector. Igor Pro Nika package was used for data reduction from the 2D-scattering profiles to 1D intensity ($I(q)$) versus scattering vector ($q$) plots [53]. A custom-built NCNR macro was used to fit the data with a polydispersed core hard-sphere model and its modified form [61]. Custom-built programs in MATLAB were also implemented to generate the azimuthal scans over a particular $q$-range and to estimate anisotropy [14, 111].

4.3 Results and Discussion
4.3.1 Effect of Temperature on the Gel Microstructure

The gelation temperature ($T_{gel}$) and moduli of the gels were captured by using shear-rheology experiments performed with an oscillation frequency ($\omega$) of 1 rad/s and strain amplitude ($\gamma_{amp}$) of 0.01 over the temperature ($T$) range of 80-20 °C and of 100-20 °C for the 10%- and the 20%-Gels, respectively. Correspondingly, to capture the evolution of the gel microstructure with decreasing temperature, RheoSAXS experiments were performed over $\approx$80 to 27 °C for the 10%-Gel, and from $\approx$120 to 27 °C for the 20%-Gel. Note that the RheoSAXS setup cannot measure the stress, therefore, the change in microstructure observed in the RheoSAXS experiments has been related to the data obtained from the shear-rheology experiments.

Figure 4.2 on page 89A displays the evolution of storage ($G'$) and loss ($G''$) moduli for 10%- and 20%-Gels as a function of temperature. At high temperatures, both gels behave like a viscous liquid (sol-state) as $G''$ is higher than $G'$. An increase in $G'$ and $G''$ with the decrease of temperature indicates the formation of a network structure in these samples. At further lower temperature, a crossover of $G'$ and $G''$ is observed, which can be identified as the gelation temperature ($T_{gel}$) corresponding to $\omega$=1 rad/s. The $T_{gel}$ has been found to be $\approx$63 °C for 10%-Gel and $\approx$85 °C for
20%-Gel, respectively. For \( T \leq 45 ^\circ C \), \( G' \) reaches a plateau with the values of 2.9 and 11.1 kPa for 10%- and 20%-Gels, respectively.

As discussed above, both PS- and PI-blocks’ good solubility at high temperatures leads to a viscous solution. At low temperatures, the polymer network is formed because of physically associated PS-blocks connected by PI-blocks [126, 66, 82, 83, 81]. A plateau in \( G' \) for both gels indicates the completion of network formation, and the microstructure is not expected to change significantly with the change of temperature in that region. A higher number of load-bearing chains in 20%-Gel as a result of higher polymer concentration leads to a higher \( G' \) value than that for 10%-Gel. Also, the higher number of chains facilitates the network formation at a relatively higher temperature, therefore the 20%-Gel has higher \( T_{gel} \).

\( T_{gel} \) determined by shear-rheology generally varies with the applied frequency (\( \omega \)), therefore, the Winter-Chambon criterion is commonly implemented to identify the true gelation temperature [135, 113, 146]. We have shown earlier that this gel does not follow the Winter-Chambon criterion, similar to a few other physically assembled gels [104, 141, 81]. It has been shown that for 10%-Gel, the \( G' \) and \( G'' \) crossover shifts by \( \approx 20 ^\circ C \) as \( \omega \) increases from 0.1 to 100 rad/s [81]. Therefore, the \( T_{gel} \) indicated here can be considered as the apparent gelation temperature, which is expected to change with applied \( \omega \). Note that the \( T_{gel} \)'s are sufficiently higher than the room temperature, therefore, the microstructure formation at room temperature is expected to be complete.

For capturing the change in gel microstructure using RheoSAXS, the samples were heated sufficiently above their \( T_{gel} \) and allowed to cool to 27 \( ^\circ C \) by natural convection (\( \approx 20 \) min). Particularly, the 10%-Gel sample was heated to 80 \( ^\circ C \) and the 20%-Gel to 120 \( ^\circ C \) and were thermally equilibrated for \( \approx 3 \) min at those temperatures. During cooling, the scattering data were collected
at every 5 °C of temperature drop with an exposure time of 0.03 s. As the sample was cooling continuously, there was a possibility of a small temperature gradient within the sample during the data collection. Figure 4.2 on page 89B and C represent the circular averaged intensity \( I(q) \) as a function of scattering vector \( (q) \) for the 10%- and 20%-Gels at different temperature. The 2D-scattering patterns presented in figure 4.2 on page 89D display a circular pattern indicating the isotropic gel microstructure without any applied strain (i.e., static condition). Note that the elongated circle near the beam center captures the low-\( q \) region (<0.0002 Å\(^{-1}\)) and is mostly an experimental artifact that has not been considered for the analysis.

For both gels, a decrease in \( T \) causes the evolution of the microstructure, which is manifested by increased intensity and narrowing of the peak at \( q \approx 0.02 \) Å\(^{-1}\). Development of a weak shoulder at \( q \approx 0.03 \) Å\(^{-1}\) is also observed. This shoulder corresponds to a low-intensity circle in the 2D-scattering profiles (figure 4.2 on page 89D1-D2). The peak at \( q \approx 0.02 \) Å\(^{-1}\) is related to the structure factor (Bragg peak) capturing inter-aggregate scattering, and the shoulder at \( q \approx 0.03 \) Å\(^{-1}\) corresponds to the form factor of spherical PS-aggregates [82, 83]. At \( T < 45 °C \), the scattering profiles overlap and those do not change significantly with a further reduction in \( T \) (figure 4.2 on page 89B-C insets) indicating a developed microstructure, which is also evident from the plateau in \( G' \) (figure 4.2 on page 89A). The peaks beyond \( q \approx 0.05 \) Å\(^{-1}\) are secondary reflections of the form factor [80]. Interestingly, the Bragg peak at \( q \approx 0.02 \) Å\(^{-1}\) and a weak shoulder at \( q \approx 0.03 \) Å\(^{-1}\) are also observed at \( T \geq T_{gel} \) for both gels, although at a lower intensity than that observed below \( T_{gel} \) (see figure 4.2 on page 89B). The initiation of the aggregate formation above the \( T_{gel} \) supports the argument that the shear-rheology experiments capture an apparent gelation temperature. Also, gelation does not occur at a single temperature but takes place over a temperature range. A similar
evolution of the structure and form factors with temperature had also been captured for acrylic gels [106, 148]. For the PS-PI-PS gels, $I(q) \propto q^{-3.2}$ over $0.0002 < q < 0.01$ Å$^{-1}$ at all temperatures signifies a rough surface fractal similar to that observed for acrylic gels [148].

A polydispersed core hard-sphere model with Percus-Yevick closure has been used to fit the scattering data for the $q$-range of $0.01 \leq q \leq 0.050$ Å$^{-1}$ [106, 148, 82, 83]. Mathematically, this model is expressed as, $I(q) \propto P(q)S_1(q)$, where $P(q)$ represents the spherical form factor and $S_1(q)$ the structure factor. As shown schematically in figure C.1 on page 165, the PS aggregates are represented by cores with mean radius $r_c$ and polydispersity $\sigma/r_c$, where $\sigma$ is the standard deviation of $r_c$ [106, 148, 82, 83, 81]. These aggregates are surrounded by a fictitious hard sphere with an average thickness $s_1$ and a volume fraction $\psi_1$. Considering that every hard-sphere is contained in a fictitious cube with a dimension $D$ (see figure C.1 on page 165), the inter-aggregate distance can be estimated as, $D_1 = (4\pi(r_c + s_1)^3/(3\psi_1))^{1/3}$ [106]. After subtracting the background, the features for $q > 0.050$ Å$^{-1}$ and $q < 0.01$ Å$^{-1}$ are not very discernible and have not been considered here for further analysis.

figure 4.3 on page 90A compares the scattering profiles for the 10%- and 20%-Gels at 27 °C. The solid lines represent the model fit, which captures the data reasonably well. Note that the structure factor peak for 10%-Gel is at slightly lower $q$ than that for 20%-Gel, indicating a higher inter-aggregate distance. The fitted parameters at different temperatures for both gels are shown in figure 4.3 on page 90B1-B2. These values are typical of the physically assembled gels in midblock-selective solvents [66, 126, 106, 148, 82, 83, 81]. For both gels, $r_c$, $s_1$, and $\psi_1$ gradually increase with decreasing $T$. For 10%-Gel, $r_c$ remains almost constant ($\approx 8.6$ nm), $s_1$ increases from 9.1 to 10.5 nm, and $\psi_1$ increases from 0.4 to 0.44 as $T$ decreases from 80 to 27 °C. Similarly, for 20% gel,
$r_c$ increases from 7.1 nm to 8.6 nm, $s_1$ increases from 6.8 to 9.2 nm, and $\psi_1$ increases from 0.29 to 0.50 while decreasing $T$ from 120 to 27 °C. For both gels, the microstructure evolves and moduli increase with decreasing temperature, but the microstructural change is not significant once the $G'$ of these gels attains a plateau (compare figure 4.2 on page 89A and figure 4.3 on page 90B1-B2).

With decreasing $T$, the PS-aggregates expel the solvent [27, 106], and this process can lead to the decrease of the aggregates radii. However, our data suggest that $r_c$ increases slightly, especially in 20%-Gel. It can be hypothesized that at higher $T$, the PS-blocks loosely associate to form smaller aggregates. Also, dangling PS-chains that are not connected to any aggregate also exist (figure 4.3 on page 90C). This is also evident from not so well-developed form factor shoulders (weaker intensity) in figure 4.2 on page 89B-C. With the decrease in $T$, those non-connected PS-blocks merge in the existing bigger aggregates leading to an increase of $r_c$. The space between two aggregates also increases slightly to accommodate the PI chains, leading to an increase in $s_1$.

In addition to the density of midblocks acting as bridges, the midblock stretch also contributes to the small strain modulus of the gels [106, 83]. The length of PI-block in the gels can be theoretically estimated by considering the mineral oil as a $\theta$-solvent at 27 °C [82, 83]. The end-to-end distance of a PI-block in $\theta$-solvent can be calculated as, $R_{e,PI} = b\sqrt{N} \approx 21.6$ nm, where $b$ (≈0.84 nm) and $N$ (≈662) are the length and number of Kuhn segments per PI-block, respectively [101, 82, 83]. We estimate the stretch ratio, $(D_1 - 2r_c)/R_{e,PI}$, for the 10%- and 20%-Gel as ≈1.08 and 0.88, respectively. This suggests the PI-blocks are slightly stretched in 10%-Gel. In reality, mineral oil is a good solvent to the PI-blocks, and that can lead to a higher value of $R_{e,PI}$ [66], therefore, the PI-blocks in 10%-Gel are not stretched as predicted for $\theta$-solvent. Similarly, the PI-blocks in
20%-Gel are expected to be more compressed in mineral oil. The compressed chains signify that the gels can achieve a higher stretch ratio before failure [82, 83].

4.3.2 Microstructure Change with Oscillatory Shear

The effect of shear deformation on the gel microstructure was explored using oscillatory shear experiments. Figure 4.4 on page 91A displays $G'$ and $G''$ for 10%- and 20%-Gels obtained from amplitude sweep experiments at 27 °C. The strain-amplitude ($\gamma_{amp}$) was varied over the range of $10^{-4}$ to 1 using $\omega$ of 1 rad/s. Over this range, the gel samples did not fail, and no noticeable change in $G'$ and $G''$ was observed. The stress-controlled rheometer used in this study could not correct the phase-angle accurately beyond $\gamma_{amp} > 1$, thus, those data have not been considered here.

In RheoSAXS experiments, the 10%-Gel was subjected to oscillatory strain-amplitude of $\gamma_{amp}=0.1$ at 27 °C, and $\gamma_{amp}=1$ at 27 °C and 40 °C, respectively. Similarly, the 20%-Gel was subjected to $\gamma_{amp}=0.1$ and 1 at 27 °C. All these experiments were conducted using $\omega=1$ rad/s. For the experiments at 27 °C, three cycles with $\gamma_{amp}=0.1$ were applied, followed by three cycles with $\gamma_{amp}=1$. The scattering data were collected during three oscillatory cycles with an exposure time of 0.03 and 0.05 s for the 10%- and the 20%-Gel, respectively. With such a short exposure time, we estimate a maximum $\approx 5\%$ change in intracycle strain value while collecting the data. The time interval between two data points was 0.157 s, resulting in $\approx 40$ data points over a strain cycle. Figure 4.4 on page 91B represents a strain cycle for $\gamma_{amp}=1$ in which thirteen representative intracycle strain values ($\gamma_1 - \gamma_{13}$) are selected. The 2D-scattering patterns corresponding to these strain values for 10%- and 20%-Gels are displayed in figure 4.4 on page 91C and D. The inset in
A strain-cycle can be divided into four quarters, for $\gamma = 0$ to $+1$, $+1$ to $0$, $0$ to $-1$, and $-1$ to $0$. For both gels, at $\gamma_1 = 0$, the scattering pattern is circular, indicating isotropic gel microstructure at the static condition (figure 4.4 on page 91C and D) [106, 148, 82, 83]. For 10%-Gel, in the first quarter, as the strain increases, the circular pattern transforms to an elliptical pattern having clear major and minor axes (for example, $\gamma_2 = 0.31$). The elliptical pattern splits into two parts, elliptical and circular patterns, with increasing strain, as presented for $\gamma_3 = 0.71$. The circular pattern has the same radius as that obtained for $\gamma_1 = 0$. With increasing strain to $\gamma_4 = 1$, the split becomes more prominent. Interestingly, the $q$-value corresponding to the intersection of circular and elliptical profiles displays higher intensity relative to the other $q$-values. This intensity is similar to that observed for all $q$-values at $\gamma_1$.

In the second quarter, as the strain values decrease to 0, the split pattern transforms to a purely elliptical pattern and then to a circular pattern at $\gamma_7 = 0$. In the 3rd quarter, the scattering pattern resembles that of the 1st quarter, however, the angle of orientation of the elliptical pattern changes because of the change in applied strain direction in an oscillatory cycle. Further, the data for the 2nd and 4th quarters are similar. Note that scattering patterns for $\gamma = 0.31$ in the 1st and 2nd quarters, i.e., for $\gamma_2$ and $\gamma_6$, are slightly different. We attribute that to the slight hysteresis in the strain cycle (figure 4.4 on page 91B inset). Note that for the same stress values ($\approx 6.7$ kPa) there are two different $\gamma$ values ($\approx 0.71$ and $\approx 0.75$), which may have affected the symmetry of the 2D-scattering pattern with respect to $\gamma$. For 20%-Gel, the strain-dependent scattering profiles are very similar to those of 10%-Gel, except that the split elliptical pattern is more prominent in 10%-Gel (figure 4.4
on page 91D). 2D-scattering profiles are also represented for both gels for $\gamma_{amp}=0.1$ in figure C.2 on page 166. For this strain value, no split in 2D-pattern is observed.

