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Phase behavior and nanomechanical mapping of block ionomer complexes

Shuying Wu, Qipeng Guo, Taiye Zhang and Yiu-Wing Mai

Block ionomer complexes SSEBS-c-PCL were prepared, as a consequence of proton transfer from the sulfonic acid of sulfonated polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene (SSEBS) to the tertiary amine of a tertiary amine terminated poly(ε-caprolactone) (APCL). The phase behavior of SSEBS-c-PCL was thoroughly investigated and the results showed that APCL in SSEBS-c-PCL displays unique crystallization behavior owing to the interaction of interactions between the amine and sulfonic acid groups as well as the effects of confinement. Further, small-angle X-ray scattering study revealed that SSEBS-c-PCL displays a less ordered micro-phase structure compared to SSEBS. A quantitative mapping of mechanical properties at the nanoscale was achieved using peak force mode atomic force microscopy. It is found that the block ionomer complex possesses a higher average elastic modulus after complexation with crystallizable APCL. Additionally, the moduli for both hard and soft phases increase and the phase with higher modulus assignable to the hard SPS component shows much more pronounced changes after complexation, confirming that APCL interacts mainly with the SPS blocks. This provides an understanding of the composition and nanomechanical properties of these new block ionomer complexes and an alternative insight into the micro-phase structures of multi-phase materials.

Introduction

Block copolymer ionomers, where one block is fully or partially ionized, have attracted considerable attention due to the combination of the individual properties of both ionomers and block copolymers. It is well-known that a block copolymer shows a micro-phase separated morphology because of its chemically distinctive polymer segments connected by covalent bonding. The chemically different blocks in a copolymer render it some interesting properties such as self-assembly, metal complexation, micellization, absorption, molecular association, etc. Block copolymers containing a small amount of ionic groups exhibit unique properties compared with the corresponding non-ionic polymers owing to the strong intermolecular association. Interaction strength and properties of a block copolymer ionomer are governed by several factors such as polymer backbone, ionic content, degree of neutralization and counterion types. And amongst these factors, the effects of counterion types on the morphologies and properties have been extensively studied. For anion-containing ionomers, the counterions are usually alkali, alkaline earth, transition, and rare earth metal cations. By contrast, the organic cations based on amine, pyridine, are also of great interest. Compared to ionomers with inorganic cations, relatively fewer studies have been reported on ionomers with organic cations which are often low molecular weight organic cations.

Sulfonated styrene-based ionomers represent one of the most important and widely studied block copolymer ionomers. The presence of sulfonic acid groups facilitates the preparation of miscible polymer blends or complexes based on some specific interactions including ion-ion, ion–dipole, hydrogen bonding, or formation of acid–base complexes, etc. For example, Lu and Weiss reported the morphology and phase behavior of blends of a lightly sulfonated styrenic block copolymer ionomer and poly(ε-caprolactone) (PCL). The miscibility of PCL in the ionomeric micro-phase was greatly enhanced by the interactions between the sulfonate groups and polyester. Moreover, partially miscible blends of sulfonated polystyrene and polyurethane were prepared due to the proton transfer from sulfonic acids to tertiary nitrogen of the polyurethane extender. Similarly, this ion–ion interaction was used to prepare complexes of polystyrene ionomers with mono- and bi-functional styrene oligomers (homo-grafts) or with butyl acrylate oligomers (hetero-grafts). Lundberg used a tertiary amine terminated poly(ε-caprolactone) to prepare complexes based on sulfonated styrene-based polymers. The resulting complex is useful as a pour depressant agent that can promote the flow of heating fuels, diesel and paraffinic oils effectively at low temperatures. But, to the best of our knowledge, up to now,
there have been no published reports on the phase behavior and nanomechanical properties of these types of complexes.

In our recent studies, we reported a class of block ionomer complexes as a template to prepare tough nanostructured epoxy thermosets.\textsuperscript{19,20} These novel block ionomer complexes, namely SSEBS-c-PCL, were prepared based on sulfonated polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene (SSEBS) and tertiary amine terminated poly(ε-caprolactone) (i.e., 3-dimethylaminopropylamine-terminated poly(ε-caprolactone) (APCL)). However, to date, little work has been done on the phase structure and properties of these novel block ionomer complexes formed due to the protonation from the sulfonic acid groups to the tertiary amine end group. The complex SSEBS-c-PCL consists of SSEBS as the hydrocarbon backbone and APCL as the side chains, leading to a kind of amphiphilic block ionomer complex, which can also be viewed as ionomers containing counterions with long organic tails or graft copolymer-like materials.

