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Principles and Functionalization of Thermoplastic Elastomers for Use in the Energy, Environment and Healthcare Sectors

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Overview of Thermoplastic Elastomers and Their Applications

Polymers are organic macromolecules that consist of a large number of repeating units and are frequently classified by their thermomechanical properties,¹ as indicated in Figure 8.1. While thermoplastics are generally solid (glassy or semicrystalline) at application temperature, they are processable as polymeric liquids (melts) at temperatures above their glass transition temperature (T_e) or melting temperature (T_m) , respectively. As examples of polymers that are not melt processable after they are formed, both elastomers and duromers (also referred to as thermosets) consist of networks generated by irreversible chemical reactions, and they display markedly different properties: elastomers are low-modulus, elastic polymers, whereas duromers are highmodulus, brittle materials. Thermoplastic elastomers (TPEs) constitute an increasingly important class of hybrid polymers that combine the elasticity of chemically-crosslinked elastomers with the melt processability of thermoplastics. To achieve this dual functionality, most TPEs are block (or "blocky") copolymers that are synthesized with hard (glassy or semicrystalline) and soft (elastomeric) moleties.²⁻⁷ Because of this molecular architecture and the range of moleties that can be integrated, TPEs afford significant advantages over conventional elastomers derived primarily from polydienes and polysiloxanes due to their tunable nanoscale structures and corresponding bulk properties, in addition to low-waste processing, low energy consumption, and excellent quality control.⁸ Major commercial uses of TPEs include automotive components,⁹ personal electronics,¹⁰ consumer goods,¹¹ and biomedical devices.^{12,13} The current global demand for TPEs is rapidly expanding and diversifying, and is forecasted to reach a production level¹⁴ of 7.4 million metric tons by 2022 and a market size¹⁵ of 27.8 billion USD by 2024. The discovery of elasticity in plasticized polyvinyl chloride (PVC), commonly referred to as "plastisol," by Semon¹⁶ in 1926 is credited for opening the door to TPEs. The subsequent development of polyurethane, polyester, polyamide, polyolefin, and polystyrene thermoplastics yields the hard segments that distinguish the families of TPEs listed in Figure 8.1: thermoplastic polyurethane (TPU), copolyester (TPC), poly(ether-b-amide) (TPA), polyolefin elastomer (TPO), and styrenic block copolymer (TPS).



FIGURE 8.1

Classification of polymeric materials and sub-classification of thermoplastic elastomers (TPEs), along with abbreviated designations.

The combination of chemically incompatible hard and soft segments in TPE molecules is essential for promoting microphase separation (i.e., phase separation that is restricted to parts of polymer molecules instead of entire molecules) under application conditions.¹⁷⁻²⁰ Upon melt processing and ensuing microphase separation, the hard segments segregate to form phase domains that serve as physical crosslinks to stabilize a molecular network composed of the soft segments in conceptually similar fashion as a chemically-crosslinked elastomer. In the case of TPU, TPC, TPA, and TPO polymers, the hard segments are crystallizable and, because of the polymerization routes employed, vary in both length and number along the copolymer chains. Synthesized by step-growth polycondensation, polyurethane is widely recognized as a highly versatile polymer.^{21,22} The segmented TPU variant is the first polymeric material to combine thermoplastic and elastomeric characteristics as a randomly-coupled (in contrast to perfectly-alternating) multiblock copolymer wherein the hard blocks crystallize while the soft blocks remain amorphous. The morphology of microphase-separated TPU is illustrated in Figure 8.2 and couples interphase mixing with intra/intermolecular hydrogen bonding in both microphases. This material possesses excellent mechanical properties for abrasion, puncture and tear resistance, in combination with substantial elasticity and good hydrolytic stability.²³⁻²⁵ For these reasons, TPU is widely used as protective and abrasion-resistant coatings. Similarly, TPCs also consist of high melting segments that are capable of crystallization and soft segments with a low Tg. In this case, the hard segments often derive from short-chain esters (e.g., tetramethylene terephthalate), and the soft segments are either polyester glycols or aliphatic polyethers.^{26,27} One TPC example, Hytrel[®], is widely popular because of its durability in mechanical gears,²⁸ medical devices,²⁹ railway technology,³⁰ and cable insulation.³¹ The TPAs are high-performance block copolymers consisting of hard and soft segments joined by amide linkages. Unlike other TPEs, these polymers possess excellent heat and solvent resistance due to strong hydrogen-bonding, and they are frequently employed in medical devices requiring good flexibility, breathability and sterilization.³²⁻³⁴ Lastly, TPOs possess physical properties that can be continuously maintained at elevated temperatures that are typically below those of the other crystallizable TPEs. This TPE class is frequently applied as roofing materials since they do not degrade upon exposure to UV radiation.³⁵



FIGURE 8.2

Schematic illustration of a semicrystalline TPE depicting the formation of an amorphous rubbery network stabilized by crystalline physical crosslinks as the temperature is lowered from the molten state (where the hard and soft blocks form a homogeneous solution).

The alternative to a crystallizable hard segment is a vitrifiable (i.e., glass-forming) hard segment, and TPEs formulated according to this synthetic strategy rely primarily on atactic polystyrene (S), although acrylic TPEs developed from poly(methyl methacrylate) (PMMA) have also been developed for this purpose.³⁶ Unlike the other TPEs discussed above, styrenic TPEs are synthesized by chain-growth polymerization mechanisms (free-radical or ionic), in which case their molecular architectures can be precisely controlled, their molecular weights can be relatively high and their dispersities can be very low (< 1.2).³⁷ In fact, commercial TPEs synthesized as triblock copolymers with styrenic endblocks and a polydiene/olefin midblock by living anionic polymerization (with dispersities < 1.1) constitute the most ubiquitous family of TPEs worldwide and account for nearly 33% of the commercial TPE market globally.³⁸ Rather than forming semicrystalline domains to serve as physical crosslinks, this class of TPEs stabilizes a subambient-Tg molecular network with glassy S microdomains having a low T_g (\approx 100 °C) relative to the melting points of the crystallizable TPEs. While commercially relevant TPEs of this genre typically contain a saturated (olefinic) midblock such as poly(ethylene-alt-propylene) (EP) or poly(ethylene-co-butylene) (EB) to ensure chemical and reaction inertness, TPSs having unsaturated polydiene midblocks afford numerous opportunities to introduce different functional moieties, such as maleic anhydride, ³⁹ polyester⁴⁰ or liquid crystalline grafts, ^{41,42} along the midblock. Moreover, the styrenic endblocks are also suitable for chemical modification and can be used to incorporate a wide range of polar moieties based on halogenated⁴³ or charged species.⁴⁴ By incorporating such species into a microphase-separated styrenic TPE (which can exhibit highly ordered nanostructures⁴⁵ since the hard/soft sequence characteristics of these copolymers are well-defined in contrast to crystallizable TPEs), these materials can exhibit tunable amphiphilicity, wherein some microdomains remain hydrophobic while others become hydrophilic.^{46,47} Hydrophilic channels capable of permeating polar liquids (including water) in these TPEs open the door to new stimuli-responsive and functional technologies,⁴⁸⁻⁵⁰ as described in later sections.

Introduction to Model Block Copolymers as TPEs

Block copolymers with precisely controlled molecular characteristics represent a technological breakthrough as TPEs in the rubber industry. Block copolymers are macromolecules that consist of at least two long, contiguous sequences ("blocks") of chemically-dissimilar repeat units.^{2,7,51,52} Due to thermodynamic incompatibility between the blocks, these materials can microphase-separate and spontaneously self-assemble into a wide variety of soft nanostructures.^{17,19,53,54} Current polymer synthetic methods provide growing opportunities to generate a broad portfolio of block copolymer families, ranging from perfectly-alternating linear multiblock copolymers⁵⁵⁻⁵⁸ to star,^{59,60} cyclic,⁶¹ branched,⁶² tapered,⁶³⁻⁶⁶ and bottlebrush block copolymers.^{67,68} Several excellent sources addressing morphological development in various block copolymers (including those with more than two constituent chemical species) are available and focus on relevant topics such as the effects of molecular architecture, composition and weight.^{19,69-74} Increases in molecular complexity greatly expand the property sets that can be realized through systematic variation in molecular design, which can be guided by predictive theory and computer simulation. The self-consistent-field phase diagram of molecularly-symmetric ABA triblock copolymers (with identical A endblocks) predicted by Matsen,¹⁹ for example, is presented in Figure 8.3 and reveals several important features. First, the thermodynamic incompatibility is expressed as the coupled parameter χN , where χ is the Flory-Huggins interaction parameter (which commonly scales as 1/T, where T

denotes absolute temperature) and N represents the number of statistical units along the copolymer backbone. Values of χ for several chemical species relative to S are ranked in **Figure 8.4**.



FIGURE 8.3

Phase diagram of ABA triblock copolymers predicted by the self-consistent field theory of Matsen.¹⁹ Included here are the close-packed spherical (S_{cp}), body-centered spherical (S), hexagonally-packed cylindrical (C), gyroid (G), *Fddd* (O⁷⁰), and lamellar (L) morphologies. (Reproduced with permission from Matsen, M.W. *Macromolecules* **2012**, *45*, 2161. Copyright 2012 American Chemical Society.)



FIGURE 8.4

Estimated values of χ between polystyrene and other species commonly found in styrenic block copolymers. (Reproduced with permission from Wang, W., *et al. Prog. Polym. Sci.* **2019**, *95*, 1. Copyright 2019 Elsevier.)

