

Self-Assembly of Partially Charged Diblock Copolymer-Homopolymer Ternary Blends

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Cite This: *Macromolecules* 2022, 55, 4766–4775



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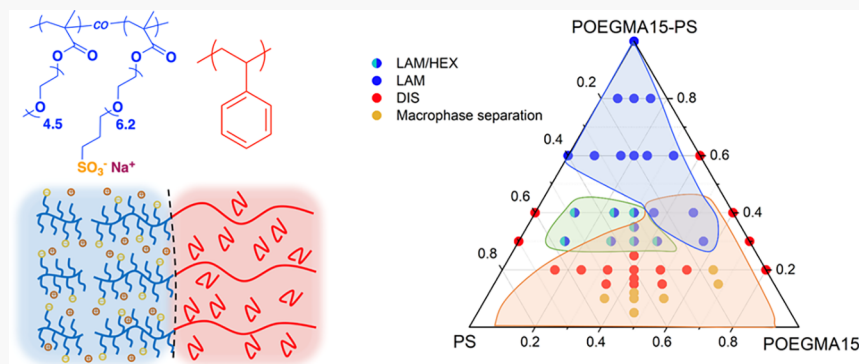
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ABSTRACT: Ternary blends comprising a diblock copolymer and the corresponding homopolymers provide ready access to a variety of morphologies, but the impact of charge on their phase behavior has not been studied extensively. Here, three partially charged ternary blends consisting of symmetric poly[(oligo(ethylene glycol) methyl ether methacrylate-*co*-oligo(ethylene glycol) propyl sodium sulfonate methacrylate)] (POEGMA#), polystyrene (PS), and POEGMA#-PS with different charge fractions were prepared, where # denotes the mole fraction of charged monomers in the POEGMA chain. The phase behavior was systematically studied using small-angle X-ray scattering, and isothermal phase diagrams at 120 °C were constructed. The resulting isothermal planes contain a wide lamellar phase window with a slight deviation from symmetry for ion-containing ternary blends due to the homopolymer size difference. Given the absence of any significant change in the phase diagrams as the charge fraction increases, the role of charge is primarily to increase the segregation strength in the ternary system, as in the case of partially charged diblock polymers. In addition, examination of the increase in domain size along the volumetrically symmetric isopleth reveals a “dry-brush”-like swelling behavior of homopolymers in all three blends, presumably due to the space-filling nature of the oligomeric ethylene glycol side chains on POEGMA.

INTRODUCTION

Polymer electrolytes have great potential in battery and fuel cell applications due to their non-volatility and non-flammability compared with low-molecular-weight liquid electrolytes.^{1,2} Among various polymer candidates, poly(ethylene oxide) (PEO) exhibits promising ionic conductivity as high as 10^{-3} S/cm⁻¹ when blended with salts.³ However, PEO-based electrolytes can suffer from poor mechanical rigidity, a crucial feature to support the structure and suppress dendrite formation in a solid-state battery.^{4,5} Ion transport and mechanical properties generally have to be decoupled in polymer materials due to the intrinsic difference in their chemical structural requirements.

One promising route is to design a polymer system that microphase separates into two continuous and interpenetrating domains, where one is responsible for ion transport and the other supports the structure. One example is the double gyroid phase identified in self-assembled block copolymers.^{6–9} However, the phase window of the gyroid is typically narrow,

posing a challenge to precisely control the polymer composition, especially when blended with different amounts of salt.^{10,11} Furthermore, the domain dimensions are constrained by the copolymer molecular weight. Blending a symmetric diblock copolymer with the corresponding homopolymers is an economically favorable alternative to access bicontinuous structures. Specifically, a polymeric bicontinuous microemulsion (B μ E), analogous to the microemulsion found in water/oil/surfactant systems, has been observed in ternary blends along the volumetrically symmetric isopleth, where equal volumes of two homopolymers A and B are added into a

Received: March 12, 2022

Revised: May 10, 2022

Published: May 27, 2022

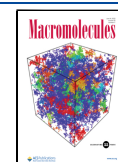


Table 1. Polymer Characteristics

	name	M_n (kDa) ^a	N^b	$f_{\text{POEGMA}\#}^c$	$\bar{D}^d = M_w/M_n$	α^f	$r = [\text{Na}^+]/[\text{EO}]$	α^g
T0	POEGMA0-PS	28.0	436	0.53	1.11	0	0	
	POEGMA0	6.76	104		1.08	0	0	0.24
	PS-6 k	6.40	101		1.05 ^e			0.23
T15	POEGMA15-PS	27.6	428	0.46	1.14	0.15	0.029	
	POEGMA15	7.42	112		1.34	0.15	0.029	0.26
	PS-4 k	4.14	65		1.09			0.15
T25	POEGMA25-PS	27.4	421	0.48	1.13	0.25	0.048	
	POEGMA25	5.96	90		1.28	0.25	0.048	0.21
	PS-4 k	4.14	65		1.09			0.15

^aNumber average molecular weight determined by SEC-MALS. ^bDegree of polymerization calculated based on a reference volume of 0.1 nm³.

^cVolume fraction of the POEGMA# block determined by ¹H NMR spectroscopy. ^dDispersity obtained from SEC-MALS. ^eFrom the supplier.

^fMole fraction of the charged POEGMA moiety in the POEGMA# block. ^g $\alpha = N_{\text{homopolymer}}/N_{\text{diblock copolymer}}$

symmetric AB diblock polymer. Since its first discovery, both experimental and theoretical evidence have supported the existence of the B μ E phase near the mean-field-predicted Lifshitz point, a multicritical point connecting disordered (DIS), multiphase, and lamellar (LAM) regions.^{12–18} With its co-continuous structure and relatively large domain size (20–200 nm), the B μ E has been used as a template to create a host of functional materials.^{19–25} However, most studies of the B μ E have focused on neutral polymer systems with relatively weak degrees of segregation defined by χN , where χ is the segment–segment interaction parameter and N is the volumetric degree of polymerization.

