Small-angle X-ray and neutron scattering studies from multiphase polymers

Kell Mortensen

The thermodynamic understanding of complex polymer systems is presently undergoing important developments. Much of the experimental input is based on structural studies that use small-angle scattering of X-rays and neutrons. These techniques provide important insight into static phase behavior and polymer conformation. In recent years, dynamical aspects have also been probed by *in situ* studies under time-varying fields. Recent progress has been made in analysing block copolymer systems and complex polymer blends using small-angle scattering.

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Current Opinion in Solid State & Materials Science 1997, 2:653–660

Electronic identifier: 1359-0286-002-00653

Abbreviations

d	characteristic length (e.g. spacing) in block-copolymer system
f	volume fraction of component A in AB-diblock copolymer
Gi	Ginzburg parameter, describing the limitation of mean-field behavior
N	degree of polymerization
ODT	order–disorder transition
OOT	order–order transition
q	scattering momentum transfer
q^*	scattering momentum transfer at maximum intensity
T_g	glass transition temperature
WSL	weak segregation limit
χ	Flory–Huggins segment–segment interaction parameter

Introduction

A key issue within modern materials science is the development of materials based on soft matter, such as polymers and liquid crystals. The industrial use of polymers and related complex fluids comprises a wide range of applications, including the use of those special properties provided by the polymeric natures such as visco- and rubber-elasticity, adhesion and lubrication.

The thermodynamics of polymer systems is dominated by the large number of degrees of freedom, weak interactions, delicate balance between enthalpy and entropy, large concentration fluctuations and macroscopic softness. The large molecular dimension of polymer systems markedly reduces the mixing entropy and provides the basis for self-organized structures.

Small-angle X-ray and neutron scattering are particularly powerful techniques for studying complex materials. In recent years a variety of new auxiliary equipment has been invented for structural studies, under specific conditions such as high pressure and shear.

Polymer blends

The most important key to a detailed understanding of binary blends of polymers, during the past two decades, has been the use of small-angle neutron scattering, with the determination of detailed phase diagrams for a variety of polymer blends. However, it is only in the last couple of years that studies have approached a conclusive level of basic understanding.

