J. Appl. Cryst. (1997). **30**, 702–707

Small-Angle Neutron Scattering Studies of the Phase Behavior and Mesophases of Homopolymers, Block Copolymers and Complex Mixtures

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(Received 23 July 1996; accepted 31 January 1997)

Abstract

Small-angle scattering of X-rays and neutrons are particularly powerful techniques for studying complex materials such as polymers, micellar solutions and lyotropic mesophases of amphiphilic molecules. In the present paper, we review some of the recent progress on polymer complex fluids made using small-angle neutron scattering. These studies include examination of the phase behavior of binary polymers where fluctuations due to the free volume significantly renormalize the critical behavior. Block copolymers phase-separate on the microscopic level given by the length scale of the polymer coils and form a variety of mesoscopic ordered phases. Blends of homopolymers and diblock copolymers show new physical phenomena where different critical behavior meets in a Lifshitz point. Block copolymers in selected solutions self-assemble into micellar structures which provide the basis for ordered structures.

1. Introduction

A key issue within modern materials science is the use and development of materials based on soft condensed matter, such as polymers, liquid crystals, micellar solutions and lyotropic mesophases of amphiphilic molecules. The value of applied polymers has already exceeded the value of materials such as metals and semiconductors. Polymers and other complex fluids have been used in a wide range of industrial applications, which is due to the special properties of the polymeric state such as visco- and rubber-elasticity, adhesion, lubrication, tension *etc.* The use of polymers is increasing greatly, with large numbers of polymer-related patent applications. Within the field of polymer blends alone, the rate of patent applications is many thousands every year.

It has become clear that polymers and other complex fluids share a number of underlying similarities such as a large number of degrees of freedom, weak interactions between chemical units, a delicate balance between enthalpy and entropy, large thermal fluctuations, macroscopic softness *etc.* Static as well as dynamic neutron scattering have been key techniques in studying the basic properties and revealing, on model systems, some of the universal structures and scaling laws.

It appears that important properties of complex fluids and polymer materials are governed by the degree of miscibility between various units in the material, *i.e.* the miscibility between polymers and a solvent, between different polymers, or between various regimes (blocks) within a single polymer chain.

While most applied polymer materials used to date have been based effectively on only one polymer component, *e.g.* poly(ethylene) or poly(vinyl chloride), new products with special properties tend to be more complex. One of the obvious ways of modifying the characteristics of polymeric materials is based on mixing polymers with different appropriate characteristics. As a general rule, however, it is found that polymers do not mix. Low-molar-mass liquids normally make an ideal mixture, which is a result of the dominating entropic contribution to the Gibbs free energy. Even though the intermolecular forces are usually repulsive, the enthalpic contribution is only small (except for special liquids like water). In polymers, on the other hand, the gain in mixing entropy is very much reduced, simply because of the large molecular dimensions, whereas the enthalpic contribution remains low as in small molecules. Therefore, in practice, it is only possible to make ideal blends of a few, special polymers.

The absence of miscibility is, on the other hand, the basis for attractive self-organizations. When various parts within a single chain are immiscible, or have different solubilities in a selected solvent, one often finds that the molecules self-assemble into well defined aggregates, which may even form paracrystalline phases on the mesoscopic length scale, *i.e.* the different (amorphous) domains order on a crystalline lattice.

Small-angle neutron scattering (SANS) and small-angle X-ray scattering (SAXS) are particularly powerful techniques for studying such complex materials, since they are sensitive to the length scale of the developed structures, which is typically of the order of 100 Å. The

SANS technique has the very important advantage in that specific features of the structure can be highlighted by the exchange of hydrogen with deuterium, which has a very different cross section for interaction with the neutrons.

In the present review, we discuss some of the recent progress made on polymers and related complex fluids using small-angle scattering techniques.

2. Polymer blends

One of the major aims of SANS over the last decade or so has been to gain a detailed understanding of binary blends of homopolymers. Only in the last couple of years, however, has the understanding of phase behavior approached a conclusive level.

Theoretical considerations in the late 1970's led to the argument that blends of polymers should show mean-field characteristics even very close to the critical point as a result of the large molecular weight (see *e.g.* de Gennes, 1979). The Ginzburg value, which describes the crossover from mean-field to Ising-like behavior, was calculated to be inversely proportional to the degree of polymerization (N): $\mathrm{Gi} \propto N^{-\alpha}$ with $\alpha = 1$.