Charge is predicted to exert a substantial influence on the phase behavior of polymer systems with strong and potentially long-range interactions. Specifically, the state of segregation for a diblock copolymer can be affected in several ways: (i) the translational entropy of ions favors disorder;²⁶ (ii) selective dissolution of ions in the polymer domain with higher dielectric constant enhances microphase separation;^{26–28} (iii) electrostatic cohesion between charged species changes χN depending on the ion size, polymer chemistry, and composition;²⁹ (iv) a “cross-linking” effect between certain segments and ions can change χN and affect polymer conformations.^{30–36} The interplay of these effects with polymer composition further complicates the overall phase behavior. “Chimney-like” phase diagrams have been observed in theoretical work by De la Cruz²⁹ et al. and Qin and Hou,²⁶ where the former considers the impact of ion correlation and the latter focuses on the solvation energy. The change in phase behavior in charged polymer systems is also reported in multiple experimental works. Experimentally, the combined effects of the above factors create a complex picture and depend on the specific system studied; for example, both linear and non-linear changes of χ with the salt concentration/ion content have been reported.^{33,37–41}

Despite extensive work on charged diblock copolymers, little is known about the phase behavior of ion-containing ternary blends and how the formation of B μ E might be affected. Recently, Irwin et al. reported the first work on a salt-doped ternary blend composed of lithium bis(trifluoromethane)-sulfonimide (LiTFSI)/polystyrene (PS)/PEO/PS-PEO.⁴² Xie et al. further extended this study and identified a wider B μ E window than the neutral system.⁴³ Single-ion-conducting polymers, where charged moieties are covalently attached to the polymer chains, have the advantage over salt/polymer blends of maximizing the transference number of the cation.^{44,45} Accordingly, Shim et al. investigated a partially

charged ternary system with anions attached to one block, along the volumetrically symmetric isopleth; a broad B μ E phase window was seen.^{46,47}

Here, we expand the scope of charged ternary blends to the full isothermal phase triangle at higher χN . The polymer system comprises poly[(oligo(ethylene glycol) methyl ether methacrylate-*co*-oligo(ethylene glycol) propyl sodium sulfonate methacrylate)] (POEGMA#), PS, and their diblock copolymer POEGMA#-PS, where # denotes the mole fraction of the charged monomer in the POEGMA chain. Three ternary blends are studied with charge fractions of 0, 15, and 25%. By tuning the volume fraction of two homopolymers and the diblock copolymer, we map out the volumetrically symmetric isopleth as well as the isothermal plane with the aid of small-angle X-ray scattering (SAXS). Near-symmetric phase behavior was observed for all three blends with a wide phase-separated region extending to a low homopolymer volume fraction, despite the variation in charge fraction. Analysis of the domain size change along the isopleth reveals that the side chains on the POEGMA lead to relatively “dry-brush” behavior. With little change in the overall phase behavior for this system, the presence of charge primarily acts to enhance the segregation strength and plays only a minor role in altering the symmetry of the isothermal planes.

EXPERIMENTAL SECTION

Polymer Synthesis. Three POEGMA#-PS diblock copolymers with different charge fractions were synthesized through reversible-addition-fragmentation chain-transfer (RAFT) polymerization and post-modification following established procedures.³⁹ Briefly, oligo-(ethylene glycol) methyl ether methacrylate and oligo(ethylene glycol) methacrylate were copolymerized using 4-cyano-4-(dodecylsulfanylthiocarbonyl)sulfanyl pentanoic acid as the chain transfer agent (CTA) and azobisisobutyronitrile (AIBN) as the initiator. The relative ratio between the two monomers was varied to change the charge fraction (#) on the POEGMA# block. Then, the macro-CTAs were chain-extended with styrene through a second RAFT polymerization. Charged moieties (–SO₃Na) were introduced through subsequent sulfonation of the side-chain-terminal hydroxyl groups on the POEGMA block. POEGMA# homopolymers were prepared following a similar procedure but with a different CTA (2-cyano-2-propyl benzodithioate). PS homopolymers were purchased from Scientific Polymer Products, Inc. and used as received.

Molecular Characterization. The polymer structure and composition were determined by proton nuclear magnetic resonance spectroscopy (¹H NMR) using a Bruker Avance III HD (400 MHz) spectrometer. Polymers were dissolved in either DMSO-*d*₆ or CDCl₃. Polymer molecular weights and dispersities were obtained from size exclusion chromatography (SEC) equipped with a Wyatt Optilab T-

rEX refractive index detector and a Wyatt HELEOS-II MALS detector. The SEC experiments were conducted using 0.05 M LiBr dimethylformamide (DMF) solution as the eluent and a flow rate of 1 mL/min at 50 °C. The refractive index increment dn/dc was obtained from Wyatt ASTRA software assuming 100% mass recovery. The polymer characteristics are summarized in Table 1.

Preparation of Ternary Blends. Three sets of ternary blends with charge fractions of 0, 15, and 25% were prepared by dissolving appropriate amounts of POEGMA#-PS, POEGMA#, and PS in 0.5 wt % butylated hydroxytoluene (BHT) benzene solution, stirring vigorously for at least 12 h, and freeze-drying for 2 days. The weight fraction of each component was then converted to volume fraction based on density. The density of polystyrene is taken as 1.05 g/cm³.⁴⁸ Densities for POEGMA#0, POEGMA#15, and POEGMA#25 are estimated to be 1.08, 1.10, and 1.11 g/cm³, respectively, using a group contribution approach.⁴⁹ Diblock copolymer density was calculated based on the volume fraction of each block, assuming that the density of each block equals that of corresponding homopolymers.