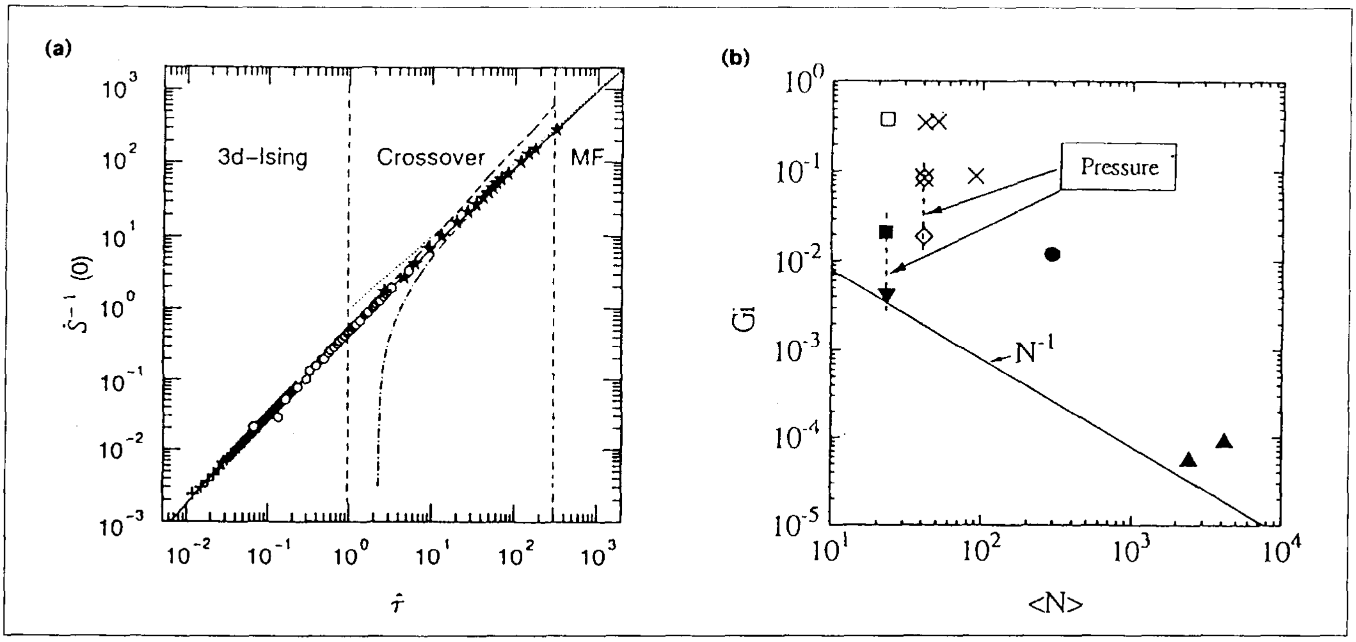
Concentration fluctuations

Based on theoretical arguments it was argued in the late 1970s that blends of polymers should show mean-field characteristics very close to the critical point where the blend phase separates in a second order phase transition [1]. The Ginzburg value, Gi, which describes the crossover from mean-field to Ising like behavior, was calculated to be inversely proportional to the degree of polymerization N; $Gi \sim N^{-1}$. A number of the polymer blends at near critical composition confirm the existence of mean-field character over large temperature ranges, as reviewed by Schwahn and coworkers [2–4].

Close to the critical point, however, the characteristics of the composition fluctuations crossover from mean-field to the 3D-Ising behavior. This crossover is analogous to classical, low-molar weight liquids (Figure 1a). This crossover was first shown in a blend of polystyrene and poly(vinylmethylether) back in 1987 [5], but has since been shown for numerous systems. These results have made it possible to experimentally probe the correlation between the molar mass and Ginzburg number. It appears that Gi does not have a universal dependence on N (Figure 1b) [2,3]. Gi was found to be much larger than predicted and it did not extrapolate to the value of low-molar mass liquids. For molecules with N of the order of 30, Gi increases by one to two orders of magnitude.

Schwahn and coworkers [2,3] analyzed the results in terms of Flory–Huggins theory and came to the conclusion that Gi, in addition to the configuration-related term of the free energy, critically depends on an entropic term in the Flory–Huggins parameter. Based on pressure experiments and data on homologous polymers with different microstructures it was concluded that the observation that fluctuation renormalizes the phase behavior far beyond

Figure 1



Phase behavior of binary homopolymer blends. **(a)** Reduced intensity $\hat{S}^{-1}(q = 0)$ versus reduced temperature $\hat{\tau}$ of various polymers, covering the two universality classes: 3D-Ising and mean-field (MF), and the crossover regime. **(b)** Ginzburg number versus degree of polymerization. □, 1 bar data of blend of deuterated poly(butadiene) with microstructure 1,4 and poly(styrene) (d-PB(1,4)PS); ■, 1 bar data of blend deuterated poly(butadiene) mixed microstructure 1,4/1,2 and poly(styrene) (d-PBC1,4/1,2)PS; ▼, 500 bar data of d-PB(1,4/1,2)PS; ⊗, 1 bar data blend of poly(phenylmethylsiloxane) and deuterated poly(styrene) (PPMS/d-PS); ◇, 1000 bar data of blend PPMS/d-PS; ×, 1 bar data of PPMS/dPS; ●, 1 bar data of PPMS/d-PS; ▲, 1 bar data of poly(dimethylsiloxane) and poly(ethylmethylsiloxane) (PDDMS-PEMS). For further detail see [2,3]. (a) and (b) are reproduced, with permission, from [2] and [3], respectively.

expectations based on mean-field, originates in the influence of the free volume [2–4,6,7].

The experimentally based conclusions have been supported theoretically [8•]. Foreman and Freed [8•] calculated the essential microscopic parameters that influence the phase separation in binary blends and found that both the stiffness disparity and the van der Waals interaction energies influence the phase behavior. Compressibility is theoretically shown to produce significant enthalpic contributions to phase separation, even when all of the van der Waals' energies are identical [8•].

