

Thermoplastic elastomers: fundamentals and applications

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Abstract

Thermoplastic elastomers are multi-functional polymeric materials that generally possess the processability of thermoplastics and the elasticity of vulcanized rubber. Intrinsic thermoplastic elastomers include microphase-separated block and segmented copolymers containing a soft (low- T_g) species. Recent achievements regarding thermoplastic elastomer block and segmented copolymers in the past year have improved the current understanding of (i) complex nanostructures in unary and multicomponent systems and (ii) the thermally-activated sphere $\rightarrow$ cylinder and cylinder $\rightarrow$ gyroid order–order transitions. The use of these materials in organogel, electro-responsive and nanocomposite applications illustrates the diversity and future potential of these technologically important materials. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Thermoplastic elastomers: an overview

Thermoplastic elastomers (TPEs) constitute a commercially relevant and fundamentally interesting class of polymeric materials. Generally speaking, they are biphasic materials that (i) possess the combined properties of glassy or semi-crystalline thermoplastics and soft elastomers, and (ii) enable rubbery materials to be processed as thermoplastics [1•]. They may be single macromolecules in which discrete thermoplastic segments capable of forming rigid nanoscale domains or channels are covalently bonded to rubbery segments that provide a soft matrix in which the rigid domains reside. Due to the covalent linkage(s) between the chemically dissimilar segments, the rigid domains can form a three-dimensional network of physical crosslink sites. The TPE, consequently, exhibits mechanical properties that are, in many ways, comparable to those of a vulcanized (covalently

crosslinked) rubber, with the exception that the network and, hence, the properties of the TPE are thermally reversible. This feature makes TPEs ideally suited for high-throughput thermoplastic processes, such as melt extrusion and injection molding. Two important types of intrinsic TPEs are microphase-separated block (including graft) copolymers and segmented polyurethanes, although additional segmented copolymers are becoming increasingly available [2••]. In some cases, TPEs can likewise be generated from existing homopolymers through reactive blending. In this work, we identify and discuss some of the recent advances regarding TPEs and their uses.

Block copolymers most notably differ from segmented (e.g. polyurethane) copolymers in terms of chemistry and molecular architecture. With regard to the latter difference, segmented copolymers can be envisaged as linear multiblock copolymers possessing a large number of blocks (m , where m can exceed 50) and typically high compositional/molecular weight polydispersity. A copolymer composed of A and B species is designated as a block copolymer when the number of discrete blocks is small, with m equal to 2

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or 3 for diblock and triblock copolymers, respectively (values of m up to 8 have been reported [3,4]). Furthermore, a block copolymer is only considered a TPE in the present work if one of its blocks is a soft (low- T_g) material, such as a polydiene (e.g. isoprene), a siloxane or a polyether (e.g. ethylene glycol). If the constituent species are sufficiently incompatible, block copolymers and segmented copolymers microphase-separate in the melt to form nanostructured (biphasic) materials that exhibit the thermo-mechanical properties of both species. Due to their generally low values of m and polydispersity, block copolymer molecules can self-organize into highly ordered morphologies, including micelles on a cubic lattice, cylinders on a hexagonal lattice, bicontinuous channels and co-alternating lamellae. An excellent description of the physical processes governing block copolymer self-organization is provided by Hamley [5^{••}], and targeted reviews of microphase-ordered block copolymers [6[•],7,8^{••},9[•],10[•],11], as well as self-organized synthetic polymers [12[•]], are also available.

Due to their generally more complex molecular architecture and higher molecular polydispersity, segmented copolymers microphase-separate into less well-defined nanostructural elements. While biphasic properties are often retained, these materials do not normally order into periodic morphologies. Polyurethanes, in particular, are employed in a very broad range of contemporary applications [13[•]], and an extensive tabulation of chemical and property data regarding various polyurethanes has been recently provided by Szycher [14[•]]. Another category of TPEs, which is only briefly mentioned here, is based on polyolefin chemistry and includes ultralow-density polyethylene [15]. In addition, TPEs can be generated through suitable chemical modification (e.g. dynamic vulcanization [16–19]) of rubbery homopolymers. General resources of interest in this vein include the edited works of Martuscelli et al. [20[•]] and Cheremisinoff [21[•]]. Process strategies such as solid-

state shear pulverization (S³P) [22[•]] and cryogenic mechanical alloying (CMA, see Fig. 1) [23,24[•]] are also under investigation as new routes by which to disperse homopolymers in blends at nanoscale dimensions and potentially produce TPEs by physical means. The importance of TPEs in commercial technology and fundamental research cannot be overstated, as reflected by the number of recent accomplishments in this fertile field. Within this brief review, it is regrettable that not all the achievements reported since December 1998 can be mentioned. In this case, we elect to focus our attention specifically on advances regarding TPE block and segmented copolymers.

2. Advances in block copolymers

The past year has witnessed a steady increase in studies relating to fundamental block copolymer issues, as well as to the broadening use of these materials. This section addresses nanostructure development, solution behavior and nanostructure dynamics in TPE block copolymers.