Small-Angle X-ray Scattering. SAXS experiments were conducted at DND-CAT 5-ID-D and 12-ID-B beamlines of the Advanced Photon Source at the Argonne National Laboratory. The isotropic 2D scattering patterns were azimuthally integrated to 1D profiles of intensity vs scattering wave vector $q = 4\pi \sin(\theta/2)/\lambda$, where θ is the scattering angle and λ is the beam wavelength ($\lambda = 0.7293$ and 0.886 Å for sector 5 and sector 12, respectively). The examined q range is approximately 0.002 – 0.2 Å^{−1} for 5-ID-D and 0.01 – 0.5 Å^{−1} for 12-ID-B. All the samples were sealed in Tzero DSC pans under a positive argon atmosphere and annealed at 120 °C for over 6 h before quenching in liquid nitrogen to trap the blend morphology. At the beamline, samples were heated directly to 120 °C and annealed at desired temperatures for 15 min before data collection. Some samples were reexamined using a Xenocs Ganesha instrument ($q = 0.007$ – 0.25 Å^{−1}, $\lambda = 1.54$ Å) at the CSE Characterization Facility, University of Minnesota. In this case, samples were sealed in stainless-steel sandwich cells containing Teflon washers, Viton o-rings, and Kapton windows.

RESULTS AND DISCUSSION

Phase Diagram along the Volumetrically Symmetric Isopleth. Charged ternary blends with either added salt^{42,43,50–52} or attached charged moieties on one of the blocks have been explored along the volumetrically symmetric isopleth.^{46,47} In both cases, the systems showed a marked resemblance to their neutral counterparts. Typically, a LAM phase persists at low homopolymer volume fractions (ϕ_H) until the Lifshitz composition is approached, which mean-field theory predicts to be equal to $1/(1 + 2\alpha^2)$ for a symmetric ternary blend along the isopleth.⁵³ At this point, LAM begins to disintegrate into a B μ E phase before macrophase separation takes place. However, it shall be noted that, in one system, a significantly curved interface was also observed along the isopleth when the ion concentration was large. Specifically, Xie et al. reported a Frank–Kasper C15 phase in a LiTFSI/PS/PEO/PS-PEO pseudo-ternary blend, which was attributed to an unequal swelling of the copolymer brush by the homopolymers.⁵¹ Shim et al. first studied partially charged POEGMA#/PS/POEGMA#-PS ternary blends with covalently attached $-\text{SO}_3\text{Na}$ moieties, and the composition window (i.e., $\Delta\phi_H$) of the B μ E channel was found to increase with increasing charge fraction.^{46,47}

Here, we examined a similar set of ternary blends with charge fractions of 0, 15, and 25%, which will be referred to as T0, T15, and T25, respectively. The molecular weights of the diblock polymers are approximately the same, around 28 kDa, with a near-symmetric composition ($f_{\text{POEGMA\#}} \approx 0.5$). Homopolymers with the same charge fraction were added to

swell the respective blocks of the diblock copolymer. The phase behaviors of T0, T15, and T25 were then studied using SAXS. Representative scattering patterns along the volumetrically symmetric isopleth at 120 °C are shown in Figure 1. Pure

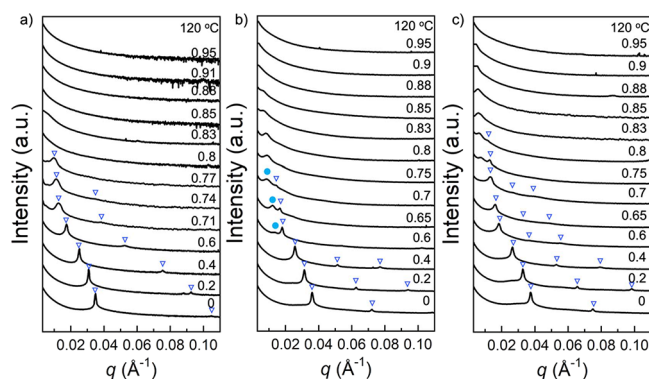


Figure 1. SAXS patterns along the volumetrically symmetric isopleths of ternary blends with (a) 0%, (b) 15%, and (c) 25% charge fraction. The blue triangles indicate the peaks assigned for LAM ($q/q^* = 1, 2, 3, \dots$), while the filled circles stand for peaks associated with the possible formation of HEX ($q/q^* = 1, \sqrt{3}, \sqrt{4}, \dots$).

diblock copolymers exhibit a LAM structure, as indicated by reflections at $q/q^* = 1, 2, \dots$, as reported before.³⁹ With higher ϕ_H , the primary peak of the LAM phase shifts to a lower q , which indicates a larger domain size upon swelling. Phase transitions appear at higher homopolymer loading. In the neutral blends (T0) the primary peak seems to be broader when ϕ_H reaches 0.6. Yet, reexamination using SAXS experiments after longer annealing time resulted in sharp peaks. No clear B μ E phase was observed prior to macrophase separation at $\phi_H = 0.8$. In T15, a second primary peak appears when $\phi_H = 0.6$ – 0.7 , which we assign as hexagonally packed cylinders (HEX). Due to the poor structure at high ϕ_H , second and third order peaks are hard to resolve at 120 °C but can be found at 180 °C for blends with $\phi_H = 0.65$ and 0.7 , as shown in the Supporting Information (Figure S5). Coexistence is also observed in T25, where a broad peak emerges along with a sharp peak at higher q when $\phi_H = 0.75$ and persists to higher ϕ_H . The coexistence is characterized as LAM/B μ E and will be discussed later.