Influence on glass transition temperature

Hashimoto and coworkers [9] studied the influence of the glass-transition temperature (T_g) on binary polymer mixtures in their single-phase state. The scattering function can typically be classified into two temperature regimes: at temperatures far above the T_g of the mixture, the data are well described by a random phase approximation; while at temperatures below T_g the scattering profiles become independent of temperature, frozen due to vitrification. For mixtures of polymers having a large difference in the T_g for each pure component, a third abnormal regime appears in the vicinity of the single-phase mixture T_g.

Shear dependence

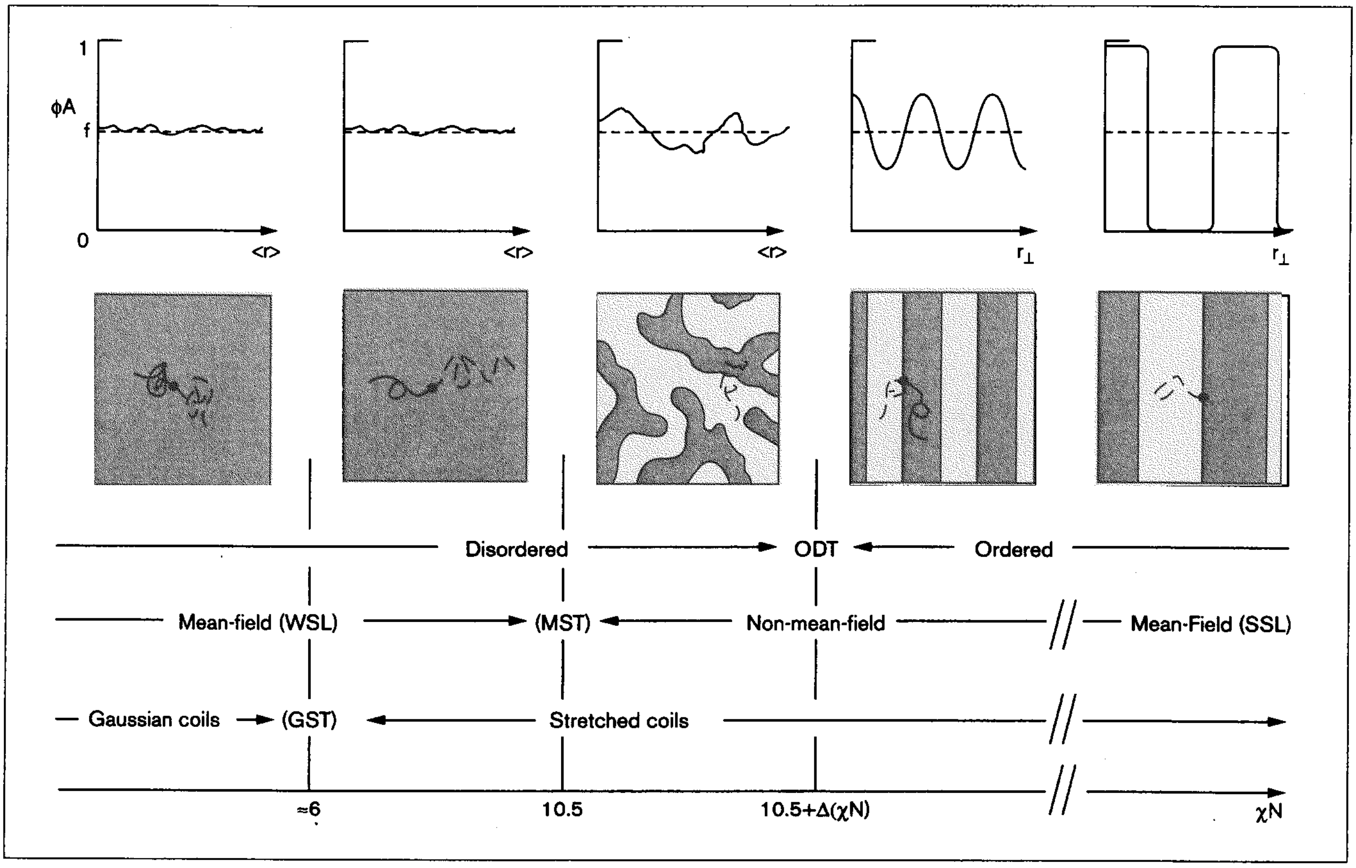
In industrial processing, polymer systems are typically exposed to large stresses and shear. It is therefore of both applied and basic interest to study the changes in phase behavior as a function of such parameters. Hobbie, Han and coworkers [10•,11] have performed scattering experiments with the goal of learning about polymer mixing properties under shear. The response for low-molar-mass blends is in good agreement with theoretical predictions, in that shear suppresses critical fluctuations and leads to a drop in the critical temperature, T_c. For high-molar-mass blends the data suggest that a mode-coupling contribution to the decay rate of composition fluctuations is significant in both the miscible and immiscible phases.