Figure 4.5 on page 92A1-A3 displays the 2D-scattering patterns for 10%-Gel at the intracycle strain of $\gamma=0$, +1, and -1. $I(q)$ vs. $q$ for different $\beta$ values have been plotted by averaging $I(q)$ over $\beta\pm5$° sector (figure 4.5 on page 92B-D). Here, $\beta$ corresponds to the angle measured from the $q_x$-axis or flow direction (figure 4.5 on page 92A). As shown in figure 4.5 on page 92B, the scattering profiles at $\beta \approx 95^\circ$ and $155^\circ$ for $\gamma=+1$, at $\beta \approx 30^\circ$ and $85^\circ$ for $\gamma=-1$, and at $\beta \approx 0^\circ$ and $90^\circ$ for $\gamma=0$ overlap. For $\gamma = \pm 1$, these $\beta$ values represent the intersection between elliptical and circular patterns. Along the minor-axis of the elliptical pattern, i.e., the scattering profiles at $\beta \approx 35^\circ$ for $\gamma=+1$ (figure 4.5 on page 92A2) and at $\beta \approx 145^\circ$ for $\gamma=-1$ (figure 4.5 on page 92A3) overlap, as shown in figure 4.5 on page 92C. Similarly, as presented in figure 4.5 on page 92D, the scattering profiles along the major-axis of the elliptical pattern, i.e., at $\beta \approx 125^\circ$ for $\gamma=+1$ (figure 4.5 on page 92A2), and at $\beta \approx 55^\circ$ for $\gamma=-1$ (figure 4.5 on page 92A3) overlap.

The $I(q) - q$ plots along the minor-axis of the ellipse for $\gamma = \pm 1$ display an additional peak at $q \approx 0.01$ Å$^{-1}$ (figure 4.5 on page 92C) compared to that for $\gamma=0$. Also, a slight decrease in the intensity of the peak at $q \approx 0.017$ Å$^{-1}$ can be noticed. A similar comparison between the $I(q) - q$ plots along the major-axis of the ellipse for $\gamma = \pm 1$, and that for $\gamma=0$ also indicates an additional peak at $q \approx 0.023$ Å$^{-1}$ (figure 4.5 on page 92D). However, this peak is in the vicinity of the form factor shoulder and is not clearly discernible. The decrease in the intensity of the structure factor peak is associated with the emergence of the additional peak signifying the change in inter-aggregate distance for some aggregates. In other words, the additional peak is also a structure factor peak with a different inter-aggregate distance. As shown in figure 4.5 on page 92C-D, both elliptical
and circular patterns are observed at \( \gamma = \pm 1 \). Further, the position and the intensity of the form factor shoulder remain similar for all \( \gamma \) values. The unchanged form factor peak signifies that the aggregates’ shape and size have not changed in the \( \gamma \)-range considered here. Similar behavior has also been observed for the 20%-Gel presented in figure 4.6 on page 93A-D. As shown in figure 4.6 on page 93B-D, at \( \gamma = \pm 1 \) and -1, additional peaks appear at \( q \approx 0.013 \ \text{Å}^{-1} \) and \( q \approx 0.025 \ \text{Å}^{-1} \), respectively. However, these additional peaks are not as prominent as in the case of 10%-Gel.

The overlapping data for \( \gamma = \pm 1 \) shown above indicate that the microstructure change during a strain cycle is independent of \( \gamma \) direction and solely depends on its magnitude (\(|\gamma|\)). Fitting a model to the extra peak of the \( I(q) - q \) data along the minor and major axes of the elliptical pattern can provide additional insights regarding the change in gel microstructure with \( \gamma \). As the aggregates remain the same, the scattering data in figure 4.5 on page 92B and figure 4.6 on page 93B can be fitted with the same polydisperse core hard-sphere model described above for the static samples. A modified form of the polydisperse core hard-sphere model, mathematically expressed as \( I(q) \sim P(q)(S_1(q)+S_2(q)) \) has been used. Here, \( S_1(q) \) represents the structure factor corresponding to the circular pattern (or intersection). \( S_2(q) \) represents the secondary structure factor corresponding to the elliptical pattern capturing the new peak. Note that the form factor \( (P(q)) \) is the same for \( S_1(q) \) and \( S_2(q) \), capturing that the features of the PS-aggregates do not change upon deformation. Note that this model results in two hard-sphere volume fractions, \( \psi_1 \) and \( \psi_2 \), because of the change in the inter-aggregate distance.

The model fittings are shown in figure 4.5 on page 92B-D and figure 4.6 on page 93B-D for 10%- and 20%-Gels, respectively, and the fitted parameters are presented in table 4.1 on the following page. The \( r_e \) values for 10%- and 20%-Gels in figure 4.5 on page 92B and figure 4.6
Table 4.1

Parameters obtained from fitting scattering data to polydispersed core hard-sphere model with Percus-Yevick closure for three different sectors at $\gamma=0$, +1 and -1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sector</th>
<th>$r_c$(nm)</th>
<th>$\sigma/r_0$</th>
<th>$s_1$(nm)</th>
<th>$\psi_1$</th>
<th>$s_2$(nm)</th>
<th>$\psi_2$</th>
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<tr>
<td>10%-Gel</td>
<td>intersection</td>
<td>10.2</td>
<td>0.01</td>
<td>11.0</td>
<td>0.43</td>
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<td>–</td>
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<td>0.48</td>
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<td></td>
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<td>9.6</td>
<td>0.46</td>
<td>–</td>
<td>–</td>
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<tr>
<td></td>
<td>minor-axis</td>
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<td>0.48</td>
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<td>0.19</td>
</tr>
<tr>
<td></td>
<td>major-axis</td>
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<td>9.6</td>
<td>0.47</td>
<td>2.9</td>
<td>0.30</td>
</tr>
</tbody>
</table>

on page 93B are slightly higher than those observed in temperature sweep experiments presented in figure 4.3 on page 90B at 27 °C, however, the change is within the limit of polydispersity ($\sigma/r_c \approx 0.2$). This is possibly due to the different cooling cycles allowed in both experiments.

Here, the samples were cooled by blowing air for $\approx 30$ min while the data related to figure 4.3 on page 90 was collected during natural cooling of the gels ($\approx 20$ min).

For the 10\%-Gel, the inter-aggregate distance ($D_1$) at the static condition ($\gamma=0$) is estimated as $\approx 45.3$ nm. For $|\gamma|=1$, two additional inter-aggregate distances ($D_2$) can be estimated corresponding to the major- and minor-axes. $D_2$ along the minor- and major-axes is expected to capture the inter-aggregate distance for the displaced aggregates because of applied strain (see figure C.3 on page 167). Similar to $D_1$, $D_2$ can be estimated as $(4\pi(r_c+s_2)/(3\psi_2))^{1/3}$ using the fitted parameters $s_2$ and $\psi_2$. We obtain $D_1 \approx 43.6$ nm from the circular profiles which is observed in addition to the elliptical profiles for $|\gamma|=1$, resembling the isotropic case of $\gamma=0$. The $D_2$ values corresponding to the major- and minor-axis are $\approx 33.1$ nm and 72.3 nm, respectively. Similarly, for 20\%-Gel, $D_1$ is $\approx 39.2$ nm, and $D_2$ values are $\approx 53.6$ nm and $\approx 29.4$ nm for the minor- and
major-axes, respectively. The lower and higher $D_2$ values represent the decrease and increase in the inter-aggregate distance, respectively.

With the applied $\gamma$, the inter-aggregate distance (or hard-sphere thickness) increases in the stretch direction. As a result, the inter-aggregate distance in the orthogonal direction decreases. The corresponding stretch or compression ratios can be estimated as $D_2/D_1$. We estimate the stretch and compression ratios are $\approx 1.66$ and $\approx 0.76$ for 10%-Gel, and $\approx 1.38$ and $\approx 0.75$ for 20%-Gel, respectively. The scattering data implies that the compression ratios are similar for these gels, whereas the stretch ratios are slightly different. These ratios can be related to the applied macroscopic deformation. For affine deformation of polymer chains, $\gamma$ can be theoretically related to the uniaxial stretch/compression ratio ($\lambda$) as $\gamma = \lambda - \lambda^{-1}$ [122]. For $\gamma=1$, this relationship provides $\lambda=1.62$ and $-0.62$, where the positive and negative signs indicate stretching and compression, respectively. The theoretical stretch ratio is similar to that obtained from the scattering data for 10%-Gel, but it is slightly higher than that for 20%-Gel. The compression ratios for the gels are slightly higher than that estimated theoretically. For the case of 20%-Gel, a deviation in the stretch ratio than that obtained theoretically can be attributed to the relatively higher inhomogeneity in the microstructure, likely aided by the slightly entangled PI-blocks [82, 83]. In addition, the thermal quenching protocol used here can also cause higher inhomogeneity in the gel microstructure. These local variations in the microstructure can be viewed as defects, which can cause strain localization, as reported for the acrylic gels [33, 32].

In summary, the oscillatory shear-rheology results indicate that the PI chains are stretched in the flow direction and are compressed in the orthogonal direction. The stretch and compression ratios are similar to those predicted theoretically. An oriented microstructure results in an elliptical 2D-
scattering pattern. However, the presence of both elliptical and circular patterns at larger intracycle strain indicates that some of the aggregates have retracted to their unperturbed condition. We hypothesize the strain-localization in these samples [33, 32], where the local strain values can be higher than the macroscopic strain value. Such higher local strain values facilitate the PS-chain pullout from the aggregates. As a result, those aggregates retract to the unstretched condition. It can also be argued that such pullout weakens the non-linear behavior like strain-stiffening responses, which are prominently observed in the acrylic gels [31, 46]. For acrylic gels, these strain-stiffening responses were related to the maximum extensibility of midblocks before being pulled out from the aggregates. Note that we have not observed any clear sign of non-linearity from the rheological responses of the gels investigated here, i.e., the $e_3$ and $v_3$ values are almost zero [35, 52, 46, 110, 63]. Most likely, the PS-blocks are pulled out of the aggregates before maximum stretchability of PI-blocks is reached. However, further investigations are needed to confirm this.

4.3.3 Stress-Relaxation Behavior

The viscoelastic nature of these gels causes stress dissipation when subjected to load. This dissipation process can be quantified through stress-relaxation experiments. In these experiments, a step shear strain ($\gamma_{step}$) was applied on the gels, and the samples were then allowed to relax. The time-dependent stress decay ($\sigma(t)$) was recorded during the relaxation process and the corresponding time-dependent shear modulus ($G(t)$) can be estimated as $\sigma(t)/\gamma_{step}$. The corresponding change in microstructure was investigated from RheoSAXS experiments. Figure 4.7 on page 94A1 represents the stress-relaxation behavior of a 10%-Gel at 40 °C over 600 s for $\gamma_{step} = 0.3$. The relaxation behavior for $0.1 \leq t \leq 1800$ is shown in figure C.4 on page 168. However, data only up
to 600 s is presented here to compare with the RheoSAXS data. Similarly, for 20%-Gel, $G(t)$ was obtained at 50 and 70 °C (figure 4.7 on page 94B1-C1). Note that for 70 °C, the relaxation process is quite fast, resulting in a steeper decrease of $G(t)$. The experiments were also conducted for both gels at 27 °C where a smooth decay of $G(t)$ is observed (see figure C.5 on page 169). For each case, $G(t)$ reaches a plateau after the relaxation process, indicating an equilibrium modulus. At higher $T$ and lower polymer concentration, a relatively steeper decrease of $G(t)$ has been noticed, followed by a lower equilibrium modulus.

RheoSAXS experiments were conducted at the same temperatures indicated above and $\gamma_{\text{step}}=0.3$ was applied. The scattering data were collected for 600 s with an X-ray exposure time of 0.03 s at an interval of 3 s. 2D-scattering profiles at different time points during the relaxation process are displayed in figure 4.7 on page 94A2-C2. Here, $t_1$ displays the circular pattern at the static condition. At $t_2$, an elliptical pattern is observed representing a stretched or oriented structure as a result of applied $\gamma_{\text{step}}$. figure C.6 on page 170 represents the $I(q) - q$ data before and after the application of strain for 20%-Gel at 50 °C. Here, we have compared the data along major- and minor-axes with that of the static condition. The shifting of structure factor peak to lower-$q$ along the elliptical pattern’s minor axis represents the sample stretch. Similarly, the data along the major-axis signifies the compression of those in the orthogonal direction. The form-factor peak display a slight change in intensity, however, the $q$-position does not change appreciably. Similar to that presented in the previous section, fitting the scattering data with polydispersed core hard-sphere model estimates stretching and compression ratios along with the minor- and major-axes as 1.15 and 0.95, respectively. These values are comparable to the theoretical prediction of 1.16 and 0.86,
respectively. For the 20%-Gel at 70 °C (figure 4.7 on page 94C2-C3), the relaxation process was very fast and the elliptical scattering pattern was captured for only one frame.

An azimuthal plot can be created by plotting average intensity over a specified $q$-range, i.e., $I(\beta)$, for $\beta$ values from 0 to 359° at any particular time point. As defined above, $\beta$ is measured from the flow/stretch direction (figure 4.5 on page 92A and figure 4.6 on page 93A). The average intensity values are estimated by taking an average over the $q$-ranges of $\approx 0.015$-$0.018 \text{ Å}^{-1}$ for 10%-Gel at 40 °C, and $\approx 0.017$-$0.021 \text{ Å}^{-1}$ for 20%-Gel at 50 and 70 °C. Since the form factor peak position and intensity almost remain the same during the relaxation process, the $q$-ranges are chosen to encompass the change in structure-factor peak position. figure 4.7 on page 94A3-C3 displays the time-lapsed azimuthal plots over 600 s. The azimuthal plot captures the peaks corresponding to the oriented elliptical pattern having uneven intensity distribution. These peaks start to fade with time, indicating a restoration of its isotropic microstructure. No significant change in azimuthal plots and 2D-scattering patterns are observed at 27 °C (figure C.5 on page 169) over 600 s indicating a slower microstructural relaxation process.