SAXS experiments were also conducted at different temperatures, which generate the phase diagrams as a function of ϕ_H displayed in Figure 2. All phases are assigned based on SAXS. Order-to-disorder transition temperatures (T_{ODT}) were only observed for neutral blends on the diblock-rich side. Further addition of the homopolymer increased T_{ODT} in T0, which became inaccessible over the temperature range explored here. Homopolymers are thus considered to stabilize microphase separation. In contrast to these observations, small homopolymers with $\alpha < 0.25$ are predicted to favor disorder, given the greater translational entropy.⁵³ For POEGMA15-PS and POEGMA25-PS, no T_{ODT} is observed even with a pure diblock copolymer. This increase in T_{ODT} is in accordance with our recent paper, where the stronger segregation strength was attributed to counterion solvation energy and a linear relation between charge fraction and χ_{eff} was established.³⁹ Macrophase separation is assigned when there are no scattering peaks observed, which is reinforced by a cloudy appearance. Shaded areas estimate the boundaries of multiphase separation based on optical observation. It is worth mentioning that the

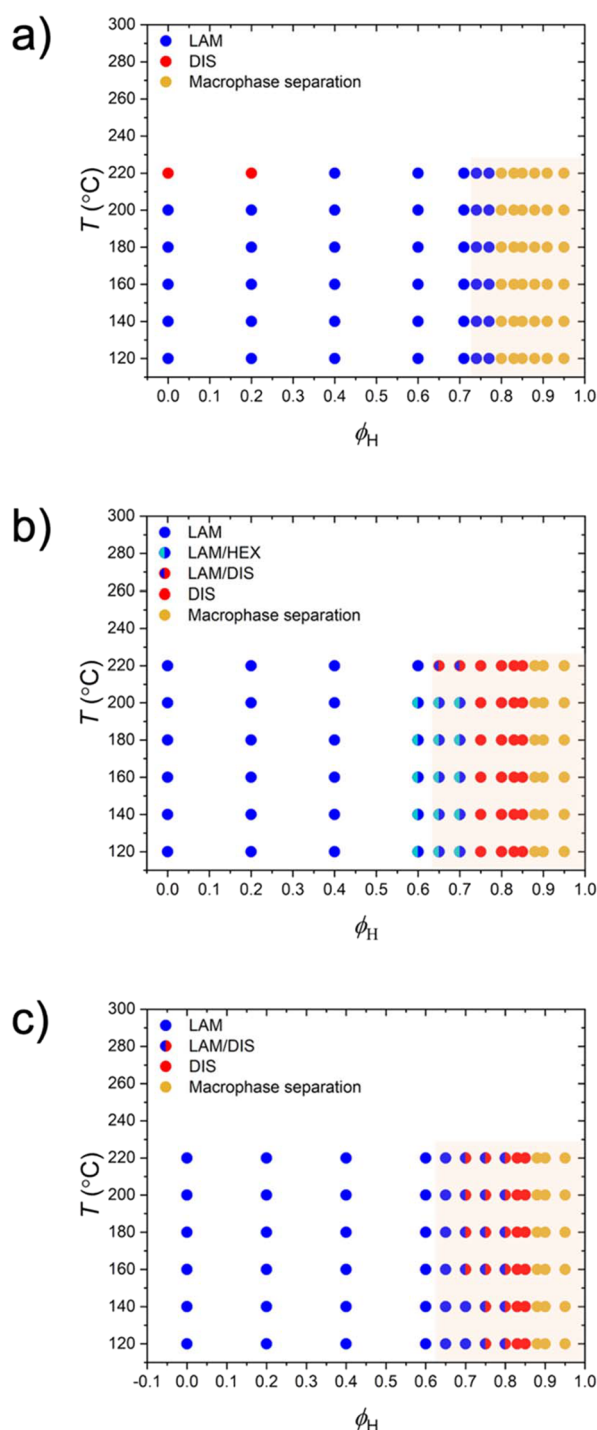


Figure 2. Volumetrically symmetric isopleth for (a) T0, (b) T15, and (c) T25 based on SAXS results. Shaded areas indicate macrophase separation based on optical turbidity.

macrophase separation region extends to strikingly low ϕ_H (~ 0.6) for all three blends; it usually first appears around $\phi_H \approx 0.8$ – 0.9 in neutral ternary blends with similar α values.⁵⁴ The scattering patterns, on the other hand, indicate the presence of LAM and LAM/HEX coexistence within the multiphase region. We conclude that copolymer-rich ordered phases coexist with homopolymer-rich disordered phases at intermediate homopolymer loadings. In the recent work of Vorselaars et al.⁵⁵ and Spencer and Matsen,⁵⁶ the stability of the B μ E phase in a ternary blend is examined by field-theoretic

simulations. They find that the pure B μ E channel is replaced by homopolymer-A-rich phase/homopolymer-B-rich phase/B μ E three-phase coexistence at equilibrium, giving way to A/B/LAM at higher χN . Such three-phase coexistence is attributed to a weak attraction between copolymer monolayers, and excess homopolymers will be excluded from B μ E or LAM domains upon loading beyond saturation. Our results agree at least qualitatively with this theoretical prediction, and the multiphase region widens for T15 and T25 with increasing segregation strength.