Block copolymers

Polymer chains comprised of blocks of different species is an alternative method of mixing chemically different polymers. The simplest type is the diblock AB-copolymer composed of an A- and a B-block, but a variety of architectures are possible, including linear multiblock and star-type polymers.

The amphiphile character of block-copolymers gives rise to compositional fluctuations or phase separation on the length-scale of the single blocks. The phase behavior is primarily determined by the Flory–Huggins parameter, χ,

Figure 2



States of segregation in a symmetric diblock copolymer. The upper panel shows local composition profiles associated with segregation patterns depicted in the lower panel. GST, Gaussian solution temperature; MST, microphase separation temperature; SSL, strong segregation limit; WSL, weak segregation limit; ϕ, local concentration of A-block; f, mean global concentration of block A-component; <r>, distance from arbitrary point at a given time in material; $r_\perp$, distance of component perpendicular to lamellaes. Reproduced with permission from [13••].

the overall degree of polymerization N, and the volume fraction, f of type A- repeat units [12,13••]. Additional factors that contribute to fluctuation and conformational asymmetry effects have been identified in both experiments [14,15] and theory [16–18,19•,20•].

States of segregation in symmetric diblock copolymers

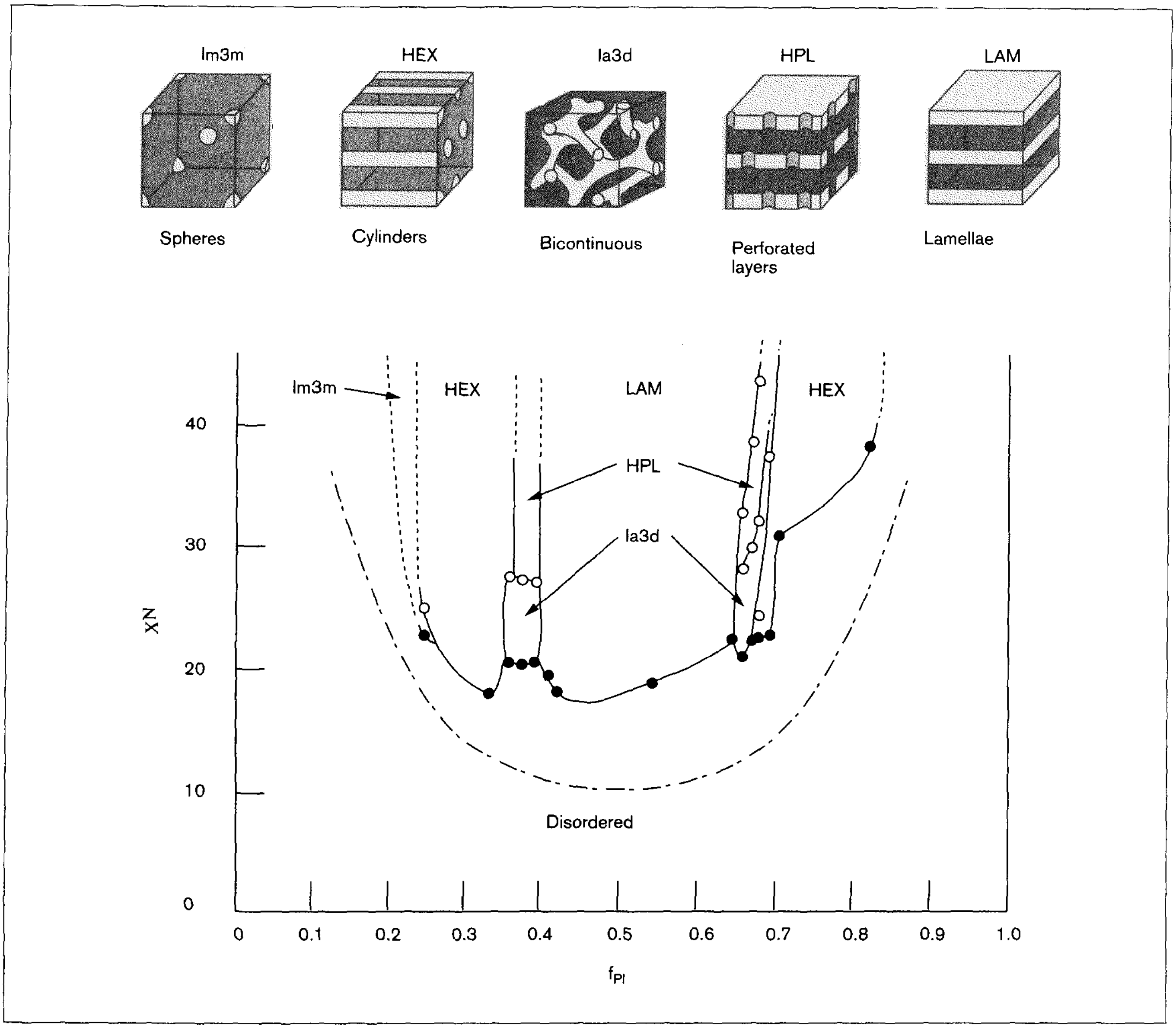
The combined parameter χN controls the degree of segregation, which is conventionally divided into three regimes: the weak and strong segregation limits and an intermediate region near the ODT (order–disorder transition) abbreviated WSL, SSL, and ISR respectively.