Copolymer composition, given by the number (volume) fraction of one block type, is designated as f in **Figure 8.3**. Within the ordered state, copolymer molecules can self-assemble into classical nanostructures: A(B) spheres typically positioned on a body-centered-cubic (bcc) or face-centered-cubic (fcc) lattice in a continuous B(A) matrix, A(B) hexagonally-packed cylinders arranged in a B(A) matrix and co-alternating lamellae.^{2,7,72} In addition, more spatially complex morphologies include

the bicontinuous gyroid⁷⁵⁻⁷⁷ (displayed in 3D for an ABA triblock copolymer^{78,79} in **Figure 8.5**), double-diamond,^{80,81} O⁷⁰,^{82,83} and the Frank-Kasper σ phase.⁸⁴ In the event that more than two species are incorporated into a block copolymer, numerous additional hybrid and unique morphologies have been predicted, simulated and observed.^{69,71,72} Unless otherwise specified, however, only bicomponent linear block copolymers will be initially considered here.



FIGURE 8.5

3D renditions of the gyroid morphology in a microphase-ordered ABA triblock copolymer: (a) experimental reconstruction from transmission electron microtomography (TEMT) and (b) calculated Schoen's gyroid surface corrected for composition. In both cases, the isoprenic matrix is transparent so that the bicontinuous styrenic channels are visible. (Reproduced with permission from Jinnai, H. and Spontak, R.J.. *Polymer* **2009**, *50*, 1067. Copyright 2009 Elsevier.)

Controlling block copolymer phase behavior and properties is routinely achieved by varying chemical species and temperature (through χ), molecular weight (through N) and block composition (through f). Several additional avenues by which to alter block copolymer attributes are now examined. The first focuses on block purity.⁸⁵ As previously mentioned, bicomponent block copolymers consist of two chemically-dissimilar species, A and B, in which case $\chi(T)$ is fixed for each polymer pair since χ is a pairwise-specific parameter. One way to alter χ without changing the two species is to generate blocks that are random copolymers, rather than pure sequences, of A and B.⁸⁶⁻⁸⁸ This special case, referred to as block random copolymers (BRCs), introduces a new experimentally tunable variable, namely, composition contrast (Δ), since each block can now contain both chemical species but at different compositions. Application of the copolymer equation for a bicomponent copolymer yields⁸⁵ $\Delta = |w_{A,1} - w_{A,2}|$, where $w_{A,i}$ corresponds to the mass fraction of A in the *i*th block (*i* = 1 or 2), so that an effective interaction parameter for the BRC (χ_{eff}) can be directly related to χ between the A and B species: $\chi_{eff} = \chi \Delta^2$. As evinced by the transmission electron microscopy (TEM) images provided for two diblock BRCs composed of S and polyisoprene (I) in **Figure 8.6**, increasing Δ from 0.25 to 0.50 at constant temperature (χ), molecular weight (~N) and block fraction (f) is accompanied by the formation of a lamellar morphology. Corresponding results from dynamic rheology confirm the existence of only one, albeit broad, Tg (from the single maximum in tan δ) when Δ = 0.25, but two distinct T_g values due to the microphase-separated blocks when Δ = 0.50. Values of the order-disorder transition temperature (T_{ODT}) discerned for

several low-dispersity BRCs (varying in N and f) from optical and rheological measurements provide values of $(\chi N)_{ODT}$, which can be corrected for composition via Δ to yield $\chi_{eff}N$, as displayed in **Figure 8.7**. In **Figure 8.7a**, $(\chi_{eff}N)_{ODT}$ is presented as a function of Δ at nearly constant f (= 0.54) to demonstrate that its average is 10.5, which corresponds well to the mean-field value of $(\chi N)_{ODT}$ for diblock copolymers at f = 0.50 in the absence of critical fluctuations commonly associated^{89,90} with block copolymers at their ODT. The results provided in **Figure 8.7b** indicate that the ODT predicted for pure diblock copolymers can be approximated as functions of only f and Δ with diblock BRCs at constant temperature (χ) and molecular weight (~N). It should be noted that the midblock of TPS triblock copolymers can likewise be synthesized as a random copolymer (with added S) to controllably increase the T_g of the midblock.⁸⁵



FIGURE 8.6

TEM images of two block random copolymers (BRCs) with identical chemical species, molecular weights and block fractions under isothermal conditions, but different block purities, as schematically depicted. The copolymer on the left possesses a single T_g according to rheology, which is indicative of a homogeneous material, whereas the one on the right possesses two T_g s expected from a microphase-separated copolymer (in agreement with the TEM images). (Adapted from Ashraf, A.R., *et al. Macromol. Rapid Commun.* **2017**, *38*, 1700207. Copyright 2017 Wiley.)

Another synthesis-based route by which to alter the phase behavior and corresponding properties of TPE block copolymers requires changes to molecular architecture through the incorporation of additional blocks. The first case considered here provides a segue from diblock to triblock copolymers as an additional endblock is progressively grown from a parent AB diblock copolymer to generate asymmetric A_1BA_2 triblock copolymers wherein the endblocks possess the same chemistry but differ in length (*i.e.*, $N_{A1} \neq N_{A2}$).^{18,91}



FIGURE 8.7

In (a), ($\chi_{eff}N$)_{ODT} presented as a function of the composition contrast (Δ) for several different BRCs possessing comparable block fractions ($f \approx 0.5$). The average of the data is 10.5, which agrees favorably with the value of (χN)_{ODT} in the mean-field limit for a comparable diblock copolymer with pure blocks (dashed line)¹⁷. In (b), the dependence of $\chi_{eff}N$ on f for copolymers possessing identical molecular weights under isothermal conditions. The theoretical ODT for diblock copolymers is included for reference (solid line). (Adapted from Ashraf, A.R., *et al. Macromol. Rapid Commun.* **2017**, *38*, 1700207. Copyright 2017 Wiley.)



FIGURE 8.8

The order-disorder transition temperature (T_{ODT}) of two copolymer series (9-17-A2 and 9-46-A2) measured by dynamic rheology as functions of (a) M_{A2} and (b) τ in molecularly-asymmetric triblock copolymers progressively grown from two parent diblock copolymers. The solid lines in (a) serve to connect the data, whereas those in (b) correspond to mean-field predictions. The diagram included in (b) illustrates several different copolymer architectures differing in τ . (Adapted from Hamersky, M.W., *et al. Phys. Rev. Lett.* **2005**, *95*, 168306. Copyright 2005 American Institute of Physics.)

In addition to exploring the utility of this approach to adjust phase behavior and properties, the systematic transition from non-networking diblock copolymers, a model material archetype capable of identifying the key elements of molecular self-assembly, to triblock copolymers, another model material archetype associated with physical network formation, can elucidate the conditions under which a triblock copolymer is first able to form an equilibrium network. To facilitate the discussion here, an asymmetry parameter (τ), defined as N_{A1}/(N_{A1} + N_{A2}), is introduced to differentiate the degree of asymmetry in this molecular progression: $\tau = 1$ is the maximum permissible value and corresponds to a diblock copolymer, whereas $\tau = \frac{1}{2}$ identifies a molecularly symmetric triblock copolymer (with $N_{A1} = N_{A2}$). It is possible, however, for $\tau < \frac{1}{2}$ when $N_{A2} > N_{A1}$. Experimental values of T_{ODT} are presented as a function of the molecular weight of the new endblock (M_{A2}) for two different copolymer systems in Figure 8.8a and immediately reveal that T_{ODT} initially decreases at low M_{A2} before increasing as expected. When M_{A2} is recast in terms of τ and temperature is related to χ for SI block copolymers, the data are in excellent quantitative agreement with the mean-field theoretical predictions of Mayes and Olvera de la Cruz⁹² (cf. Figure 8.8b). Similar results acquired from small-angle X-ray scattering (SAXS) and self-consistent field analysis of ordered morphologies, as well as dynamic melt rheology,93 confirm that the diblock \rightarrow triblock transition is not a simple interpolatable process, especially when M_{A2} is relatively small (and τ lies between 1 and $\frac{1}{2}$).



FIGURE 8.9

In (a), illustration of a microphase-separated ABA triblock copolymer identifying the microphases and matrix present, along with the four possible midblock conformations: bridges (B), loops (L), dangles (D), and unsegregated (un). Corresponding midblock fraction (F) values extracted from DPD simulations are provided as functions of (b) χ N at constant f and (c) f at constant χ N (color-coded, labeled). The solid lines serve to connect the data, and the gray boxes in (b) correspond to predictions from self-consistent field theory (which does not account for dangles or unsegregated chains). (Adapted from Tallury, S.S., *et al. J. Chem. Phys.* **2014**, *141*, 244911. Copyright 2014 American Institute of Physics.)



FIGURE 8.10

In (a), midblock fractions presented as functions of τ from DPD simulations (color-coded open symbols, labeled), whereas those from MC simulations are designated by filled symbols and those from self-consistent field theory are provided as solid lines. The value of τ at which F_B identifies the formation of a network is given by τ_N , and the value of τ discerned from the most pronounced changes in phase behavior, nanostructural dimensions and melt rheology (τ^*) is displayed as the gray region. In (b), molecular asymmetry is used in conjunction with β (or f) to control morphological development in molecularly asymmetric triblock copolymers. In the super strong-segregation regime, coexisting lamellae and micelles can develop in A₁BA₂ triblock copolymers with short A₂ blocks (c), and the phase diagram (from MC simulations) showing the range over which such interstitial micelles form is included in (d). The solid lines in (d) serve as guides for the eye, and the dashed curve corresponds to a theory⁹⁹ for free micelles. (Adapted from Tallury, S.S., *et al. J. Chem. Phys.* **2014**, *141*, 121103 and Woloszczuk, S., *et al., Phys. Rev. E* **2015**, *91*, 010601. Copyright 2014 and 2015 American Institute of Physics.)