2.1. Nanostructure development

Ongoing theoretical and simulation developments seek to further elucidate the factors governing the stability of block copolymer nanostructures in thin films [25[•],26,27^{••},28^{••}] and bulk systems [29[•],30^{••},31^{••},32]. Since most of the copolymers employed in thin film studies are not TPEs, we have not elaborated on them here. Some of the most exciting developments in TPE block copolymers have arisen in terms of novel molecular architectures and binary copolymer blends. Gido, Mays and co-workers have continued their detailed investigation of non-linear copolymers, such as model graft [33[•]] and star [34] molecules. The morphologies of these copolymers

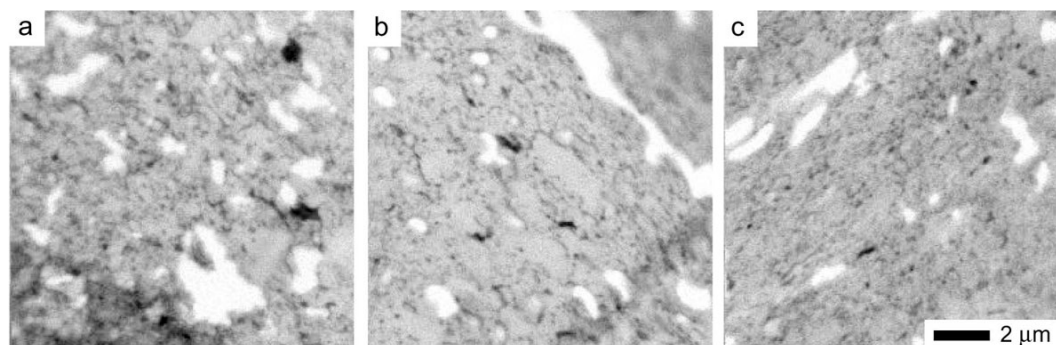


Fig. 1. X-Ray microscopy images of polyisoprene/poly(methyl methacrylate) blends prepared by CMA for 5 h and annealed at 150°C for: (a) 0; (b) 15; and (c) 60 min prior to being quenched to ambient temperature. These images have been acquired at 285.3 eV (isoprene appears dark) and demonstrate that, due to polyisoprene crosslinking, little phase coarsening occurs [23,24[•]].

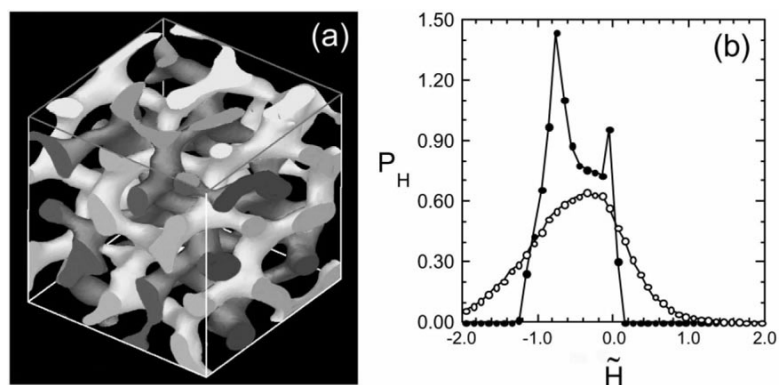


Fig. 2. In (a), a three-dimensional TEM image of the gyroid morphology in a microphase-ordered triblock copolymer. Probability distributions of the interfacial mean curvature ($\tilde{H}$), displayed in (b), are obtained from the image in (a), as well as from the mathematical description of the gyroid surface [37^{••}]. These data are denoted by (O) and (●), respectively.

have been investigated by transmission electron microscopy (TEM) and small-angle scattering (SAS) and related to linear analogs, as well as existing theory, to ascertain the effect of molecular architecture on nanostructure stability. In addition to novel copolymer architectures, complex (bicontinuous) nanostructures in neat block copolymers remain an important issue, since such morphologies (e.g. the gyroid) are capable of endowing copolymers with superior mechanical properties [35^{••},36[•]]. Jinnai et al. [37^{••}] have directly measured the interfacial curvature distributions of the gyroid morphology in a neat ABA triblock copolymer from three-dimensional TEM images (see Fig. 2), whereas Ahn and Zin [38] have investigated a shear-induced perforated lamellar morphology.

Tricomponent (ABC) molecular architectures and their complex nanostructures remain a subject of in-

tense experimental investigation [39^{••},40^{••}]. Abetz and co-workers have also pioneered new routes to complex nanostructures, such as the core-shell gyroid displayed in Fig. 3, by blending ABC copolymers [41^{••},42–44[•]]. In a similar vein, analyses [45^{••},46[•]] of chemically dissimilar diblock copolymers have been instrumental in elucidating molecular miscibility criteria. While the blends mentioned thus far have been composed of two copolymers, other blends of fundamental and technological relevance are those composed of two homopolymers and a block copolymer. In-depth studies of A/B/C-*b*-D [47[•]] and A/B/A-*b*-C [48] ternary blends (each letter designates a different chemical species) have revealed two important compatibilization considerations: (i) the order-disorder transition (ODT) of the copolymer must be lower than the melt-mixing temperature, and (ii) the block lengths must be sufficiently short to preclude