The degree of microstructure orientation can be quantified by estimating the anisotropic factor ($\Omega$). The $\Omega$ values are displayed in the right axis of figure 4.7 on page 94A1-C1. A point in the 2D-scattering plot can be represented in the form of a unit vector, $\vec{u} = u_x i + u_y j$, where $u_x$ and $u_y$ represent the components of $I(\beta)$ parallel and perpendicular to the flow direction. The $\Omega$ can be mathematically expressed as [64, 51, 14, 111]:

$$\Omega = \left[ \left( \langle u_x^2 \rangle - \langle u_y^2 \rangle \right)^2 + 4\langle u_x u_y \rangle^2 \right]^{1/2}$$ (4.1)
Table 4.2

Parameters obtained by fitting the stretched exponential function to the stress-relaxation and anisotropy factor data for 10%- and 20%-Gels at different temperatures. Here $T$ represents experimental temperature, $\alpha$ stretch parameter, $G_0$ zero-time shear modulus, $\tau_{SR}$ stress-relaxation time, $\Omega_0$ anisotropy at $t \approx 0$, i.e., after the application of strain, and $\tau_\Omega$ microstructure recovery time.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T$ (°C)</th>
<th>$\alpha$</th>
<th>$G_0$ (Pa)</th>
<th>$\tau_{SR}$ (s)</th>
<th>$\Omega_0$</th>
<th>$\tau_\Omega$ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10%-Gel</td>
<td>27</td>
<td>0.30±0.00</td>
<td>3398±5</td>
<td>955±5</td>
<td>0.14±0.00</td>
<td>99928±5320</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>0.30±0.00</td>
<td>3668±4</td>
<td>40.2±0.2</td>
<td>0.17±0.00</td>
<td>38.2±1.0</td>
</tr>
<tr>
<td>20%-Gel</td>
<td>27</td>
<td>0.26±0.00</td>
<td>9714±15</td>
<td>3433±26</td>
<td>0.27±0.00</td>
<td>2.23e6±1.33e5</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.22±0.00</td>
<td>12454±17</td>
<td>6.1±0.1</td>
<td>0.61±0.01</td>
<td>4.6±0.2</td>
</tr>
<tr>
<td></td>
<td>70</td>
<td>0.28±0.00</td>
<td>12780±23</td>
<td>0.18±0.00</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

where $\langle \ldots \rangle$ represents $I(\beta)$ weighted average quantity as,

$$
\langle u^2_2 \rangle = \frac{\int_0^{2\pi} I(\beta) \cos^2 \beta d\beta}{\int_0^{2\pi} I(\beta) d\beta}, \quad \langle u^2_3 \rangle = \frac{\int_0^{2\pi} I(\beta) \sin^2 \beta d\beta}{\int_0^{2\pi} I(\beta) d\beta}, \quad \text{and} \quad \langle u_x u_y \rangle = \frac{\int_0^{2\pi} I(\beta) \cos \beta \sin \beta d\beta}{\int_0^{2\pi} I(\beta) d\beta}
$$

Before the application of strain, $\Omega$ is as low as $\approx 0.020$ for all the cases. The $\Omega$ increases with the application of step strain as the oriented elliptical pattern emerges. At higher $T$, the increase of $\Omega$ is relatively higher (see figure C.5 on page 169A-B). For example, for the 10%-Gel at 40 °C, $\Omega$ jumps from $\approx 0.01$ to 0.1. Such behavior is due to the higher mobility of chains at elevated $T$ facilitating the orientation development. As shown in figure 4.7 on page 94A1-C1, with time $\Omega$ decreases for all cases, a trend similar to $G(t)$. Due to the faster relaxation of 20%-Gel at 70 °C, the $\Omega$ value jumps from 0.041 to 0.010 rapidly.

The relaxation modulus, $G(t)$ can be reasonably captured by a stretched exponential function, mathematically represented as $G(t) = G_0 \exp(-t/\tau_{SR})^{\alpha}$ [106, 30, 149, 82, 83]. Here, $G_0$ is
zero-time shear modulus, $\tau_{SR}$ is the characteristic relaxation time, and $\alpha$ represents the stretch in the relaxation time spectrum. Note that $\alpha \to 1$ represents the Maxwell-type fluid with a single relaxation time. Although two exponent models can be used [12, 111], the stretch exponential function is widely used to capture the stress-relaxation behavior of self-assembled gels with a broad distribution of relaxation time originated from their inhomogeneous microstructure [106, 30, 149, 82, 83]. Here, we fit this model to $G(t)$ over the time scale of 0.1 to 1800 s. $G_0$, $\tau_{SR}$, and $\alpha$ have been treated as floating parameters and the results are shown in Table 4.2 on the preceding page. Note that fitting the data up to 600 s does not display a significant variation in the fitting parameters.

An increase in $G_0$ and $\tau_{SR}$ with polymer concentration can be attributed to the higher number of PI-blocks participating as the load-bearing chains [141, 81]. A decrease in $\tau_{SR}$ at higher $T$ signifies increased chain mobility along with the increase in the solubility of PS-blocks in mineral oil [66, 82]. Both of these factors lead to a faster pullout of PS-blocks among the aggregates. The $\alpha$ values of both gels vary from 0.2-0.3 indicating a distributed $\tau_{SR}$ due to the inhomogeneous microstructure of gels. For 20%-Gel, $\alpha$ is slightly lower than that of 10%-Gel suggesting a higher inhomogeneity of the microstructure [106, 149, 82, 83].

As shown in figure 4.7 on page 94A1-C1, the stress-relaxation and microstructure relaxation follow a similar trend. This suggests that the microstructure recovery time can also be represented in the form of stretched-exponential function as $\Omega(t) = \Omega_0 \exp\left(-t / \tau_\Omega \right)^\alpha$, where $\Omega(t)$ is the time-dependent anisotropic factor, $\Omega_0$ signifies the anisotropy at $t = 0$, i.e., just after the application of strain, and $\tau_\Omega$ represents the characteristic recovery time of the microstructure, which is referred here as the microstructural relaxation time. Similar to $\tau_{SR}$, the $\tau_\Omega$ is also expected to have a broad
distribution due to inhomogeneous microstructure, therefore, we have fixed the $\alpha$ values to those obtained from the fitting of stress-relaxation data. The fitted model captures the data reasonably well (figure 4.7 on page 94A1-C1), and the fitted parameters are shown in Table 4.2 on page 84.

Interestingly, for 10%-Gel at 40 °C and for 20%-Gel at 50 °C, $\tau_{SR}$ and $\tau_{\Omega}$ are similar. For 70 °C, due to fast relaxation time, sufficient microstructure data could not be collected. It signifies that the microstructural relaxation time is less than the sampling time in RheoSAXS (3 s). At 27 °C, $\tau_{\Omega}$ is approximately two orders of magnitude higher than the $\tau_{SR}$, which warrants further discussion.

After the application of step-strain, several processes can take place in a sample. The applied strain facilitates the end-block (PS-block) pullout, and such a process results in stress relaxation. The relaxation of PI-blocks also contributes to the stress-relaxation process. It has been shown that for the same endblock length, the stress relaxation is slower for longer midblock chains, particularly that with entanglements [126, 83, 81]. The overall multimode relaxation process has the characteristic time scale of $\tau_{SR}$. The pulled-out endblocks can reassociate to an existing aggregate, or multiple of the endblocks associate to form new aggregates. Both chain pullout and chain exchange have to be completed to observe the microstructural relaxation in the scattering profile. It appears that the process is much slower than the stress-relaxation process. We attribute this to the endblock diffusion process through the crowded environment retarded by the high chain density and entanglements of PI-blocks [95, 82, 83]. This is further evident from the 20%-Gel sample in which higher polymer concentration leads to the larger difference between $\tau_{SR}$ and $\tau_{\Omega}$. In addition to these processes, various other mechanisms like corona screening, double activation, and walking diffusion are also shown to affect the relaxation dynamics in gels [143, 142, 95]. Note
that microstructure recovery is faster during the oscillation experiments facilitated by the applied mechanical deformation.

4.4 Conclusions

We have related the microstructure and rheology results for 10 and 20 wt% of PS-PI-PS triblock copolymer gels in mineral oil during temperature-dependent gelation, subjected to large amplitude oscillatory strain, and during the stress-relaxation process. During gelation, loosely bounded aggregates are observed at higher temperatures than $T_{gel}$ obtained from shear-rheology experiments. The microstructure evolved with decreasing temperature, and at room temperature, the microstructure evolution is complete. Correspondingly, $G'$ reaches a plateau. With the application of strain, the gel microstructure orients in the stretching direction. This results in the transformation of the circular scattering pattern in the isotropic state to an oriented elliptical scattering pattern. However, in an oscillatory strain cycle, a split in scattering pattern has been observed with increasing $\gamma$, displaying both ellipse and circle. This has been attributed to chain pullout caused by strain localization. A polydisperse core hard-sphere model can capture the scattering data both at the static and under loading conditions. The estimated results are comparable to that estimated using affine deformation. In the stress-relaxation experiments, the microstructure relaxes faster at higher temperatures. The characteristic stress-relaxation time and microstructural relaxation time, estimated using a stretched-exponential model, are similar at higher temperatures but deviate significantly at room temperature. This has been attributed to the complex PS-block association process. Further understanding of the relaxation behavior needs experimental investigations such as dielectric measurement [131], and SANS with appropriate contrast matching [95], which can
capture the PS-block pullout and PI-block relaxation process. Future experiments will also involve the investigation of the microstructural relaxation process by varying the A- or B-block lengths.
Temperature dependent gelation process. (A) Storage modulus ($G'$) and loss modulus ($G''$) as a function of temperature ($T$) for 10%- and 20%-Gels captured using shear-rheology experiments with an oscillatory amplitude ($\gamma_{amp}$) of 0.01 and frequency ($\omega$) of 1 rad/s. A cooling rate of 2 °C/min with a soak time of 300 s was applied. Intensity ($I(q)$) as a function of scattering angle ($q$) for (B) 10%-Gel at 27, 40, 50, 60, 70, and 80 °C, and for (C) 20%-Gel at 27, 50, 70, 90, 100, and 120 °C. The curves are shifted along the $q$-axis for clarity. The insets in B and C represent the $I(q)$ vs. $q$ without shifting. The 2D-scattering patterns above $T_{gel}$ and at room temperature are shown for (D1) 10%-Gel and (D2) 20%-Gel.
Evolution of gel microstructure as a function of temperature. (A) Comparison of $I(q)$ vs. $q$ for 10%- and 20%-Gels at $T=27$ °C (markers), and fitting with a polydispersed core hard-sphere model (lines). (B) Fitted parameters, viz. the core radius ($r_c$), hard-sphere thickness ($s_1$), and hard-sphere volume fraction ($\psi_1$) are presented as a function of temperature for the (B1) 10%-Gel and (B2) 20%-Gel. (C) Schematic representing the assembly of PS- and PI-blocks leading to the formation of network structure with the change of temperature.
Figure 4.4

Shear-rheology and RheoSAXS results for oscillatory shear experiments at 27 °C. (A) Storage modulus ($G'$) and loss modulus ($G''$) as a function of strain amplitude ($\gamma_{amp}$) for 10%- and 20%-Gels using a frequency ($\omega$) of 1 rad/s. The results for $\gamma_{amp}=1$ are highlighted. The error bars, smaller than the markers in some cases, represent one standard deviation. (B) Schematic of one oscillatory strain cycle as a function of time for $\gamma_{amp}=1$ at $\omega=1$ rad/s. The inset displays the stress vs. strain plot for 20%-Gel displaying a small hysteresis of the gel. The markers on the strain cycle correspond to the 2D-scattering patterns presented in (C) for 10%-Gel, and (D) for 20%-Gel. In C and D, $q_x$ represents $v$ or flow direction and $q_y$ represents $\nabla v$ or velocity gradient direction.
Figure 4.5

Scattering patterns and $I(q) - q$ plots for 10%-Gel at 27 °C for the strain amplitude of 1 and for the static condition. The azimuthal angle $\beta$ is defined in (A1). The 2D-scattering patterns are shown for (A1) $\gamma$=0, (A2) $\gamma$=+1 (clockwise), and (A3) $\gamma$=-1 (anticlockwise). 1D-scattering patterns and model fit are shown for (B) circular pattern and the intersection between circle and ellipse, (C) minor-axis of the ellipse, and (D) major-axis of the ellipse.
Figure 4.6

Scattering patterns and $I(q) - q$ plots for 20%-Gel at 27 °C for the strain amplitude of 1 and for the static condition. 2D-scattering patterns are shown for (A1) $\gamma=0$, (A2) $\gamma=+1$ (clockwise), and (A3) $\gamma=-1$ (anticlockwise). 1D-scattering patterns and model fit are shown for (B) circular pattern and intersection between circle and ellipse, (C) minor-axis of the ellipse, and (D) major-axis of the ellipse.
Stress-relaxation behavior obtained from shear-rheology and RheoSAXS experiments. Data for the applied step strain of 0.3 for the (A) 10%-Gel at 40 °C, and 20%-Gel at (B) 50 °C and (C) 70 °C. (A1, B1, C1) Time-dependent modulus ($G(t)$), obtained from shear-rheology experiments, and anisotropy factor ($\Omega$) estimated from RheoSAXS experiments. Lines represent stretched exponential model fitted to $G(t)$ and $\Omega$ data. (A2, B2, C2) 2D-scattering patterns before the application of strain ($t_1$), after the application of strain ($t_2$), after $t = \tau_{SR}$ determined from stress-relaxation data ($t_3$), and at 600s ($t_4$). The $q$-range considered for the calculation of anisotropy factor is indicated by two dashed-circles in each $t_1$-image. For model fitting, the time-scale was shifted appropriately. (A3, B3, C3) Azimuthal plots as a function of time for different $\beta$ values are shown.
CHAPTER V

INVESTIGATING THE REAL-TIME MICROSTRUCTURAL CHANGE IN
PMMA-PNBA-PMMA TRIBLOCK COPOLYMER GELS AS A FUNCTION OF
TEMPERATURE AND STRAIN

5.1 Introduction

ABA triblock copolymer gels are a class of physically assembled gels, which have been studied widely in the literature due to their tunable mechanical properties [1, 67, 68, 66, 126, 106, 108, 10, 109, 31, 33, 30, 32, 46, 149, 148, 95, 82, 83, 98, 99, 141, 81]. These gels consist of an ABA triblock copolymer dissolved in a B-selective solvent. Here, the A-blocks are generally glassy and the B-blocks are rubbery at room temperature. The gelation mechanism in these gels originates from a strong temperature-dependent solubility of A-blocks in the solvent while the solubility of B-blocks is rather insensitive to the temperature [106, 148]. Also, it is required that the A- and B-blocks are incompatible with each other at room temperature [70]. Upon dissolving the polymer in the solvent at high temperature, a clear polymer solution is formed, signifying a good solubility of both blocks. With a decrease in temperature, the A-block solubility decreases and these blocks form small nanometer-size of physically associated aggregates with those in their vicinity. These aggregates behave like crosslinks for the swollen B-blocks, which act as load-bearing or elastically active chains [10, 106, 108]. Therefore, the network is a three-dimensional crosslinked polymer swollen in the solvent.
Due to temperature-driven associations, these gels are thermoreversible and often referred to as thermoplastic elastomeric gels. The thermo-mechanical properties of these gels are shown to be tuned by temperature [106, 149, 86, 82, 83, 81], polymer concentration [56, 106, 99, 81], length of A- and B-block [108, 20, 19], choice of solvent [148], and inclusion of homopolymer [109] and nanoparticles [149]. Such diverse ways of tuning make these gels attractive for many applications like prosthetics consumer products [22], and ballistics [86]. Also, understanding the structure-property relationship of these gels can be applied to other gels containing solubility triggered aggregates like in double network gels or hybrid gels [21].