The WSL is characterized by small deviations in local composition around an average value of f. Within mean-field theory this regime covers the entire disordered regime and extends slightly into the ordered state. For symmetric diblock copolymers, where $f = 0.5$, theory predicts that when $\chi N = 10.5$, a second-order critical point occurs and a lamellar ordered phase is formed.

The structure factor is characterized by a peak at a scattering momentum q^* where q^* is determined by the polymer size, R_g. In the lamellar ordered phase, q^* directly reflects the periodicity d as $d = 2\pi/q^*$. According to the WSL-theory (small χN-values), d scales as $N^{1/2}$ whereas the SSL-theory (large χN-values) predicts $d \propto N^{2/3}$. As the amplitude of the composition profile grows with increasing χN, the shape of the profile becomes nonsinusoidal and the chains get stretched beyond their Gaussian dimension. Almdal *et al.* [21] found, by measuring q^* for a number of symmetric PEP–PEE block copolymers, that the WSL-to-ISR crossover occurs in the disordered regime at $\chi N = 5$, far above T_{ODT}. Extended experimental studies have shown that the ISR-to-SSL crossover appears at $\chi N = 30$ [22•], in agreement with theory [23,24•]. Figure 2 illustrates the states of segregation.

At T_{ODT} structural data shows an anomaly in polymer chain compressibility in conflict with present theories. Such an anomaly was observed, primarily, using combined pressure and temperature studies [6,25•] but additional

Figure 3



Phase diagram of PI–PS (polyisoprene–polystyrene) diblock copolymer. HEX, hexagonal; HPL, hexagonal perforated lamellar; LAM, lamellar. Reproduced with permission from [28••].