An improved understanding of this molecular transition can be realized through the use of computer simulations and their unique ability to quantify the different types of accessible chain conformations.⁹⁴⁻⁹⁶ **Figure 8.9a** is an illustration of the conformations that a microphase-separated ABA triblock copolymer can adopt: bridges (B), loops (L) and dangles (D). Depending on the magnitude of χN , some chains can also remain unsegregated (un). Bridges are associated with midblock network formation since they connect neighboring (glassy) microdomains serving as physical crosslinks (knotted loops are not considered here). Included in **Figures 8.9b** and **8.9c** are

the fractions of these conformations (F_B, F_L, F_D, and F_{un}) extracted from dissipative particle dynamics (DPD) simulations as functions of (i) χN at constant f and (ii) f at constant χN , respectively. Two important observations are apparent from these results: (1) as χN increases and the copolymer eventually enters the strong-segregation regime ($\chi N > 100$), F_B increases to a plateau and becomes independent of χN ; and (2) as the block fraction (f) increases and the copolymer morphologies transform from spheres to cylinders and finally to lamellae, F_B monotonically decreases since the interfacial area/volume likewise decreases. These findings establish that simulations can be used to monitor the molecular conformations of network-forming block copolymers in moderate-to-strong segregation regimes, and that this methodology can be applied to molecularly asymmetric A₁BA₂ copolymers.⁹⁷ When τ = 1.00, F_D = 1.0, whereas F_B = F_L = 0.0, in Figure 8.10a. A reduction in τ is initially accompanied by increases in F_B and F_L and a systematic decrease in F_D , according to DPD simulations. At τ_N , F_B becomes independent of τ , indicating the formation of a thermodynamically equilibrated network. The value of F_B in this limit agrees well with Monte Carlo (MC) simulations and self-consistent field calculations (the latter of which do not, however, account for the presence of dangles). The increase in F_L beyond τ_N reflects the continuing decrease in $F_{\rm D}$. The value of τ^* (= 0.79) highlighted in **Figure 8.10a** identifies the molecular asymmetry corresponding to pronounced minima in independent experimental measurements of the ODT temperature,¹⁸ the microdomain period and the melt modulus,⁹³ as well as a maximum in the invariant from SAXS.⁹¹

Taken together, the results provided in **Figure 8.10a** indicate that short A_2 endblocks remain mixed in the B matrix and only occasionally serve as bridges between A₁ microdomains, thereby yielding flocs that become increasingly prevalent as both M_{A2} and F_B increase (and τ decreases). At sufficiently high M_{A2} (< M_{A1}), these flocs ultimately merge to form the contiguous, load-bearing network expected of a TPE. Molecular asymmetry in a triblock copolymer can also be used to drive morphological transitions at constant copolymer composition, expressed as either β (= N_B/N_{A1}) or f (the B block fraction) in Figure 8.10b. At very high χN and very low M_{A2} levels, a somewhat unexpected phenomenon is also observed: dual morphologies coexisting in a single bicomponent block copolymer.⁹⁸ Although coexisting morphologies have been reported in neat (*i.e.*, non-mixed) bicomponent block copolymers, they typically arise due to either nonequilibrium processing or close proximity to an order-order transition (OOT). They also develop in tricomponent block terpolymers.^{69,71,72} Here, coexistence involves the independent self-assembly of the A_1 and A_2 endblocks under high χN conditions in the super strong-segregation regime. The outcome, displayed in Figure 8.10c, consists of alternating A1 lamellae separated by a single array of hexagonally-arranged A₂ micelles that exist within the (transparent) B lamellae. The boundary conditions between which these micelles form are included in Figure 8.10d and indicate that they become less stable as the fraction of A_2 endblocks (f_{A_2}) increases since longer endblocks will ultimately start to interact with the A₁ microdomains by adopting bridge or loop conformations. Interestingly, the initial formation of these molecularly confined micelles (relative to dangling ends) can be accurately modeled as free (i.e., non-confined) micelles according to the theoretical framework proposed by Semenov and co-workers.⁹⁹ Although this predicted coexistence discerned from MC simulations has not yet been experimentally validated, it suggests that TPEs based on the design pictured in Figure 8.10c could exhibit greater extensibility. Through the implementation of cutting-edge synthetic protocols, this strategy of adding blocks to copolymer molecules to control the phase behavior and property development of TPSs has successfully spawned new materials such as perfectly-alternating linear multiblock copolymers possessing either constant block weight (and variable molecular weight)⁵⁵ or constant molecular weight (and variable block weight),⁵⁶ as well as perfectly-alternating tapered multiblock copolymers arranged in linear^{57,58} and nonlinear⁶⁶

architectures. Another intriguing variation of triblock copolymers introduces bottlebrush blocks,⁷⁴ as depicted in **Figure 8.11**.



FIGURE 8.11

Schematic diagrams of three TPE molecular architectures containing bottlebrush (bb) blocks: (left) A-B_{bb}-A, (middle) A_{bb}-B_{bb}-A_{bb} and (right) (A_{bb}-B_{bb})₃ star. (Reproduced with permission from Wang, W., *et al. Prog. Polym. Sci.* **2019**, *95*, 1. Copyright 2019 Elsevier.)

All of the previous modifications to block copolymers discussed here involve the synthesis of designer molecules, which might not always be economically viable. An alternative approach often chosen to vary block copolymer phase behavior and morphology/property development involves post-synthesis chemical functionalization.¹⁰⁰⁻¹⁰² While this topic will be discussed in detail later, one particular reaction is commonly utilized. As mentioned earlier, typical TPSs include triblock copolymers in which the midblock is either a polydiene or its saturated analog. For this reason, hydrogenation is considered here since it is routinely used to generate saturated midblocks from unsaturated ones.¹⁰³ Hydrogenation is a catalytic reaction that can be performed with a homogeneous (unsupported) or heterogeneous (supported) catalyst solution.¹⁰⁴ The results discussed below employ nickel(II) bis(2-ethylhexanoate) dissolved in cyclohexane to yield a homogeneous solution. Representative proton nuclear magnetic resonance (¹H NMR) spectra of S-I copolymers at different degree of hydrogenation (DOH) levels are supplied in Figure 8.12a to demonstrate the gradual and quantifiable disappearance of unsaturated bonds. Although hydrogenated SIS and poly(styrene-b-butadiene-b-styrene) (SBS) triblock copolymers are the most commercially relevant TPEs since they yield SEPS and SEBS copolymers, respectively, we monitor here the hydrogenation of S-I BRCs since their properties can be precisely adjusted¹⁰⁵ to provide a more complete picture of hydrogenation (otherwise, hydrogenating SIS and SBS copolymers could yield relatively little insightful information before thermal degradation). For instance, the unaltered BRC possesses a relatively low TODT, as ascertained by dynamic rheology in Figure 8.12b. Progressive hydrogenation to a DOH level of 93 mol% clearly signifies that the T_{ODT} is systematically increased to over 200 °C (due to increased incompatibility) and that this dependence, measured by both dynamic rheology and SAXS, is unexpectedly linear for two different BRCs in Figure 8.12c. By casting associated SAXS profiles into the form proposed by Vonk¹⁰⁶ in Figure 8.12d, it is possible to extract information regarding the interphase thickness (w) that exists between chemicallydissimilar microdomains. The dependence of w on DOH is included in the inset of Figure 8.12d and reveals that the interphase is relatively broad (> 3 nm) for the unaltered BRC (at 0 mol% DOH) but abruptly narrows when the DOH exceeds 58 mol% (eventually approaching ~ 1 nm). Since w ~ $\chi^{-\%}$ in the limit of strong-segregation behavior according to Helfand and Tagami,¹⁰⁷ this dependence corroborates the results from T_{ODT}(DOH), verifying that increasing hydrogenation boosts copolymer incompatibility.



FIGURE 8.12

In (a), ¹H NMR spectra acquired from a BRC at different DOH levels (labeled), as quantified by the disappearance of unsaturated bonds (shaded area). In (b), the dynamic storage modulus (G') is displayed as a function of temperature for a BRC varying in DOH (color-coded, labeled). Values of T_{ODT} extracted from such rheological data for two different BRCs (color-differentiated) are supplied in (c) as a function of DOH and reveal a linear dependence (solid lines). In (d) SAXS data collected from four BRCs differing in their DOH are provided in the form suggested by Vonk¹⁰⁶ (where s denotes the scattering vector) to extract the interphase thickness (w), values of which are given as a function of DOH in the inset of (d). (Adapted from Ashraf, A.R., *et al. ACS Appl. Mater. Interfaces* **2018**, *10*, 3186. Copyright 2018 American Chemical Society.)