Numerous polymer blends at near-critical composition have been investigated during the last decade and it has been revealed that mean-field behavior is certainly the dominating feature over large regimes. Close to the critical point, however, the three-dimensional Ising characteristic clearly appears, as in classical low-molar-mass liquids. This was first proved in a blend of deuterated poly(styrene) (dPS) and poly(vinyl methyl ether) PVME (Schwahn, Mortensen & Yee-Madeira, 1987), but has since been found for numerous other polymer mixtures, as shown in Fig. 1(*a*). Studies of polymer blends with different molecular sizes have been made in an attempt to investigate experimentally the Ginzburg number. It has been demonstrated that the Ginzburg number (Gi) does not have a universal dependence on molecular size (Fig. 1*b*). Gi is much larger than predicted and seems to depend on the entropic part of the free energy which, for polymer blends, appears as a segmental quantity in addition to the usual configurational term. The segmental entropy term is determined by the free volume, *i.e.* the degree of packing of the molecules. The Ginzburg number for polymer blends therefore does not extrapolate to the Gi value of low-molar-mass liquids and polymers are accordingly not just extended versions of small molecules. For molecules with length N of the order of 30, the Ginzburg number typically increases by one to two orders of magnitude (Fig. 1*b*), depending on the molecular microstructure (Schwahn, Meier, Mortensen & Janssen, 1994). Experimentally, the segmental entropy contribution, and thus the Ginzburg number, can be controlled by application of hydrodynamic pressure. For polymer blends, there appears to be a universal relationship whereby pressure reduces the Ginzburg number and thus reduces the Ising regime (Janssen, Schwahn, Springer & Mortensen, 1995). This probably relates to the reduction of free volume, and thereby a change in the entropic term of the Flory–Huggins parameter, upon application of pressure.

3. Phase behavior of block copolymers

A linear polymer chain can be composed of more than one type of monomer. The chain may, for example, be organized in two covalently bonded blocks: one block A_n of A monomers and one block B_n of B monomers, thus obtaining the AB-diblock copolymer. Equally, there may be triblock copolymers composed of three blocks (ABA or ABC, for example) or more complex structures including random organization of the different blocks.

The amphiphilic character of the block copolymers gives rise to a fluctuation in composition or even (micro)phase separation on the level of single blocks in the melting of block copolymers (see *e.g.* Bates *et al.*, 1994). Using mean-field theory, Leibler (1980) calcu-

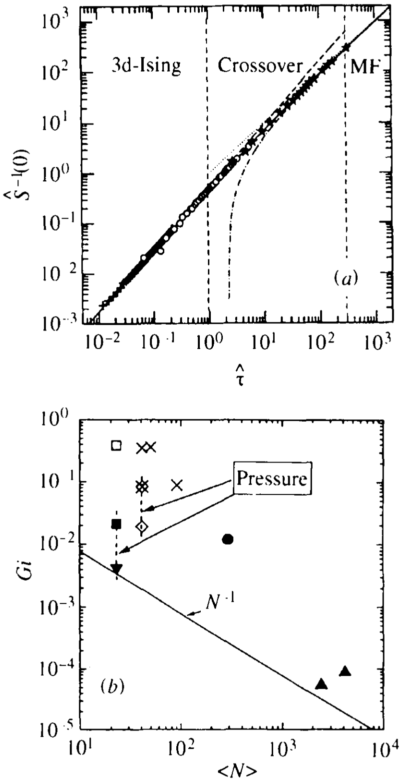

Fig. 1. The phase behavior of binary homopolymer blends. (*a*) Double logarithmic plot of reduced intensity $\hat{S}(q = 0)$ *versus* reduced temperature $\hat{\tau}$ (Meier, Schwahn, Mortensen & Janssen, 1993) for a variety of polymers and polymer sizes: PS–PB (○), PVME–PS (+), PPMS–PS (*) [PS poly(styrene); PB poly(butadiene); PVME poly(vinyl methyl ether); PPMS poly(phenylmethylsiloxane)]. (*b*) Ginzburg number *versus* degree of polymerization for various polymers. The notation 'Pressure' shows changes upon application of hydrodynamic pressure (for details, see Schwahn, Meier, Mortensen & Janssen, 1994).