Herein, we report a detailed study of the phase behavior and nanomechanical properties of these new block ionomer complexes. A unique micro-phase morphology is expected due to the presence of a rubbery phase (poly(ethylene-ran-butylene), EB blocks), a hard phase (sulfonated polystyrene, SPS blocks), and semicrystalline component (PCL side chains) in the SSEBS-c-PCL. This study will also provide new insights into how the crystallization behavior is affected by a restricted geometry (block copolymer ionomer micro-domains) and interactions with the block copolymer ionomer. Further, nanomechanical mapping techniques based on peak force mode atomic force microscopy (AFM) were used to obtain elastic modulus maps, which have enabled the investigation of the physico-chemical properties of these chemically and mechanically heterogeneous materials at the nanoscale.

Experimental section

Materials and preparation of samples

Polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene (SEBS) containing 29 mol% of styrene blocks was purchased from Sigma-Aldrich Co. The average molecular weight $M_w$ of the SEBS block copolymer was 95 600 with $M_w/M_n=1.05$ (and $M_n$ is number-average molecular weight) measured by GPC in tetrahydrofuran (THF) relative to the polystyrene standard. All the number-average molecular weight) measured by GPC in tetrahydrofuran (THF) relative to the polystyrene standard. All the number-average molecular weight was 95 600 with $3\text{acid (96\%), 1,2-dichloroethane (DCE), isopropyl alcohol (IPA), chemicals including acetic anhydride, concentrated sulfuric hydro-furan (THF) relative to the polystyrene standard. All the number-average molecular weight was 95 600 with $3\text{acid (96\%), 1,2-dichloroethane (DCE), isopropyl alcohol (IPA), chemicals including acetic anhydride, concentrated sulfuric hydro-furan (THF) relative to the polystyrene standard. All the number-average molecular weight was 95 600 with $3\text{acid (96\%), 1,2-dichloroethane (DCE), isopropyl alcohol (IPA)},$ 3-dimethylaminopropylamine and THF were reagent grade.

Sulfonation of SEBS was conducted in 1,2-dichloroethane at 50–55 °C under nitrogen atmosphere described in detail in our previous paper.\textsuperscript{19} The sulfonation degree of SSEBS, i.e., the percentage of polystyrene blocks grafted with sulfonic acid groups, was obtained by titration with standard sodium hydroxide solution (0.1 N) using phenolphthalein as indicator. SSEBS with four different sulfonation degrees were prepared by adjusting the feed amount of acetyl sulfonate. In terms of appearance, the color of SSEBS becomes darker with increasing degree of sulfonation. 3-Dimethylaminopropylamine-terminated poly(ε-caprolactone) (APCL) was synthesized by ring-opening polymerization of ε-caprolactone with 3-dimethylaminopropyl-amine as initiator in the presence of the catalyst, Sn(Oct)$_2$.\textsuperscript{19} The resultant SSEBS and APCL were characterized by FTIR and $^1$H NMR and $M_n$ of APCL was estimated to be ~2000 g mol$^{-1}$.\textsuperscript{19}

The block ionomer complex SSEBS-c-PCL was synthesized by neutralization of SSEBS with APCL as previously described.\textsuperscript{19} In the present work, four block ionomer complexes SSEBS-c-PCL were prepared from SSEBS with four different degrees of sulfonation. The characteristics of these four block ionomer complexes are given in Table 1. The sulfonation degree, i.e., the molar percentage of polystyrene grafted with sulfonic acid groups, varies from 14.2 to 41.5 mol%. The corresponding block ionomer complexes are denoted by 1SSEBS-c-PCL, 2SSEBS-c-PCL, 3SSEBS-c-PCL and 4SSEBS-c-PCL, respectively. The formation of the block ionomer complex is due to the proton transfer from the sulfonic acid group, which is naturally acidic\textsuperscript{12} to the tertiary amine end group of APCL, leading to an ionic linkage. The block ionomer complex SSEBS-c-PCL was characterized by FTIR and $^1$H NMR.\textsuperscript{19}

Fourier transform infrared (FTIR) spectroscopy

FTIR spectra of all samples were measured with a Bruker Vertex 70 FTIR spectrometer. The THF solutions of samples were dropped onto the KBr disks. The solvent was evaporated at room temperature and the disks were further dried under vacuum at 100 °C before measurement. The spectra were recorded by the average of 32 scans in the standard wave-number range 600–4000 cm$^{-1}$ at a resolution of 4 cm$^{-1}$.