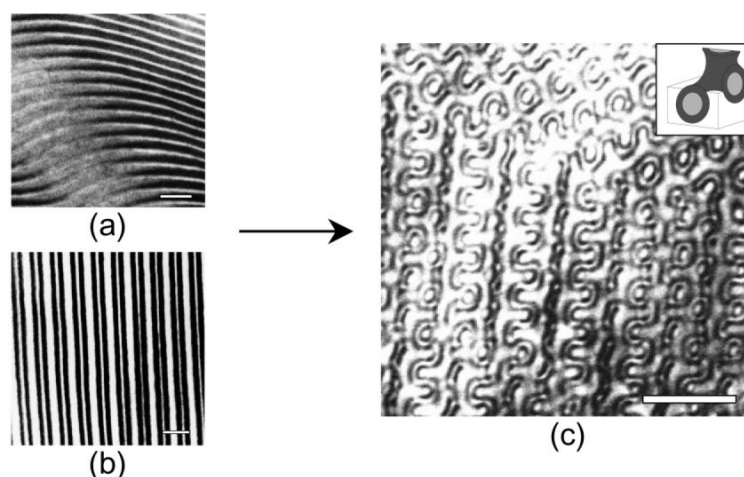


Fig. 3. TEM images of a poly(butadiene-*b*-methyl methacrylate) (BM) diblock copolymer (a) and a poly(styrene-*b*-butadiene-*b*-methyl methacrylate) (SBM) triblock copolymer (b) and the core-shell gyroid morphology [44[•]] generated in a 20:80 w/w BM/SBM blend of the two copolymers (c). Scale bars: 100 nm in (a) and (b); 250 nm in (c). (courtesy of V. Abetz).

entanglement and molecular entrapment. In more conventional A/B/A-*b*-B ternary blends, Morkved et al. [49•] have examined the formation of swollen lamellae and a microemulsion, as well as the onset of phase separation, in blends composed of poly(ethylene) and poly(dimethylsiloxane). They have identified a re-entrant microemulsion — a bicontinuous nanostructure that is stable at one temperature and then becomes unstable and, later, stable again as the temperature is lowered. Microemulsion formation is predicted [50••] to be greatly facilitated, thereby opening potentially new stability windows, through the combined use of two compatibilizing diblock copolymers differing in chain length. Smith et al. [51] have prepared compatibilized ternary blends by CMA and find that the impact strength of their TPE blends increases with increasing block copolymer concentration.

2.2. Solution behavior

Numerous efforts have elucidated the phase behavior [52••,53•] and properties [54•,55] of aqueous block copolymer solutions. While these studies are insightful and beneficial to the development of cosmetics and pharmaceuticals, they are not TPE block copolymers and are not considered further. Likewise, hybrid isotropic/liquid crystalline block copolymers in the presence of a liquid crystal solvent [56••,57•] are mentioned here due to the multiple levels of supra-molecular organization they exhibit, as well as the promise they show in electro-responsive applications. The phase behavior of block copolymers can also be influenced by compressible solvents, such as supercritical carbon dioxide [58•,59••,60•]. In contrast, TPE block copolymer solutions typically consist of a triblock composed of styrenic (S) endblocks and a diene (saturated or unsaturated) midblock dissolved in a midblock-selective organic solvent and subsequently permitted to self-organize into nanostructural elements (e.g. micelles). At copolymer concentrations above the critical gel concentration, the solution (microphase-ordered or disordered) consists of a connected network and behaves as a physical gel in the same fashion as non-TPE block copolymer gels in aqueous systems [53•]. Laurer et al. [61••] have examined the nanostructure and property development of two chemically-related ABA copolymers in the presence of mineral oil, while van Vlimmeren et al. [62••] have used density functional theory to simulate the three-dimensional nanostructures that form in concentrated triblock copolymer solutions.

Laurer et al. [61••] have also provided TEM images of stained micelles showing the coronal (looped) midblocks and the network-forming bridged midblocks (evident in Fig. 4a as molecular bundles). Zheng et al.

[63••] report similar findings for unstained micelles of an amphiphilic block copolymer composed of poly(ethylene oxide) and polybutadiene, as imaged by cryo-TEM (see Fig. 4b). Quintana et al. [64•] have found that, by judiciously varying the composition of a mixed solvent, they could alter the solution nanostructure by gradually switching the solvent from being midblock-selective to endblock-selective. Jackson et al. [65•] have investigated the incorporation of poly(phenylene oxide) into the S-rich micelles of a TPE block copolymer gel and report increases in micelle size, viscosity and transition temperature, whereas Kleppinger et al. [66•] have used SAS to explore the effect of thermal processing on the long-range order arising in TPE block copolymer gels. In complementary fashion, Konak et al. [67] have employed light scattering and nuclear magnetic resonance to probe the dynamics of comparable gels and have identified three different molecular processes, one relaxational and two diffusive in nature. From their results, they deduce that their semi-dilute copolymer solutions consist of large-scale inhomogeneities. Extensions of these studies have resulted in the production of: (i) block copolymer mesogels, in which a solvent selectively swells the midblock microdomains of a microphase-ordered triblock copolymer [68]; (ii)