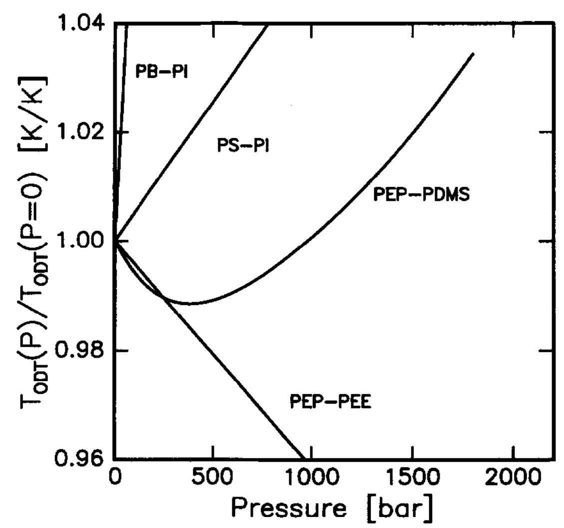
indications are given based on a SANS (small-angle neutron scattering) study of a blend of deuterated and protonated diblock copolymers, providing the possibility for direct measurement of the polymer radius of gyration [26].

Phase diagram

The composition parameter *f* is primarily responsible for the ordered state symmetry. The experimentally observed phase behavior of block copolymers shows, in general, a complexity far beyond both mean-field [12] and fluctuation renormalized theories [16]; which both predicts a symmetric phase diagram of lamellar, hexagonal rod-structure and body centered ordered spheres (Im$\bar{3}$m). The true phase diagram is typically nonsymmetric with respect to *f* [13••], and additional mesophases have been documented: hexagonally modulated lamellar (ML), and the bicontinuous gyroid-phase (Ia$\bar{3}$d). Figure 3 shows the phase-diagram of polyisoprene–polystyrene (PI–PS) [27]. Transitions from one ordered state to another occur only when the lattice spacing is closely matched, thus highlighting the importance of epitaxy and molecular conformation [28••].

Based on reproducibility and dynamics in experimental data, the HML (hexagonal modulated lamellar) and HPL (hexagonal perforated lamellar) structures were originally identified as being thermodynamically stable. Theories,

Figure 4



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Pressure dependence of the order–disorder temperature for a variety of diblock copolymers. PB, poly(butadiene); PDMS, poly(dimethylsiloxane); PE, poly(ethylene); PEP, poly(ethylene propylene); PI, poly(isoprene); PS, poly(styrene). The data are based on values given in [4,25•,33–35].

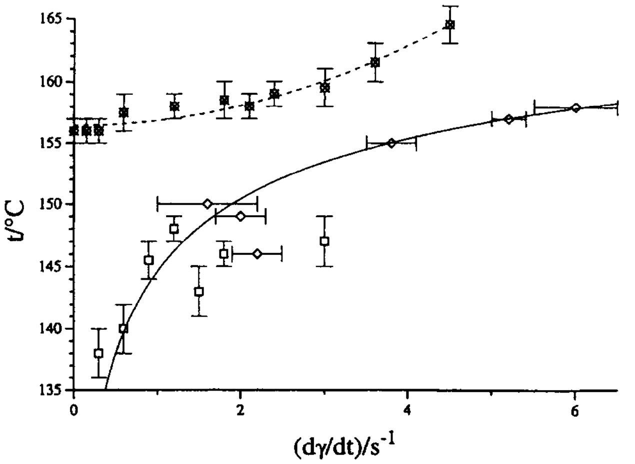
however, indicate that these phases are metastable, developed from anisotropic fluctuations in the weak segregation limit [19•,20•].

The complex phases are critically dependent on thermal fluctuations which are more pronounced in low-molar mass systems. This has been verified in studies of low-molar mass systems of poly(ethylene oxide) and poly(ethylene ethylene) [28••] and poly(ethylene propylene)-poly(dimethylsiloxane) [29].