Physical Modification of Nonpolar TPEs and Their Applications

Recent progress has established that TPEs can be physically modified to achieve properties beyond their inherent mechanical limitations.¹⁰⁸⁻¹¹¹ For instance, the lowest modulus achievable in TPSs is dictated by the plateau modulus of the middle rubbery block. In some emerging applications, however, a lower modulus might be desirable, in which case a sound physical strategy must be developed to achieve a tunable reduction in modulus while still maintaining control over morphological development. Within this section, we examine one approach to attain this objective

through the physical incorporation of a low-volatility aliphatic oil, which serves as a midblockselective solvent, to yield thermoplastic elastomer gels (TPEGs). These soft, stretchy and selfhealing materials are of tremendous general interest due to their unique abilities to, for example, mimic mammalian skeletal muscle,¹¹² show little evidence of mechanical hysteresis,¹¹³ become responsive to electrical stimulation,¹¹⁴⁻¹¹⁸ and dampen compression and vibrations.¹¹⁹ They can be used as anthropomorphic surrogates^{120,121} to test ballistics^{122,123} or crash/explosion survival,¹²⁴ or replace cadavers in surgical training,¹²⁵ and they can be used for controlled drug delivery¹²⁶ and microfluidics.¹²⁷ As shock-absorbing media, they are suitable for underground housing for fragile fiber optics in the telecommunications industry.^{128,129} Moreover, as electroresponsive media, they can be used for soft robotics,^{130,131} haptic devices,¹³² and even energy-harvesting media. Lastly, this general materials design can be readily extended to yield pressure-sensitive adhesives^{133,134} with tunable properties, high-precision shape-memory materials¹³⁵⁻¹³⁷ and unparalleled polymeric systems that exhibit time-composition rheological equivalence under isothermal conditions. 138,139 While the TPEGs of most interest here consist of a saturated TPS that is selectively swollen with a primarily aliphatic oil (e.g., mineral oil, MO), the phase diagram¹⁴⁰ displayed in Figure 8.13, generated from SAXS analysis, confirms that the morphologies observed in neat block copolymer systems are retained in ternary physical blends composed of a nonpolar SEPS copolymer with a midblock-selective MO and an endblock-selective oligostyrene. This level of morphological consistency substantiates our contention that mixing paradigms developed for miscible block copolymer blends and amphiphilic block copolymers apply to these TPEGs.



FIGURE 8.13

Ternary phase diagram generated from synchrotron SAXS for a TPE (SEPS copolymer) physically modified with a midblock-selective mineral oil (MO) and an endblock-selective oligostyrene (OligoS). The colored regions correspond to the color-coded morphologies. (Adapted from Krishnan, A.S., *et al. Macromolecules* **2012**, *45*, 6056. Copyright 2012 American Chemical Society.)



FIGURE 8.14

Dimensionless temperature-composition ($T^*-\phi_s$, where ϕ_s denotes the fraction of midblock-selective solvent) phase diagrams from MC computer simulations for triblock copolymers varying in molecular composition (f): (a) 0.2, (b) 0.4, (c) 0.6, and (d) 0.8. In addition to lamellae (L), perforated lamellae (PL), bicontinuous (B), cylinders and rods (C and R), and spherical micelles (M), a new morphology denoted by OCT (for octahedron) is identified and depicted. (Adapted from Woloszczuk, S., *et al. ACS Appl. Mater. Interfaces* **2017**, *9*, 39940. Copyright 2017 American Chemical Society.)

Most styrenic TPEs of commercial relevance commonly possess 20-33 wt% S at surprisingly few molecular weights. This shortage of available, well-defined TPSs severely limits experimental inquiry, in which case computer simulations again demonstrate their obvious value by exploring key parameters in phase space.¹⁴¹⁻¹⁴³ The MC simulations in **Figure 8.14a-d**, for instance, focus on the effect of midblock solvation for ABA triblock copolymers differing in f (the A fraction). While (perforated) lamellae, cylinders, rods and spherical micelles constitute most of the morphologies identified, a unique nanostructure, referred to as the truncated octahedron (OCT, depicted in

Figure 8.14d), is predicted to be stable in TPEGs when the copolymer is 80% endblock (which is more representative of a rubber-reinforced plastic than a true TPE). The corresponding bridge fractions evaluated at different isotherms are included in Figure 8.15 and corroborate that discrete micellar morphologies tend to exhibit the highest level of midblock bridging. Dynamic rheological analysis of TPEGs at relatively low ABA triblock copolymer loading levels (ϕ) in **Figure 8.16a** reveals that network behavior (as evidenced by the dynamic storage modulus, G', being independent of oscillatory frequency, ω , and greater than the dynamic loss modulus, G") is observed down to 2 wt% copolymer. In addition, the low-o G' measured for TPEGs composed of SEBS copolymers possessing similar molecular compositions but different molecular weights scales as ϕ^k , where $k \approx 2$, suggesting that entanglements dominate the rheological contribution to G', in favorable agreement with previous independent studies,^{144,145} as well as the theoretical studies of de Gennes¹⁴⁶ proposed for entangled homopolymers in solution. Associated simulations of the midblock bridging fraction for TPEGs containing ABA triblock copolymers varying in chain length at constant composition (cf. Figure 8.16b) indicate that the copolymer composition (ϕ_{ea}) required to achieve equilibrated molecular networks at F_{B,net} varies inversely with copolymer chain length, and the scaling relationship extracted from the inset in **Figure 8.16b** is given by $\phi_{eq} \sim N^{-1.4}$.



FIGURE 8.15

Midblock bridging fraction as a function of ϕ_s at four different isotherms (T*) – 1 (\bigcirc), 2 (\bigcirc), 3 (\blacktriangle), and 4 (\triangle) (see **Figure 8.14**) – for four triblock copolymers varying in molecular composition (f): (a) 0.2, (b) 0.4, (c) 0.5, and (d) 0.6. The solid lines serve to connect the data, and the vertical red lines indicate the onset of the ODT. The red dots identify order-order transitions from the corresponding phase diagrams displayed. (Reproduced with permission from Woloszczuk, S., *et al. ACS Appl. Mater. Interfaces* **2017**, *9*, 39940. Copyright 2017 American Chemical Society.)



FIGURE 8.16

In (a) frequency spectra of G' (open symbols) and G" (filled symbols) at different copolymer fractions (colorcoded, labeled). The inset in (a) displays G' at low ω as a function of ϕ for four SEBS copolymers possessing similar composition (f \approx 0.3) but different molecular weights. The lines in the inset correspond to power-law regressions to the data. In (b), the midblock bridging fraction from DPD simulations is presented as a function of ϕ for copolymers differing in chain length (N, labeled) at f = 0.3. The value of F_B signaling network formation is identified (F_{B,net}), as is the composition at which it occurs (ϕ_{eq}), and the solid lines serve to connect the data. The dependence of ϕ_{eq} on N in included in the inset in (b), and the solid line is a power-law regression. (Adapted from Tuhin, M.O., *et al. J. Chem. Phys.* **2018**, *148*, 231101. Copyright 2018 American Institute of Physics.



FIGURE 8.17

In (a), DPD simulations of TPEGs composed of (AB)_nA multiblock copolymers (n varies from 1 to 3) at different solvent compositions (labeled). The midblock conformations displayed in (b) yield the midblock conformation index (MCI) values (included) developed to describe the topologies of TPEG physical networks. A description of the MCI is provided in the text. (Adapted from Tuhin, M.O., *et al. Macromolecules* **2018**, *51*, 5173. Copyright 2018 American Chemical Society.)

A series of DPD simulations generated¹⁴³ from linear multiblock copolymers of the form (ABA)_n, where n varies from 1 to 3 to include triblock (n = 1), pentablock (n = 2) and heptablock (n = 3), at constant chain length is presented at different midblock-solvation levels in **Figure 8.17a**. Due to the starting composition of these copolymers (20 wt% hard block), they all exhibit spherical micelles. The ensemble of molecular conformations possible in these three TPEG series is depicted in **Figure 8.17b**, and each can be uniquely differentiated to yield a midblock conformation index (MCI), which is expressed by 4 numbers: [number of connected micelles, number of bridges, number of loops, number of dangles]. Careful examination of the chain trajectories in computer simulations yields the most probable copolymer conformation in each TPEG. These are provided in schematic form and as functions of ϕ in **Figure 8.18** and signify that the pentablock and heptablock molecules prefer not to be fully extended (since each exhibits a loop). Also included in this figure is the total fraction of bridged molecules in each TPEG series. Similarly detailed topological analyses of networks have been reported¹⁴⁷⁻¹⁴⁹ for several other polymer systems.



FIGURE 8.18

Midblock bridging fractions determined from DPD simulations (see **Figure 8.17**) as a function of copolymer composition (ϕ) for TPEGs composed of triblock (circles), pentablock (diamond) and heptablock (square) copolymers of constant composition and molecular weight. Except for the case of triblock-based TPEGs, these results identify the most probable conformation (filled symbols, depicted with its MCI designation) and total values (open symbols). The solid lines serve to connect the data. (Reproduced with permission from Tuhin, M.O., *et al. J. Chem. Phys.* **2018**, *148*, 231101. Copyright 2018 American Institute of Physics.)

Rheological investigation of TPEGs fabricated from matched pentablock and heptablock copolymers imply that G' ~ ϕ , in which case it follows that physical crosslinks dominate G' (in marked contrast to the triblock-based TPEG governed by entanglements). Complementary quasistatic uniaxial tensile tests of these TPEGs can be analyzed in the context of the Slip-Tube Network (STN) model proposed by Rubinstein and Panyukov¹⁵⁰ to distinguish the contributions of elastic crosslinks and chain entanglements to the shear modulus (G_c and G_e, respectively) in polymer networks. Results obtained¹⁵¹ by fitting tensile data at ambient temperature are presented in **Figure 8.19** and verify that the physical crosslinks of these TPEGs are important at low copolymer levels but entanglements dictate the response of all TPEGs at high ϕ , with the crossover consistently between ~20 and 25 wt% copolymer. While similar behavior is observed from dynamic rheology for the TPEGs composed of pentablock and heptablock copolymers, the apparent difference in the case of the triblock-based TPEGs is attributed to the extent to which the samples are deformed (the rheological tests were performed on a stress-controlled rheometer with a constant stress amplitude of 1 Pa in the linear viscoelastic regime, whereas the tensile data were examined up to 200% strain). Detailed mechanical analyses such as these provide a starting point to develop a more fundamental and comprehensive understanding of how network topology governs the mechanical properties of TPEGs.