lated the structure factor and phase diagram for diblock copolymers, showing that such systems are characterized by undergoing weak first-order transitions from the disordered phase into microphase-separated phases characterized by ordered domain structure: lamellar, hexagonal rod structure or body-centered ordered spheres (where the rods and spheres contribute the minority component). In the symmetric case, Leibler theory predicts a second-order transition critical point. The structure factor of diblock copolymers is characterized by a peak at a scattering momentum q^* given solely by the molecular sizes. The scattering intensity at $q = q^*$, $S(q^*)$, is proportional to the square of the amplitude of the first harmonic, ψ_1, of the composition field $\psi\bar{r}$. $S(q^*)$ thus represents the order parameter of the system, following $S^{-1}(q^*) \propto \chi$ where χ is the Flory–Huggins segmental interaction parameter which changes linearly with T^{-1}.

In real diblock copolymer systems, however, $S^{-1}(q^*)$ shows pronounced deviation from the linear T^{-1} dependence, indicating that the thermal fluctuations in analogy with the homopolymer blends discussed above markedly renormalize the order parameter. Fredrickson & Helfand (1987, 1988) have consistently included the fluctuations using the Hartree approximation and thereby calculated the phase behavior and structure factor. The resulting $S(q)$ has the same form as the mean-field formula, but with a renormalized Flory–Huggins parameter: $(\chi_{\text{ren}}N) = (\chi N) - \tilde{c}[S(Q^*)/(V\bar{N})]^{1/2}$ with $\tilde{c}$ depending on molecular parameters and V being the molecular volume. The degree of fluctuations is determined by the generalized polymerization parameter defined by $\bar{N} = (R_o^3/V)^2$. The quantity $\bar{N}$ characterizes the average number of chains in the volume R_o^3, where R_o is the end-to-end distance of the linear polymer ($R_o^2 = 6R_g^2$). The parameter $\bar{N}$ can be thought of as the Ginzburg parameter used for homopolymer blends. The mean-field theory is valid for $S(Q^*)/V \ll 1$ and/or $\bar{N} \gg 1$ which is fulfilled for temperatures very far from T_S and/or in the case of molecules approaching infinite size.

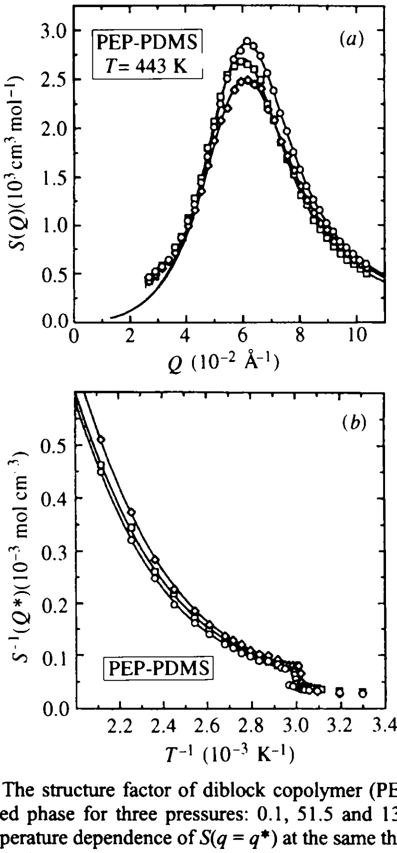

Fig. 2. (*a*) The structure factor of diblock copolymer (PEP–PDMS) in disordered phase for three pressures: 0.1, 51.5 and 136.5 MPa. (*b*) The temperature dependence of $S(q = q^*)$ at the same three pressures, showing clear deviation from mean-field behavior (Schwahn, Friedlinghaus, Mortensen & Almdal, 1996).

Fig. 2 shows a typical example of the structure factor of block copolymers and the temperature dependence of the inverse peak intensity. The present block copolymer system did not show any significant change in the Ginzburg number as a function of pressure (Schwahn, Friedlinghaus, Mortensen & Almdal, 1996), as expected based on experience from homopolymer blends. The order–disorder transition (ODT), however, showed unusual pressure dependence: with increasing pressure the ODT temperature first decreases and then increases as shown in Fig. 3 (Schwahn *et al.*, 1996).

