Cosolvent-regulated time–composition rheological equivalence in block copolymer solutions

Arjun S. Krishnan, Sönke Seifert, Byeongdu Lee, Saad A. Khan and Richard J. Spontak

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The morphological and mechanical attributes of triblock copolymer solutions composed of miscible, midblock-selective solvents are investigated by small-angle scattering and dynamic rheology. Variation in cosolvent composition at constant copolymer concentration has little effect on copolymer morphology, but promotes large differences in matrix relaxation, as evinced by changes in the shape of isothermal frequency spectra. Shifting these spectra in the frequency domain reveals the existence of time–composition equivalence, wherein shift factors scale with the viscosity of the cosolvent mixture.

Introduction

Block copolymers, macromolecules composed of two or more long, covalently linked sequences of chemically dissimilar repeat units, constitute one of the most widely investigated classes of soft condensed matter due largely to their inherent ability to spontaneously self-assemble. The resultant nanostructures, which can impart multifunctionality to, or serve as templating media for, designer materials, reflect the thermodynamic interplay between interblock incompatibility and interfacial chain packing. Periodic morphologies include A(B) spheres positioned on a body/face-centered cubic (bcc/fcc) lattice in a B(A) matrix, A(B) cylinders on a hexagonal lattice in a B(A) matrix, bicontinuous channels, and alternating lamellae. These morphologies, as well as several aperiodic nanostructures, have likewise been reported for block copolymers in the presence of another (co)polymer, a solvent or nanoparticles. In the present study, we focus on selectively solvated triblock copolymer systems at solvent concentrations where the copolymer molecules self-organize into spherical micelles at equilibrium.

Triblock copolymers possessing glassy/crystalline A endblocks and a soft (low glass transition temperature, \( T_g \)) B midblock are routinely referred to as thermoplastic elastomers due to their shape-memory capability. Incorporation of a midblock-selective solvent into such a copolymer at the concentration levels considered here (vide infra) yields thermoplastic elastomer gels, which are capable of returning to their initial dimensions upon large or cyclic deformation and providing considerable vibration dampening. Mechanical attributes such as these are important in technologies ranging from pressure-sensitive adhesives and cable casings to sporting goods and dielectric elastomers. Thermoplastic elastomer gels derived specifically from ABA triblock copolymers also provide fundamental insight into molecular networks, which in this case are stabilized by dispersed micelles that act as physical crosslink sites. Of particular interest in this regard are those copolymer molecules whose midblocks are anchored in, and thus serve to bridge, neighboring micelles. Previous efforts on this topic almost exclusively address systems containing a single selective solvent.

Recent studies have confirmed earlier predictions that the polymer conformational behavior responsible for bulk properties and phase behavior can be controllably manipulated through the judicious use of miscible cosolvents. Cosolvents have been found to alter solution viscosity and polymer solubility, as well as trigger molecular aggregation/collapse. While immiscible (organic + aqueous) cosolvents have yielded a wealth of nanostructures in amphiphilic triblock copolymer systems, few studies have, however, sought to explore the effect of miscible, organic cosolvents on the morphologies and properties of thermoplastic elastomer gels. Quintana et al. have employed cosolvents as a physical route by which to tune solvent quality in their investigation of copolymer micellization, whereas Bates and co-workers have elucidated the compatibilizing efficacy of triblock copolymers in the presence of partially miscible asphalt blends. The objective of the present work is to discern how miscible cosolvents influence the morphological characteristics and viscoelastic properties of thermoplastic elastomer gels.