FIGURE 8.19

Values of G_c and G_e (color-coded, labeled) obtained from regressions of the Slip-Tube Network model¹⁵⁰ to quasistatic uniaxial tensile test data and presented as a function of ϕ for TPEGs composed of triblock (n = 1), pentablock (n = 2) and heptablock (n = 3) copolymers of constant composition and molecular weight. The solid lines are power-law fits to the data. (Reproduced with permission from Yan, J., *et al. J. Chem. Phys.* **2020**, *153*, 124904. Copyright 2020 American Institute of Physics.)

One final aspect of styrenic TPEGs that warrant mention is that their dynamic properties can exhibit isothermal time-composition superpositioning $(tCS)^{138,139}$ (also referred to as rheological equivalence), in contrast to conventional time-temperature superpositioning (tTS).¹ In this case, a cycloaliphatic resin (CR) that behaves as a tackifying resin with a T_g above ambient temperature is added to MO to yield ternary, rather than binary, TPEGs. While TPEGs formulated with MO consistently exhibit network behavior at copolymer loading levels above the critical gel concentration according to dynamic rheology, those prepared with CR display evidence of viscoelastic behavior in which G" exceeds G' up to a crossover point in frequency spectra. To ensure that these midblock-selective cosolvents are miscible at all compositions, T_g values of MO/CR mixtures have been measured over the entire composition range and subsequently analyzed according to the Couchman equation to confirm infinite miscibility.¹⁵² Frequency spectra acquired from ternary TPEGs composed of a commercial SEBS copolymer physically swollen with MO/CR

mixtures are included in **Figure 8.20a** and reveal that a gel network is retained up to 60 wt% CR in the cosolvent. At and above 80 wt% CR in **Figure 8.20b**, the TPEGs exhibit viscoelastic behavior. Shifting the frequency spectra in **Figures 8.20a** and **8.20b** yields the master G' and G" curves as functions of adjusted frequency over 10 decades (up to 12 decades have been recorded) in **Figure 8.20c**. While the master curve for G' appears relatively seamless, the one for G" displays variation in the low-frequency limit. This characteristic is attributed to the onset of a second relaxation mechanism. Rheological equivalence derives from a single relaxation mechanism, typically due to chain entanglements. The second mechanism evident in **Figure 8.20c** reflects endblock-hopping when a copolymer endblock pulls out from one glassy micelle and re-enters another one.¹⁵³ For this reason, this manifestation becomes amplified (and superpositioning fails) with copolymers possessing short endblocks, but disappears altogether with copolymers having long endblocks. The shift factor obtained from tTS (a_T) is commonly related to temperature through an Arrhenius expression or the Williams-Landel-Ferry (WLF) equation, whereas the one from tCS (a_c) is found to scale with the zero-shear cosolvent viscosity, and the corresponding scaling exponents vary linearly with copolymer loading level.¹³⁹



FIGURE 8.20

In (a) and (b), frequency spectra of G' (open symbols) and G" (filled symbols) for TPEGs consisting of triblock copolymers with a midblock-selective cosolvent composed of MO and a cycloaliphatic resin (CR, the fraction of which is provided in the legend of each panel). Time-composition superpositioning yields the master curves displayed in (c), as well as the van Gurp-Palmen plot of phase angle (δ) vs. complex modulus (G*), which assesses the quality of superpositioning by how well the data superimpose. Variations evident in superpositioned G" at low frequency imply the existence of a second relaxation mechanism (due to endblock hopping¹⁵³). (Adapted from Krishnan, A.S., *et al. Soft Matter* **2010**, *6*, 4331. Copyright 2010 Royal Society of Chemistry.)

While most studies of TPEGs have focused on those produced from TPSs, Shull and co-workers¹⁵⁴⁻¹⁵⁷ have pioneered TPEGs derived from acrylic triblock copolymers (these TPEGs are designated here

as ATPEGs to reflect their acrylic content). Those efforts have focused on various mechanical attributes, as well as important thermal transitions. An important aspect of ATPEGs that immediately distinguishes them from styrenic TPEGs is that they can incorporate polar solvents¹¹⁶ (e.g., dioctyl phthalate, DOP), which can be highly beneficial in stimuli-responsive applications (discussed below). Alternatively, TPEGs can also be generated from TPOs. For example, addition of MO to polyolefin TPEs composed of randomly-coupled high-density polyethylene hard blocks and poly(ethylene-co- α -octene) soft blocks yields olefinic TPEGs (OTPEGs) that can exhibit altogether different property sets due to the ability of this TPE to crystallize.^{117,158} Since this copolymer only contains polyethylene, it is suitable for various biomedical applications.¹⁵⁹ As before, the MO serves to swell the soft blocks, while the hard blocks stabilize the network composed of swollen soft blocks. Thermal calorimetry of OTPEGs differing in copolymer concentration confirms that the degree of copolymer crystallinity, which can be controllably varied by adjusting the hard/soft segment ratio, only undergoes a noticeable reduction from its neat copolymer limit at low copolymer loading levels (< 10 wt%). This observation indicates that the presence of MO has little influence on copolymer crystallization. Moreover, unlike styrenic TPEGs that exhibit low mechanical hysteresis (with little irrecoverable strain) during cyclic tensile deformation, OTPEGs initially suffer from substantial irrecoverable strain (that can exceed 100%),¹⁵⁸ accompanied by a large hysteretic energy, due to plastic deformation. Incorporation of relatively little MO (~20 wt%) into these TPOs,

however, promotes an unexpected property development. While styrenic TPEGs are generally hyperelastic and routinely surpass over 1500% strain, OTPEGs can achieve strain levels exceeding 4000% before failure^{117,158}.

Chemical Modification of Nonpolar TPEs and Their Applications

Block copolymers are often used as compatibilizing agents to reduce interfacial tension and the size of dispersed phase domains in phase-separated polymer blends.¹⁵⁹⁻¹⁶¹ By localizing along the interface, they promote adhesion through chain entanglements and thus improve mechanical properties. Unfortunately, as evinced in Figure 8.21, straightforward use of styrenic TPEs do not always promote compatibilization if the timescale for diffusion to the polymer/polymer interface is insufficiently short, in which case the TPE molecules self-assemble instead.¹⁶² Since few block copolymers are available for specific polymer blends, customizable compatibilizers have become increasingly important. One successful example incorporates maleic anhydride into TPEs so as to introduce polarity to a nonpolar block copolymer.¹⁶³ In this spirit, the strategy discussed here relies on the post-functionalization of premade TPEs possessing well-defined molecular attributes. In the case of TPSs, both of the styrenic endblocks, as well as unsaturated polydiene midblocks, are amenable to modification. First, we consider chemically altering the midblock of a partially hydrogenated SIS copolymer (partial hydrogenation helps to prevent undesirable chemical crosslinking).¹⁶⁴ One promising chemical approach to do this relies on thiol-ene click chemistry, which affords mild reaction conditions, relatively high yields and rapid reaction rates.¹⁶⁵ By applying thiol-ene click chemistry, a library of polar moieties can be grafted onto nonpolar TPEs to enhance their compatibility with various polymers and polymer blends.^{166,167} One illustrative exemplar uses the thiol-ene click chemistry depicted in Figure 8.22a to generate esterified SEPS, which is then suitable for toughening poly(lactic acid) (PLA). The inherent brittleness and poor mechanical properties of PLA prevent this sustainable bioplastic from being used to replace conventional plastics derived from fossil fuel sources in numerous commodity applications. The esterified SEPS constitutes a facile and low-cost route by which to rubber-toughen PLA and profoundly improve its mechanical properties.¹⁶⁴ Representative ¹H NMR spectra confirming ester substitution on the midblock are provided in **Figures 8.22b** (before reaction) and **8.22c** (after reaction), and several mechanical performance metrics are included in **Figures 8.22d** and **8.22e**. According to these results, a Goldilocks composition range exists from 1 to 5 wt% copolymer wherein the tensile strength does not vary noticeably, but the elongation at break and fracture toughness increase by about 2300% and 1500%, respectively, at 1 wt%. These results are not only competitive with more exotic means of toughening PLA, but the design paradigm is sufficiently general and can also be extended to other polyesters as well.



FIGURE 8.21

A series of cross-sectional TEM images acquired from bicomponent fibers composed of isotactic polypropylene (iPP) and poly(lactic acid) (PLA). The entire fiber is visible in (a), and a reference displaying a SEBS copolymer in PLA is included in (b). The unexpected morphologies of the copolymer in (c) PLA-sheath and (d) PLA-core fibers reveal the effect of nonequilibrium processing on copolymer self-assembly. The "peas-in-a-pod" (micelles within nanotubes) arrangement is evident in the inset of (c). (Reproduced with permission from Arvidson, S.A., *et al. Macromolecules* **2012**, *45*, 913. Copyright 2012 American Chemical Society.)



FIGURE 8.22

In (a), the thiol-ene click reaction used to esterify the midblock of a TPE SIS copolymer (the actual material used is partially hydrogenated to prevent undesirable side reactions). The ¹H NMR spectra presented in (b) and (c) confirm the chemical conversion. Resultant mechanical properties of PLA modified with the esterified copolymer are included in (d) and (e) and confirm that properties associated with fracture resistance are greatly improved. (Adapted from Yan, J. and Spontak, R.J. *ACS Sustainable Chem. Eng.* **2019**, *7*, 10830. Copyright 2019 American Chemical Society.)