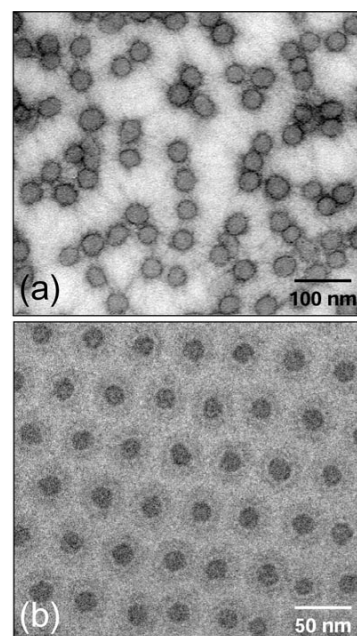


Fig. 4. In (a), a TEM image of a TPE gel composed of 10 wt.% poly(styrene-*b*-isoprene-*b*-styrene) triblock copolymer and mineral oil [61••]. The OsO₄-stained polyisoprene appears dark, revealing the location of looped midblocks and bridged midblock bundles. The core-shell structure of an unstained poly(ethylene oxide-*b*-butadiene) diblock copolymer in a 1-wt.% aqueous solution [63••] is also evident in a cryo-TEM image (b). (courtesy of Y. Talmon).

the development of acrylic adhesives [69]; and (iii) TPE gels possessing connected solvent-rich pores on the micrometer length scale [70•].

2.3. Dynamic processes

The dynamic processes discussed here relate to molecular architecture, ordering transitions and shear-induced alignment. Chrissopoulou et al. [71••] have discovered that inverse starblocks possess an additional relaxation process relative to linear tetrablock copolymers, while Buzza et al. [72••] have demonstrated that the ODT of a four-arm (A_2B_2) star copolymer differs from that of its AB analog by more than can be accounted for using established theories. They propose that this anomaly reflects different extents of non-Gaussian chain stretching. In the case of a highly asymmetric diblock copolymer, SAS and dynamic rheology have been used [73••] to identify the reversible lattice disorder/order transition (LDOT, the temperature above which micelles lose their periodic order and behave liquid-like) and demicellization/micellization transition (DMT, the temperature above which micelles become unstable and convert to unimers). Within the ordered regime, order–order transitions (OOTs) have recently come under intense investigation. Floudas et al. [74••] have employed SAS and rheology to probe several OOTs and not only found evidence that the cylinder $\rightarrow$ gyroid transition occurs by nucleation and growth, but also provided an experimental measure of the activation barrier encountered during this transformation. Several efforts have specifically focused on the sphere $\rightarrow$ cylinder OOT in the presence [75] and absence [76•,77•,78••] of a flow field. Flow fields have also been used to induce bulk or surface alignment of the lamellar [79•] and gyroid [80] morphologies in microphase-ordered copolymers.

3. Advances in segmented copolymers

As alluded to earlier, one of the most commonly produced classes of segmented copolymers consists of polyurethanes, which are employed extensively in the manufacture of biomedical devices due to their potential biocompatibility [81••]. Recent studies have also demonstrated that these materials can exhibit intriguing electro-responsive [82,83•,84•] and optical [85•] properties. While several works have focused on the synthesis of novel segmented polyurethanes [86,87], others have faced contemporary technological challenges, such as biodegradation [88•]. Fundamental nanostructural issues have been addressed in studies reported by Musselman et al. [89••], who employed SAS and calorimetry to discern the impact of prepolymer polydispersity on the degree of copolymer microphase separation, and Sakurai et al. [90•], who investigated the effect of hard-segment chain length on the nanostructure of segmented poly(urethaneurea)s. The response of segmented copolymers to deformation also remains an active area of research. Lee and co-workers [91•,92] have used synchrotron SAS and spectroscopy to ascertain the effect of uniaxial tension on the orientation of rigid microdomains in various segmented copolymers, whereas Stribeck et al. [93•] have concentrated their complementary efforts on segmented poly(ether ester)s. Depending on molecular factors (e.g. chemistry and composition), the nanostructures of segmented copolymers can not only endow these copolymers with excellent mechanical properties, but may also promote beneficial gas-separation properties [94•, 95•,96].

4. Conclusions

Numerous achievements in both the understanding and development of thermoplastic elastomers have

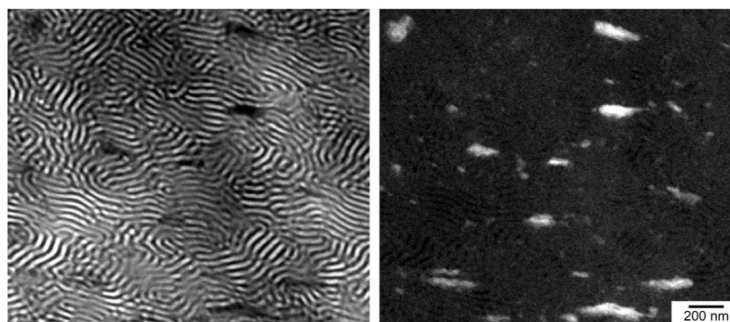


Fig. 5. Energy-filtered TEM images of a nanocomposite composed of a microphase-ordered polystyrene-polybutadiene block copolymer and siliceous particles, which appear dark at an energy loss (ΔE) of 0 eV (left) and bright at $\Delta E = 250$ eV (right). The polybutadiene block is stained with OsO_4 and appears consistently dark (most clearly seen in the zero-loss image).

ensured that this class of materials will continue to capture the attention of researchers interested in nanostructured elastomeric polymers amenable to variable processing. While we have elected to highlight accomplishments pertaining specifically to neat TPE block and segmented copolymers and their blends in the present work, advances in TPEs possessing inorganic species, e.g. clays [97•] or metal nanoparticles [98•], have demonstrated that these hybrid materials hold tremendous promise as TPE nanocomposites (see Fig. 5). Expedient design of the copolymer nanostructure in such multicomponent materials, as well as in conventional TPEs, will benefit enormously from innovative combinatorial screening methods, such as those recently introduced by Drolet and Fredrickson [99••].