Compared to T0, T15 charged blends feature LAM/HEX coexistence. Two factors can contribute to such phase behavior. First, the asymmetry in the size of homopolymers can lead to interfacial curvature. Janert and Schick constructed phase diagrams of neutral ternary blends with a symmetric diblock polymer and varying homopolymer sizes using self-consistent field theory (SCFT).⁵⁷ Shorter homopolymers have a better ability to swell the corresponding block, which would induce the interface to bend. Therefore, more homopolymers with longer chains are required to balance this “wedge” effect. In our work, POEGMA15 ($\alpha = 0.26$) is larger than PS-4 k ($\alpha = 0.15$) in terms of molecular volume. As predicted by their calculation, the phase diagram along the isopleth would experience a transition from LAM to a LAM/HEX window, where POEGMA15 lies in the core of the cylindrical phase. The other factor to be considered here is the conformational asymmetry between POEGMA# and PS. The statistical segment length (b) of PS is reported to be 6.8 Å based on the volume of a styrene monomer (~ 165 Å³).⁵⁸ On the other hand, poly(ethylene glycol) methacrylate with ~ 9 EO repeating units on the side chain is reported to have a statistical segment length of only 2.5 Å based on the same reference volume.⁵⁹ Despite the absence of extensive data for $b_{\text{POEGMA\#}}$, it is still reasonable to expect a large extent of conformational asymmetry in the current system given the brush-like structure of POEGMA. In the case of neat diblock polymers, the block with a larger statistical segment length will reside in the inner side of the interface to release stretching energy.⁶⁰ However, the trend is reversed in the ternary blends. Assuming the “wet-brush” swelling situation, the interface may curve toward the block with a smaller statistical segment length (POEGMA15) as the PS block has a larger coil size and tends to swell more, which would strengthen the curvature change induced by the homopolymer size difference.⁵⁴ Further examination of the complete phase diagram reveals that POEGMA15 lies in the inner side of HEX under the combined effect of the size difference and conformational asymmetry.

Bicontinuous Microemulsions (B μ Es). Upon the addition of homopolymers, the LAM domain spacing along the isopleth increases until the bending energy of the LAM structure and the thermal fluctuation become comparable, where a B μ E phase is observed.¹² The detailed structure of the B μ E in neutral ternary blends has been experimentally investigated by small-angle neutron scattering, SAXS, and rheological measurements and directly observed using transmission electron microscopy.^{12,14,16,61–65} Here, we examine the possible formation of B μ E in partially charged POEGMA#/PS/POEGMA#-PS blends based on SAXS. Although not observed in T0, a broad peak, indicative of a disordered structure, is present around $\phi_H \sim 0.8$ in blends T15 and T25, as shown in Figure 1. To characterize the structure, the Teubner–Strey model was applied to fit the scattering curves.⁶⁶

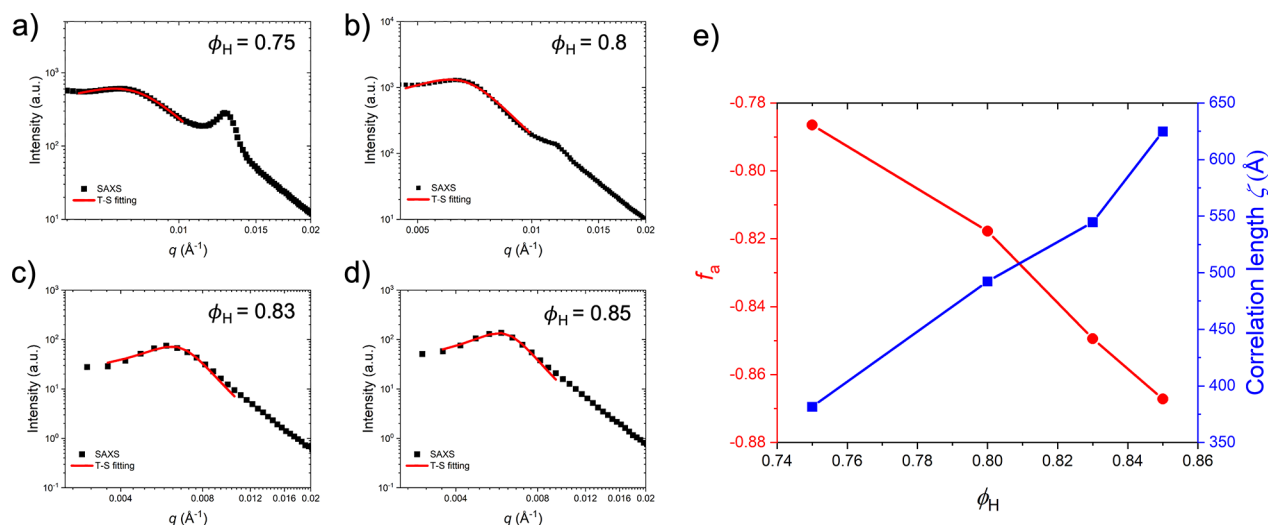


Figure 3. SAXS profiles of T25 with ϕ_H = (a) 0.75, (b) 0.8, (c) 0.83, and (d) 0.85. The red line is the Teubner–Strey fitting. (e) Amphiphilicity factor f_a (red) and correlation length ξ (blue) as a function of ϕ_H .

$$I(q) = \frac{1}{a_2 + c_1 q^2 + c_2 q^4} \quad (1)$$

where I is the scattering intensity and a_2 , c_1 , and c_2 are the fitting parameters. Using these parameters, the structure of B μ E can be well described by the amphiphilicity factor f_a , correlation length ξ , and domain size $d_{B\mu E}$, given, respectively, as

$$f_a = \frac{c_1}{\sqrt{4a_2c_2}} \quad (2)$$

$$\xi = \left[\frac{1}{2} \left(\frac{a_2}{c_2} \right)^{1/2} + \frac{1}{4} \left(\frac{c_1}{c_2} \right) \right]^{-1/2} \quad (3)$$

$$d_{B\mu E} = 2\pi \left[\frac{1}{2} \left(\frac{a_2}{c_2} \right)^{1/2} - \frac{1}{4} \left(\frac{c_1}{c_2} \right) \right]^{-1/2} \quad (4)$$