In the last three decades, significant studies have been made towards understanding the mechanical properties of physically assembled gels while tuning their microstructure. Various combinations of A-blocks, B-blocks, and solvents were utilized and compared to deduce similarities in their behavior [66, 126, 56, 106, 93, 95, 141, 81]. A few of such common characteristics of these gels are (1) lower gelation temperature for the gels with higher polymer concentration [141, 81], shorter B-block [108], and longer A-blocks [108, 83], (2) micellar microstructure at low-to-moderate polymer concentrations evolving into cylindrical micelles with an increase in polymer concentration [66, 106, 148, 95, 82, 83, 81], (3) higher moduli at higher polymer concentration [106, 108, 99, 81], also at longer A-block length [108], and at lower temperatures [126, 149, 148], (4) strain-rate dependent moduli for the gels with B-block entanglements [20, 19, 82, 83, 81].

Interestingly, features like strain stiffening [31, 46] and temperature-independent stress relaxation mechanism [30, 81] are a few that are not common to all these systems. The gel explored in the present study is one example of such type of gels and consists of poly(methyl methacrylate)–poly(n-butyl acrylate)–poly(methyl methacrylate) [PMMA-PnBA-PMMA] in 2-ethyl-1-hexanol, referred
here as acrylic gel. Although it has been investigated extensively for its gelation mechanism [10, 106, 107], a direct observation of its real-time microstructure evolution with temperature and strain is not available in the literature. Relating such development of microstructure with stress responses is also useful to engineer gels for targeted applications. This acrylic gel is known to display inhomogeneous microstructure leading to a distribution of the relaxation time [106, 108, 149]. Also, this gel displays a strain stiffening behavior at low polymer concentration due to the finite extensibility of PnBA-chains, as proposed theoretically. Such inhomogeneity results in shear bands within the gel leading to its failure at a relatively lower strain than that proposed theoretically [32, 33].

In this chapter, four gels consisting of PMMA-PnBA-PMMA polymer in 2-ethyl-1-hexanol are studied. In the first section, a gel with high-polymer volume fraction ($\phi$) – referred to as 30%-Gel or high-$\phi$ gel – composed of 30% v/v of LA 2330 polymer will be presented. The investigation is focused on exploring its change in microstructure with temperature and large amplitude oscillatory strain using the RheoSAXS technique. This technique allows us to capture the microstructural change in the gel with a very short exposure time (\(\approx 0.03 \text{ s}\)). Such microstructural change has been also related to the stress responses using shear-rheometry. In the second section of the chapter, the large amplitude responses of the high-$\phi$ gel are compared with those for three low-$\phi$ gels, of varying PMMA-blocks (A) and PnBA-blocks (B) lengths, by using shear-rheometry and RheoSAXS techniques. Their designation as $A_{25}B_{104}A_{25}$, $A_{12}B_{96}A_{12}$, and $A_{8}B_{54}A_{8}$ gels, indicates the blocks length (kg mol$^{-1}$) of the polymer used to prepare the gel.
5.2 Experiments
5.2.1 Materials

High polymer concentration gel

The triblock copolymer LA 2330 poly(methyl methacrylate)–poly(n-butyl acrylate)–poly(methyl methacrylate) [PMMA–PnBA–PMMA] was kindly provided by Kuraray America Inc. Based on the manufacture data-sheet, the molecular weight of PMMA and PnBA are \( M_{PMMA} = 12 \) and \( M_{PnBA} = 96 \) kg mol\(^{-1}\). The solvent, 2-ethyl-1-hexanol, was purchased from Sigma Aldrich. Both reactants were used as received. The gel was prepared by adding 30% v/v of the polymer to the solvent. The mixture was placed overnight in the oven maintained at 80°C to obtain a clear polymer solution. The gel was obtained upon cooling the solution to room temperature (RT, 27°C). For shear-rheometry, the hot polymer solution was poured over a flat surface and allowed to cool down for \( \approx 15 \) min to RT, forming a gel sheet. Square shapes of gel were cut with a scalpel from the sheet for further testings. For RheoSAXS experiments, the hot solution at 80°C was poured gently on the RheoSAXS setup. A waiting time of \( \approx 15 \) min was allowed for the sample to cool down to RT before any test.

Low polymer concentration gels

The triblock copolymer used for the preparation of the gels was also PMMA-PnBA-PMMA (Kuraray America Inc.), however, the molecular weight of PMMA- and PnBA-blocks is different for all of them. For the first gel, 3% (v/v) of LA 2550 copolymer, which has PMMA-block length \( M_{PMMA} \) of 25 kg mol\(^{-1}\) and PnBA-block length \( M_{PnBA} \) of 104 kg mol\(^{-1}\), was used and referred as \( A_{25}B_{104}A_{25} \) gel in this chapter. The second gel was prepared with the 4% (v/v) of LA 2330 polymer, which has \( M_{PMMA} = 12 \) and \( M_{PnBA} = 96 \) kg mol\(^{-1}\), and referred as \( A_{12}B_{96}A_{12} \) gel.
And the third gel was prepared with the 5% (v/v) of LA 2140E, which has $M_{PMMA}=8.05$ and $M_{PnBA}=53.9 \text{ kg mol}^{-1}$, and referred as $A_8B_{54}A_8$ gel. The procedure to prepare these low-$\phi$ gels is the same followed for the preparation of the principal gel.

### 5.2.2 Shear-rheometry

For the shear-rheometry experiments, a Discovery HR-2 hybrid rheometer from TA Instruments was used. The rheometer was equipped with a Peltier plate and a 25 mm parallel plate geometry. The polymer solution was poured on the bottom plate of the geometry, maintaining a temperature of the plate at 80°C, and afterward, the gap was adjusted to 1 mm and cooled down to RT to form the gel. A conditioning time of 120 s after loading the sample was used before every test. Amplitude sweep experiments were performed at RT using an oscillatory strain ($\gamma$) range from $10^{-4}$ to 1 and a frequency ($\omega$) of 1 rad s$^{-1}$. Temperature sweep experiments were performed using a strain amplitude ($\gamma_{amp}$) of 0.01 and $\omega=1 \text{ rad s}^{-1}$ over a temperature range of 65 to 20°C. The temperature step used was 2°C min$^{-1}$ with an equilibration time of 180 s. Stress-relaxation experiments were performed at RT applying a $\gamma_{amp}=0.01$ in 0.01 s, after which the samples were allowed to relax for 1800 s.

### 5.2.3 RheoSAXS experiments

The RheoSAXS experiments were performed with a custom-built shear-stage attached to a DND-CAT small X-ray scattering setup from the Advanced Photon Source at Argonne National Laboratory (ANL, Chicago, IL). The shear-stage was equipped with an annular cone and plate geometry. The cone angle of the geometry was 5°, and the outer and inner diameter values of the plates were 50 and 30 mm, respectively. The X-ray beam of wavelength 0.7293 Å passed
through a pinhole, located on the bottom plate of the geometry, in parallel to the cone angle. More information about the setup can be found in Chapter IV. Next, the beam passed through the sample capturing the 1-2 plane (2 dimensional), and the scattering data was captured by a CCD detector and was saved for analysis. For the analysis of the scattering data, IgorPro software and Nika macros were used to reduce the data from 2D to 1D data. An NCNR macro and a polydispersed core hard-sphere model were used to fit the data. For the observation of the temperature effect on the system, after loading the sample to the setup, the temperature of the gel was increased to 70 °C at static conditions, which means no $\gamma_{amp}$ was applied. After which the hot solution is allowed to cool to form the gel while capturing the data with a beam-exposure time of 0.03 s every 5 °C. For oscillatory shear experiments, the gel was subjected to $\gamma_{amp}=0.5$ and $\omega=1$ rad s$^{-1}$ for 3 cycles. A beam-exposure time of 0.03 s captured the data every 0.157 s. This latter procedure and parameters were kept the same for oscillatory shear experiments performed in the low-$\phi$ gels. However, for the low-$\phi$ gels, the loading temperature for the samples was 55, 45, and 35° C for $A_{25}B_{104}A_{25}$, $A_{12}B_{96}A_{12}$, and $A_{8}B_{54}A_{8}$ gels, respectively.

5.3 Result and Discussion
5.3.1 Effect of Temperature on the High-$\phi$ Gel Microstructure

figure 5.1 on the following pageA displays the evolution of storage ($G'$) and loss modulus ($G''$) over a temperature ($T$) range of 65°C to 20°C obtained from shear-rheometry experiments. In these experiments, an oscillatory strain amplitude ($\gamma_{amp}$) of 0.01 and a frequency ($\omega$) of 1 rad s$^{-1}$ were used with a temperature step of 2°C min$^{-1}$. At high temperatures, $G' < G''$ indicating a liquid-like behavior of the sample. An evolution of $G'$ and $G''$ with decrease in $T$ signifies the network formation. At further lower temperature, the polymer network becomes strong enough to
Temperature dependent moduli and scattering patterns at different temperatures for the 30%Gel. (A) Storage modulus ($G'$) and loss modulus ($G''$) as a function of temperature ($T$) obtained from shear-rheometry experiments using amplitude strain ($\gamma_{amp}$) of 0.01 and oscillation frequency ($\omega$) of 1 rad s$^{-1}$ obtained from RheoSAXS experiments. (B) Intensity $I(q)$ as a function of scattering angle ($q$) at 70, 60, 50, 40, and 27°C along with 2D-scattering patterns showing the development of the microstructure at 70, 50, and 27°C. (C) $I(q) - q$ curve at room temperature (27°C) fitted with a polydispersed core hard-sphere model. The inset displays the development of the curves with respect to temperature.

bear the load displaying a soft solid-like behavior. This critical point is identified as a crossover of $G'$ and $G''$, which can be defined as the gelation temperature ($T_{gel} \approx 57°C$). Below $T_{gel}$, $G' > G''$ suggesting a soft solid-like behavior of the gel. At room temperature ($\approx 27°C$), the $G' \approx 39.4$ kPa and is slightly higher than one order of magnitude than the $G''$, displaying the elastic nature of the gel.

By using RheoSAXS experiments, the real-time change in the gel microstructure was captured during natural cooling of the polymer solution from $\approx 70°C$ to $\approx 27°C$. The data was collected at every 5°C of temperature change. In figure 5.1B, $I(q)$ is plotted against log scale of $q$ at 70, 60, 50, 40, and 27 °C, and the 2D patterns images corresponding to 70, 50, and 27 °C are shown aside. In these images, the circular pattern shows an increase in intensity with a decrease in $T$. A circular 2D
pattern indicates an isotropic microstructure of gels. In the corresponding \( I(q) - q \) plots, the peaks represent the inter-aggregate scattering while the shoulders provide information about the shape and size of aggregates [80]. Figure 5.1 on the preceding page displays \( I(q) \) against \( q \) at room temperature (RT, 27°C) fitted with the polydisperse core hard-sphere model. With a decrease in \( T \), the evolution of structure factor peak at \( q \approx 0.02 \, \text{Å}^{-1} \) and development of a form-factor shoulder at \( q \approx 0.04 \, \text{Å}^{-1} \) can be noticed (figure 5.1 on the previous page inset).

For the shear-rheometry data, a plateau in \( G' \) value in the vicinity of room temperature suggests that the formation of the gel microstructure is complete and that it is not sensitive to the temperature change [106, 82]. It is well-established in the literature that the gelation mechanism of this system is triggered by the strong temperature-dependent solubility of PMMA-blocks. On the contrary, the solubility of PnBA-blocks does not change appreciably with temperature [106, 107, 148]. The reduced solubility of PMMA-blocks leads to their collapse to form physically associated crosslinks at low temperatures, often referred to as aggregates. The swollen PnBA-blocks connect those aggregates acting as elastically active chains, also referred to as bridges.

In the RheoSAXS results, for \( q < 0.01 \, \text{Å}^{-1} \), \( I(q) \sim q^{3.3} \) indicating a rough surface originated from the fractal nature of the polymer network in the gel. The microstructure of the gel was interpreted in the range of \( 0.01 \leq q \leq 0.05 \, \text{Å}^{-1} \) encompassing the form factor and structure factor. A fitting with a polydisperse core hard-sphere model captures the data reasonably well for all temperatures (figure 5.1 on the preceding page and table 5.1 on the next page) [80, 106, 148, 82, 83, 81]. Here the core represents the PMMA aggregates of mean radius \( r_c \) with a Gaussian dispersion factor \( \sigma \). The hard-spheres are concentric with the cores and have a thickness \( s \) with volume fraction \( \psi \). Data beyond \( q > 0.05 \, \text{Å}^{-1} \) can be understood as secondary reflections from
Table 5.1

Fitting parameters for $I(q) - q$ data for the 30%-Gel obtained by using a polydispersed core hard-sphere model at different temperatures and static conditions. Core radius ($r_c$), sphere thickness ($s$), and volume fraction ($\psi$) as a function of temperature ($T$).

<table>
<thead>
<tr>
<th>$T$ (°C)</th>
<th>70</th>
<th>65</th>
<th>60</th>
<th>55</th>
<th>50</th>
<th>45</th>
<th>40</th>
<th>35</th>
<th>30</th>
<th>27</th>
</tr>
</thead>
<tbody>
<tr>
<td>$s$ (nm)</td>
<td>5.6</td>
<td>5.9</td>
<td>6.0</td>
<td>6.5</td>
<td>7.0</td>
<td>7.2</td>
<td>7.4</td>
<td>7.4</td>
<td>7.4</td>
<td>7.4</td>
</tr>
<tr>
<td>$\psi$</td>
<td>0.30</td>
<td>0.42</td>
<td>0.43</td>
<td>0.46</td>
<td>0.48</td>
<td>0.49</td>
<td>0.50</td>
<td>0.51</td>
<td>0.51</td>
<td>0.51</td>
</tr>
</tbody>
</table>

polydispersed spherical form factor. Table 5.1 displays the fitted parameters over $70 \leq T \leq 27$°C.