The experimentally observed phase behavior of block copolymers shows in general a complexity far beyond the theory of both Leibler and Fredrickson–Helfand. The phase diagram is typically nonsymmetric with respect to composition f. This is believed to be a result of configurational asymmetry of the blocks. Beyond the classical LAM, HEX and $Im\bar{3}m$ phases, identification of additional phases has been made, namely hexagonally modulated (HML) and perforated lamellar (HPL) phases and the bicontinuous $Ia\bar{3}d$ phase. Fig. 4 shows the phase diagram of polyisoprene–polystyrene, PI–PS (Khandpur *et al.*, 1995). The stabilization of the complex phases is probably critically dependent on the thermal fluctuations and can therefore be expected to be more pronounced in relatively low-molar-mass liquids. A relatively low-

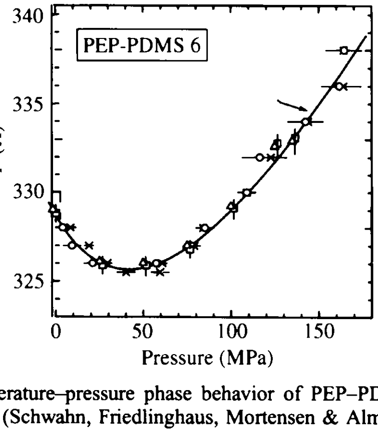

Fig. 3. Temperature–pressure phase behavior of PEP–PDMS diblock copolymer (Schwahn, Friedlinghaus, Mortensen & Almdal, 1996).

molar-mass diblock copolymer of poly(ethylene oxide) and poly(ethylene ethylene), PEO–PEE, has within a single block copolymer five ordered phases beyond the disordered phase at high temperature (Hillmyer, Bates, Almdal, Mortensen & Ryan, 1996). The five ordered phases are a lamellar phase of crystalline PEO and amorphous PEE, a lamellar phase in which both PEO and PEE are amorphous, a modulated lamellar phase, the cubic $Ia\bar{3}d$ and a hexagonal rod phase.

The low-temperature lamellar phase has a different origin from the fluctuation-induced phases. For PEO-based block copolymers, one often finds that below 310–320 K (depending on molecular size) the PEO blocks form extended lamellae of crystalline PEO, separated by amorphous poly(propylene oxide), PPO. The result is a lamellar phase with a relatively large periodicity due to highly stretched PEO in the crystalline phase. In fact, the PEO lamellae have a thickness which corresponds to the integer number of chain folding, typically with zero, one or two folds depending on the thermal and mechanical history (Ryan, Hamley & Fairclough, 1996). Upon heating, the crystalline PEO lamellae melt and, depending on the Flory–Huggins parameter, the sample undergoes an order–disorder or an order–order transition. In the PEO–PEE system studied by Hillmyer *et al.* (1996) the PEO crystallization/melting gives rise to a lamellar-to-lamellar order–order transition, while block copolymer systems of PEO with PPO (Mortensen, Brown & Jørgensen, 1994) and poly(ethylene butylene), PBO (Ryan, Hamley, Bras & Mant, 1995) and PS (Mortensen, Brown, Almdal, Alami & Jada, 1997) undergo order–disorder transitions at the PEO melting point. The disorder–order transition induced by the PEO crystallization thus has a different origin from the Leibler type of ODT and is much more first order. A very powerful technique for such investigations is combined small-angle and wide-angle scattering instruments as used by Ryan *et al.* (1995).

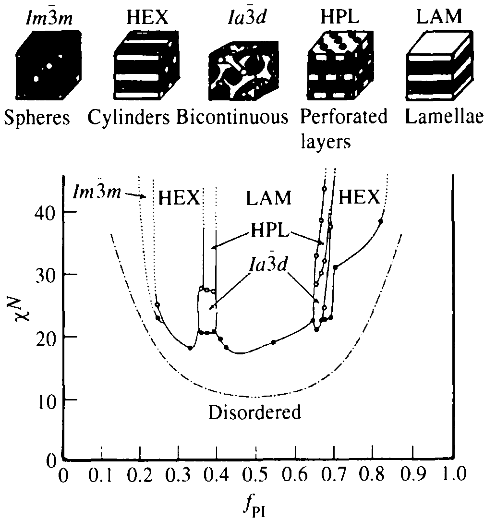

Fig. 4. Phase diagram (χN *versus* f_{PI}) of PI–PS diblock copolymer with $\bar{N}$ of the order of 1×10^3 (Khandpur *et al.*, 1995).