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References and recommended reading

- of special interest
- of outstanding interest
- [1] Holden G. Understanding thermoplastic elastomers. Munich: Hanser, 2000.
- [2] Holden G, Legge NR, Quirk RP, Schroeder HE. Thermoplastic elastomers. 2nd ed. Munich: Hanser, 1996.
- [3] Smith SD, Spontak RJ, Satkowski MM, Ashraf A, Lin JS. Microdomain contraction in microphase-separated multi-block copolymers. *Phys Rev B* 1993;47:14555–14558.
- [4] Cho CS, Jeong YI, Kim SH, Nah JW, Kubota M, Komoto T. Thermoplastic hydrogel based on hexablock copolymer composed of poly (γ -benzyl-L-glutamate) and poly (ethylene oxide). *Polymer* 2000;41:5185–5193.
- [5] Hamley IW. The physics of block copolymers. New York: Oxford University Press, 1998.
- [6] Abetz V. Assemblies in complex block copolymer systems. In: Ciferri A, editor. *Supramolecular polymers*. New York: Marcel Dekker, 2000:215–262.
- [7] Pietkiewicz D, Roslaniec Z. Liquid crystalline block copoly(ether-ester)s. *Polimery* 2000;45:69–80.
- [8] Bates FS, Fredrickson GH. Block copolymers — designer soft materials. *Phys Today* 1999;52:32–38.
- [9] Spontak RJ, Alexandridis P. Advances in self-ordering macromolecules and nanostructure design. *Curr Opin Coll Interface Sci* 1999;4:140–146.
- [10] Alexandridis P, Spontak RJ. Solvent-regulated ordering in block copolymers. *Curr Opin Coll Interface Sci* 1999;4:130–139.
- [11] Xie H-Q, Xie D. Molecular design, synthesis and properties of block and graft copolymers containing polyoxyethylene segments. *Prog Polym Sci* 1999;24:275–313.
- [12] Pojman JA. Self organization in synthetic polymeric systems. • *Ann NY Acad Sci* 1999;879:194–214.
- [13] Uhlig K. Discovering polyurethanes. Munich: Hanser, 1999.
- [14] Szycher M. Handbook of polyurethanes. Boca Raton: CRC Press, 1999.
- [15] Haward RN. The application of non-Gaussian chain statistics to ultralow density polyethylenes and other thermoplastic elastomers. *Polymer* 1999;40:5821–5832.
- [16] Zhang XF, Zhang Y, Peng ZL, Shang XY, Zhang YX. Dynamically vulcanized nitrile rubber/polyoxymethylene thermoplastic elastomers. *J Appl Polym Sci* 2000;77:2641–2645.
- [17] Lesser AJ, Jones NA. Fracture behavior of dynamically vulcanized thermoplastic elastomers. *J Appl Polym Sci* 2000;77:763–770.
- [18] George J, Varughese KT, Thomas S. Dynamically vulcanised thermoplastic elastomer blends of polyethylene and nitrile rubber. *Polymer* 2000;41:1507–1517.
- [19] Aoyama T, Carlos AJ, Saito H, Inoue T, Niitsu Y. Strain recovery mechanism of PBT/rubber thermoplastic elastomer. *Polymer* 1999;40:3657–3663.
- [20] Martuscelli E, Musto P, Ragosta G. Advanced routes for polymer toughening. Amsterdam: Elsevier, 1996.
- [21] Cheremisinoff NP. Handbook of engineering polymeric materials. New York: Marcel Dekker, 1997.
- [22] Furgiele N, Lebovitz AH, Khait K, Torkelson JM. Novel strategy for polymer blend compatibilization: solid-state shear pulverization. *Macromolecules* 2000;33:225–228.
- [23] Smith AP, Ade H, Balik CM, Koch CC, Smith SD, Spontak RJ. Cryogenic mechanical alloying of poly(methyl methacrylate) with polyisoprene and poly(ethylene-*alt*-propylene). *Macromolecules* 2000;33:2595–2604.
- [24] Smith AP, Spontak RJ, Ade H, Smith SD, Koch CC. High-energy cryogenic blending and compatibilizing of immiscible polymers. *Adv Mater* 1999;11:1277–1281.
- [25] Tang WH. Confinement of symmetric diblock copolymer thin films. *Macromolecules* 2000;33:1370–1384.
- [26] Huinink HP, Brokken-Zijp JCM, van Dijk MA, Sevink GJA. Asymmetric block copolymers confined in a thin film. *J Chem Phys* 2000;112:2452–2462.
- [27] Wang QA, Yan QL, Nealey PF, de Pablo JJ. Monte Carlo simulations of diblock copolymer thin films confined between two homogeneous surfaces. *J Chem Phys* 2000;112:450–464.
- [28] Geisinger T, Muller M, Binder K. Symmetric diblock copolymers in thin films. I. Phase stability in self-consistent field calculations and Monte Carlo simulations. *J Chem Phys* 1999;111:5241–5250.
- [29] Kolbet KA, Schweizer KS. Real space structure of associating polymer melts. *Macromolecules* 2000;33:1443–1458.
- [30] Cho JH. Analysis of phase separation in compressible polymer blends and block copolymers. *Macromolecules* 2000;33:2228–2241.
- [31] Matsen MW, Thompson RB. Equilibrium behavior of symmetric ABA triblock copolymer melts. *J Chem Phys* 1999;111:7139–7146.
- [32] Aksimentiev A, Holyst R. Single-chain statistics in polymer systems. *Prog Polym Sci* 1999;24:1045–1093.
- [33] Beyer FL, Gido SP, Buschl C et al. Graft copolymers with regularly spaced, tetrafunctional branch points: morphology and grain structure. *Macromolecules* 2000;33:2039–2048.
- [34] Beyer FL, Gido SP, Uhrig D, Mays JW, Tan NB, Trevino SF. Morphological behavior of A₂B₂ star block copolymers. *J Polym Sci B: Polym Phys* 1999;37:3392–3400.