With decrease in $T$ from 70 to 45°C, $r_c$ increases 8.0 nm to 9.2 nm, $s$ increases from 5.6 nm to 7.2 nm, and $\psi$ increases from 0.30 to 0.49. For $T < 45$°C, the fitted parameters do not significantly change, with as $r_c \approx 9.2$ nm, $s \approx 7.4$ nm, and $\psi \approx 0.51$. The polydispersity ($\sigma/r_c$) varies over a range of 0.07-0.19 over $70 \leq T \leq 27$°C.

The presence of an inter-aggregate peak at $T > T_{gel}$ suggests the presence of cores even at high $T$. Due to a relatively high solubility of PMMA in 2-ethyl-1-hexanol at high $T$, the cores are expected to be loosely bounded with significant solvent within. At high $T$, some PMMA-blocks are also expected to not be connected to any aggregate. With a decrease in $T$, those PMMA-blocks associate to existing aggregates or form new aggregates, leading to an increase in $r_c$ and a decrease in $s$. In contrast, it is shown that with a decrease in $T$, the cores expel out the solvent, due to poor solubility of PMMA-blocks in the solvent, leading to a decrease in $r_c$ and an increase in $s$ [10, 106]. An interplay of these two mechanisms causes a weak temperature-dependent change of $r_c$ and $s$. The formation of new aggregates with a decrease in $T$ leads to an increase in $\psi$, which increases the number density of aggregates. The calculation of inter-aggregate distance

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\( D = 4\pi (r_c + s)^3 / (3\psi) \) reveals a slight increase in \( D \) [106], from 32.7 to 33.5 nm, over 70-27°C. Therefore, the end-to-end length of PnBA-block in the gel \( (D - 2r_c) \) slightly decreases from 16.7 to 15.1 nm with a decrease in \( T \) from 70-27°C. Knowing that the Kuhn length of PnBA is \( b = 1.7 \) nm and a C-C bond length is \( \approx 1.5 \) Å, the molar mass of the Kuhn segment can be roughly estimated as \( \approx 0.715 \) kg mol\(^{-1}\) [101]. Correspondingly, the number of Kuhn segments in the PnBA-segment can be estimated as \( N \approx 135 \). At high polymer concentration, the 2-ethyl-1-hexanol can be treated as \( \theta \)-solvent to PnBA, therefore, the end-to-end distance \( (R_{e-e}) \) of PnBA can be estimated as \( b\sqrt{N} \approx 19.7 \) nm. The \( R_{e-e} \) is higher than \( D - 2r_c \) suggesting that the PnBA-blocks are slightly compressed in the gel. The fitted parameters do not change significantly from a temperature below 45 °C (\( < T_{gel} \)) indicating the completion of microstructure formation, also indicated by a plateau in \( G' \). Also, knowing the entanglement molecular weight of PnBA \( (M_{e-PnBA}) \) as 22 kg mol\(^{-1}\), we do not expect any entanglement of the PnBA-chain in our gel as the theoretical formulation estimates \( \phi^{5/4}(M_{PnBA}/M_{e-PnBA}) \approx 0.97 < 1 \) [101, 20, 19, 82], where \( \phi \) is the polymer volume fraction.

### 5.3.2 Effect of Oscillatory Strain on the High-\( \phi \) Gel Microstructure

To study the dynamic microstructure of the gel when applying oscillatory strain, it is necessary to have minimal relaxation in the gel while deforming. Concretely, the data collection time must be significantly lower than the gel relaxation time to treat the data as a static microstructure. We have used stress-relaxation experiments to obtain the relaxation time of the gel, as performed in the literature [30, 149]. In our experiments, the sample was applied with a step strain \( (\gamma_{step}) \) of 0.01 in 0.01 s and allowed to relax for 1800 s. The data obtained from shear-rheometry experiments
is shown in figure 5.2 on page 117 and the time-dependent shear modulus \( G(t) \) is fitted with a stretched-exponential model.

The fitting model can be mathematically represented as, \( G(t) = G_0 \exp\left(-\frac{t}{\tau_{SR}}\right)^\alpha \) [30, 149, 82, 81]. Here, \( G_0 \) is zero-time shear modulus, \( \tau_{SR} \) is the characteristic relaxation time, and \( \alpha \) signifies the stretch in the relaxation time spectrum. \( \alpha = 1 \) signifies Maxwell type fluid with a single relaxation time, and as the \( \alpha \to 0 \), \( \tau_{SR} \) displays a broader relaxation time. Our fitting estimates \( G_0 = 43231 \pm 492 \text{ Pa}, \tau_{SR} = 5328 \pm 506 \text{ s}, \) and \( \alpha = 0.26 \pm 0.01 \). Here, all the parameters were kept floating and the \( G_0 \) value is very similar to that observed in figure 5.1 on page 101A at 27 \(^\circ\)C.

Figure 5.3 on page 118 displays the 2D pattern of the gels at different \( \gamma \) values while the gel was applied with an oscillatory strain of \( \gamma_{amp} = 0.5 \) with \( \omega = 1 \text{ rad s}^{-1} \). Three strain cycles were applied with an interval of 0.157 s between cycles and an X-ray exposure time of 0.03 s, which estimates \( \approx 40 \) data points per cycle. Note that the \( \tau_{SR} \) is \( 10^6 \) times higher than the data collection time, therefore, a minimal effect of microstructure relaxation can be expected during data collection. As can be observed, the 2D pattern is circular for \( \gamma = 0 \). With an increase in \( \gamma \) from 0 to 0.5, the circular pattern transforms to elliptical and elongates towards a \( \beta \)-angle of 130\(^\circ\) as major-axis and \( \beta = 40\(^\circ\) \) as minor-axis of the ellipse. The pattern restores back to the isotropic structure as \( 0.5 \leq \gamma \leq 0 \). During the negative half-cycle of strain, the 2D pattern displays the same behavior qualitatively, however, the elongation shifts to 40\(^\circ\) as major-axis and to 130\(^\circ\) as minor-axis.

The transition from a circular to an elongated 2D pattern represents the change in orientation of the microstructure with applied strain. In the three cycles applied to the gel, the 2D pattern was found to be similar for each cycle. This suggests that no major damage occurred to the gel microstructure during shearing.
figure 5.4 on page 119A represents the $G'$ and $G''$ evolution as a function of $\gamma_{amp}$ varying from $10^{-4}$ to 1 using $\omega=1$ rad s$^{-1}$ obtained from shear-rheometry. Over the studied range of $\gamma_{amp}$, no significant change in $G'$ and $G''$ can be observed. Beyond $\gamma_{amp} > 1$, the phase angle correction could not be performed accurately by our rheometer, therefore, we do not consider that data to be reliable. Note that for lower concentrations of this gel a strain-stiffening behavior can be observed.

To characterize the change in the gel microstructure, the 1D $I(q) - q$ curves obtained from the RheoSAXS experiments were utilized. As shown in figure 5.4 on page 119B, at $\gamma=+0.5$ the pattern elongates towards the second quadrant displaying the major axis of the pattern at $\beta \approx 130^\circ$ and minor axis at $\approx 40^\circ$. We have used a sector $\beta \pm 5^\circ$ to estimate an average value of $I(q)$ and reported the results for that $\beta$-angle. A comparison of $I(q) - q$ curves for $\gamma = 0$ is made with those at $|\gamma|=0.5$ along major and minor axes and depicted in figure 5.4 on page 119C. At $\gamma = 0$, a sector average at any angle and circular averaged intensity curve overlap (figure 5.4 on page 119D) displaying an isotropic microstructure. As depicted in figure 5.4 on page 119E, for the case of $\gamma = \pm 0.5$, the sectors along the minor-axis of the ellipse ($\beta_{\gamma=0.5} \approx 40^\circ$, $\beta_{\gamma=-0.5} \approx 140^\circ$) also overlap. Similarly, figure 5.4 on page 119F displays an overlap of the sector average $I(q) - q$ curves along the major-axis of the pattern ($\beta_{\gamma=+0.5} \approx 130^\circ$, $\beta_{\gamma=-0.5} \approx 50^\circ$).

The overlapping of $I(q) - q$ curves suggests that the extent of change in microstructure is independent of the strain direction and solely dependent on the strain amplitude ($|\gamma|$). This supports our previous observation of 2D patterns in figure 5.3 on page 118 that the transient microstructure does not depend on $\gamma$-direction. The structure factor corresponding to the circular pattern (circle) located at 0.021 Å$^{-1}$ shifts to 0.024 Å$^{-1}$ with slightly lower intensity for the major-axis sector and to 0.018 Å$^{-1}$ with slightly higher intensity for the minor-axis sector.
Table 5.2

Sector and corresponding strain $\gamma$ and $\beta$-angle considered for analysis along with the fitted parameters for the $I(q) - q$ data of 30\%Gel at applied $\gamma$=1. Here, $r_c$ is core radius, $s$ hard-sphere thickness, and $\psi$ hard-sphere volume fraction.

<table>
<thead>
<tr>
<th>Sector</th>
<th>$\gamma$</th>
<th>$\beta$ (°)</th>
<th>$r_c$ (nm)</th>
<th>$s$ (nm)</th>
<th>$\psi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Circle</td>
<td>0</td>
<td>0</td>
<td>9.2</td>
<td>7.4</td>
<td>0.50</td>
</tr>
<tr>
<td>Minor-axis</td>
<td>+0.5</td>
<td>40</td>
<td>9.2</td>
<td>9.1</td>
<td>0.49</td>
</tr>
<tr>
<td>Major-axis</td>
<td>+0.5</td>
<td>130</td>
<td>9.2</td>
<td>5.5</td>
<td>0.49</td>
</tr>
</tbody>
</table>

To characterize the gel microstructure, we have fitted the data in figure 5.4 on page 119D-F with a polydispersed core hard-sphere model over $0.01 \leq q \leq 0.1 \text{ Å}^{-1}$ with $r_c$ fixed to 9.2 nm. The data is reasonably well captured by the model and the fitted parameters are indicated in table 5.2. The fitted parameters for the case of $\gamma$=0 are similar to those observed in table 5.1 on page 103 at 27 °C. For all the cases, the $r_c$ value does not change, indicating that in this $\gamma$-range, the PMMA aggregates remain intact. Also, any pullout events of PMMA-blocks from an aggregate does not occur that can potentially reduce the $r_c$. As expected, the hard-sphere thickness displays a higher value along the minor-axis and the least value for the major-axis. This suggests that the aggregates orient towards the applied strain leading to two possible arrangements. When $\gamma$ is applied, the aggregates displace along the $\gamma$-direction (see figure C.3 on page 167). The microstructure also experiences a compression in the perpendicular direction. The resultant structure is a combination of a compressed and stretched microstructure resulting in an elliptical 2D pattern. The PnBA length can be calculated with the expression $D = \left(\frac{4\pi(r_c + s_1)^3}{3\psi_1}\right)^{1/3}$ [106], estimating a value of 33.7 nm for the circular pattern at static conditions ($\gamma = 0$), similar to that obtained from table 5.1 on page 103 at room temperature. $D_2$=37.4 and 30.1 nm along with the sectors of minor and major
axes, respectively, representing two inter-aggregate distances related to stretch and compression of aggregates. Consecutively, the stretch and compression ratio can be calculated as, \( D_2/D_1 \) resulting in values of 1.11 and 0.89. These ratios can be compared with the applied deformation by converting \( \gamma \) to the elongation ratio (\( \lambda \)) [122]. Using the affine deformation model, it can be shown that \( \lambda - \lambda^{-1} = \gamma \). When \( \gamma=0.5 \), the relationship is satisfied for \( \lambda=1.25 \) and -0.75, representing elongation and compression, respectively. The model predicts a slightly higher extension ratio as obtained from characterizing the scattering data. This can be attributed to the inhomogeneities in the gel microstructure.

To gain insight into the anisotropy in the microstructure during deformation, we have analyzed the 2D-scattering patterns over three strain cycles for anisotropic factor (\( \Omega \)) and anisotropic angle (\( \chi \)). We have utilized the region \( 0.015 \geq q \geq 0.025 \text{ Å}^{-1} \) encompassing the structure factor peak movement with \( \gamma \) (see figure 5.4 on page 119C). The \( \Omega \) captures the degree of orientation in the microstructure while the \( \chi \) represents the direction of orientation with respect to the applied strain direction. Mathematically, \( \Omega = [((\langle q_x^2 \rangle - \langle q_y^2 \rangle)^2 + 4\langle q_x q_y \rangle)^{1/2} \) and \( \chi = 0.5 \tan^{-1} \left( 2\langle q_x q_y \rangle/((\langle q_x^2 \rangle - \langle q_y^2 \rangle) \right) \). Here \( \bar{q} \) corresponds to a point in the azimuthal plot of intensity \( I(\beta) \) making an angle \( \beta \) from \( q_x \) axis. The average values can be estimated as, \( \langle q_x^2 \rangle = \frac{\int_0^{2\pi} \cos^2(\beta) I(\beta) d\beta}{\int_0^{2\pi} I(\beta) d\beta} \), \( \langle q_y^2 \rangle = \frac{\int_0^{2\pi} \sin^2(\beta) I(\beta) d\beta}{\int_0^{2\pi} I(\beta) d\beta} \), and \( \langle q_x q_y \rangle = \frac{\int_0^{2\pi} \cos(\beta) \sin(\beta) I(\beta) d\beta}{\int_0^{2\pi} I(\beta) d\beta} \). Figure 5.5 on page 120A represents the \( \gamma \) and \( \chi \) as a function of time displaying a microstructure orientation at \( \approx 40^\circ \) as soon as \( \gamma \) is applied. Similarly, figure 5.5 on page 120B displays \( \Omega \) as a function of time. With an increase in \( |\gamma| \), a smooth increase in \( \Omega \) can be observed from \( \approx 0.01 \) to \( \approx 0.10 \), which comes back to the initial value as \( \gamma \) approaches to 0. This is a consequence of connected
aggregates experiencing a stretch in one direction and compression in another direction, therefore, the resultant displacement shifts 40° away from the direction of applied stretch.

5.4 Comparison with Low-ϕ Gels

This part of the study provides a comparative study of mechanical properties and real-time change in the microstructure of four gels with different polymer concentrations. The responses of the 30%-Gel (30% v/v of LA 2330 polymer), referred here as high-ϕ gel, are compared with three low-ϕ gels. The low-ϕ gels are $A_{25}B_{104}A_{25}$, $A_{12}B_{96}A_{12}$ gel, and $A_{8}B_{54}A_{8}$, respectively. As mentioned in the materials section, these low-ϕ gels were prepared with different concentrations of PMMA-PnBA-PMMA polymers with varying block lengths. Note that $A_{25}B_{104}A_{25}$ and $A_{12}B_{96}A_{12}$ gels have similar PnBA (midblock) molecular weight and that $A_{12}B_{96}A_{12}$ and $A_{8}B_{54}A_{8}$ gels have similar PMMA (endblock) molecular weight. With these similarities between low-ϕ gels, it is also possible to estimate the effect of midblock and endblock lengths on the gel responses to load.