Experimental

Two commercial poly[styrene-b-(ethylene-co-butylene)-b-styrene] triblock copolymers (BCs, Kraton G1650 and G1651) were obtained from Kraton Polymers (Houston, TX). Their number-average molecular weights (polysidispersities), as measured by SEC, were 95 000 (1.05) and 267 000 (1.10), respectively, and their compositions ranged from 30 to 33 wt% S. One cosolvent was an aliphatic/alicyclic white mineral oil (MO, Hydrobrite 380) with a molecular weight of ~500, manufactured by Sonneborn, Inc. (Tarrytown, NY). The other cosolvent, a hydrogenated resin (HR, Escorez 5380) containing cyclic C5 and C9 moieties, was acquired from ExxonMobil (Houston, TX). Binary and ternary gels were prepared by melt mixing according to the procedure described earlier. Copolymer concentrations (expressed in terms of mass fraction, \( w_{BC} \)) ranged from 0.15 to 0.35 in 0.05 increments. For each copolymer concentration, the mass fraction of HR in the cosolvent was varied from 0.00 to 1.00. To minimize oxidative degradation during mixing, 1 wt% Irganox B220 was added as an antioxidant. Resultant gels were compression-molded at 180 °C and quenched to ambient temperature, yielding films measuring 2–3 mm thick.

The morphologies of gels varying in \( w_{HR} \) at constant \( w_{BC} \) were examined by small-angle X-ray scattering (SAXS) using the...
differential diffractometer maintained in undulator beamline 12ID-C at Argonne National Laboratory. The beam size, total flux and sample-to-detector distance were 0.5 mm × 0.1 mm, 3 × 10^{12} photons s^{-1} and 2.8 m, respectively. Two-dimensional scattering patterns of the gels were collected on a MAR CCD detector with 1024 × 1024 pixels after an exposure time of 10–200 ms. Images were collapsed to intensity patterns by first correcting the images for dark background, specimen transmittance, pixel efficiency and beam inhomogeneities, followed by azimuthal integration of intensity along the momentum transfer (q), where q = (4π/λ)sin(θ/2), λ is the X-ray wavelength (0.1332 nm) and θ is the scattering angle.

Dynamic shear rheology was performed on specimens at ambient temperature on a Rheometrics RMS-800 strain-controlled rheometer equipped with 25 mm parallel plates separated by a 2 mm gap. Isochronal strain sweeps identified the linear viscoelastic (LVE) limit of each specimen. Frequency (ω) spectra were acquired from 10^{-2} to 10^{2} rad s^{-1} at strain amplitudes ranging from 0.3 to 2% to avoid overloading the load cell while remaining in the LVE regime. Resultant datasets were analyzed using the IRIS Rheo-Hub software suite. Zero-shear viscosity measurements were also performed at 25 °C and above on cosolvent mixtures (without copolymer). The Tg's of cosolvent mixtures were measured by differential scanning calorimetry (DSC) with a TA Q2000 calorimeter operated from 25 °C to 80 °C at a heating rate of 5 °C min^{-1}, whereas the thermal signatures of gels were examined by dynamic mechanical thermal analysis (DMTA) conducted on a TA Q800 instrument operated from 30 °C to 100 °C at a cooling rate of 5 °C min^{-1} and a frequency of 1 Hz. Values of Tg were extracted as DSC inflection points (cosolvent mixtures) and maxima in dynamic loss moduli (triblock copolymer gels).

**Results and discussion**

A series of SAXS patterns acquired from a gel with w_{BC} = 0.30 at several values of w_{HR} is presented in Fig. 1. The binary BC/MO gel and the two ternary BC/MO/HR gels exhibit well-defined scattering maxima due to the difference in electron density between the S-rich micelles and the MO-rich matrix. Conversely, the scattering pattern obtained from the binary BC/HR gel is nearly featureless because of similar electron densities. The positions of the form factor peaks at high q, which depend on micelle size and shape, are nearly constant in the MO-containing gels and, along with the positions of the minima, confirm that the micelles in all cases are spherical. Analysis of these patterns with the Percus–Yevick model for hard-sphere micelles reveals that the mean micellar radius varies from 13.7 to 14.7 nm. The corresponding polydispersities (9.4–13%) and hard-sphere radii (23.8–25.0 nm) likewise show little variation, verifying that the morphologies of these gels do not change appreciably with cosolvent composition.