Particularly, f_a provides a metric of B μ E quality, where $f_a = -1$ indicates a LAM phase and $f_a = 0$ corresponds to the “Lifshitz” line. The correlation length ξ , on the other hand, assesses the coherence of the periodic structure. Typically, a B μ E phase is considered to be well structured with $-1 < f_a < 0$ and a relatively large ξ . Selected samples of T25 were examined, and the fitting results are shown in Figure 3a–d. The broad peaks agree well with the T-S model, showing a characteristic q^{-4} decay at larger q . For $\phi_H = 0.75$ and 0.8, a sharp peak at higher q is also observed, which we assigned as the LAM phase, as no other ordered phase appears in the vicinity of this composition. Examination of the domain size of B μ E and the LAM phase in this coexisting window using eqs 4 and 5 reveals that B μ E has a much thicker domain than the LAM phase at the same composition, as shown in Figure S8. A further increase in ϕ_H leads to the disappearance of the sharp LAM peak and leaves a single broad peak at $\phi_H = 0.83$ and 0.85. The coexistence of LAM/B μ E has been reported before in multiple ternary blends.^{42,67,68} The changes in f_a and ξ with ϕ_H are summarized in Figure 3e. Both the decrease in f_a and the increase in ξ indicate a more structured B μ E with higher ϕ_H . This counterintuitive behavior can actually be explained by the composi-

tional change of the B μ E phase. With the LAM structure weakening upon homopolymer swelling, a higher fraction of POEGMA25-PS is incorporated into the coexisting B μ E phase, which strengthens the B μ E structure.

Although a wide composition window ($\Delta\phi_H \sim 10\%$) of B μ E coexisting with other phases is observed for charged ternary blends, it is hard to isolate the effect of charge on the formation of B μ E given the existence of the homopolymer size difference in T15 and T25. However, the current results show the feasibility of targeting a B μ E phase over a broad composition range by adjusting both the charge fraction and homopolymer size.

Domain Size along the Symmetric Isopleth. The domain size d and the average area per junction A_c can be used to characterize the polymer distribution in a given phase, where d indicates the thickness of a domain while A_c gives information on the lateral crowding. For the LAM phase in the systems studied here, these metrics can be calculated using eqs 5 and 6, respectively

$$d_{\text{LAM}} = \frac{2\pi}{q^*} \quad (5)$$

$$A_c = \frac{2M_{\text{POEGMA\#-PS}}}{N_A \rho_{\text{POEGMA\#-PS}} (1 - \phi_H) d_{\text{LAM}}} \quad (6)$$

where $M_{\text{POEGMA\#-PS}}$ and $\rho_{\text{POEGMA\#-PS}}$ are the molecular weight and density of POEGMA#-PS, respectively, and N_A is Avogadro's constant. The resulting d relative to that in the pure diblock copolymer (d/d_0) and A_c are plotted as a function of ϕ_H and shown in Figures 4 and 5, respectively. The changes in d/d_0 and A_c can be further interpreted regarding the swelling behavior of homopolymers. Setting aside the issue of macrophase separation, there are two limits to be considered, namely, the wet-brush and dry-brush limits. In the wet-brush limit, homopolymers mix well with the corresponding block and distribute uniformly in the block polymer.⁶⁹ In the dry-brush limit, on the other hand, homopolymers are expelled from the block polymer brush and form a homopolymer-rich region in the middle of the corresponding domain. Due to these differences in homopolymer distribution, the domain size will change differently with ϕ_H along the isopleth. Usually, the

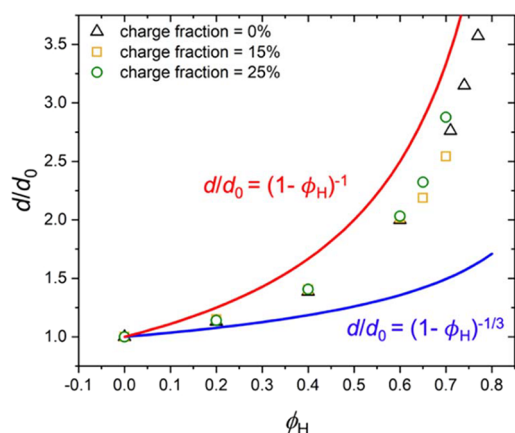


Figure 4. Relative domain size (d/d_0 , d_0 denotes the domain size when $\phi_H = 0$) change with ϕ_H along the isopleth at 120 °C. The red line and the blue line represent the dry-brush and wet-brush swelling limits, respectively.

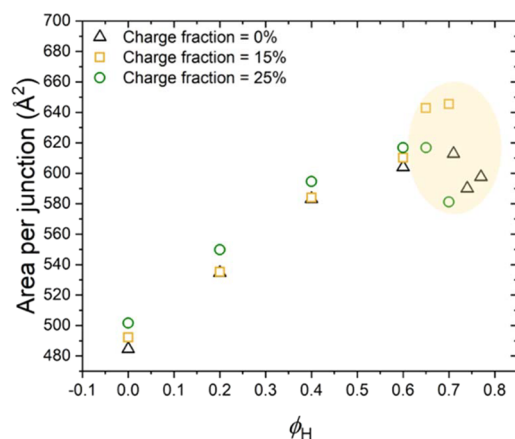


Figure 5. Area per junction of the POEGMA#-PS interface calculated from the LAM phase at 120 °C along the isopleth of T0 (black triangle), T15 (yellow square), and T25 (green circle). The shaded area coincides with macrophase separation based on optical appearance.