Figure 5.6 on page 121A shows the evolution of $G'$ and $G''$ over a temperature range of 18 to 60°C for all three low-ϕ gels. At high temperatures, the torque measurement of the rheometer attains its lower limit, and the data at those temperatures were not very reliable. Therefore, we only consider for the analysis the data lower than ≈40, 50, and 55°C for $A_{25}B_{104}A_{25}$, $A_{12}B_{96}A_{12}$, and $A_{8}B_{54}A_{8}$ gels, respectively. In this limit, at high temperatures $G' < G''$ for all three gels, signifying the liquid-like behavior of the samples. A decrease in temperature causes an increase in both moduli until reaching a crossover between $G'$ and $G''$ – considered as gelation temperature ($T_{gel}$). The $T_{gel}$ of $A_{25}B_{104}A_{25}$, $A_{12}B_{96}A_{12}$, and $A_{8}B_{54}A_{8}$ gels are 52°C, 42°C, and 32°C, respectively. At lower values of temperature, $G' > G''$ signifying the solid-like behavior of the samples. At RT,
all gels reach similar values of $G' \approx 100$ Pa, which allows us to compare the three gels in further experiments. Interestingly, for $T < T_{gel}$, the $G''$ values are lower for the gels with lower $\phi$, indicating a lower dissipation of elastic energy for the $A_{25}B_{104}A_{25}$ gel.

5.4.1 Shear-rheometry

Figure 5.6 on page 121B displays the results of amplitude sweep experiments in which $G'$ and $G''$ are plotted as a function of $\gamma_{amp}$ over a range of $10^{-4}$ to 100. Below $\gamma_{amp} \approx 0.6$, $G' \approx 100$ Pa and has a similar value for all three gels. However, the ratio of $G'$ and $G''$ varies from $\approx 5$ to 10 times. Here, $G''$ is higher for $A_{8}B_{54}A_{8}$ showing a more viscous behavior than the other gels, followed by $A_{12}B_{96}A_{12}$ gel. Above $\gamma_{amp} \approx 0.6$, all gels show strain-stiffening behavior. Also, above $\gamma_{amp} \approx 4$, all these gels fracture despite different molecular weights of PMMA- and PnBA-blocks.

In figure 5.6 on page 121C, $G'$ and $G''$ are plotted as a function of $\omega$ for all low-$\phi$ gels. In the $\omega$-range of 0.1 to 30 rad s$^{-1}$ considered here, $G'$ does not change significantly, however, the $G''$ displays a minimum which becomes more prominent for the gels with higher PnBA-block length.

At room temperature, $G'$ is not significantly different for all three samples, but $G''$ varies from $\approx 3$ to 20 Pa. Despite the different chain density in the gels, $G'$ is similar probably due to the difference in midblock stretching and the bridge density. It can be observed that $T_{gel}$ is higher for $A_{25}B_{104}A_{25}$ and $A_{12}B_{96}A_{12}$ gels, compared to $A_{8}B_{54}A_{8}$ gel, signifying that longer midblocks facilitate the network formation even at high temperatures. Additionally, the $T_{gel}$ of $A_{25}B_{104}A_{25}$ is higher than that of $A_{12}B_{96}A_{12}$ gel, which implies that longer endblocks facilitate the network connection to form the gel. Note that, due to lower $\phi$ and higher molecular weight, $A_{25}B_{104}A_{25}$ gel has the lowest number density of polymer chains, followed by $A_{12}B_{96}A_{12}$ gel.
Despite a lower chain density of $A_{25}B_{104}A_{25}$, it can form a stronger network to bear the load at higher temperatures. This can be attributed to the longer PMMA-chains in LA 2550 polymer that promotes the gelation by forming stronger aggregates. The $A_8B_{54}A_8$ gel shows the highest value of $G''$, followed by $A_{12}B_{96}A_{12}$ gel, signifying that $G''$ increases for lower endblock lengths and lower midblock lengths. A high value of $G''$ in this case signifies higher viscous dissipation probably due to a higher number of loops and dangling chains present in the $A_8B_{54}A_8$ gels as the longer PnBA-blocks lead to a higher bridging fraction [10, 19, 81, 106]. A similar fracture $\gamma_{amp}$ for all three gels suggests that the midblocks are more stretched for the $A_{25}B_{104}A_{25}$ gel, followed by the $A_{12}B_{96}A_{12}$, therefore, the entropic penalty is higher for stretching the PnBA-chains in $A_{25}B_{104}A_{25}$. A minimum in the $G''$ at $\omega \approx 3$ rad s$^{-1}$ for $A_{25}B_{104}A_{25}$ and $A_{12}B_{96}A_{12}$ gels can be attributed to the difference in the relaxation times of longer midblock and gel, similar to what observed in the case of other endblock associative triblock copolymer gels [90, 70, 83].

When comparing the values with the high-$\phi$ gel, we find that its $G' \approx 39.4$ kPa, which is $\approx 400$ times higher than that for its low-$\phi$ gel. This signifies that the chain density significantly affects the elastic behavior of gels by providing a higher number of load-bearing chains.

Stress-relaxation experiments were performed on the low-$\phi$ gels. A $\gamma_{step}=0.01$ was applied to the gels in 0.01 s and allowed to relax for 1800 s at RT. As shown in figure 5.7 on page 122, the fitting of $G(t)$ over time obtained from shear-rheometry with a stretched-exponential model provides the characteristic relaxation time of gels. The fitting parameters are shown in table 5.3 on the next page. Here, all gels display similar values of $G_0$, which are not significantly different than the $G'$ obtained at RT in figure 5.6 on page 121A. The $\alpha$-values also vary over a small range, from
Table 5.3

Fitted parameters for stress-relaxation experiments of $A_{25}B_{104}A_{25}$, $A_{12}B_{96}A_{12}$, and $A_8B_{54}A_8$ gels obtained from shear-rheometry. Here, $G_0$ is zero-time shear modulus, $\tau_{SR}$ the characteristic relaxation time, and $\alpha$ the stretch exponent.

<table>
<thead>
<tr>
<th>Gel</th>
<th>$G_0$ (Pa)</th>
<th>$\tau_{SR}$ (s)</th>
<th>$\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{25}B_{104}A_{25}$</td>
<td>104±2</td>
<td>756±57</td>
<td>0.22±0.01</td>
</tr>
<tr>
<td>$A_{12}B_{96}A_{12}$</td>
<td>135±6</td>
<td>3.4±0.6</td>
<td>0.21±0.00</td>
</tr>
<tr>
<td>$A_8B_{54}A_8$</td>
<td>120</td>
<td>0.63±0.05</td>
<td>0.28±0.00</td>
</tr>
</tbody>
</table>

0.21 to 0.28, however, $\tau_{SR}$ varies significantly. The characteristic $\tau_{SR}$ for $A_8B_{54}A_8$ gel of 0.63 s, is three orders of magnitude lower than that for $A_{25}B_{104}A_{25}$ gel of 756 s.

The difference in $\tau_{SR}$ values signifies that the relaxation time of gels is governed by both PMMA- and PnBA-block length. However, $\tau_{SR}$ of $A_{25}B_{104}A_{25}$ gel is two orders of magnitude higher than that of $A_{12}B_{96}A_{12}$ gel suggesting that the endblock length effect is more prominent than the midblock length. The presence of loops and dangling chains increases the viscous dissipation. In addition, for a smaller PMMA-block, the endblock exchange mechanism is faster leading to a faster relaxation of $A_8B_{54}A_8$ gel. When compared to the high-$\phi$ gel (30% v/v LA 2330), with a $\tau_{SR}$ of $\approx$180 times higher than that for its low-$\phi$ (4% v/v LA 2330, $A_{12}B_{96}A_{12}$) gel, it can be understood that the concentration plays a significant role in dictating the relaxation behavior of gels by including more number of chains in the relaxation mechanism.

5.4.2 RheoSAXS

Figure 5.8 on page 123A1-C1 shows the 2D-scattering patterns of $A_{25}B_{104}A_{25}$, $A_{12}B_{96}A_{12}$, and $A_8B_{54}A_8$ gels at static conditions ($\gamma$=0). Circular patterns are observed for all the samples, however, the intensity appears to be higher for $A_{25}B_{104}A_{25}$ gel. The pattern of $A_{12}B_{96}A_{12}$ gel
depicts a more prominent ring of higher intensity, with a higher diameter than the circular pattern of $A_{25}B_{104}A_{25}$ gel. The pattern of $A_{8}B_{54}A_{8}$ gel depicts a diffused ring with higher radius than the other gels. These observations are supported by the circular averaged $I(q) - q$ plots of the low-$\phi$ gels, shown in figure 5.8 on page 123A2-C2. Here, the intensity of structure factor peak highest for $A_{25}B_{104}A_{25}$ gel, followed by $A_{12}B_{96}A_{12}$ gel. This peak is located at $q \approx 0.013$ Å$^{-1}$ for $A_{25}B_{104}A_{25}$ and $A_{12}B_{96}A_{12}$ gel, while for the $A_{8}B_{54}A_{8}$ gel, it lies at $q \approx 0.017$ Å$^{-1}$. The peak seems to be more narrow for $A_{12}B_{96}A_{12}$ gel. The form factor shoulder of $A_{25}B_{104}A_{25}$ gel can be observed at $q \approx 0.028$ Å$^{-1}$, whereas for $A_{12}B_{96}A_{12}$ and $A_{8}B_{54}A_{8}$ gel, it is located at $q \approx 0.030$ Å$^{-1}$, and $q \approx 0.038$ Å$^{-1}$, respectively.

A circular scattering pattern indicates the isotropic microstructure for all gels. A higher intensity in the pattern signifies a higher number density of aggregates present in the gel. We attempted to fit the data with the polydispersed hard-sphere model but could not obtain a good fit. Recall that the polydispersed core hard-sphere model assumes that the gel microstructure consists of two phases – PMMA aggregates and PNBA-blocks swollen in the solvent. Particularly, this model does not consider the contrast between solvent and the PnBA as the PnBA chains are swollen in solvent and are dispersed. It is well known that at low polymer concentrations, the PnBA-blocks are more involved in forming the loops as the aggregates are sparsely distributed. These loops behave like a corona around the PMMA aggregates, therefore, to characterize the polymer network quantitatively, the $I(q) - q$ data was fitted with a core-shell model combined with hard-sphere structure factor as $I(q) \propto P(q) \times S(q)$. Here $P(q)$ is a summation of core and shell form factors, and $S(q)$ considers the shell as hard-spheres. The fitting parameters are displayed in table 5.4 on the next page for $\gamma = 0$. The fitted parameters indicate that the cores are bigger for the $A_{25}B_{104}A_{25}$ gel, followed
Table 5.4

Fitting parameters for $I(q) - q$ data at $\gamma = 1$ and different sectors for $A_{25}B_{104}A_{25}$, $A_{12}B_{96}A_{12}$, and $A_{8}B_{54}A_{8}$ gels obtained by using a polydispersed core hard-sphere model. Here, $\gamma$ is strain, $\beta$ the considered angle, $r_c$ core radius, $s$ hard-sphere thickness, and $\psi$ hard-sphere volume fraction.

<table>
<thead>
<tr>
<th>Gel</th>
<th>Sector</th>
<th>$\gamma$</th>
<th>$\beta$ (°)</th>
<th>$r_c$ (nm)</th>
<th>$s$ (nm)</th>
<th>$\psi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{25}B_{104}A_{25}$</td>
<td>Circle</td>
<td>0</td>
<td>0</td>
<td>9.0</td>
<td>12.7</td>
<td>0.22</td>
</tr>
<tr>
<td></td>
<td>Minor-axis</td>
<td>+1</td>
<td>35</td>
<td>9.5</td>
<td>13.6</td>
<td>0.22</td>
</tr>
<tr>
<td></td>
<td>Major-axis</td>
<td>+1</td>
<td>125</td>
<td>9.3</td>
<td>13.3</td>
<td>0.10</td>
</tr>
<tr>
<td>$A_{12}B_{96}A_{12}$</td>
<td>Circle</td>
<td>0</td>
<td>0</td>
<td>8.3</td>
<td>13.9</td>
<td>0.18</td>
</tr>
<tr>
<td></td>
<td>Minor-axis</td>
<td>+1</td>
<td>35</td>
<td>8.7</td>
<td>13.5</td>
<td>0.24</td>
</tr>
<tr>
<td></td>
<td>Major-axis</td>
<td>+1</td>
<td>125</td>
<td>8.8</td>
<td>13.4</td>
<td>0.21</td>
</tr>
<tr>
<td>$A_{8}B_{54}A_{8}$</td>
<td>Circle</td>
<td>0</td>
<td>0</td>
<td>6.7</td>
<td>8.9</td>
<td>0.19</td>
</tr>
<tr>
<td></td>
<td>Minor-axis</td>
<td>+1</td>
<td>35</td>
<td>6.7</td>
<td>8.9</td>
<td>0.19</td>
</tr>
<tr>
<td></td>
<td>Major-axis</td>
<td>+1</td>
<td>125</td>
<td>6.9</td>
<td>9.2</td>
<td>0.15</td>
</tr>
</tbody>
</table>

by $A_{12}B_{96}A_{12}$ gel. This is a consequence of longer PMMA-blocks [20, 19, 112, 124]. A higher inter-aggregate distance ($r_c + s$) for $A_{25}B_{104}A_{25}$ gel signifies that the aggregates are relatively more distant than in other gels, which is expected, due to a lower chain density in this gel. A similar hard-sphere volume fraction ($\psi$) for all gels elucidates that the aggregates in the $A_{12}B_{96}A_{12}$ and $A_{8}B_{54}A_{8}$ gels are loosely connected.

The microstructure of gels was also analyzed for $\gamma = \pm 1$, as shown in figure 5.9 on page 124 and table 5.4 along the major-(M) and minor-axes (m). Unlike the high-$\phi$ gel, not a significant change in the gel microstructure was observed, however, the fitting parameters suggest a slight stretch of PnBA-blocks with the applied strain.