Differential scanning calorimetry (DSC)

Calorimetric measurements were made on a TA Q200 differential scanning calorimeter in dry nitrogen. Indium and tin standards were used for calibration of the low- and high-temperature regions, respectively. Samples of about 8 mg were placed in the DSC pan. All samples, except when indicated otherwise, were first heated to 100 °C from 0 °C at a rate of 20 °C min$^{-1}$ (first heating scan) and kept at that temperature for 5 min; they were subsequently cooled at a rate of ~10 °C min$^{-1}$ to detect crystallization (cooling scan). Following the cooling scan, a second scan was conducted at the same heating rate as the first. The $T_g$ values were taken as the mid-point of the transition in the second scan of the DSC curves. The crystallization temperature ($T_c$) was determined from the minimum of the

<table>
<thead>
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<th>Table 1</th>
<th>Characteristics of block ionomer complexes</th>
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<tr>
<td>Sulfonated</td>
<td>Sulfonation degree (mol%)</td>
</tr>
<tr>
<td>SEBS</td>
<td>14.2%</td>
</tr>
<tr>
<td>(SSEBS)</td>
<td>18.8%</td>
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<tr>
<td>29.8%</td>
<td>28.6%</td>
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<tr>
<td>41.5%</td>
<td>44.4%</td>
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exothermic peak, whereas the melting temperature \( T_m \) was obtained from the maximum of the endothermic peak.

**Polarizing Optical Microscopy (POM)**

The semi-crystalline morphology of SSEBS-c-PCL was examined using a Nikon eclipse-80i optical microscope under polarized light. Solutions of SSEBS-c-PCL were spread as thin films on glass slides and dried in a vacuum oven.

**Small-angle X-ray scattering (SAXS)**

The SAXS experiments were performed at the Australian Synchrotron on the small/wide angle X-ray scattering beam-line utilizing an undulator source that allowed measurement at a very high flux to moderate scattering angles and a good flux at the minimum \( q \) limit (0.012 nm\(^{-1}\)). The intensity profiles were interpreted from the plot of scattering intensity \( I \) versus scattering vector, \( q = (4\pi/\lambda) \sin(\theta/2) \) (where \( \theta \) is scattering angle and the wavelength \( \lambda \) is 0.062 nm).

**Measurements of nanomechanical properties**

Nanomechanical measurements were performed using the PeakForce QNM (Quantitative NanoMechanics) mode which is based on the Derjaguin–Muller–Toropov (DMT) model on an AFM system under ambient conditions. The AFM system is a Bruker MultiMode™ 8 SPM equipped with a Nanoscope V controller and Nanoscope analysis software (Bruker Nano Surface Business, Santa Barbara, CA 93117, USA). Following a proper calibration procedure, samples were scanned using the SNL-A probe with a nominal radius of 2 nm and a nominal spring constant of 0.35 N m\(^{-1}\).

Peak-force tapping AFM is an operating mode that can control the maximum normal force (“peak force”) applied on the samples at each point of the map. Nanoscale property and peak force are obtained by collecting a force curve at each pixel. The force–separation curves are subsequently analysed to obtain information on sample adhesion, surface deformation and topography. Adhesion force is the minimum force depending on the interaction between the tip and sample while deformation is the difference of the separation from the force equal to zero to the peak force. The reduced elastic modulus \( E^* \) is obtained by fitting the experimental data using the Derjaguin–Muller–Toropov (DMT) model given by:

\[
F_{\text{tip}} = (4/3)E^*(Rd)^{1/2} + F_{\text{adh}}
\]

where \( F_{\text{tip}} \) is the force on the tip, \( F_{\text{adh}} \) is the constant adhesion force during contact, \( R \) is the tip end radius, and \( d \) is the tip to sample separation. The reduced modulus \( E^* \) is related to the sample elastic modulus \( E_s \) by:

\[
E^* = [(1 - \nu_s^2)/E_t + (1 - \nu_s^2)/E_s]^{-1}
\]

where \( \nu \) and \( E \) are the Poisson’s ratio and Young’s modulus and the subscripts “t” and “s” stand for the tip and sample, respectively. In our materials system, the tip modulus, \( E_t \), is much larger than \( E_s \) so that the first term of eqn (2) can be neglected. Hence, \( E_s \) is calculated easily given the Poisson’s ratio \( \nu_s \).

