

Block copolymers – Their microdomain formation (in solid state) and surfactant behaviour (in solution)

Pratap Bahadur

Department of Chemistry, South Gujarat University, Surat 395 007, India

Block copolymers are linear macromolecules that consist of different blocks (often incompatible) of different types of monomers. The two or more distinct and incompatible moieties provide unique solid state and solution properties to block copolymers which in turn lead to various applications. The microphase separation in block copolymers gives rise to formation of different types (e.g. spherical, cylindrical, lamellar, etc.) of microdomains in the solid state. In addition to this, they show micellization and adsorption characteristics in suitable solvents. The present article reviews the properties of block copolymers in the solid and solution state with special reference to ethylene oxide-propylene oxide block copolymers in solution.

POLYMERS are long chain molecules and their properties like light weight, good mechanical strength and easy processibility make polymers useful materials for a variety of uses. Sometimes, the desired properties are obtained by preparing mixtures of two polymers (say A and B); such physical mixtures are called polyblends or polymer alloys. The polymer blends, however, tend to phase-separate, especially when the constituent polymers are incompatible. Another difficulty in mixing polymers at molecular level arises from the fact that polymer molecules are quite large in size. Thus to prepare a polymer blend, it is desirable to have a chemical bond between the constituent polymer molecules so that they cannot segregate. This is achieved in block copolymers.

A block copolymer is a linear arrangement where two often incompatible blocks obtained from different monomers are covalently linked together. It is possible to prepare diblock (A-B), triblock (A-B-A and B-A-B) and multi-block (or segmented) polymers as shown in Figure 1.

Unlike polyblends, where the constituting polymers separate at macroscopic scale, for block copolymers only microhomogeneous scale separation is possible, due to the covalent bond linking the blocks of different polymers, which forces them to regroup in smaller domains. The reasons for demixing of two blocks of the copolymer are the same as those for demixing of low

molecular mass liquids. However, it becomes predominant for mixtures of polymers or in a block copolymer when the chains are very long or/and the constituting polymers differ considerably. When a diblock copolymer is mixed with a homopolymer A, the mixture may exist as an ordered or disordered single phase or undergo macrophase separation. Thus phase diagrams of mixtures containing a block copolymer and a homopolymer exhibit fascinating complexity involving macrophase or microphase separation.

Two general methods used in the synthesis of block copolymers involve step and chain polymerization¹. In the first, two polymers with functional end groups are reacted while in the later, sequential polymerization² involving initiation of other monomers on the active site of a macromolecular chain of one monomer is considered (Figure 2).

Block copolymers possess unique structural features resembling those of surface active agents which have two distinct moieties in their molecule that behave differently. Thus, block copolymers get adsorbed onto

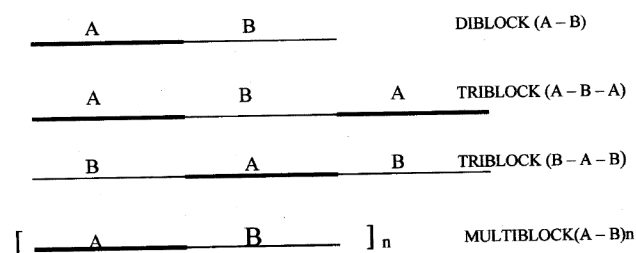


Figure 1. Schematic representation of different types of block copolymers.

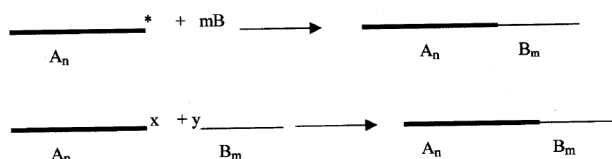


Figure 2. Synthetic routes for block copolymers.

interfaces and self-assemble to form micelles in solutions in addition to their microdomain formation in solid state. This makes these multiphase systems useful for a variety of applications. It is, therefore, not surprising that block copolymers have aroused worldwide interest of physicists, chemists and chemical engineers. Several commercial products are available as thermoplastic elastomers (e.g. styrene-diene block polymers as Solprene (*Philips*), Kraton (*Shell*); segmented polyester-polyurethane as Estane (*Goodrich*), Spandex (*Dupont*) and surfactants e.g. ethylene oxide-propylene oxide as Pluronics (*BASF, ICI*)).