Block copolymer phase behavior near the ODT

Both mean-field and fluctuation renormalized theories predict that microphase-separation is accompanied by first-order disorder-order transition. Scattering studies on poly(styrene)-poly(isoprene) diblock copolymers with $f_{PS} = 0.3$ indicate, however, that a micellar state, with liquid- like order between the disordered and the ordered phase exists [30•] in analogy with block copolymers in selective solutions [31•]. Schwab and Stühn [30•] found that while the micelles gradually appear as the temperature is lowered, the formation of the ordered state occurs discontinuously. Time-resolved experiments indicating that the growth of micelles occurs at a time scale clearly separated from that of their ordering was taken as further evidence for the presence of micelles [30•]. Other studies using shear to control the state have shown, however, that the fluctuations have similar features with a characteristic time-scale significantly different from that of the order-disorder process [32].

Figure 5



Ordering temperature of PEP–PEE diblock copolymer as a function of shear rate. The solid line represents the stability limit [32,44•]. ⊗, Order–disorder transition temperature measured upon heating; □, disorder–order transition measured during cooling; ◇, disorder–order transition measured upon change in shear. Reproduced with permission from [44•].

Pressure dependence

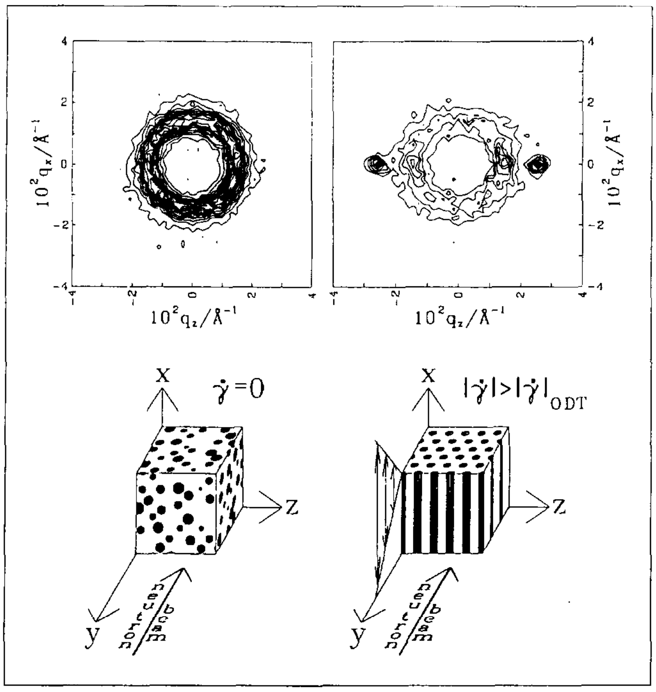
The structure factor maximum $S(q^*)$ represents the order parameter of the system. According to mean-field theory it follows that $S^{-1}(q^*) \propto \chi$ where χ changes linearly with T^{-1}.

Experimentally, however, $S^{-1}(q^*)$ shows pronounced deviation from the linear T^{-1}-dependence, indicating that fluctuations markedly renormalize the order parameter, in analogy with polymer blends. The renormalization is determined by the generalized polymerization parameter defined by $\bar{N} = (R_0^3/V)^2$, where R_0 is the end-to-end distance of the linear polymer [16] and $\bar{N}$ can be thought of as the Ginzburg parameter.

In contrast to homopolymer blends, block-copolymer systems do not show any significant change in the Ginzburg number as a function of pressure [4,25•]. The order-disorder transition temperature, T_{ODT}, however, has a marked pressure dependence. Figure 4 shows the pressure dependence of various block copolymers [4,25•,33–35]. It appears that the pressure dependence is rather diverging, with both positive and negative slopes of T_{ODT} versus P. Most unusual is the phase behavior of PDMS-(poly(dimethylsiloxane))-systems, showing first a decreases in T_{ODT} and then an increase. The divergent behavior of T_{ODT} versus P reflects that the free energy of the system is determined by critical competition between entropic and enthalpic terms [4,25•].