**Results and discussion**

**Phase behavior and crystallization**

The thermal behaviors of SEBS, SSEBS and SSEBS-c-PCL were investigated by DSC. The second scan DSC thermograms of SEBS and block ionomer complex SSEBS-c-PCL are shown in Figs. 1 and 2.

Fig. 1a presents the second heating scan of SEBS and SSEBS with different degrees of sulfonation. The corresponding
cooling scan is shown in Fig. 1b. The parent SEBS with two immiscible distinct blocks is known to have a micro-phase separated structure consisting of a rubbery phase of EB blocks and hard micro-domains of PS blocks. Thus, two different $T_g$, i.e., one at $-40$ °C for the EB block and another at ca. 80–90 °C for the PS block should be observed.\textsuperscript{14,23} However, from the DSC curve for SEBS (Fig. 1a), it is noted that there is no discernible $T_g$, which might be due to the insensitivity of DSC for detecting $T_g$. Meanwhile, a broad endotherm between $-20$ and $30$ °C can be ascribed to the melting of small crystallites formed by long sequences of ethylene.\textsuperscript{14,23} After sulfonation, an obvious $T_g$ was found, which can be ascribed to the SPS block of SSEBS. For 14.2SSEBS, the $T_g$ is located at 107 °C and increases gradually with increasing degree of sulfonation, reaching $122$ °C for 41.5SSEBS. It is known that strong hydrogen bonding interactions usually occur between SO$_3$H groups in SPS blocks, restricting the chain mobility and thereby generally resulting in a higher $T_g$ for PS block.\textsuperscript{22}

From the cooling scan (Fig. 1b), an exothermic peak is readily seen for all the SSEBSs which can be attributed to the crystallization of ethylene segments.\textsuperscript{14} It is also noticed that the crystallization temperatures ($T_c$) of SSEBSs were slightly lower than that of the parent SEBS. The hydrogen bonding interaction between the SO$_3$H groups in the SPS block can act as the physical crosslink, which simultaneously confines the mobility of the EB chains owing to the covalent bonding between SPS and EB blocks. Therefore, the restriction of chain mobility can be responsible for the depression of crystallization of the ethylene segments in SSEBS.\textsuperscript{24} Furthermore, it is shown that $T_c$ of the ethylene segments decreases slightly with increasing sulfonation degree.

Fig. 2a shows clearly that neat APCL displays a melting point ($T_m$) at $-48$ °C. After the neutralization with SSEBS, noticeable changes in the crystallization behavior of APCL can be seen. There are sharp endothermic peaks assignable to the melting of APCL in the DSC curves of all block ionomer complexes except 1SSEBS-c-PCL which has the least APCL content (11.8 wt%). APCL in block ionomer complexes shows almost the same $T_m$ as neat APCL. 1SSEBS-c-PCL, however, does not display the melting peak of APCL, indicating that APCL is either dissolved or at least partially dissolved in SSEBS, since the melting point depression is a typical characteristic of a miscible polymer blend.

Fig. 2b shows the crystallization behavior of APCL in block ionomer complexes. Neat APCL displays a sharp exothermic peak at $-29$ °C assignable to the crystallization of APCL. By contrast, SSEBS-c-PCLs with relatively higher APCL contents (3SSEBS-c-PCL and 4SSEBS-c-PCL) exhibit two exothermic peaks assignable to the crystallization of APCL. Compared to $T_g$ of neat APCL ($-29$ °C), one of these two $T_c$ values is slightly higher (31 and 32 °C) and the other is lower (21 and 28 °C). By contrast, 2SSEBS-c-PCL shows a weak exothermic peak at 20 °C due to the crystallization of APCL, which is much lower than that of neat APCL whereas 1SSEBS-c-PCL does not show a noticeable exothermic peak assignable to the crystallization of APCL.