4. Blends of block copolymers and homopolymers

Ternary blends of homopolymers and diblock copolymers offer unique physical systems in which one may expect critical phenomena with competing length scales. While pure block copolymers, as discussed above, tend to phase-separate on the microscopic length scale given by the polymer radius of gyration (characteristic momentum $q^* \simeq 1/R_g$), homopolymer blends phase-separate macroscopically ($q^* = 0$). Theory predicts that in the block-copolymer-rich regime, a line of order–disorder transitions with finite wavevector $q^* > 0$ should be observed, whereas in the homopolymer-rich regime there should be a line of critical points with $q^* = 0$. The two lines will meet in an isotropic Lifshitz point (Broseta & Fredrickson, 1990), as shown in Fig. 5.

While Lifshitz critical behavior has been widely discussed in theory, experiments have only recently proved the existence of the isotropic Lifshitz (Lp) point, namely in studies of a three-component mixture of *A* and *B* homopolymers and a symmetric *AB*-diblock copolymer (Bates *et al.*, 1995). Within mean-field theory, blending the two symmetric systems connects the homopolymer critical point and the block copolymer order–disorder transition by a λ line of second-order transitions as shown in Fig. 5. Above the λ line the system is disordered. Adding homopolymer to the lamellar phase continuously increases the repeat distance *D* until a transition (UT) where the system separates into two phases. The high-temperature end of the UT line terminates at the Lp point. Fig. 5 also shows the experimental phase diagram of a mixture of poly(ethylene), PE, with size $N_{PE} = 392$, poly(ethylene propylene), PEP, with $N_{PEP} = 409$ and PE–PEP symmetric block copolymer with $N_{PE-PEP} = 1952$, as obtained from small-

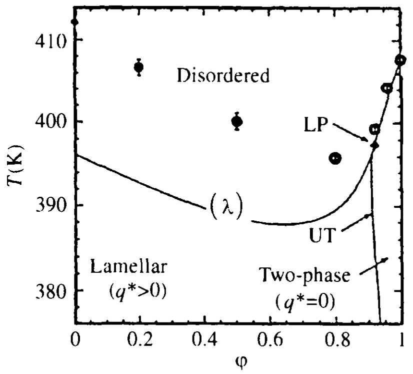

Fig. 5. Phase diagram of block copolymer–homopolymer blends (Bates *et al.*, 1995). The symbols represent experimental points; the full line is the theoretical phase boundary.

angle scattering experiments. The agreement with the theoretical picture is remarkable, including the Lp point at $\varphi = 0.91$ (Bates *et al.*, 1995).

In the disordered phase rich in block copolymers, *i.e.* above the ODT line, the scattering function follows the Leibler function (Leibler, 1980) characteristic for diblock copolymers with a peak in intensity at $q^* \neq 0$. In the mixed phase rich in homopolymers, *i.e.* above the line of demixing critical temperatures, Ornstein–Zernike characteristics ($\Gamma^{-1} \propto q^2$) are found. Both the block copolymer- and homopolymer-dominated regimes show marked deviations from the mean-field $\Gamma^{-1} \propto T^{-1}$ behavior as discussed above for pure diblock copolymers and pure binary homopolymer mixtures.

In the mean-field picture, *i.e.* ignoring renormalizations due to fluctuations, the second-order fluctuation term in the Landau free energy vanishes at the Lifshitz point (Broseta & Fredrickson, 1990), and $\Gamma^{-1}(q) \propto q^4$ and $\Gamma^{-1}(q = 0) \propto T^{-1}$characteristics are expected. This is exactly the form found experimentally (Bates *et al.*, 1995), which seems quite surprising given that fluctuations markedly renormalize the behavior in both block copolymers and homopolymer blends.

5. Block copolymers in selected solutions, micelles

Solutions of di- and triblock copolymers have been extensively studied, in particular in solvents where only one of the blocks (say the *A* block) is soluble. In this case, a variety of aggregates may be formed, depending on the molecular architecture. Often the polymers self-associate into microscopic well defined aggregates, micelles, where the nonsoluble *B* block (in the *AB* type of polymers) forms a core shielded from the solution by the soluble *A* blocks. Such micellar aggregates may have the form of spherical objects, or they may be elongated rod- or worm-like systems, or flat discs. More complex structures can also be found, for example networks of micelles or bicontinuous complex microemulsions.