Similarly diverse methods designed to functionalize the styrenic endblocks of TPSs are available, and one of the most versatile routes involves chloromethylation.¹⁶⁸ Although the presence of a halogen on a TPS is advantageous for functional membranes and ion exchange resins,¹⁶⁹ this modification is amenable to further chemical reaction to introduce, for example, phosphonium or ammonium cations, which could interact strongly with polyamides. The 90° peel strength results provided in **Figure 8.23a** indicate that these chemical alterations to a SEBS copolymer greatly benefit the compatibilization of polar nylon-6 and nonpolar linear low-density polyethylene (LLDPE).¹⁷⁰ Selective sulfonation of styrenic TPEs, however, constitutes one of the most mature routes to alter the functionality of inherently nonpolar macromolecules by making them amphiphilic.^{171,172} While most sulfonation efforts (including the seminal studies of Weiss and coworkers^{173,174}) have specifically targeted the styrenic endblocks of TPSs, targeted sulfonation of

unsaturated midblocks has also been successfully achieved (without chemical crosslinking) through the use of a 1,4-sulfur trioxide-1,4-dioxane complex,¹⁷⁵ and the resulting material is capable of substantial swelling in water without dissolving since the properties of the nonpolar styrenic endblocks are not compromised (as they would be in the case of endblock-sulfonated materials). The major drawback of endblock-sulfonated TPSs is that, in the presence of a polar liquid, the endblocks responsible for network stabilization either become plasticized or, depending on the degree of sulfonation (DOS), dissolve so that the network altogether fails. A relatively recent solution to this shortcoming requires the introduction of a multivalent cation that can complex with and physically crosslink the sulfonated styrenic endblocks.¹⁷⁶ This strategy permits styrenic TPEGs to remain stable at temperatures far above the Tg of polystyrene. An alternative solution focuses on a TPS composed of a midblock-sulfonated pentablock polymer: poly[tert-butylstyrene-b-(ethylenealt-propylene)-b-(styrene-co-styrenesulfonate)-b-(ethylene-alt-propylene)-b-tert-butylstyrene] (TESET). Since the tert-butylstyrene endblocks cannot be sulfonated, they remain intact in the presence of a polar liquid and maintain the integrity of the swollen molecular network. The EP intermediate blocks serve a vital role in that they prevent this material from becoming brittle, as is analogous triblock copolymer:¹⁷⁷ poly(tert-butylstyrene-b-(styrene-cothe case of an styrenesulfonate)-*b-tert*-butylstyrene) (TST).



FIGURE 8.23

In (a), 90° peak peel strength results from laminates of polar nylon-6 and nonpolar LLDPE separated by a thin film of SEBS copolymer in which the endblocks are chemically functionalized (labeled) and homopolymer adhesion is clearly improved. Similar results measured from the same laminates separated by an endblock-sulfonated SEBS copolymer (sSEBSn, where n denotes the DOS) are displayed in (b). While the neat sSEBS copolymer moderately improves interfacial strength, two other possibilities are possible: "easy-off" (shaded blue), referring to the addition of water to swell the copolymer and reduce interfacial adhesion by decompatibilization, and "easy-on" (shaded gold), referring to the addition of Cu⁺ ions to the copolymer to improve adhesion by compatibilization. (Adapted from Ryan, J.J. and Spontak, R.J. *Compatibilization of Polymer Blends.* **2020**, pp. 57-102. Copyright 2020 Elsevier.)

While sulfonation can promote the development of unexpected, but nonetheless interesting, properties in TPSs, here we first consider the use of sulfonated copolymers for compatibilization

and decompatibilization, as discerned from peel tests similar to those mentioned above. We refer to this class of compatibilizers in Figure 8.23b as "easy-on/easy-off" since this designation accurately describes the uniquely contrary ability of these materials to either promote or reduce interfacial adhesion between chemically-dissimilar polymers. Endblock sulfonation of a SEBS triblock copolymer, for example, introduces charged species that can interact with a polar polymer (such as nylon-6), whereas the olefinic midblock would prefer to interact with a nonpolar polymer (such as LLDPE). The result, as with the cationic TPSs generated from endblock-chloromethylated SEBS, is a considerable net reduction in interfacial tension and, hence, improved compatibilization between the two incompatible homopolymers (the 90° peak peel strength between nylon-6 and LLDPE without a compatibilizer is very low, 0.06 kN/m). A practical challenge that arises with sulfonated TPSs is, however, that they are sensitive to thermal degradation at elevated temperatures. One way to overcome this drawback and concurrently improve compatibilization is through metal ion complexation.¹⁷⁶ Neutralization of a sulfonated SEBS copolymer with Cu²⁺ cations yields a processable material that increases the nylon-6/LLDPE peak peel strength in Figure 8.23b to 2.5 kN/m, which is comparable to the phosphonium modification in Figure 8.23a. In marked contrast, the inherent hydrophilicity of non-neutralized sulfonic acid groups is likewise suitable for a vastly different purpose. By introducing water to trilayered laminates containing a thin middle layer of sulfonated SEBS, the laminates can be readily separated (as the peak peel strength drops to 0.01 kN/m). In this case, selective swelling of the sulfonated SEBS copolymer serves to increase interfacial tension and reduce interfacial adhesion, thereby facilitating separation of the homopolymers. Such decompatibilization is of commercial interest in the separation of bicomponent fibers to yield hollow or nanoscale fibers, depending on the cross-sectional fiber geometry.

Morphological Development and Applications of Charged TPEs

Templatable Self-Assembly

Here, we examine the morphological characteristics and emerging applications of ion-containing TPSs, specifically those modified with sulfonic acid groups, to identify relevant thermodynamic considerations and opportunities for technological breakthroughs. For this purpose, we focus on the TESET TPS due to its ability to imbibe polar liquids because of the sulfonated midblock and behave as a tough physical hydrogel due to retention of the intact (non-sulfonated) endblocks. While non-sulfonated TPSs can be easily melt-processed without loss of properties, the TESET materials must be cast from solvent, in which case the choice of solvent is critically important. Since the polar and nonpolar blocks are highly incompatible (cf. Figure 8.4), identifying a common solvent is challenging, but tetrahydrofuran (THF) satisfies the requirements. Alternatively, a polar/nonpolar cosolvent of, for instance, toluene and isopropyl alcohol (referred to here as TIPA) can also be used to achieve dissolution, but care must be exercised with regard to solvent templating. Mineart et al.¹⁷⁸ have used a combination of SAXS and small-angle neutron scattering (SANS) to explore the size and composition dependence of TESET micelles in TIPA varying in composition and report that the micellar size increases with increasing toluene content due to nonpolar coronal swelling. Concurrently, the extent to which the isopropyl alcohol partitions between the bulk solvent and the polar core also increases so that resultant films retain this micellar morphology. In marked contrast, THF-cast films exhibit a mixed morphology composed of lamellae and hexagonally-packed cylinders.¹⁷⁹ Electron microscopy images of these distinctively different morphologies are displayed

for comparison in **Figure 8.24**. Results from a DPD computer simulation⁴⁵ of the TESET TPS are included in this figure and indicate that the anticipated equilibrium morphology is lamellar, which suggests that the experimental morphologies are nonequilibrated, although the THF-cast films possess lamellae, as discerned from cross-sectional curvature analysis of the corresponding 3D reconstructions. For non-sulfonated TPEs, equilibration is commonly achieved by thermal annealing, but this approach cannot be used here.



FIGURE 8.24

TEM (a,b) and TEMT (c,d) images collected from the TESET charged pentablock polymer cast from the TIPA cosolvent (a,c) and THF (b,d). The contrast between the TEM and TEMT images is reversed. Included for comparison in (b) are results from a DPD simulation of the morphology under equilibrium conditions. (Adapted from Mineart, K.P., *et al. Macromol. Rapid Commun.* **2015**, *36*, 432 and *Macromolecules* **2016**, *49*, 3126. Copyright 2015 Wiley and 2016 American Chemical Society.)



FIGURE 8.25

In (a), time-resolved SAXS profiles in 2 min intervals obtained from the TESET material cast from TIPA and subsequently subjected to SVA in THF at ambient temperature. The peak positions (identified by arrows) indicate the transformation to a highly-ordered lamellar morphology, which is confirmed by the TEM image displayed in (b). The corresponding 2D SAXS patterns in (c) also reveal that the newly-formed lamellae can be highly oriented. (Adapted from Mineart, K.P., *et al. Macromolecules* **2016**, *49*, 3126. Copyright 2016 American Chemical Society.)