The crystallization behavior of APCL in block ionomer complexes can also be inferred from the FTIR results as shown in Fig. 3. The carbonyl stretching vibration band of neat APCL is located at 1724 cm$^{-1}$, which can be ascribed to the crystalline conformation of APCL. By contrast, we can clearly see a slightly broader main peak at 1724 cm$^{-1}$ with a shoulder at 1737 cm$^{-1}$ in the spectra of block ionomer complexes, which are ascribed to the crystalline and amorphous conformations of APCL, respectively.\textsuperscript{25} The crystalline peak decreases in intensity and shifts to a higher frequency (1730 cm$^{-1}$), whereas the peak at 1737 cm$^{-1}$ corresponding to the amorphous state becomes more discernible with decreasing APCL content and is especially noticeable in the spectra of 1SSEBS-c-PCL containing the least amount of APCL.

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**Fig. 2** DSC curves of APCL and block ionomer complexes SSEBS-c-PCL: (a) second heating scan at 20 °C min$^{-1}$; and (b) cooling scan at −10 °C min$^{-1}$.

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These unique crystallization characteristics may result from the complex multi-phase morphology and the miscibility between the components. For the 1SSEBS-c-PCL, the APCL is probably completely dissolved in SPS micro-domains due to the interaction between the sulfonic acid groups and tertiary amine end group of APCL. Hence, no APCL crystallites are present in this block ionomer complex, which is consistent with the SAXS results to be discussed later. With increasing molar ratio of amine/acid from 0.11 for 1SSEBS-c-PCL to 0.16 for 2SSEBS-c-PCL (see Table 1), there may be some APCL not completely dissolved but crystallized with confinement in the SPS micro-domains. It is known that in the case of a block copolymer when the crystallization is confined in micro-domains, the crystallization is often depressed compared with the neat crystallizable homopolymer.\textsuperscript{14,26} Therefore, 2SSEBS-c-PCL exhibits a lower $T_c$ than neat APCL. For block ionomer complexes with a higher APCL content, the presence of two crystallization peaks most possibly originates from two different population of APCL crystallites, i.e., inside the SPS micro-domains and APCL matrix outside the SPS micro-domains.\textsuperscript{14} For APCL confined within SPS micro-domains, the crystallization is depressed showing lower crystallization temperature, but the APCL matrix shows higher crystallization temperature arising from possible heterogeneous nucleation effects of the neighboring micro-domains in this multi-phase system.

Apart from the crystallization of APCL, another obvious crystallization peak can also be found for all block ionomer complexes which could be ascribed to the crystallization of the ethylene block (see Fig. 2b). Compared to neat SSEBS, the crystallization temperature of the ethylene block in block ionomer complexes is slightly increased. For example, $T_c$ of the ethylene block in 4SSEBS-c-PCL increases to 7 °C while the ethylene block in the corresponding SSEBS (41.5SSEBS) shows a crystallization peak at 3 °C. Moreover, $T_c$ increases with increasing APCL content in the block ionomer complexes, confirming that the incorporation of APCL has some effect on the crystallization of the ethylene block. The crystallization of a polymer involves two crucial steps, i.e., nucleation and growth of the crystallites.\textsuperscript{26} The crystallization temperature of the ethylene block is lower than that of APCL which, hence, may act as the nucleus for crystallization of ethylene. Also, the presence of APCL might interfere with the hydrogen bonding interaction between SO$_3$H groups in the SPS block, enabling better mobility of ethylene segments. Therefore, it becomes easier to rearrange due to the plasticization effects of APCL resulting in a higher crystallization temperature.

The semi-crystalline morphology of the block ionomer complexes was examined using a polarizing optical microscope (POM). Fig. 4 shows the polarized images revealing that block ionomer complexes SSEBS-c-PCL contain spherulites. For neat APCL, a very well-developed spherulitic structure can be found. The spherulitic morphology becomes coarser in SSEBS-c-PCLs. Indeed, the spherulites become smaller and less regular with decreasing APCL content. For 1SSEBS-c-PCL, small but clear spherulitic structures are visible, possibly caused by the existence of ethylene crystallites. This speculation is based on the absence of crystallization and melting peaks of APCL but the presence of the corresponding peaks for the ethylene block in the DSC curves of 1SSEBS-c-PCL.