5.5 Conclusions

This investigation work explores the change in the microstructure of a gel with 30% v/v of PMMA-PnBA-PMMA triblock copolymer (LA 2330) in 2-ethyl-1-hexanol as a function of

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temperature and strain using RheoSAXS. We also relate those changes to the stress responses using shear-rheometry. Our analysis provides evidence that the $G'$ plateau is related to the saturation of the microstructure evolution. The fitting of the scattering data with a polydispersed core hard-sphere model reveals that at high temperatures, the aggregates appear as loosely bounded. With a decrease in temperature, new aggregates form leading to an increase in inter-aggregate distance. Upon application of strain, an orientation of microstructure was observed as a result of the displacement of aggregates. Interestingly, the shape and size of aggregates remain intact upon loading. Deduction of stretch and compression ratio (1.11 and 0.89) of hard-spheres from fitted parameters reveals a deviation from those obtained through the affine deformation model (1.25 and 0.75), indicating an inhomogeneous microstructure. A high stress-relaxation of gel in comparison to X-ray exposure time minimizes the possibility of change in microstructure during data collection in oscillatory shear RheoSAXS experiments. The degree of anisotropy in the gel microstructure was studied by the anisotropic factor and angle. Our analysis reveals that the microstructure orientation is independent of strain direction and that the microstructure orients at $\approx 40^\circ$ from the direction of applied strain.

Investigations were also conducted on the low-$\phi$ gels with different PMMA- and PnBA-blocks molecular weights. These gels were composed of 3% LA 2550 ($A_{25}B_{104}A_{25}$), 4% LA 2330 ($A_{12}B_{96}A_{12}$), and 5% LA 2140 E ($A_{8}B_{54}A_{8}$) polymers in 2-ethyl 1-hexanol. The study reveals that the gelation temperature is prominently dictated by the length of PnBA-blocks while the strength of aggregates is governed by the PMMA-blocks. A longer PMMA-block length also increases the stress relaxation time significantly. Strain sweep experiments reveals that despite a significant difference in PnBA-block length, all the gels fracture at similar strain values. This is probably a
result of the lower polymer concentration of the gels with longer PnBA-blocks due to which the PnBA-chains are in pre-stretched condition. A microstructure analysis reveals that the gel with longer PnBA-blocks has lesser aggregate number density and that the core radius is dictated by the length of PMMA-blocks. The application of strain does not show a prominent effect on the low-\(\phi\) gels as for the high-\(\phi\), 30%-Gel.
Stress-relaxation data obtained from shear-rheometry of 30\%(v/v) of $A_{12}B_{96}A_{12}$ gel, where time-dependent shear modulus ($G(t)$) is plotted as a function of time. The solid line denotes the model fit with a stretched-exponential model over the range of 0.01 s to 1800 s.
Shear strain effect on the microstructure of the 30%-Gel at room temperature. At the center, the strain ($\gamma$) curve as a function of time indicates relevant $\gamma$-values, and the origin of $\beta$-angle measurement is indicated in the image of $\gamma=0$. The corresponding 2D patterns obtained from RheoSAXS experiments are arranged around it in a clockwise direction.

Figure 5.3
Oscillatory strain effect on the 30%-Gel at room temperature. (A) Storage modulus ($G'$) and loss modulus ($G''$) as a function of strain amplitude ($\gamma_{amp}$) using an oscillatory frequency ($\omega$) of 1 rad s$^{-1}$ obtained from shear-rheometry experiments. (B) 2D pattern at $\gamma=+0.5$ and $\omega=1$ rad s$^{-1}$ indicating relevant sector angles ($\beta$). Intensity ($I(q)$) as a function of scattering vector ($q$) for (C) the circular pattern at static conditions ($\gamma=0$, $\beta=0$) along with the major-axis and minor-axis for comparison ($\gamma=+0.5$). $I(q) - q$ data fitted with a polydispersed core hard-sphere model for (D) the circular pattern at $\gamma=0$, $\beta=0^\circ$ and $90^\circ$ and circular average, for (E) the minor-axis of the ellipse at $\gamma=+0.5$ and $\beta=40^\circ$ and at $\gamma=-0.5$ and $\beta=140^\circ$, and for (F) the major-axis of the ellipse at $\gamma=+0.5$ and $\beta=130^\circ$ and at $\gamma=-0.5$ and $\beta=50^\circ$. 

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Estimated anisotropic factor of gels. (A) Strain ($\gamma$) on left-y-axis and anisotropy angle ($\chi$) on right-y-axis as a function of time. (B) $\gamma$ on left-y-axis and anisotropy factor ($\Omega$) on right-y-axis as a function of time. RheoSAXS experiments were performed with an oscillatory $\gamma$ of amplitude 0.5 and frequency of 1 rad s$^{-1}$.
Temperature, amplitude, and frequency sweep results for $A_{25}B_{104}A_{25}$, $A_{12}B_{96}A_{12}$, and $A_8B_{54}A_8$ gels obtained from shear-rheometry. (A) Temperature sweep results for the three low-$\phi$ gels displaying $G'$ and $G''$ as a function of temperature. A $\gamma_{amp}=0.01$ and $\omega=1$ rad s$^{-1}$ were used with a temperature ramp of 2°C min$^{-1}$ and equilibration time of 120 s. The estimated $T_{gel}$s are $\approx52$, 42, and 32 °C for $A_{25}B_{104}A_{25}$, $A_{12}B_{96}A_{12}$, and $A_8B_{54}A_8$ gels, respectively. (B) Amplitude sweep results for the three low-$\phi$ gels displaying $G'$ and $G''$ as a function of $\gamma$ using $\omega=1$ rad s$^{-1}$ at RT. (C) Frequency sweep results for the three low-$\phi$ gels displaying $G'$ and $G''$ as a function of $\omega$ using $\gamma_{amp}=0.01$ at RT.
Stress-relaxation results for $A_{25}B_{104}A_{25}$, $A_{12}B_{96}A_{12}$, and $A_{8}B_{54}A_{8}$ gels obtained from shear-rheometry. $G(t)$ as a function of time is plotted for three low-$\phi$ gels. The lines represent the fitting of data using a stretched-exponential model.
RheoSAXS results for $A_{25}B_{104}A_{25}$, $A_{12}B_{96}A_{12}$, and $A_{8}B_{54}A_{8}$ gels at static conditions. Images of the (-1) 2D-scattering patterns at $\gamma=0$ and corresponding (-2) $I(q) - q$ curves in which the lines represent the fitting of data using a core-shell model for (A) $A_{25}B_{104}A_{25}$, (B) $A_{12}B_{96}A_{12}$, and (C) $A_{8}B_{54}A_{8}$ gels.
Strain effect on $A_{25}B_{104}A_{25}$, $A_{12}B_{96}A_{12}$, and $A_{8}B_{54}A_{8}$ gels obtained from RheoSAXS experiments. Images of the (-1) 2D-scattering patterns at $\gamma=+1$ (clockwise) and corresponding $I(q) - q$ curves for the (-2) major-axis, $M$, and (-3) minor-axis, $m$, of the pattern for (A) $A_{25}B_{104}A_{25}$, (B) $A_{12}B_{96}A_{12}$, and (C) $A_{8}B_{54}A_{8}$ gels. The lines represent the fitting of data using a core-shell model. The measurement of $\beta$-angles is also indicated.
6.1 Concluding Remarks

This dissertation advances the understanding of the structure-property relationship of microstructurally complex gels towards their potential practical applications. Here, two types of gel systems are investigated.

The first gel system studied here is a stretchable hydrogel synthesized through a simple free-radical copolymerization reaction. The microstructure of this gel consists of both physical and chemical crosslinks. The gel is obtained by choosing an appropriate ratio of hydrophilic AAc and MAM monomers to hydrophobic PPGDA polymer and is shown to display a high stretchability ($\lambda \approx 8.6$) and resilience as high as $\approx 98\%$, in a typical loading cycle, with negligible residual strain ($\approx 2\%$). For the first time, retraction experiments are performed on a gel. After released from the stretched state, the gel samples achieve a retraction velocity of $\approx 16$ m s$^{-1}$ with an acceleration of $4 \times 10^3$ m s$^{-2}$. These properties resemble naturally occurring elastomeric biopolymers like resilin. Furthermore, based on the results presented here, it can be hypothesized that designing materials for power-amplified activities require a high tensile modulus to gel density ratio, high stretchability, and minimal energy dissipation or high energy recovery. The high resilience and stretchability of this gel have also been utilized in a power amplified activity like catapulting a small projectile over a distance of $\approx 8$ m.
By varying the PPGDA polymer concentration from 0.1 to 0.3, 1, and 3 wt%, it is shown that the stretchability and the ultimate failure stress of these gels can be changed. The low strain modulus of the gels appears to be less affected by the PPGDA concentration, yet at high strain values, the resultant stress increases significantly with an increase in the PPGDA concentration. Interestingly, the resilience for a given loading cycle is found to be highest for the gel with 1 wt% of PPGDA concentration and decreases with further increase in PPGDA concentration. These gels display a remarkable swelling behavior in water and absorb water up to $12 \times 10^5$ times their dry weight. Such a high swelling behavior is essentially due to the anionic PAAc chains that attract water. These anionic chains are shielded by salt cations, which diffuse to the water upon immersion in a water bath. Swelling experiments were also performed with saline solutions of concentration 0.2, 0.4, and 0.8 M of NaCl. These experiments indicate $\approx 40$ times lower swelling capability in 0.2 M solution in comparison to that in water, which further decreases to $\approx 240$ times in 0.8 M solution.

Polymer gels display non-linear responses at large strain values as a consequence of the change in their microstructure. Such a transient change in microstructure was studied in the second gel system. Two different physically crosslinked gels with different polymer concentrations have been used. The study successfully captures and characterizes the change in the microstructure of the gels during temperature-induced gelation, subjected to large amplitude oscillatory strain, and during the stress-relaxation process. The change in microstructure is also related to the stress responses of gels.

The first physically crosslinked gel is composed of 10 and 20 wt% of PS-PI-PS in mineral oil. Small-angle X-ray scattering experiments of the gel samples are performed on a RheoSAXS setup, and the corresponding stress responses are measured on a rheometer. During gelation, the
scattering data suggests that loosely bounded PS-aggregates are observed even at temperatures higher than $T_{gel}$, obtained from shear-rheology experiments. The microstructure evolves with decreasing temperature and the evolution is shown to be complete at room temperature, as depicted by a plateau in $G'$. The application of large deformations orients only a fraction of aggregates towards the strain direction, as represented by a circle and ellipse in the 2D-scattering patterns. A modified form of polydisperse core hard-sphere model with two hard-spheres can capture the scattering data at the static and under loading conditions. The affine deformation model predicts the stretch and compression equivalent to 100% strain as 1.62 and 0.62, respectively, while the scattering analysis displays those values as 1.66 and 0.76 for 10%-Gel and 1.38 and 0.75 for 20%-Gel. The deviation from the theoretical prediction is higher for 20%-Gel, suggesting an increase in inhomogeneity at higher polymer concentrations. The stress-relaxation data is fitted with a stretched-exponential model and suggests that the microstructure relaxes faster at higher temperatures.

These results are compared with another physical gel consisting of 30% v/v of PMMA-PnBA-PMMA polymer ($A_{12}B_{96}A_{12}$) in 2-ethyl-1-hexanol. This gel, denominated as 30%-gel or high-$\phi$ gel, is also investigated for the change in microstructure during gelation, oscillatory shear, and stress relaxation at different temperatures. The microstructural change of the 30%-Gel is also related to the stress responses, captured by using shear-rheology. The scattering is fitted with a polydisperse core hard-sphere model suggesting that at high temperature, the PMMA-blocks form loosely bounded aggregates. With a decrease in temperature, an increase in inter-aggregate and core radius was observed. This is attributed to a higher number of PMMA-blocks contributing to the aggregates with a decrease in temperature. Upon application of strain, the scattering data
suggests an orientation in microstructure as a result of the displacement of aggregates, however, unlike in the case of PS-PI-PS gel, the homogeneous distribution of load is observed. The deduction of stretch and compression ratios (1.11 and 0.89) of hard-spheres reveals a slight deviation from those obtained through the affine deformation model (1.25 and 0.75), indicating an inhomogeneous microstructure. Upon the application of 50% strain amplitude, an anisotropic factor of ≈0.1 was observed with a microstructure orientation towards ≈40° from the direction of applied strain.

The results presented above for the high-ϕ gel are also compared with those for three acrylic gels of low polymer volume fraction through shear-rheology and scattering experiments. The gels are investigated in a similar manner but at zero-load conditions. The low-ϕ gels are prepared with polymers of different lengths of PMMA-block (A) and PnBA-block (B) in 2-ethyl-1-hexanol. Their designations \( A_{25}B_{104}A_{25}, A_{12}B_{96}A_{12}, \) and \( A_{8}B_{34}A_{8} \) express the blocks length (kg mol$^{-1}$) of the polymer used to prepare the gel. The polymer volume fraction used for the \( A_{25}B_{104}A_{25}, A_{12}B_{96}A_{12}, \) and \( A_{8}B_{34}A_{8} \) gel is 3, 4, and 5% v/v, respectively. The volume fractions are adjusted to keep a similar \( G' \) for all low-ϕ gels. The study reveals that the gelation temperature is prominently dictated by the length of PnBA-blocks and that a higher length of both blocks increases the gelation temperature, as a higher length of PMMA-blocks increases the strength of aggregation. A higher PMMA-block length increases the stress relaxation time significantly. Despite a variation in the length of PnBA-blocks, all the gels fracture at the similar strain values. This is due to the lower volume fraction of polymer in the gels with longer PnBA-blocks, which leads to a lower number density of aggregates resulting in a pre-stretched PnBA-blocks. X-ray scattering data reveals that the gel with longer PnBA-blocks has a lower number density of aggregates and that the core radius
is dictated by the length of PMMA-blocks. The application of strain in these gels causes a relatively less prominent change in the microstructure as compared to the high-\(\phi\), 30%-Gel.