Block copolymers in solid state

Block copolymers with incompatible sequences exhibit characteristic morphological behaviour and interesting properties. For example, incompatible and noncrystallizable A & B blocks form microdomain structures due to microphase separation. The conditions of microphase separation and equilibrium domain sizes and their various morphologies, viz. spherical, cylindrical and lamellar, etc. are predictable in terms of interaction parameters and molecular characteristics of the copolymer^{3,4}. A few common structures encountered in block copolymers are shown schematically in Figure 3.

The repulsive interactions between A and B blocks cause the domains to grow in thickness (thickness of the lamellar domains and radius of the spherical and cylindrical domains) so as to reduce the surface-to-volume ratio. This is counterbalanced by two forces of entropic origin, i.e. loss of conformational entropy in maintaining uniform segment density and the loss of placement entropy in confining A-B junction in the interfacial region. Statistical thermodynamical calculations⁵ have been used to obtain information on the characteristics of the interphase zone, where chains of two constituent polymers interdiffuse. Partial miscibility in the interfacial zone depends on the nature of the blocks, type and molecular characteristics of block copolymer and temperature (Figure 4). Chain diffusion functions and segment density functions for block copolymers in microphase separated systems are available in literature⁶.

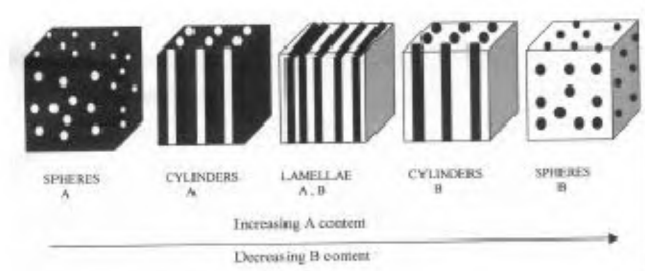


Figure 3. Block copolymers of different morphologies.

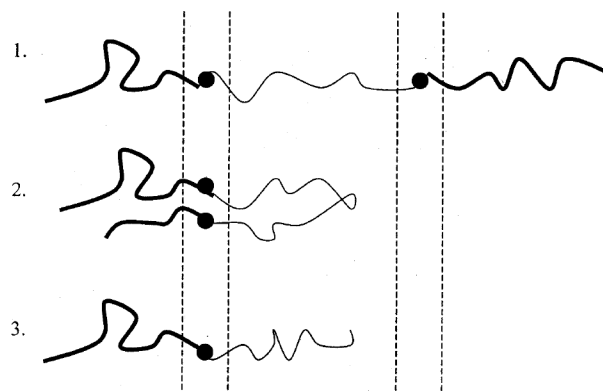


Figure 4. Schematic representation of microphase separation of diblock (3) and triblock copolymers (1 and 2).

At a certain temperature when the free energy of mixing of both blocks is zero, complete mixing of the phases would occur. Thus order-disorder transition from microphase separated domains into a disordered phase would occur which can be clearly observed from mechanical behaviour. The phase transition is evident for copolymers when the chains are sufficiently short. With increase in temperature, thermal agitation increases and the system gets disordered. At this stage, the molecules diffuse into the entire volume and the copolymer now accommodates stresses by restructuring itself rapidly. It behaves like a conventional viscoelastic polymer liquid. The force required to maintain it in a deformed shape decreases rapidly in a few milliseconds. The deformation is then permanent.

Several experimental techniques have been used for studying morphological behaviour and characterizing mesomorphic structures and their domain size for block copolymers. In particular, electron microscopy⁷ and small angle neutron scattering⁸ have been extensively used for these studies. Morphologies of copolymers with amorphous blocks in general, and styrene-diene block copolymers in particular, have shown that the constituents of segregated microphase can be spherical, cylindrical or lamellar depending upon the relative composition of the two blocks. While the lamellar form a regularly repeating lamellae order, the cylinders arrange themselves in a two-dimensional hexagonal lattice and the spheres in a cubic lattice. The domain size for a given morphology depends on structure, molecular weight and polydispersity, block composition, temperature and polymer-polymer interaction parameter. For styrene-butadiene-styrene triblock copolymer (PS-PB-PS), it has been observed that: (i) for PB volume up to 16%, there is a cubic structure of PB spheres in PS matrix; (ii) for PB volume in the range of about 16–18%, there is an orthorhombic structure formed by short rods of PB in PS matrix; (iii) for PB volume in the range of about 18–36%, there is a hexagonal structure

of PB cylinders in PS matrix; (iv) for PB volume in the range of about 36–60% there is a lamellar structure formed by PB and PS layers alternately arranged; (v) for PB volume in the range of about 60–80% there is an inverse hexagonal structure of PS cylinders in PB matrix; (vi) for PB volume above 80%, there is an inverse cubic structure of PS spheres in PB matrix.