**Self-assembly and nanostructures**

SAXS measurements for parent SEBS, SSEBS and block ionomer complexes SSEBS-c-PCLs were performed at room temperature to study the micro-phase structures. Fig. 5a shows the SAXS results of SSEBS with different degrees of sulfonation and Fig. 5b shows SAXS results of their corresponding block ionomer complexes.

For parent SEBS, multiple scattering peaks can be observed in the SAXS profile, which indicates that ordered nanoscale structures may exist in SEBS. The first-order scattering peak is centered at a value of the scattering vector $q*$ corresponding to a long spacing of 34 nm. There are higher order reflections clearly visible at the positions of $q/q^* = 1, 2, 3, 4$ and 5, which are characteristic of a lamellae arrangement.\textsuperscript{27} For all SSEBSs, the SAXS profiles show well-defined peaks, indicating they are micro-phase separated at the nanoscale. But, compared to the SAXS profile of SEBS, the first-order scattering peaks become broader and a smaller number of secondary peaks are observed in the SAXS profiles of SSEBSs. This suggests that a less ordered micro-phase structure exists in SSEBSs where the sulfonate groups are attached to PS blocks. According to previous studies, light sulfonation of PS blocks may introduce two competing effects on morphology and thereby the properties.\textsuperscript{7,28,29} Firstly, the introduction of ionic groups onto the PS blocks leads to a greater driving force for phase separation owing to the increased difference in solubility parameters between constituent blocks. Secondly, phase separation may be simultaneously hindered by the reduced mobility of ionic blocks due to some
Fig. 4 Polarized optical microscopy images (Mag. ×100) of (a) neat APCL, (b) 4SSEBS-c-PCL, (c) 3SSEBS-c-PCL, (d) 2SSEBS-c-PCL, and (e) 1SSEBS-c-PCL.

Fig. 5 SAXS profiles of (a) SEBS and SSEBS with different sulfonation degrees; and (b) block ionomer complexes from the corresponding SSEBS at room temperature. Each profile is shifted vertically for clarity.
specific interactions, e.g., hydrogen bonding or ion–ion interactions. Even though the results of these competing effects are not yet fully understood, based on the obtained SAXS results, it seems that the second effect dominates.

Also, it is shown from the SAXS profile of 14.2SSEBS that the primary scattering peak is located at a position corresponding to a long spacing of 27 nm. With increasing sulfonation degree, the primary scattering peak shifts slightly to a lower scattering vector, reflecting an increase in the average distance between neighboring micro-domains. This probably originates from the fact that more sulfonate groups are grafted onto the PS block for SSEBS with a higher sulfonation degree. Further, it is clear that the characteristic scattering peaks become broader, which indicates reduced ordering for SSEBS with higher sulfonation degree. Thus, there is only one broad secondary scattering peak for 41.5SSEBS and the long spacing increases to 34 nm.

After neutralization with APCL, the micro-phase structure of the block ionomer becomes less ordered, which is demonstrated by the presence of broader scattering peaks and a smaller number of secondary peaks (Fig. 5b). Block ionomer complexes with a higher APCL content (4SSEBS-c-PCL and 3SSEBS-c-PCL) exhibit no higher order reflections in SAXS profiles, indicating the deterioration of the micro-phase structure. The micro-phase structure of the block copolymer ionomer goes through a transition from a relatively ordered arrangement to a disordered structure by introduction of APCL. It is also noticed that the long spacing between micro-domains increases remarkably for all complexes compared with the corresponding SSEBS. For example, after the incorporation of APCL into 18.8SSEBS, the long spacing increases from 30 to 39 nm for the corresponding complex 2SSEBS-c-PCL. This is consistent with the morphology studies using AFM in our previous paper, i.e., the SPS phase is remarkably swollen after the incorporation of APCL. The interaction between APCL and SPS enhances the miscibility leading to a lower \( T_c \) of the SPS block due to the plasticization effect and also disrupts the hydrogen bonding between SO\(_3\)H groups within the SPS phase. From this viewpoint, it should be easier for the block ionomer complex to self-assemble into well-ordered structures caused by the increased mobility of the SPS sub-chains. However, it is well-established that the micro-phase structure of a block copolymer is controlled by the phase parameter \( \chi N \), where \( \chi \) is interaction parameter and \( N \) is the degree of polymerization. As \( \chi N \) increases, the equilibrium block copolymer micro-phase structure transforms from the disordered phase, to bcc spheres, hexagonally packed cylinders, and lastly to lamellae. In the block ionomer complex SSEBS-c-PCL, the introduction of APCL has disrupted the strong interaction between SO\(_3\)H groups which acts as a physical crosslink in SSEBS. Thus, the apparent molecular weight (degree of polymerization) \( N \) decreases and so does \( \chi N \). This possibly explains why the micro-phase structure experiences a transition to a poorly ordered structure after the introduction of APCL into SSEBS.