6.2 Future Directions

In present investigation, a hydrogel consist of chemical and physical crosslinks was synthesized using a simple reaction route. This gel displays retractable capability, however, the properties of these gels can be further improved by optimizing the chemical compositions. First, this study on retractable hydrogels can be extended to investigate the effect of PPGDA molecular weight on the mechanical properties of gels. The literature suggests that longer chains cause friction within the aggregates while shorter chains form weak aggregates, therefore, finding an optimum chain length is necessary for achieving optimized properties. Second, a series of gels need to be investigated with different ratios of hydrophilic ionic monomers of AAc to MAM. This investigation combined with a study of the microstructure at zero load and upon deformation can essentially relate the microstructure to the mechanical properties of gels. Such a study can be conducted with a combination of tensile test setup and X-ray scattering experiments. Third, in addition to the optimization of the present system, other combinations of hydrophilic and hydrophobic polymers like poly(ethylene glycol) [PEG] or poly(\(\varepsilon\)-caprolactone) [PCL] can be investigated [11, 93]. Since the retraction properties are governed by the aggregation of hydrophobic chains, a stronger hydrophobic interaction is expected to improve the retraction velocity. Fourth, the present synthesis scheme is limited to hydrogels, which can be potentially extended for organogels. Organogels are known to be rather environmentally stable and have a longer shelf life. A retractable organogel can extend the applications of retractable gels.
The study on physically assembles gels investigates the dynamic change in the microstructure of gels with different compositions. This study can be expanded to investigate the change in the gel microstructure in various solvents. Since most of the studies are focused on polymer architecture and concentration, this study will reveal how the solvent compatibility to each block affects their extensibility, aggregation strength, and gelation. Second, the present study does not account for loops and dangling chains, which can potentially lead to an overestimated bridge density and aggregation number. A combination of small-angle neutron scattering study (SANS) with contrast match and dielectric study can provide more information about the gel microstructure and reveal how the loops are affected by the polymer concentration and block lengths [131]. Third, although this dissertation elucidates the effect of block lengths influencing the mechanical properties and microstructure of gels, the effect of oscillation frequency and amplitude contributing to their non-linear behavior needs to be studied. Such a study might explain the origin of non-linear stress responses in these gels. Fourth, the study of transient change in microstructure can be extended and compared with ABA triblock hydrogels like PCL-PEG-PCL or PPO-PEO-PPO gel systems, which further can be related to the microstructure of retractable gels at large deformations.
REFERENCES


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APPENDIX A

ACHIEVING HIGH-SPEED RETRACTION IN STRETCHABLE HYDROGELS
A.1 Figures and tables related to chapter II
Swelling behavior of gels. (A) As-prepared 17%- , 27%- , and 37%-Gels. (B) Dried gels after 72 h of drying. (C) Gels after swelling for 24 h.
Figure A.2

Dimensions of dogbone samples with marked-lines. (A1) Schematic of the dogbone-shape specimen for tensile experiments representing the dimensions. Images of tensile testing indicating the marked lines on the sample (17%-Gel) that were used to measure the strain ($\varepsilon$) and strain-rate ($\dot{\varepsilon}$). (A2) Unstretched sample, $\varepsilon=0$, and (A3) stretched sample, $\varepsilon=8.45$. 
Gel stretchability and strain-rate dependence. Images of a 17%-Gel (A1) at the unstretched condition ($\varepsilon=0$) and (A2) the maximum stretched condition ($\varepsilon=8.45$). Images of 27%-Gel (B1) at the unstretched condition ($\varepsilon=0$) and (B2) the maximum stretched condition ($\varepsilon=6.54$). Images of 37%-Gel (C1) at the unstretched condition ($\varepsilon=0$) and (C2) the maximum stretched condition ($\varepsilon=4.46$). (D) Nominal stress ($\sigma$) as a function of strain ($\varepsilon$) for a 27%-Gel obtained from tensile testing experiments at strain-rate ($\dot{\varepsilon}$) 0.048 s$^{-1}$ (dark green triangles) and 0.48 s$^{-1}$ (light green open circles). The error bars represent the standard deviation.
Figure A.4

Tensile modulus of gels. Nominal stress ($\sigma$) as a function of strain ($0 \leq \varepsilon \leq 0.35$) for 17%-Gel, 27%-Gel, and 37%-Gel fitted with the neo-Hookean model for uniaxial loading. The corresponding tensile modulus ($E$) values for 17%-Gel, 27%-Gel, and 37%-Gel have been estimated as $\approx 15.1$, 56.8, and 103.1 kPa, respectively. The error bars represent the standard deviation.
Cyclic loading results of a 17% Gel. (A) Nominal stress ($\sigma$) as a function of strain ($\varepsilon$) obtained from cyclic loading of 10, 20, and 30 kPa. (B) Cycles are moved along the $\varepsilon$-axis for clarity and visualization.
Cyclic loading results of a 27\%-Gel. (A) Nominal stress ($\sigma$) as a function of strain ($\varepsilon$) obtained from cyclic loading of 10, 20, 30, 40, and 50 kPa. (B) Cycles are moved along the $\varepsilon$-axis for clarity and visualization.
Cyclic loading results of a 37% Gel. (A) Nominal stress ($\sigma$) as a function of strain ($\varepsilon$) obtained from cyclic loading of 10-130 kPa with a step of 10 kPa. (B) Cycles are moved along the $\varepsilon$-axis for clarity and visualization.
Line positions as a function of time during retraction. The positions of seven marked lines on the samples as a function of time from retraction experiments with $\lambda=6$ for a 37%-Gel sample. The symbols display the values obtained from image processing, and the lines indicate the fifth-order Fourier fit.
Table A.1

Results of swelling behavior of gels. The results indicate the water content in as-prepared gels and the swelling water capacity.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Water content in as-prepared samples [%, g g⁻¹]</th>
<th>Swelling ratio after swell in water [g g⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>17%-Gel</td>
<td>80.87 ± 0.88</td>
<td>87.85 ± 14.92</td>
</tr>
<tr>
<td>27%-Gel</td>
<td>67.64 ± 0.15</td>
<td>44.16 ± 1.35</td>
</tr>
<tr>
<td>37%-Gel</td>
<td>64.92 ± 0.09</td>
<td>34.55 ± 0.05</td>
</tr>
</tbody>
</table>
Resilience of gels. Maximum stress, strain, and resilience (\%) values for 17\%-Gel, 27\%-Gel, and 37\%-Gel samples corresponding to the highest stress cycle applied during cyclic-loading experiments.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Maximum stress [kPa]</th>
<th>Maximum strain</th>
<th>Resilience [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>17%-Gel</td>
<td>30</td>
<td>4.8</td>
<td>88.6</td>
</tr>
<tr>
<td>27%-Gel</td>
<td>50</td>
<td>3.9</td>
<td>90.3</td>
</tr>
<tr>
<td>37%-Gel</td>
<td>130</td>
<td>2.2</td>
<td>97.7</td>
</tr>
</tbody>
</table>
APPENDIX B

INVESTIGATING THE EFFECT OF HYDROPHOBIC POLYMER CONCENTRATION IN STRETCHABLE HYDROGELS
B.1 Figures and tables related to chapter III
Figure B.1

Translucent and transparent dogbone-shaped gels. As-prepared samples of (A) 0.3%-Gel and (B) 3%-Gel.
Strain-rate dependence for 0.3%-Gel on tensile experiments. Tensile experiment results displaying stress ($\sigma$) as a function of strain ($\varepsilon$) for 0.3%-Gel at strain-rate ($\dot{\varepsilon}$) of 0.048 and 0.48 s$^{-1}$ at room temperature. The error bars, smaller than the symbols in some cases, represent the standard deviation.
Figure B.3

Cyclic-loading curves for gels. Cyclic-loading (loading and unloading) curves for (A) 0.1%-Gel, (B) 0.3%-Gel, and (C) 1%-Gel. (A1, B1, C1) displays the cyclic-loading curves shifted along the strain-axis for clarity, and (A2, B2, C2) displays the cyclic-loading curves compared with the tensile curve of the corresponding gel.
Images of dried gel samples and after immersion in water. The images show the (-1) dried samples and (-2) the same specimens after immersion in water for 144 h of (A) 0.1%-Gel and (B) 0.3%-Gel. The images correspond to the data at 0 h and 144 h shown in figure 3.3 on page 62A.
APPENDIX C

CAPTURING THE TRANSIENT MICROSTRUCTURE OF A PHYSICALLY ASSEMBLED

GEL SUBJECTED TO TEMPERATURE AND LARGE DEFORMATIONS
C.1 Figures and tables related to chapter IV
Table C.1

Gel nomenclature, polymer concentration in wt%, polymer volume fraction ($\phi$), and PS and PI content in the gels (wt%).

<table>
<thead>
<tr>
<th>Sample</th>
<th>wt%</th>
<th>$\phi$ (v/v)</th>
<th>PS (wt%)</th>
<th>PI (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10%-Gel</td>
<td>10</td>
<td>0.089</td>
<td>2.9</td>
<td>7.1</td>
</tr>
<tr>
<td>20%-Gel</td>
<td>20</td>
<td>0.181</td>
<td>5.8</td>
<td>14.2</td>
</tr>
</tbody>
</table>
Schematic representing gel structure. 3D crosslinked network formed by poly(styrene)-poly(isoprene)-poly(styrene) [PS-PI-PS] triblock copolymer in mineral oil, where the PS-blocks form aggregates bridged by PI-blocks. The PS-aggregates of core radius $r_c$ are surrounded by a fictitious hard sphere of thickness $s$ contained in a cube with dimension of $D_1$. 
2D-scattering patterns for gels at 27 °C during a strain cycle with $\gamma_{amp}$ of 0.1. 2D-scattering patterns are shown for $\gamma$ (intracycle strain) equal to 0, 0.1, and -0.1 for the (A) 10%-Gel and (B) 20%-Gel. The dashed lines in the $\gamma_1$ images indicate the analyzed $q$-range.
Gel structure at the static condition and after the application of a shear strain. (A) Gel structure formed by PS-aggregates surrounded by a fictitious hard sphere contained in a cube with dimension $D_1$ at the static condition. (B) The change of structure after a shear strain is applied, displaying compressed, and stretched chains. The corresponding cube has dimension of $D_2$. 

Figure C.3
Stress relaxation for 10%- and 20%-Gels over 1800 s at different temperatures obtained from shear rheology experiments. Time-dependent modulus ($G(t)$) over time with an applied step strain ($\gamma_{step}$) of 0.3, and fitted with a stretched exponential function for the (A) 10%-Gel at 27 and 40 °C, and the (B) 20%-Gel at 27, 50, and 70 °C.
Results for the stress relaxation experiments at 27 °C, azimuthal plots, and 2D-scattering patterns for gels. Time-dependent modulus ($G(t)$) fitted with stretched exponential function, 2D-scattering patterns at different time points, and stacked azimuthal plots over time are shown for the (A) 10%-Gel and (B) 20%-Gel. Here, $t_2$ is just after the strain is applied. The dashed lines in the $t_1$-images indicate the analyzed $q$-range for each case.
Figure C.6

$I(q) - q$ data corresponding to $t_2$ obtained from RheoSAXS experiments for 20%-Gel at 50 °C. A step strain $\gamma_{step}=0.3$ was applied and the gel was allowed to relax. Here, the sector averages along major- and minor-axis ($\beta=125^\circ$ and $30^\circ$) are compared with the circular average data at the static condition ($\gamma_{step}=0$). The inset represents the oriented 2D-scattering pattern along with the azimuthal angles ($\beta$) corresponding to the major- and minor-axes.
C.2 Model description

Model fit for the gels at static conditions: We have characterized the gel microstructure using a polydispersed core hard-sphere model for the gels at static conditions. According to this model, the PS-aggregates can be viewed as cores having a Gaussian distribution in radius. The cores have a mean radius $r_c$ with polydispersity $\sigma/r_c$. The cores are surrounded by fictitious hard spheres, concentric to the cores, with thickness $s_1$ estimating the radius of hard spheres as $r_c + s_1$. The hard spheres occupy a volume fraction $\phi_1$ in the gel. The model is a combination of a spherical form factor ($P(q)$) multiplied with hard-sphere structure factor ($S(q)$), mathematically represented as $I(q) \propto P(q) \times S_1(q)$. The inter-aggregate distance, approximately representing the end-to-end distance of a PI-block in the gel can also be calculated as $D_1 = (4\pi R^3/(3\psi_1))^{1/3}$ [106], where $R = r_c + s_1$ is the radius of the hard-sphere. The above model is also used for the cases in which the gel is under deformation but the 2D scattering pattern does not display a split.

Model fit for the gels at stretched conditions: For the gels at $\gamma = \pm 1$, a modified polydispersed core hard-sphere model was used for the fitting. The model is justified as follows. At these $\gamma$ values, we observed a circular pattern and an elliptical pattern. The circular pattern resembling the scattering pattern at the static condition. The oriented microstructure displays an elliptical pattern. The $I(q) - q$ curve displays two length scales viz. (1) along the minor-axis, displaying the increase in the inter-aggregate distance as a result of applied $\gamma$, and (2) along the major-axis, signifying a decrease in the inter-aggregate distance or compression as a consequence of stretching in the orthogonal direction (minor-axis). The state of the hard spheres in case-1 and -2 can be referred to as stretched and compressed, respectively, when compared with those at static conditions. Therefore, at a particular $\gamma$, three inter-aggregate distances can be envisaged -
unperturbed, increased, and decreased. Along with the minor-axis sector, the $I(q) - q$ data signifies two arrangements of hard spheres- unperturbed and stretched. Similarly, along the major-axis, the data represents unperturbed and compressed hard spheres. Note that our data indicates an intact form factor peak, meaning that the aggregates do not change the size and shape during deformation. Since the value of the hard-sphere radius ($R$) signifies the inter-aggregate distance, the changed inter-aggregate distance can be conveniently represented by adding a hard-sphere in the model while keeping the form factor the same. We represent the modified polydisperse hard-sphere model as $I(q) \propto P(q) \times (S_1(q) + S_2(q))$, where $S_2(q)$ is the structure factor related to the new hard-sphere to capture the characteristics of displaced hard spheres.

**Mathematical expression:** Here, the structure factor is calculated based on Percus-Yevick closure as

$$S(q) = \frac{1}{1 + 25\psi G(A)/A} \quad (C.1)$$

where $A = 4\pi qR$, $R$ is the radius of hard sphere, and $\psi$ is the hard-sphere volume fraction.

$$G(A) = \alpha (\sin A - A \cos A) + \beta/A^3 \left(2A \sin A + (2 - A^2) \cos A - 2 \right) + \gamma \left(-A^4 \cos A + 4((3A^2 - 6) \cos A + (A^3 - 6A) \sin A + 6) \right)/A^5 \quad (C.2)$$

and

$$\alpha = \frac{(1 + 2\psi)^2}{(1 - \psi)^4} \quad (C.3)$$

$$\beta = -6\psi \left(1 + \frac{\psi}{2} \right)^2 / (1 - \psi)^2 \quad (C.4)$$

$$\gamma = \frac{\psi \alpha}{2} \quad (C.5)$$
Form factor of sphere can be mathematically expressed as:

\[ P_1(q, r) = \left( \frac{4\pi r_c^3}{3} \right)^2 \left( \frac{3}{qr_c} \right)^3 \left( \sin(qr_c) - qr_c \cos(qr_c) \right)^2 \]  \hspace{1cm} (C.6)

The polydispersity is \( \sigma/r_c \), where \( \sigma \) is the variance of distribution in aggregate radius \( r_c \). And the average form factor is:

\[ \langle P(q, r, \sigma) \rangle = \int_0^\infty \frac{1}{\sigma (2\pi)^{1/2}} \exp \left( -\frac{(r - r_c)^2}{2\sigma^2} \right) F(q, r) dr \]  \hspace{1cm} (C.7)