- [35] Dair BJ, Honeker CC, Alward DB et al. Mechanical properties and deformation behavior of the double gyroid phase in unoriented thermoplastic elastomers. *Macromolecules* 1999;32:8145–8152.
- [36] Kossuth MB, Morse DC, Bates FS. Viscoelastic behavior of cubic phases in block copolymer melts. *J Rheol* 1999;43:167–196.
- [37] Jinnai H, Nishikawa Y, Spontak RJ, Smith SD, Agard DA, Hashimoto T. Direct measurement of interfacial curvature distributions in a bicontinuous block copolymer morphology. *Phys Rev Lett* 2000;84:518–521.
- [38] Ahn JH, Zin WC. Structure of shear-induced perforated layer phase in styrene–isoprene diblock copolymer melts. *Macromolecules* 2000;33:641–644.
- [39] Hückstädt H, Goldacker T, Göpfert A, Abetz V. Core-shell double gyroid morphologies in ABC triblock copolymers with different chain topologies. *Macromolecules* 2000;33:3757–3761.
- [40] Shefelbine TA, Vigild ME, Matsen MW et al. Core-shell gyroid morphology in a poly(isoprene-*block*-styrene-*block*-dimethylsiloxane) triblock copolymer. *J Am Chem Soc* 1999;121:8457–8465.
- [41] Abetz V, Goldacker T. Formation of superlattices via blending of block copolymers. *Macromol Rapid Commun* 2000;21:16–34.
- [42] Goldacker T, Abetz V, Stadler R. Blends of block copolymers. *Macromol Symp* 2000;149:93–98.
- [43] Goldacker T, Abetz V. A new way to the ‘knitting pattern’ via blending of ABC triblock copolymers. *Macromol Rapid Commun* 1999;20:415–418.
- [44] Goldacker T, Abetz V. Core-shell cylinders and core-shell gyroid morphologies via blending of lamellar ABC triblock and BC diblock copolymers. *Macromolecules* 1999;32:5165–5167.
- [45] Vaidya NY, Han CD. Temperature–composition phase diagrams for binary blends consisting of chemically dissimilar diblock copolymers. *Macromolecules* 2000;33:3009–3018.
- [46] Kimishima I, Jinnai H, Hashimoto T. Control of self-assembled structures in binary mixtures of A–B diblock copolymer and A–C diblock copolymer by changing the interaction between B and C block chains. *Macromolecules* 1999;32:2585–2596.
- [47] Chun SB, Han CD. Morphology of model A/B/(C-*block*-D) ternary blends and compatibilization of two immiscible homopolymers A and B with a C-*block*-D copolymer. *Macromolecules* 2000;33:3409–3424.
- [48] Hlavata D, Horak Z, Hromadkova J, Lednický F, Pleska A. Compatibilization of polystyrene polypropylene blends by styrene–butadiene block copolymers with differing polystyrene block lengths. *J Polym Sci B: Polym Phys* 1999;37:1647–1656.
- [49] Morkved TL, Chapman BR, Bates FS, Lodge TP, Stepanek P, Almdal K. Dynamics of ternary polymer blends: disordered, ordered and bicontinuous microemulsion phases. *Faraday Disc* 1999;112:335–350.
- [50] Thompson RB, Matsen MW. Improving polymeric microemulsions with block copolymer polydispersity. *Phys Rev Lett* 2000;85:670–673.
- [51] Smith AP, Ade H, Koch CC, Smith SD, Spontak RJ. Addition of a block copolymer to polymer blends produced by cryogenic mechanical alloying. *Macromolecules* 2000;33:1163–1172.
- [52] Ivanova R, Lindman B, Alexandridis P. Effect of glycols on the self-assembly of amphiphilic block copolymers in water. 1. Phase diagrams and structure identification. *Langmuir* 2000;16:3660–3675.
- [53] Derici L, Ledger S, Mai SM, Booth C, Hamley IW, Pedersen JS. Micelles and gels of oxyethylene–oxybutylene diblock copolymers in aqueous solution: the effect of oxyethylene–block length. *Phys Chem Chem Phys* 1999;1:2773–2785.