Fig. 2 shows the dependence of the dynamic storage and loss moduli (G' and G''), respectively) on ω for a series of gels containing 25 wt% low-molecular-weight copolymer at ambient temperature. At low w_{HR} (Fig. 2a), the moduli are effectively independent of ω over the entire ω range examined, indicating that the materials behave as gels consisting of physically crosslinked molecular networks, as previously reported for binary BC/MO blends. At w_{HR} = 0.60 in Fig. 2a, however, G'' displays a modest upturn at high ω. This upturn becomes more pronounced and shifts to lower ω as w_{HR} increases further in Fig. 2b. Another important feature of the ω spectra in Fig. 2b is that a well-defined G'–G'' crossover frequency (ω_c) is discernible at 40 rad s^{-1} when w_{HR} = 0.80. As w_{HR} is increased to 0.90 and beyond, ω_c shifts to markedly lower frequencies. The relaxation time (τ_R), given by 1/ω_c, correspondingly increases by more than 3 decades from ~25 ms to ~89 s as w_{HR} increases from 0.80 to 1.00. A crossover point, expected in the ω spectra of viscoelastic materials, normally delineates viscous behavior at ω < ω_c from elastic.

![Fig. 1](image1.png)  
**Fig. 1** Series of SAXS patterns acquired from triblock copolymer gels containing 30 wt% high-molecular-weight triblock copolymer at different cosolvent compositions (labeled).

![Fig. 2](image2.png)  
**Fig. 2** Dynamic storage (G', open symbols) and loss (G'', filled symbols) moduli presented as a function of frequency (ω) for gels containing 25 wt% low-molecular-weight triblock copolymer at different cosolvent compositions (labeled) and ambient temperature. Results obtained from gels with low and high concentrations of HR are displayed in (a) and (b), respectively.
behavior at \( \omega > \omega_c \). The data seen in Fig. 2b contradict this expectation up to \( w_{HR} = 1.00 \). In the limit of pure HR, however, a second, conventional \( \omega_c \) emerges at a higher \( \omega \) (shorter \( t_R \)).

Shifting the \( \omega \) spectra portrayed in Fig. 2 in the \( \omega \) domain yields a single master curve, which is presented in Fig. 3. The existence of two crossover frequencies is evident in this figure and reveals that the gels exhibit viscous behavior over a relatively narrow frequency (or time) range. This result is consistent with observations of the gels after they are stretched: gels with a high MO content behave elastically by abruptly snapping back to their relaxed size and shape, whereas gels with a high HR content undergo an initially abrupt dimensional change, followed by a slower, more gradual return to their original size and shape. We attribute this behavior in the HR-rich gels to molecular-level competition between the elasticity of the copolymer network, which promotes shape retention, and the high viscosity of the HR (vide infra), which impedes shape change. Theoretical developments are, however, warranted to substantiate this interpretation and discern the relative importance of such factors on mixed-matrix relaxation.

The process of time–composition superposition (tCS) used to generate Fig. 3 greatly expands the accessible frequency range under isothermal conditions. Unlike classical time–temperature superposition (TTS),

\[ \omega_c \] 

\[ \frac{\omega}{\omega_c} \] 

tCS affords a unique opportunity to explore changes in mechanical behavior without exposing an organic polymer to temperatures that may promote degradation or a phase change. The quality of tCS in Fig. 3 can be established from a van Gurp–Palmen plot,

\[ \omega \] 

\[ \frac{\omega}{\omega_c} \] 

wherein the phase angle (\( \delta \)) vs. complex modulus (\( G^* \)). Data collected from gels with varying HR levels satisfactorily superimpose in the inset of Fig. 3, confirming that tCS satisfactorily describes relaxation of the cosolvent-rich matrix. Superpositioning is only valid when fundamental relaxation mechanisms remain unaffected by changes in the parameter responsible for frequency shifts, which explain the poor superposition of \( G'' \) at low \( \omega \) in Fig. 3. The slope of these upturns, attributed to the pullout of S endblocks from micelles during shear, is \(-0.24\), which is close to \(-0.23\) reported\(^{28}\) for endblock relaxation of triblock copolymer in solution. Since this relaxation depends on the energy of endblock/(co)solvent interactions, lack of tCS in this regime implies that the quality of the cosolvent mixture changes with composition. While a detailed account of this observation is beyond the scope of the present work, this topic will be addressed in a forthcoming publication.