Crystallization of APCL may also have some impact on the micro-phase structure of SSEBS-c-PCL. From the DSC studies discussed above we know that there are APCL crystallites in the block ionomer complexes except 1SSEBS-c-PCL. To study the effect of crystallization of APCL on the micro-phase structure, SAXS tests were conducted at 70 °C, which is above the melting point of APCL. At this temperature, the crystalline APCL becomes a melt, resulting in a micro-phase separated structure of amorphous APCL and SSEBS. The obtained SAXS profiles are shown in Fig. 6. We can see that there is almost no change in the profile of 1SSEBS-c-PCL, indicating that no changes occur in the micro-phase structure at this temperature. By contrast, multiple scattering peaks are discernible for the other three complexes unlike the profiles obtained at room temperature, indicating the presence of some ordered nanostructures. This remarkable change is particularly obvious for 4SSEBS-c-PCL. Hence, it is evident that crystallization of APCL has a profound impact on the micro-phase structure of block ionomer complexes. Based on the SAXS results and AFM investigation in our previous paper, a schematic illustration of the self-assembly is given in Fig. 7.
Quantitative mechanical property mapping at the nanoscale
Recent development in peak force mode AFM techniques offers the potential for imaging the mechanical properties of a material at the nanoscale.\textsuperscript{32–35} It has now become possible to obtain truly quantitative material property mapping with high resolution and precision, including elastic modulus, adhesion, deformation, and dissipation maps of nanostructured materials. Such maps can be used to identify and characterize successfully the composition and properties of multi-phase materials. However, little work has been reported using this technique to characterize block copolymers. Herein, we use it to evaluate the nanomechanical properties of SSEBS-c-PCL. The results discussed below, except when indicated otherwise, are for 18.8SSEBS and its corresponding block ionomer complex 2SSEBS-c-PCL.

The triblock copolymer SEBS consists of hard and soft components and usually displays micro-phase separated microstructures as revealed by AFM investigations.\textsuperscript{36–38} Fig. 8

Fig. 8 Topographic images and elastic modulus maps of (a) SEBS, (b) SSEBS and (c) SSEBS-c-PCL.
shows simultaneously generated topography and elastic modulus maps of SEBS, SSEBS and SSEBS-c-PCL by peak force QNM. A distinct contrast in these maps suggests that there are at least two different phases with different properties. Surface topography images in Fig. 8a1, b1 and c1 demonstrate worm-like micro-phase structures in SEBS which remain almost unchanged in SSEBS and SSEBS-c-PCL except for slight changes in the domain sizes. From the corresponding elastic modulus maps, it can be found that there are two distinct phases showing different elastic moduli. Consider SEBS, the bright region in Fig. 8a2 shows a higher elastic modulus. By contrast, there is another phase showing a lower modulus. Owing to the difference in viscoelasticity between PS and PEB components, the phase with the higher elastic modulus can be attributed to the hard PS-rich phase while that with the lower elastic modulus is probably due to the soft PEB-rich phase.36–38

To further study the properties of each phase and their variation from SEBS, SSEBS to SSEBS-c-PCL, DMT modulus ($E_s$) maps and the corresponding histograms are shown in Figs. 9 and 10, respectively. The DMT elastic modulus profiles along the dotted lines in the modulus maps are also displayed in Fig. 9, which clearly indicate that the bright region has higher modulus values and the dark region, lower values. The dark and bright dots marked on the modulus maps are two typical points showing higher and lower moduli, respectively, for the corresponding hard and soft phases. The elastic modulus ($E_s$) values vary from 5.87 to 35.84 MPa for SEBS, 10.24 to 36.91 MPa for SSEBS, and 11.27 to 51.46 MPa for SSEBS-c-PCL along the cross-sections.