- [54] Daniel C, Hamley IW, Mingvanish W, Booth C. Effect of shear on the face-centered cubic phase in a diblock copolymer gel. *Macromolecules* 2000;33:2163–2170.
- [55] Mallamace F, Chen SH, Liu YC, Lobry L, Miceli N. Percolation and viscoelasticity of triblock copolymer micellar solutions. *Physica A* 1999;266:123–135.
- [56] Schneider A, Müller S, Finkelmann H. Lyotropic mesomorphism of AB block copolymers in nematic solvents. *Macromol Chem Phys* 2000;201:184–191.
- [57] Schneider A, Geppert S, Spontak RJ, Gronski W, Finkelmann H. Effect of composition on the morphology and electro-optical properties of physically crosslinked liquid crystals. *Mater Res Soc Symp* 1999;559:177–182.
- [58] Vogt BD, Brown GD, RamachandraRao VS, Watkins JJ. Phase behavior of nearly symmetric polystyrene-*block*-polyisoprene copolymers in the presence of CO₂ and ethane. *Macromolecules* 1999;32:7907–7912.
- [59] Wignall GD. Neutron scattering studies of polymers in supercritical carbon dioxide. *J Phys-Condens Matter* 1999;11:R157–R177.
- [60] Liu LZ, Cheng ZG, Inomata K, Zhou SQ, Chu B. Synchrotron SAXS and laser light scattering of aggregation behavior of poly(1,1-dihydroperfluorooctyl acrylate-*b*-vinyl acetate) diblock copolymer in supercritical carbon dioxide. *Macromolecules* 1999;32:5836–5845.
- [61] Laurer JH, Khan SA, Spontak RJ et al. Morphology and rheology of SIS and SEPS triblock copolymers in the presence of a midblock-selective solvent. *Langmuir* 1999;15:7947–7955.
- [62] van Vlimmeren BAC, Maurits NM, Zvelindovsky AV, Sevink GJA, Fraaije JGEM. Simulation of 3D mesoscale structure formation in concentrated aqueous solution of the triblock polymer surfactants (ethylene oxide)₁₃(propylene oxide)₃₀(ethylene oxide)₁₃ and (propylene oxide)₁₉(ethylene oxide)₃₃(propylene oxide)₁₉. Application of dynamic mean-field density functional theory. *Macromolecules* 1999;32:646–656.
- [63] Zheng Y, Won YY, Bates FS, Davis HT, Scriven LE, Talmon Y. Directly resolved core-corona structure of block copolymer micelles by cryo-transmission electron microscopy. *J Phys Chem B* 1999;103:10331–10334.
- [64] Quintana JR, Hernaez E, Inchausti I, Katime I. Thermal behavior and association properties of polystyrene-*b*-poly(ethylene/butylene)-*b*-polystyrene triblock copolymer in n-octane/4-methyl-2-pentanone solutions. *J Phys Chem B* 2000;104:1439–1446.
- [65] Jackson NR, Wilder EA, White SA, Bukovnik R, Spontak RJ. Modification of a thermoplastic elastomer gel through the addition of an endblock-selective homopolymer. *J Polym Sci B: Polym Phys* 1999;37:1863–1872.
- [66] Kleppinger R, Mischenko N, Reynaers HL, Koch MHJ. Long-range order in physical networks of gel-forming triblock copolymer solutions. *J Polym Sci B: Polym Phys* 1999;37:1833–1840.
- [67] Konak C, Fleischer G, Tuzar Z, Bansil R. Dynamics of solutions of triblock copolymers in a selective solvent: effect of varying copolymer concentration. *J Polym Sci B: Polym Phys* 2000;38:1312–1322.
- [68] King MR, White SA, Smith SD, Spontak RJ. Mesogel networks via selective midblock swelling of lamellar triblock copolymers. *Langmuir* 1999;15:7886–7889.
- [69] Flanigan CM, Crosby AJ, Shull KR. Structural development and adhesion of acrylic ABA triblock copolymer gels. *Macromolecules* 1999;32:7251–7262.