wet-brush limit is expected when the homopolymer is much smaller than the corresponding block ($\alpha \ll 1$) and the scaling follows $d/d_0 = (1 - \phi_H)^{-1/3}$, while in the dry brush limit, the homopolymer size is comparable with or larger than the block polymer ($\alpha \gtrsim 1$) and d increases more rapidly following $d/d_0 = (1 - \phi_H)^{-1}$. Both limits are drawn in Figure 4, with blue and red lines. Note that, for all three blends studied here, $\alpha < 0.3$, which is a typical value for wet-brush behavior. The actual trends of d/d_0 as a function of ϕ_H , on the other hand, disagree with this expectation. At a very low ϕ_H ($\phi_H \leq 0.2$), all three blends show swelling behavior closer to the wet-brush limit. However, a dramatic increase in domain size is observed upon further addition of homopolymers, where the scaling is much closer to a dry-brush limit. Such swelling behavior has been reported before for ion-containing ternary systems with small α values.⁵² Meanwhile, in the previous work, this was attributed to the presence of free ions, which caused an increase in segregation strength, and direct comparison among the three systems in our work shows that the poor solubility of the homopolymer toward the corresponding block has little relation with the charge fraction. In Figure 5, all three blends show a similar trend of A_c with ϕ_H , regardless of the difference

in charge fraction and homopolymer size, increasing almost linearly at low ϕ_H before deviating at $\phi_H > 0.6$. Such an increase in the lateral dimension indicates a growing interfacial area between POEGMA# and PS due to homopolymer swelling. It shall also be noted that the deviation in A_c when $\phi_H > 0.6$ is in accordance with the optically observed macrophase separation regime. The inconsistent change of A_c at high ϕ_H strengthens the idea that we can no longer assume that homopolymers are confined to the LAM domains after ϕ_H reaches 0.6.

The similar swelling behavior along the isopleth in T0, T15, and T25 suggests the hypothesis that it is the side chains on POEGMA# that undermine its solubility. Specifically, the free energy gained from the translational entropy of mixing POEGMA# homopolymers with the block polymer is outweighed by the penalty of conformational entropy loss of the POEGMA chain. The outcome of such poor solubility is that the diblock copolymers saturate at relatively low ϕ_H , and POEGMA homopolymers are expelled from the brush to form an inner layer. A future research direction would be to quantify the effect of side chains on the swelling behavior in homopolymer/block polymer blends.

Isothermal Plane. Altering the ratio of the two homopolymer volume fractions in a ternary blend can induce a change in the interfacial curvature, leading to the formation of various phases. The interactions between homopolymers and the diblock copolymer in neutral blends have been well studied, yet little is known when ions are involved. In the recent work of Xie et al., the phase behavior of a ternary system of LiTFSI-doped PS/PEO/PS-PEO was systematically investigated.⁴³ At a relatively low salt concentration ($[Li^+]/[EO] = 0.03$), a wide B μ E phase window was observed. More surprisingly, a C15 Laves phase was found for a range of compositions in blends with higher salt loading ($[Li^+]/[EO] = 0.06$). The emergence of this large curvature change was attributed to the high effective χN induced by the salt, coupled with the differential wet-brush to dry-brush transition for PS vs PEO.⁵² As anions are confined to the polymer chains in the current system, the phase behavior may differ from salt-blended systems. As noted above, the prior work of Shim et al. focused on the volumetrically symmetric isopleth, where the composition window over which the B μ E was observed apparently increased with charge fraction, for reasons that remain to be elucidated.^{46,47} To understand the effect of attached charge groups on the phase behavior of ternary blends, we construct the isothermal planes for T0, T15, and T25 at 120 °C using SAXS, as summarized in Figure 6. Phase boundaries are drawn to guide the eye and should not be interpreted quantitatively. These isothermal triangles show the following features. (i) A wide LAM regime dominates the phase diagram, without the appearance of another pure ordered phase. (ii) A small region of phase coexistence is observed in both T15 and T25. (iii) Macrophase separation appears at lower ϕ_H compared to neutral ternary blends with similar α values and extends to the POEGMA#-rich side.

By means of SCFT, Janert and Schick predicted an isothermal triangle with various phases for a neutral symmetric diblock copolymer blended with two homopolymers with $\alpha_A = 0.2$ and $\alpha_B = 0.3$.⁵⁷ Given the difference in homopolymer size, the isothermal plane also tilted toward the homopolymer with lower M_n , namely, the A-rich side. In comparison to a phase diagram with multiple ordered phases, our results show a LAM-dominated isothermal plane for all three ternary blends.