From the modulus maps in Fig. 9, the average, maximum and minimum modulus values determined by QNM can be obtained. The mean modulus increases from 18.20 MPa for

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**Fig. 9** Elastic modulus maps of (a1) SEBS, (b1) SSEBS and (c1) SSEBS-c-PCL. Numerical values in each image across the sections indicated by the dotted lines in (a1) (b1) and (c1) are shown in (a2), (b2) and (c2), respectively. The dark and bright dots marked on the modulus maps correspond to the points in the modulus profiles indicated by the dashed lines, exhibiting higher and lower moduli, respectively.
SEBS and 19.51 MPa for SSEBS to 36.1 MPa for SSEBS-c-PCL. Further, the maximum modulus increases only slightly from 40.20 MPa for SEBS to 42.49 MPa for SSEBS, but dramatically to 63.11 MPa for SSEBS-c-PCL. The minimum modulus values for SSEBS and SSEBS-c-PCL (9.30 and 6.5 MPa, respectively) also increase compared to SEBS (4.58 MPa). The histograms in Fig. 10 demonstrate the distribution of the modulus values. It is clearly seen that the elastic modulus of the majority of the scanned surfaces (peak in the distribution curve) increases, especially for SSEBS-c-PCL.

All results obtained above indicate that sulfonation and subsequent complexation with APCL increase the modulus of both phases consisting of stiff PS blocks and soft PEB blocks. The increase in modulus with sulfonation is most likely caused by the presence of strong interactions between sulfonic acid groups in SPS blocks which serve as physical crosslinks. For the block ionomer complex, the presence of APCL side chains ionically linked to the SPS block may bring about two competing factors contributing to the modulus. First, APCL forms ionic linkage with SO$_3$H groups in SPS blocks leading to the interference of hydrogen bonds between SO$_3$H groups. Second, APCL tends to crystallize in the block ionomer complex even though this process is depressed to some extent compared to neat APCL. From the obtained results, it may be inferred that the latter factor is more dominant, yielding an increased modulus. Also, the phase with the higher modulus assignable to the hard PS components shows much more pronounced changes after sulfonation and complexation. Especially, complexation of SSEBS with APCL increases the modulus of the hard phase (SPS phase) dramatically, confirming that APCL interacts mainly with SPS blocks. Although no chemical changes take place for PEB blocks during sulfonation and complexation, there exist some changes in the properties of the soft phase (PEB component) from SEBS to SSEBS-c-PCL, which is very likely due to the covalent bonding with the hard phase consisting of PS or SPS.

There exist some inconsistencies between the properties at nanoscale and those of bulk samples. The minimum modulus obtained from peak force QNM is slightly lower than that of bulk PEB samples. The maximum modulus, however, is much lower than that of bulk PS samples. These results suggest that the soft and hard segments may mutually affect each other. Similar results have been reported by other groups, namely, the properties at nanoscale may not agree with those of the bulk samples due to the microstructure effects exerted on each other. For example, there are rubbery layers in the probed volume such that the soft PEB blocks may surround or lie underneath the hard PS blocks leading to dramatic decreases of the modulus values. Furthermore, other possible factors like contact area, tip geometry and local value of Poisson’s ratio may also contribute to the elastic modulus reductions.

Conclusions

Block ionomer complexes, SSEBS-c-PCL, were prepared based on sulfonated SEBS and a tertiary amine-terminated PCL. DSC results revealed that APCL exhibited a unique crystallization behavior due to the effects of miscibility and restriction imposed by the SPS micro-domains. Crystallization was generally depressed compared with neat APCL and two crystallization peaks were observed for the complexes with a relatively higher APCL content (3SSEBS-c-PCL and 4SSEBS-c-PCL). Spherulitic semi-crystalline structures were observed for neat APCL, which became smaller and irregular in block ionomer complexes. SAXS results showed that the micro-phase structure of the block ionomer underwent a transition from a relatively ordered structure to a poorly ordered morphology by the introduction of APCL. Quantitative mapping of mechanical properties at the
nanoscale using AFM indicated that the block ionomer complex showed a higher average elastic modulus than SEBS and SSEBS. In addition, the elastic moduli for both hard and soft phases increased, and the phase with higher modulus assignable to the hard SPS component shows much more noticeable change after sulfonation and complexation.

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