Solvent-vapor annealing (SVA) is frequently used to controllably alter the morphologies of block copolymer thin films^{180,181} (often measuring < 50 nm thick) and occasionally thick films.^{182,183} In the same fashion as thermal annealing conducted above the upper Tg of a TPS to enhance molecular mobility, SVA relies on solvent swelling and subsequent plasticization to achieve the same objective. While several solvents are suitable candidates for SVA, the vapor of THF has proven to be the most effective for TESET films cast from either THF or TIPA. In fact, a time sequence of SAXS profiles acquired⁴⁵ from a TIPA-cast TESET bulk film is provided in Figure 8.25a and confirms that the initially micellar morphology rapidly and completely transforms into lamellae after an exposure time of just a few minutes. Longer exposure times serve to refine the lamellar morphology, which is confirmed by the TEM image shown in Figure 8.25b, and simultaneously increase the grain size. An unexpected and added benefit of SVA is that the orientation of the lamellae also improves with increasing exposure time, as evidenced by the 2D SAXS pattern included in Figure 8.25c. Since equilibration of charged block copolymers is a well-known challenge, the use of SVA to overcome this difficulty and yield near-equilibrium morphologies in bulk polymer films represents a notable breakthrough that is not limited to the present sulfonated TPS. Two other points warrant mention at this juncture. First, the SVA-induced transformation process is much faster and complete for TIPA-cast films than for THF-cast films since the former are kinetically trapped much further from equilibrium. Second, according to SAXS measurements of SVA-equilibrated films, an increase in the DOS from 26 to 52 mol% yields a systematic increase in the extent of microdomain swelling (as evidenced by a corresponding increase in the lamellar period from 38 to 45 nm).⁴⁵ A distinctively different and irreversible transformation that occurs in TIPA-cast TESET films is induced by exposure to liquid water. Upon swelling, the morphology drastically evolves¹⁸⁴ from discrete micelles to highly interconnected, but irregular, channels that promote superabsorbency at elevated temperature.¹⁸⁵

Now that the factors governing morphological development in the TESET material have been elucidated, we turn our attention to the broad spectrum of applications suitable for this sulfonated TPS. Several applications are classified below according to three contemporary global concerns in the energy, environment and healthcare sectors.



FIGURE 8.26

In (a), a sequence of digital images acquired at different times (labeled) of a TESET-based IPMC infused with glycerol during electroactuation at 7 V. In (b), values of κ L as a function of electroactuation time for the same IPMCs at 3 different voltages (labeled, with different filled symbols) and Nafion (labeled, with the cation in parentheses and smaller open symbols) at 2 V. The effect of Pt coating on electroactuation is also displayed (O, labeled with the number of Pt cycles). The dashed lines serve to connect literature data, whereas the solid lines correspond to model fits to the TESET data. (Adapted from Vargantwar, P.H., *et al. Macromol. Rapid Commun.* **2012**, *33*, 61. Copyright 2012 Wiley.)

Energy-Related Applications

Nonpolar, midblock-swollen TPEGs (without sulfonation) exhibit excellent electromechanical properties as dielectric elastomers, 114,117,120,186-191 a class of electroactive polymers¹⁹² (EAPs) that change shape due to the onset of a compressive Maxwell stress upon application of an external electric field. In the presence of an electrolyte solution, the TESET material can also function as an ionic polymer-metal composite (IPMC),¹⁹³ another type of EAP that relies on the diffusion of ionic species in the presence of a polar solvent, including water.¹⁹⁴⁻¹⁹⁸ In this scenario, a film is plated with electrodes and solvated ions migrate to the oppositely-charged electrode upon application of a potential across the film, resulting in solvent-rich and solvent-lean regions of the film and, consequently, a bending motion. One way to characterize such deformation is through the product of the length of the cantilever (L) and its principal curvature ($\kappa = 1/R$, where R is the radius of curvature) as the film undergoes electroactuation. In Figure 8.26, real-time actuation, along with the corresponding time dependence of KL, measured from the TESET polymer (swollen with glycerol and imbibed with Li⁺ ions) at different potentials is compared to the gold standard, Nafion[™], with different cations. One obvious difference between the two IPMC designs is that, unlike those fabricated from Nafion[™], the IPMCs derived from the TESET material do not display evidence of back-relaxation. In addition, the level of electroactuation, as indicated by the magnitude of κL , is much higher (at higher potentials) in the case of the TESET-based IPMCs relative to the NafionTM-based IPMCs. While it is important to recognize that the polar solvent is different in the two systems, application of the microelectromechanical model proposed by Asaka and Oguro¹⁹⁹ reveals that the diffusivity of the glycerol (with a viscosity ~900x that of water at 25 °C) is ~ 10^{-7} cm²/s, which is slightly lower than that exhibited by water in Nafion[™]. Another energy-related application benefiting from ion diffusion through the midblock-sulfonated TESET polymer upon solvation is Li⁺ batteries, but this topic is too embryonic to be included at the time of this writing.



FIGURE 8.27

Photocurrent densities of photosensitive dye-containing TESET materials presented as a function of voltage for two solar cell designs: (a) leaf surrogates, employing only a cationic Ru dye and a sulfonated anionic dye; and (b) DSSCs, each containing one of three different Ru dyes in the presence of TiO₂. Dye ratios are varied in (a), whereas the HD15 dye in (b) is highlighted (thick solid line) because it is hydrophobic, unlike the other two dyes. Note the difference in photocurrent density scale. (Adapted from Al-Mohsin, H.A., *et al. Adv. Energ. Mater.* **2015**, *5*, 1401941 and *Sol. RRL* **2018**, *2*, 1700145. Copyright 2015 and 2018 Wiley.)

Alternatively, since the TESET polymer self-assembles into a nanostructure composed of both hydrophobic and hydrophilic microdomains, it can be fabricated into organic photovoltaic devices (OPDs). Solar cells afford a highly attractive alternative to fossil fuels due to climate change considerations,^{200,201} and the most common commercial family of solar cells relies on the use of specialty inorganics, such as single/multicrystalline silicon, and complicated processes by which to fabricate solar-cell panels so that harmful environmental factors are largely mitigated over relatively long application lifetimes.²⁰² While OPDs employing polymer nanolaminates hold tremendous promise as a replacement for silicon-based solar cells,^{203,204} they are not considered further. In one TESET design considered here, the OPD mimics the performance of natural leaves through the incorporation of photosensitive dye molecules without the use of TiO₂ nanoparticles.²⁰⁵⁻²⁰⁷ Although these OPDs inherently possess very low efficiencies and photocurrents from a practical standpoint, they demonstrate that hydrated TESET materials, which do not require sealants due to their natural adhesiveness or micropatterning due to their spontaneous self-assembly and which exhibit favorable dry/wet mechanical properties, can be used for light harvesting.²⁰⁸ In Figure 8.27a, photocurrent densities are displayed as a function of voltage for TESET-based OPDs containing tris(2,2'-bipyridine) ruthenium(II) hexahydate, $Ru(bpy)_3$, as the photosensitive cationic dye and 9,10-dimethoxy-2-anthracenesulfonic acid, DAS, as the anionic dye at different Ru(bpy)₃/DAS concentration ratios to illustrate the effect of composition on performance (indicated by the short-circuit current density, open voltage and fill factor). Alternatively, the OPD can be designed to operate on the principle of dye-sensitized solar cells^{209,210} (DSSCs) with added TiO_2 in the presence of a single photosensitive Ru-based dye molecule that can be either hydrophilic (e.g., N719 and NCSU10) or hydrophobic (HD15). Representative results obtained by Al-Mohsin et al.²¹¹ are displayed in Figure 8.27b and reveal that relatively high fill factors can be achieved with both types of dyes, but the short-circuit photocurrent density level and net efficiency differ significantly. The highest fill factor, short-circuit current density and efficiency values reported for non-optimized DSSCs based on the TESET TPS are 0.67, 15.1 mA/cm² and 7.0%, respectively.

Environment-Related Applications

One of the most critical concerns facing the world today pertains to global climate change due to the emission of greenhouse gases, primarily CO₂, from various industrial sources.²¹² While ethoxylated TPAs have been successfully employed²¹³⁻²¹⁵ to remove CO₂ from mixed gases (since polyethers have an inherently high chemical affinity for CO_2), the TESET TPS, as an anionic macromolecule, operates on a different principle to selectively permeate CO_2 , as well as other polar gases. Recall that this material swells considerably, but remains intact, in the presence of water and that polar gases tend to be highly soluble in water. As an example, the single-gas permeation data acquired by Ansaloni et al.²¹⁶ and presented in Figure 8.28 establishes that NH₃, a basic gas, can be easily separated from N₂ (and, by inference, from similar gases possessing a larger molecular size and a lower water solubility such as CH_4), especially when the fully hydrated TESET separation membrane exhibits a specific morphology, which is dictated by the casting solvent. At high humidity levels, the permeability of NH_3 exceeds 5000 Barrer and the NH_3/N_2 selectivity approaches 1900, making this membrane ideally suited for this gas-phase separation, which is particularly important for methane "sweetening" of biogas. Relative to Nafion[™] (of significant commercial interest for use in fuel cells), the diffusivity and solubility of water are found²¹⁶ to be higher in the TESET material at high humidity levels. Since permeation equals the product of diffusivity and solubility in the solution-diffusion transport mechanism, this combination results in

reasonably high CO_2 permeation and CO_2/N_2 selectivity, where ideal selectivity denotes the permeability ratio of the two penetrant species being compared. In contrast, mixed-gas measurements are conducted with mixtures of CO_2 and N_2 to account for the possibility of CO_2 inducing plasticization, and the resulting transport performance metrics (including the separation factor, which is equivalent to selectivity) are determined from gas chromatographic analysis.



FIGURE 8.28

Permeability of NH_3 and N_2 through TESET membranes with 26 mol% DOS cast from two different solvents and exposed to dry and fully humidified (wet) gases (labeled and color-coded). (Adapted from Ansaloni, L., *et al. Adv. Mater. Interf.* **2017**, *4*, 1700854. Copyright 2017 Wiley.)