The significant pressure dependence of the thermodynamic parameters may have an important influence in

Figure 6



Contour plots of PEP–PEE for high and low shear rate near the ordering temperature. Reproduced with permission from [44•].

industrial processing. The pressure-dependence of the glass-transition in a block copolymer may also affect the material characteristics. In a diblock copolymer of poly(styrene) and poly(methylstyrene) an apparent decrease of T_{ODT} with increasing pressure appeared to reflect changes in T_g [36•].

Shear dependence

It is well known that shear and flow can transform polycrystalline block copolymer mesophases into a well oriented monodomain texture. Lamellae, for example, were observed to respond by stacking parallel to the plane of shear. Bates and coworkers discovered [37], however, that depending on the shear condition perpendicular orientation can also be formed. Recent studies have aimed at elucidating the dynamics of orientation [38•,39,40•,41]. Wiesner and coworkers [38•] demonstrated that the orientation depends both on shear and on thermal history. Amorphous samples annealed at temperatures far below T_{ODT} align parallel, while samples quenched from above T_{ODT} preferentially align perpendicularly. A characteristic flip from parallel to perpendicular orientation was observed depending on the deformation [40•]. Measurements performed *in situ* during the oscillatory deformation revealed large dynamic lattice transformations [42•].

Shear not only affects microstructural texture, it also reduces fluctuations [13••]. Shear-induced disorder-order transitions have accordingly been observed in both diblock (as shown in Figures 5 and 6) [32,43,44•] and in triblock copolymers [45] shear induced disordering are also observed [46,47]. Dynamic experiments using shear quench have revealed a stability limit in the isotropic state [32,47]. Recent data by Hajduk *et al.* [47] indicates this limit is kinetic rather than thermodynamic in origin.

Block copolymers mixed with liquids and homopolymers

Block copolymers in solution, selective for only one block, tend to segregate into micellar aggregates of spherical, rod or disc-shaped form depending on the molecular architecture. The interaction potential is typically close to hard-sphere like, and for sufficiently high concentrations micelles may organize themselves into ordered structures [31•]. Triblock copolymers with the soluble block in the center also form micelles, but such systems form interconnected networks of micelles connected through the soluble middle block, producing a gel [48]. Ordering of the micelles in such materials provides quite unique gel-systems, where the micellar cross-links are located on a crystalline lattice [49•]. In analogy to the self-assembling of block copolymers in solution, Hillmyer and coworkers [50•] have used the selective solvation of an epoxy precursor to form epoxy-block copolymer nanocomposites with highly-organized microstructures.

Like surfactants block complex copolymer systems may also form isotropic microemulsions. The isotropic sponge phase was first discovered in an aqueous solution of triblock copolymers [51], and more recently in ternary blends of homopolymers and diblock copolymers [52•,53•].

Conceptually, mixtures of high-molar mass homopolymers and block copolymers are closely related to traditional microemulsions. AB-diblock copolymers will primarily localize at the interface boundary separating discrete phases rich of A and B homo-polymers. Such ternary blends offer, however, a unique physical system in which one may expect critical phenomena, as manifested by the concentration fluctuations discussed above, with competing length-scales. While pure block copolymers tend to phase separate on the length-scale given by the polymer size, homopolymer blends phase separate macroscopically. The two phenomena will, according to mean-field theory, meet in a Lifshitz point (LP). Bates and coworkers [54] reported that near the LP the critical scattering exhibits surprisingly perfect mean-field character. Very near the predicted LP, however, a catastrophic failure of mean-field theory is observed, in coincidence with the fluctuation-induced formation of a bicontinuous microemulsion (K Mortensen *et al.*, unpublished data).

Conclusions

In the present review, I have attempted to provide an overview of recent polymer studies based on the small-angle scattering techniques. The field is extremely active and many excellent studies could not be included. It is clear from the review that small-angle scattering provides a unique tool for experimental studies of advanced complex materials. The technique provides data which can be used directly in the design and optimization of new polymeric materials. Furthermore, the experimental scattering studies of complex polymer systems provides a challenge for exploring new physical phenomena.

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