- [70] Fukahori Y, Mashita N, Wakana Y. Structure formation and dynamic properties in physical gels of thermoplastic elastomer and oil. *Kobunshi Ronbunshu* 1998;55:768–779.
- [71] Chrissopoulou K, Tselikas Y, Anastasiadis SH et al. Macromolecular architecture effects on block copolymer dynamics: linear tetrablocks and inverse starblocks. *Macromolecules* 1999;32:5115–5126.
- [72] Buzza DMA, Hamley IW, Fzea AH et al. Anomalous difference in the order–disorder transition temperature comparing a symmetric diblock copolymer AB with its hetero-four-arm star analog A_2B_2 . *Macromolecules* 1999;32:7483–7495.
- [73] Han CD, Vaidya NY, Kim D, Shin G, Yamaguchi D, Hashimoto T. Lattice disordering/ordering and demicellization/micellization transitions in highly asymmetric polystyrene-block-polyisoprene copolymers. *Macromolecules* 2000;33:3767–3780.
- [74] Floudas G, Ulrich R, Wiesner U, Chu B. Nucleation and growth in order-to-order transitions of a block copolymer. *Europhys Lett* 2000;50:182–188.
- [75] Park C, Simmons S, Fetters LJ, Hsiao B, Yeh F, Thomas EL. Spherical-to-cylindrical microdomain transformation by application of a flow field. *Polymer* 2000;41:2971–2977.
- [76] Krishnamoorti R, Silva AS, Modi MA, Hammouda B. Small-angle neutron scattering study of a cylinder-to-sphere order–order transition in block copolymers. *Macromolecules* 2000;33:3803–3809.
- [77] Kimishima K, Koga T, Kanazawa Y, Hashimoto T. Thermoreversible order–order transition between spherical and cylindrical microdomain structures of block copolymer. *ACS Symp Ser* 2000;739:514–530.
- [78] Ryu CY, Lodge TP. Thermodynamic stability and anisotropic fluctuations in the cylinder-to-sphere transition of a block copolymer. *Macromolecules* 1999;32:7190–7201.
- [79] Laurer JH, Pinheiro BS, Polis DL, Winey KI. Persistence of surface-induced alignment in block copolymers upon large-amplitude oscillatory shear processing. *Macromolecules* 1999;32:4999–5003.
- [80] Dair BJ, Avgeropoulos A, Hadjichristidis N, Capel M, Thomas EL. Oriented double gyroid films via roll casting. *Polymer* 2000;41:6231–6236.
- [81] Zdrahala RJ, Zdrahala IJ. Biomedical applications of polyurethanes: a review of past promises, present realities, and a vibrant future. *J Biomater Appl* 1999;14:67–90.
- [82] Liu RB, Zhang QM, Cross LE. Experimental investigation of electrostrictive polarization biased direct apparent piezoelectric properties in polyurethane elastomer under quasistatic conditions. *J Appl Polym Sci* 1999;73:2603–2609.
- [83] Kyokane J, Ishimoto H, Yugen H, Hirai T, Ueda T, Yoshino K. Electrostriction effect of polyurethane elastomer (PUE) and its application to actuators. *Synth Met* 1999;103:2366–2367.
- [84] Watanabe M, Hirai T, Suzuki M, Amaike Y. Electric conduction in bending electrostriction of polyurethanes. *Appl Phys Lett* 1999;74:2717–2719.
- [85] Nair B, Osbourne MAR, Hammond PT. Synthesis and characterization of new segmented copolymers with side chain liquid crystalline soft segments. *Macromolecules* 1998;31:8749–8756.
- [86] Shirasaka H, Inoue S, Asai K, Okamoto H. Polyurethane urea elastomer having monodisperse poly(oxytetramethylene) as a soft segment with a uniform hard segment. *Macromolecules* 2000;33:2776–2778.
- [87] Paul CJ, Nair MRG, Koshy P, Idage BB. Segmented block copolymers of natural rubber and bisphenol A-toluene diisocyanate oligomers. *J Appl Polym Sci* 1999;74:706–721.
- [88] Dupret I, David C, Colpaert M, Loutz J-M, Vander Wauven C. Biodegradation of poly(ester-urethane)s by a pure strain of micro-organisms. *Macromol Chem Phys* 1999;200:2508–2518.
- [89] Musselman SG, Santosusso TM, Barnes JD, Sperling LH. Domain structure and interphase dimensions in poly(urethaneurea) elastomers using DSC and SAXS. *J Polym Sci B: Polym Phys* 1999;37:2586–2600.
- [90] Sakurai S, Okamoto Y, Sakaue H, Nakamura T, Banda L, Nomura S. Structure and properties of segmented poly(urethaneurea)s with relatively short hard-segment chains. *J Polym Sci B: Polym Phys* 2000;38:1716–1728.
- [91] Lee HS, Yoo SR, Seo SW. Domain and segmental deformation behavior of thermoplastic elastomers using synchrotron SAXS and FTIR methods. *J Polym Sci B: Polym Phys* 1999;37:3233–3245.
- [92] Lee HS, Park HD, Cho CK. Domain and segment orientation behavior of PBS–PTMG segmented block copolymers. *J Appl Polym Sci* 2000;77:699–709.
- [93] Stribeck N, Fakirov S, Sapoundjieva D. Deformation behavior of a poly(ether ester) copolymer. Quantitative analysis of SAXS fiber patterns. *Macromolecules* 1999;32:3368–3378.
- [94] Bondar VI, Freeman BD, Pinnau I. Gas transport properties of poly(ether-*b*-amide) segmented block copolymers. *J Polym Sci B: Polym Phys* 2000;38:2051–2062.
- [95] Bondar VI, Freeman BD, Pinnau I. Gas sorption and characterization of poly(ether-*b*-amide) segmented block copolymers. *J Polym Sci B: Polym Phys* 1999;37:2463–2475.
- [96] Ha SY, Park HB, Lee YM. Percolational effect of siloxane content in poly(amideimide siloxane) on the gas permeation behavior. *Macromolecules* 1999;32:2394–2396.
- [97] Ren JX, Silva AS, Krishnamoorti R. Linear viscoelasticity of disordered polystyrene–polyisoprene block copolymer based layered-silicate nanocomposites. *Macromolecules* 2000;33:3739–3746.
- [98] Hashimoto T, Harada M, Sakamoto N. Incorporation of metal nanoparticles into block copolymer nanodomains via in-situ reduction of metal ions in microdomain space. *Macromolecules* 1999;32:6867–6870.
- [99] Drolet F, Fredrickson GH. Combinatorial screening of complex block copolymer assembly with self-consistent field theory. *Phys Rev Lett* 1999;83:4317–4320.