To illustrate the influence of polymer nanostructure on transport properties, recall that hydrothermal treatment of the TESET polymer can induce an irreversible morphological transformation¹⁸⁴ from dispersed ionic micelles to continuous ionic channels, as illustrated in the TEMT images provided in Figure 8.29. The color coding employed in these images identifies ionic microdomains that are physically connected, which is why TEMT is needed to examine the 3D nature of the nanostructural elements. According to the measurements⁴⁹ displayed in Figure 8.30 for TESET membranes cast from different solvents with and without subsequent water submersion at ambient temperature, such treatment is capable of promoting a substantial increase in mixedgas CO₂ permeation from less than 100 Barrer to nearly 500 Barrer at high humidity levels, thereby confirming improved CO₂ diffusivity. Note that the morphology already possessing continuous ionic channels (as-cast from THF) is the least affected by hydrothermal treatment. The negligible change in CO_2/N_2 selectivity implies that the transport of N_2 molecules likewise benefits from the morphological transformation. These results are compiled in Figure 8.31 and favorably compare to the upper bound established by Robeson²¹⁷ on the basis of empirical observations regarding the trade-off between permeability and selectivity in polymer membranes near ambient temperature. Another route by which the morphological characteristics can be physically modified is through the addition of a low-volatility hydrophilic species that, during solvent casting, ultimately swells the ionic microdomains in similar fashion as the nonpolar TPEGs discussed earlier. In this case, a CO₂philic ionic liquid such as 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim][BF4]) can be incorporated into TESET membranes to afford a relatively facile means by which to improve CO_2/N_2 selectivity, especially since it has a similar outcome when added to Nafion[™].²¹⁸ Doing so increases the CO₂/N₂ selectivity beyond 100 (up to ~130) at ambient temperature.²¹⁹



FIGURE 8.29

TEMT slices of an as-cast TESET film highlighting the presence of both (a) discrete micelles and (b) micelles connected by filaments (circled). In (c), micelles are color-coded to indicate the number of connected micelles: 2 (blue), 3 (orange), 4 (red), 5 (green), and 9 (purple). A TEMT image of a membrane after submersion in water for 1 h is displayed in (d), and the same image is color-coded in (e) to confirm the presence of a single ionic network (yellow). All scalebars correspond to 100 nm. (Adapted from Mineart, K.P., *et al. Appl. Phys. Lett.* **2016**, *108*, 101907. Copyright 2016 American Institute of Physics.)



FIGURE 8.30

The dependence of (a,b) CO_2 permeability and (c,d) CO_2/N_2 selectivity of TESET membranes containing 52 mol% DOS and cast from different solvents (color-coded and labeled) before (a,c) and after (b,d) submersion in deionized water on RH. The solid lines serve to connect the data. (Reproduced from Dai, Z., *et al. NPG Asia Mater.* **2019**, *11*, 1. Copyright 2019 Nature Publishing Group.)



FIGURE 8.31

 CO_2/N_2 selectivity as a function of CO_2 permeability for TESET membranes cast from four solvents (labeled and color-coded) before and after submersion in water (filled and open symbols, respectively). The dotted line represents the Robeson²¹⁷ upper bound, and the color-coded lines connect the data. (Reproduced from Dai, Z., *et al. NPG Asia Mater.* **2019**, *11*, 1. Copyright 2019 Nature Publishing Group.)

Healthcare-Related Applications

The global healthcare system is presently facing one of its greatest challenges, the COVID-19 pandemic,²²⁰ which has paralyzed much of the world during 2020-2021 and resulted in over 5 million lost lives as of the time of this writing.²²¹ While efforts to apply antibacterial methods to thwart the spread of the SARS-CoV-2 virus (prior to the production of safe vaccines) have been met with sporadic success, a new healthcare paradigm has emerged and focuses on infection control through the use of broad-spectrum, self-disinfecting materials that operate on the mechanisms of either photodynamic inactivation^{222,223} or anionic inactivation.^{50,224,} Although the SARS-CoV-2 virus is spread primarily by the droplets and aerosols emanating from a person's nose and/or mouth upon coughing or sneezing, independent studies have established^{225,226} that the virus can survive for extended periods of times (days or more) on common surfaces, where it can be transmitted due to direct contact. Indeed, this is the route by which many infective microbes proliferate, in which case the development of self-disinfecting coatings can help to prevent the spread of disease, especially in healthcare facilities and highly populated locales. A plethora of different materials have been developed for this purpose, and many of them have been successful at combating specific microbes.²²⁷⁻²²⁹ The fight against pathogens must, however, address a wide range of bacteria (including those that are or are becoming antibiotic-resistant²³⁰), (non)enveloped viruses and fungi, but the inactivation mechanisms employed by current antimicrobial materials simply cannot meet this requirement, a fact that becomes suddenly alarming when pathogens undergo mutation and successfully developed vaccinations fail to afford the desired or expected level of protection.231

As an anionic macromolecule, the TESET material possesses a truly unique antimicrobial mechanism that contradicts the conventional design paradigm requiring a cationic surface: in the

presence of moisture, protons from the sulfonic acid groups migrate to the surface and create a deadly, low-pH (< 1.0) environment that comprehensively and non-specifically inactivates a broad spectrum of microbes. This mechanism is illustrated in Figure 8.32. Examples of pathogens tested include Gram-positive/negative bacteria (including the commonly fatal C. difficile²³²), antibioticresistant bacteria (including methicillin-resistant S. aureus,²²⁴ also known as the "superbug" MRSA), highly contagious viruses (including SARS-CoV-2 and influenza-A) and dangerous fungi (including A. niger, which is responsible for black mold).^{50,224} The remarkable aspect of this self-disinfecting material is that the exposure time needed to achieve minimum detection (often relating to 99.9999% inactivation) is 5 minutes or less. The survivability of various microbes illustrating this exceptional level of performance is presented in Figure 8.33. This discovery by Peddinti et al.^{50,224} completely dismisses the contention that anionic macromolecules cannot be antimicrobial (in comparison to their cationic counterparts), and introduces a revolutionary design paradigm that brings a TPE to centerstage in the escalating war against pathogens. This approach has been successfully translated⁵⁰ to selectively-sulfonated bicomponent TPSs, as well as to Nafion[™]. If the sulfonic acid moieties become neutralized due to exposure to free cations during application, the TESET material can be fully rejuvenated upon exposure to a weak aqueous acid.²²⁴ Moreover, since the pH-drop responsible for killing microbes does not target specific functionalities on microbes in the same fashion as medications or metals, future microbial resistance is also highly unlikely. The TESET polymer with 52 mol% DOS has been designated as BiaXam[™] by Kraton Corporation, and it has been issued an emergency exemption for use in 2021 by the Environmental Protection Agency (EPA)²³³ and has likewise been awarded approval to be used in commercial airports.²³⁴



FIGURE 8.32

Schematic illustration of the TESET substrate after self-assembly and the mechanism by which it inactivates a contacting microbe (displayed is the SARS-CoV-2 virus). Upon hydration, protons from sulfonic acid groups in contiguous ionic microdomains (dark features in the TEM image) transport to the surface and lower the surface pH to below 1.0, which fully inactivates a wide range of microbes in minutes. The topology transition zone indicates that the bulk polymer morphology likely restructures at the surface due to the presence of water.



FIGURE 8.33

Survival of (a) Gram-positive and (b) Gram-negative bacteria comprising most of the *ESKAPE* family of bacteria²²⁴ primarily responsible for nosocomial infections after exposure to two different TESET surfaces (TESETn, where n denotes the DOS, labeled) for 5 min. Survival kinetics are also provided in (c) and (d) for SARS-CoV-2 and methicillin-resistant *S. aureus* (MRSA), respectively. Included in (c) are values measured for the virus on a Cu substrate,²²⁵ and a life-dead assay is provided for MRSA on TESET52 after 5 min in (d). (Adapted from Peddinti, B.S.T., *et al. Mater. Horiz.* **2019**, *6*, 2056 and *Adv. Sci.* **2021**, *8*, 2003503. Copyright 2019 Royal Society of Chemistry and 2021 Wiley.)

Concluding Remarks

Since their inception, new TPEs have been emerging, and many of them afford excellent properties for a wide range of mature applications, as well as new opportunities for the development of currently needed technologies, such as gas-separation membranes, solar cells, and self-disinfecting surfaces. This class of materials can effectively serve as building blocks that are simultaneously capable of spontaneous self-assembly and network formation, with little, if any, process waste and no need for curing. At their core, the TPEs considered in this chapter essentially rely on physical crosslinks formed by hard (glassy or semicrystalline) microdomains to stabilize a soft, elastic molecular network upon microphase separation of various copolymer molecules differing in chemistry and architecture, in addition to other molecular characteristics. While the range of TPEs continues to expand, physical or chemical modification of existing copolymers provides novel routes to stimuli-responsive and functional macromolecules that benefit from possessing both a nanostructure and a network. A key feature of TPEs responsible for making this class of materials particularly popular in both numerous and diverse applications is their facile melt processability, which can be retained in many of the applications discussed herein if the TPEs are physically modified through the use of additives. In the event that melt processability is compromised because of chemical functionalization, the advantage of the new material relative to its processing requirements must be assessed. In the case of creating highly effective and broad-spectrum antimicrobial materials from sulfonated TPSs, for instance, the need for solvent-based processing represents a small price to pay to improve global healthcare. Similarly, the production of membranes capable of high CO_2 permeability and selectivity via the same process route is clearly worthwhile if climate change can be mitigated. While applications such as these are unequivocally important, the advances in polymer physics and chemistry responsible for such new materials and their properties likewise offer guidance and yield new strategies to design and develop materials that will overcome future challenges. Block polymers, and TPEs in particular, introduce abundant opportunities for the exploration of next-generation (multi)functional materials that will become increasingly important in the 21st century.

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