Shift factor \( (a_c) \) values derived by tCS from the gels with \( w_{BC} \) ranging from 0.15 to 0.35 are shown as a function of HR concentration in Fig. 4a. The \( \omega \) spectra have all been arbitrarily shifted relative to \( w_{HR} = 0.60 \) so that \( a_c = 1.0 \) at this cosolvent composition. Although the shift factors increase monotonically with increasing \( w_{HR} \), further supporting the validity of tCS, we must ensure that the cosolvents are sufficiently miscible. The inset in Fig. 4a reveals that each cosolvent mixture (without BC) exhibits a single \( T_g \), which verifies cosolvent miscibility.\(^{28}\) Note that the neat HR exhibits a \( T_g \) just above ambient temperature, in which case it possesses a much higher viscosity than the MO. Another consideration in this vein is the miscibility of the ternary gel matrix. According to complementary DMTA measurements (not shown here), a single, lower \( T_g \) is evident for each gel, confirming that the cosolvents remain homogeneously mixed in the presence of the BC. Values of this \( T_g \) further
reveal that the presence of copolymer serves to suppress the $T_g$ of each cosolvent mixture due to the low $T_g$ of the EB midblock. From this battery of analyses, we conclude that the MO and HR cosolvents uniformly distribute within the highly swollen EB-rich matrix.

In tTS, shift factors derived from a selectively solvated triblock copolymer relate directly to changes in solvent viscosity, which, in turn, is a function of molecular free volume. Here, $a_C$ is observed to vary nearly linearly with the lower $T_g$ discussed above, which suggests that $a_C$ likewise depends on solvent viscosity and, by inference, molecular free volume. To discern the nature of this dependence, $a_C$ is displayed as a function of cosolvent zero-shear viscosity ($\eta_{0,s}$) in Fig. 4b for all the gels examined here. In cases where $\eta_{0,s}$ was too large to measure directly, data acquired at elevated temperatures have been fitted to an Arrhenius expression to obtain $\eta_{0,s}$ at 298 K. The results provided in this figure indicate the existence of a scaling relationship of the form $a_C \sim \eta_{0,s}^{-\psi(w_{BC})}$, where $\psi$ is a function of $w_{BC}$. The apparent linear dependence of $\psi$ on $w_{BC}$ in the inset of Fig. 4b yields $\psi = 1.01 - 1.64w_{BC}$, which allows the above relationship to be approximated as $a_C \sim \eta_{0,s}^{-1.64}$. This result resembles the Flory exponent (3/5) for a good solvent. Although the MO and HR cosolvents employed in this work are good solvents for the aliphatic midblock of the BC, universal assignment of $n = 0.61$ is nearly equal to the Flory exponent (3/5) for a good solvent. This battery of analyses, we conclude that the MO and HR cosolvents relate directly to changes in solvent viscosity, which verifies that the cosolvent matrix is largely frequency/time domain by varying cosolvent composition under conditions of interest.

Conclusions

This study establishes the existence of time–composition equivalence in triblock copolymer gels containing miscible organic cosolvents. Previous studies reporting such behavior are severely limited and have thus far been restricted to plasticized homopolymers, surfactant solutions and interfacial monolayers. The present result permits investigation of mechanical properties over an expanded frequency/time domain by varying cosolvent composition under isothermal conditions. In the gels examined here, the cosolvents are found to be fully miscible alone, as well as in the presence of the copolymer, which verifies that the cosolvent matrix is largely homogeneous. Since the cosolvents differ significantly in viscosity and since the tCS shift factors scale with cosolvent zero-shear viscosity, it follows that TC equivalence is a consequence of the variation in molecular free volume promoted by cosolvent mixing. While these observations reveal a viable means of broadly tuning/probing the mechanical behavior of solvated triblock copolymer networks, theoretical guidance is needed to elucidate the physical relaxation mechanism underpinning these results so that tCS can be more fully understood and generally applied as a predictive tool in the same fashion as tTS.

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