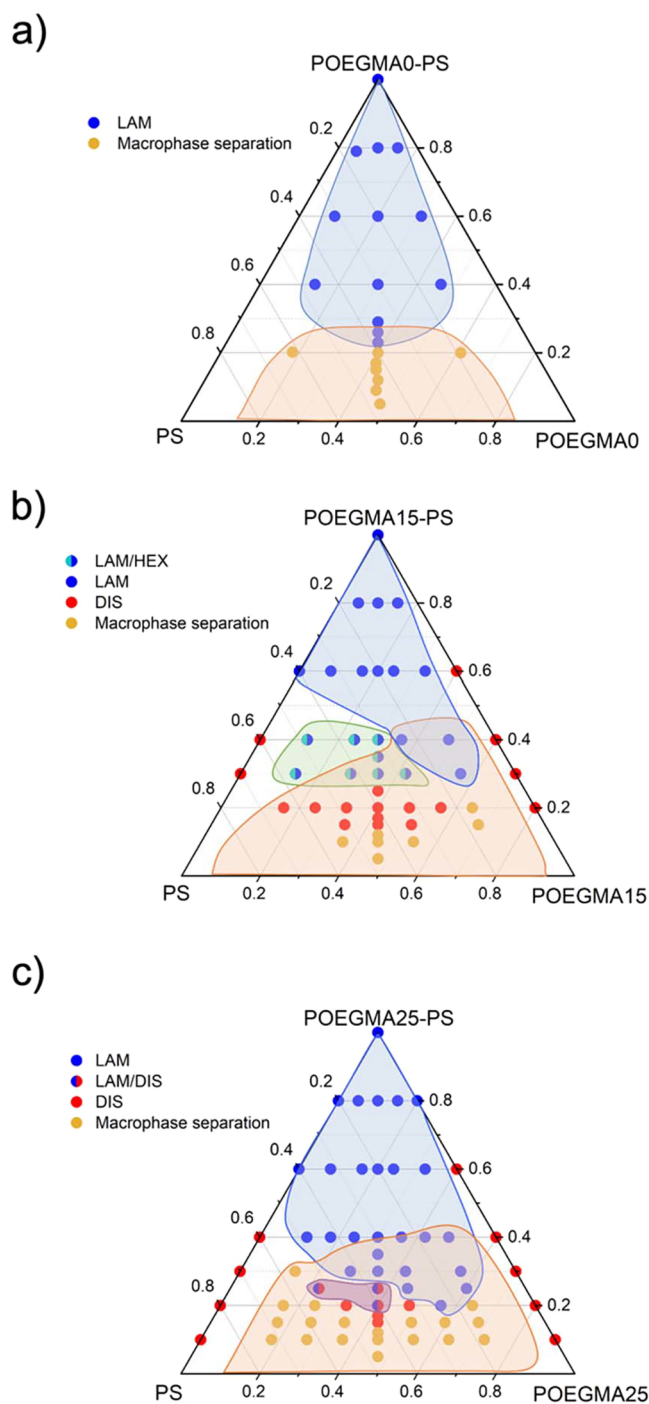


Figure 6. (a–c) Isothermal phase diagram for T0, T15, and T25 at 120 °C based on scattering results. Phase boundaries are estimated and drawn with blue (LAM), green (LAM/HEX coexistence), purple (LAM/DIS coexistence), and orange (macrophase separation) shaded areas.

This is nevertheless in accordance with the dry-brush-like swelling of our system. As homopolymers are expelled from the diblock copolymer, they form an inner layer located between neighboring LAM domains. Such localized solubilization reduces the conformational change of the polymer chain upon homopolymer addition and helps stabilize a flat interface. In the meantime, the LAM phase is also stabilized as the charge fraction increases due to stronger effective χN .

The phase coexistence windows observed on the isopleths of T15 and T25 extend outward on the isothermal planes, which appears to tilt toward the PS-rich side. Regarding the HEX/LAM coexistence phase in T15, such a tilted phase window indicates that more POEGMA#15 is required to balance the interfacial curvature, which indicates that POEGMA#15 lies in the inner side of the HEX phase due to its weaker “wedge” effect. Another prominent feature in these three isothermal planes is the appearance of wide phase separation regimes. Based on the analysis of the domain size change along the isopleth, such phase behavior can be rationalized by the poor solubility of the POEGMA# homopolymer due to the existence of side chains. In fact, the phase-separation regime extends to the POEGMA#-rich side in T15 and T25, which is another sign that POEGMA# is the main contributor to the poor swelling behavior.

Self-assembly of partially charged diblock copolymers has been studied theoretically and experimentally. With the combined effect of translational entropy of ions, solvation energy, ion correlation, and the cross-linking effect between ions and polymer chains, introducing moderate amounts of ions into the diblock copolymer is found theoretically to not only enhance phase separation but also result in an asymmetric phase diagram.^{26,29} Blending the diblock copolymer with the homopolymer intrinsically changes the content of two monomers and is considered to have a similar effect as changing the volume fraction of one block in the copolymer. Therefore, the isothermal plane of T15 and T25 is expected to be tilted with the presence of charged species. However, all three ternary blends remain symmetric with a stabilized LAM phase. Despite the impact of the POEGMA side chain on the swelling behavior, direct comparison between the three isothermal planes reveals that the charge has minor or no influence on the symmetry of the isothermal plane. Instead, charged moieties merely increase the segregation strength, as in the case of pure diblock copolymer POEGMA#-PS reported in our recent work.³⁹ This indicates that the dominant effect is the solvation energy of the ions, given the significant dielectric constant mismatch between the two polymers.

SUMMARY

The phase behavior of three ternary blends composed of POEGMA#/PS/POEGMA#-PS has been systematically studied using SAXS, where LAM, LAM/HEX, and LAM/DIS phases were observed. The emergence of the coexisting phases in T15 and T25 is attributed to the unequal homopolymer size as well as the strong segregation strength in the regime examined. Strikingly, based on optical observation, macrophase separation extends to quite a low homopolymer content ($\phi_H \sim 0.6$), where ordered phases coexist with disordered homopolymer-rich phases. Further investigation of the domain size change along the isopleth indicates that the poor swelling behavior of homopolymers can be related to the grafted nature of POEGMA, where all three blends show almost the same trend of domain size increase despite the difference in homopolymer size and charge fraction. A direct comparison was also made among the isothermal planes of T0, T15, and T25 at 120 °C, where the increase in the charge fraction was found to have no dramatic influence on the phase diagrams but rather raise the segregation strength as in the pure diblock copolymer case. However, quantitative analysis of the effect of charge is inaccessible due to the complexity of the current

system involving conformational asymmetry, homopolymer size difference, and the coil-brush-like polymer architecture.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.macromol.2c00518>.

Synthetic details, SEC traces, ^1H NMR spectra, and SAXS data (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The work was supported by grant DE-SC0017809 funded by the U.S. Department of Energy (DOE), Office of Science. SAXS experiments were carried out in sector 5 (DuPont-Northwestern-Dow Collaborative Access Team, DND-CAT) and sector 12 of the Advanced Photon Source (APS). DND-CAT is supported by Northwestern University, the Dow Chemical Company, and DuPont de Nemours, Inc. This research used resources of the Advanced Photon Source, a U.S. DOE Office of Science User Facility operated for the DOE Office of Science by the Argonne National Laboratory under contract no. DE-AC02-06CH11357. Parts of this work were carried out in the Characterization Facility, University of Minnesota, which receives partial support from the NSF through the MRSEC (award number DMR-2011401) and the NNCI (award number ECCS-2025124) programs.

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