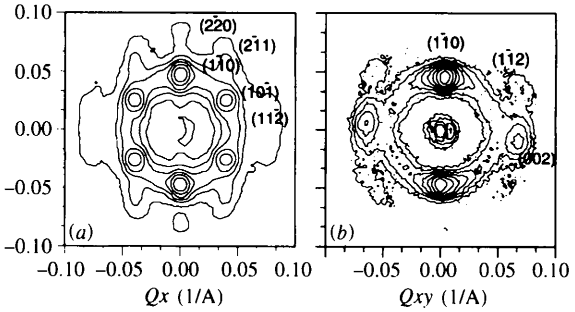

Fig. 6. The two-dimensional scattering function of the mono-domain cubic mesophase of spherical micelles (28% $EO_{88}PO_{40}EO_{88}$ in water), as obtained with (*a*) shear axis horizontal and shear gradient parallel to the beam ([111]); and (*b*) as observed when the sample is rotated 35° around the vertical axis ([110]).

Below, we focus on block copolymers which self-associate into micellar aggregates. Such *AB*-diblock as well as *ABA*-triblock copolymers organize as a general rule in individual micellar aggregates which interact through a near hard-sphere-like potential. *BAB*-triblock copolymers with the soluble block in the center may also form individual micelles, but this implies that all polymer chains start and end in the same micelle and have the middle *A* block dispersed into the solvent. It is more likely that such micelles form interconnected networks of micellar cores connected through the soluble *A*-polymer block.

An important class of such block copolymers is that in which water is a selective solvent. One of the most important classes of polymers used in industry appears also to be among the most interesting from a physical point of view. This is triblock copolymers of poly(ethylene oxide) and poly(propylene oxide). While PEO is water soluble within the whole 273–373 K temperature range, PPO is only soluble at low temperatures and at relatively low polymer concentrations. We have, therefore, a handle on the amphiphilic character of the block copolymer, just by varying the temperature.

Experiments clearly verify this (Mortensen, 1996). SANS experiments have revealed that at low temperatures and low polymer concentrations, the polymers are dissolved in the water phase as individual molecules with near-Gaussian random-walk conformation. When the temperature is increased above a certain temperature, the critical micellation temperature T_{cml}, some polymers aggregate into spherical objects, micelles, with a core of PPO and a corona of PEO dispersed into the water phase. The micellar volume fraction, *i.e.* the volume fraction corresponding to hard spheres given by the micellar interaction radius, increases more or less linearly with both temperature and polymer concentration up to the value of $\varphi \simeq 0.53$ where the suspension undergoes a hard-sphere crystallization (Mortensen, Brown & Nordén, 1992). The remarkable thing to note is that melting occurs by lowering the temperature and crystallization by increasing the temperature. Application of hydrostatic pressure equivalently melts the crystal (Mortensen, Schwahn & Janssen, 1993).

Upon application of shear the solid paste-like phase of PEO–PPO–PEO micelles transforms into a mono-domain crystal. Such shear-aligned samples can be used for crystallographic studies. Fig. 6 gives the two-dimensional scattering pattern of the mesophase of spherical $EO_{96}PO_{39}EO_{96}$ micelles (28% polymer concentration) in two different orientations relative to the beam, revealing b.c.c. symmetry (Mortensen, 1996).

6. Block copolymer gels

While the *ABA* kind of block copolymers in *A* solvent forms individual micelles which interact through hard-sphere-like repulsions, quite different behavior can be expected for the *BAB* kind of aggregates in *A* solvent.

In the PPO–PEO–PPO *BAB* kind of system, such polymers also form spherical micelles within a wide range of temperatures and concentrations. Since the water-soluble block is in the middle, however, aqueous solutions form opaque suspensions because of the interconnected domain structures (Mortensen *et al.*, 1994). In the scattering pattern, such domains of micellar networks are characterized by a major low-angle scattering on top of the pattern observed for individual micelles. At higher polymer concentrations a micellar network of cubic ordered micelles has been observed. Also, this ordered network can be shear aligned into a mono-domain phase (Mortensen, 1997).

The *BAB* micellar systems have potentially interesting elastic properties as a result of the network structure. One may design well defined network structures in which one is able to control both size and position of network knots and length of the connecting polymer strands.

7. Concluding remarks

In the present review, we have described a variety of recent polymer studies performed using the SANS technique. It is clear from these studies that SANS is a unique tool for studying advanced complex materials. The technique provides experimental data which can be used directly in the design and optimization of new polymeric materials. Moreover, the experimental scattering studies of complex polymer systems provide a challenge for exploring new physical phenomena.

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