Morphological studies on copolymers with amorphous and crystalline blocks show that the crystalline lamellae usually consist of one or two layers of folded crystallizable blocks. Such structures depend on crystallization temperature, molecular weight and the nature of amorphous and crystalline blocks. For example, while well-organized periodic structures have been observed in styrene–ethylene oxide block polymer, the multiblock copolymers segmented polyurethanes shows microphase separation without any periodic structure. In general, the system shows lamellar structures when both of the blocks of the block copolymers are crystallizable.

Block copolymers in solution

Block copolymers often consists of blocks which are either water or oil compatible and in such cases they exhibit adsorption characteristics and micelle formation in solution. These two fundamental properties which can be suitably controlled provide unique applications to both surface active agents and block copolymers.

Adsorption from solution

The adsorption of polymers onto surfaces plays an important role in many industrial processes. When a surface is exposed to a polymer solution, one of two diametrically different processes generally occurs. In the first, the polymer is enriched in the surface zone (adsorption), while in the second, the surface zone is depleted with respect to the polymer. Since the change in entropy on adsorption is negative (due to the restriction of the translational freedom and of the number of possible conformations of the polymer) adsorption would occur only if the gain in energy is larger than the loss in entropy. Thus there is a critical energy of adsorption which determines whether adsorption or depletion occurs. The value of the critical energy is generally quite small, typically a few tenths of a kT , due to a large number of adsorption sites. Block copolymers, due to their amphiphilic nature are adsorbed on to surfaces as trains, tails and loops (Figure 5).

The efficient adsorption of block copolymers from solution on to the surface of colloidal particles provides a long term stability to the colloidal solutions. Napper⁹ has pointed out that the mechanism of polymeric stabilization of colloidal solutions is governed by steric stabilization or depletion stabilization. In the former

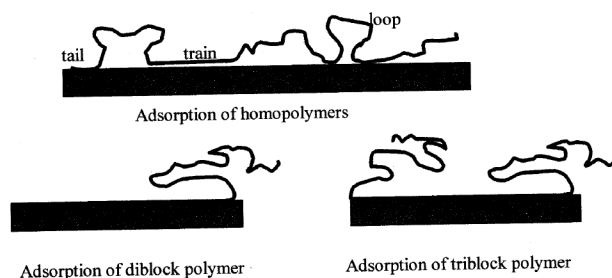


Figure 5. Polymer adsorption at interfaces.

case the particles are stabilized by the attached or adsorbed polymer. The depletion stabilization is provided by unanchored, unattached polymer molecules in the dispersion phase. There have been experimental studies on the conformation of chains confined to solid–liquid interface. Techniques, viz. small angle neutron scattering^{10,11}, nuclear magnetic resonance¹², surface force measurements^{13–15}, different hydrodynamic techniques^{16,17}, etc. have been employed for studying adsorption of polymers. These studies mostly involve equilibrium aspects of the conformations of adsorbed polymer molecule. Techniques that provide kinetic aspects of adsorption were radio labelling¹⁸, total internal reflection fluorescence¹⁹, IR spectroscopy²⁰, reflectometry²¹, and ellipsometry^{22,23}. Surface force measurements provide insight into the structures of adsorbed amphiphile on surface²⁴. Tirrell^{25,26} and coworkers' pioneering studies on the adsorbed block copolymer by surface force apparatus showed that block copolymers are adsorbed with their lyophobic block anchored to the solid surface at a high concentration, leaving the lyophilic block highly extended from their random coil configuration. Small angle neutron scattering gives concentration profile of the polymer segments normal to the interface and thus volume fraction profile.

The majority of the theories of the adsorbed block copolymers are based on the concepts developed by Alexander²⁷ and de Gennes²⁸. These theories assume that polymers are grafted to the surface by one end only. The comprehensive theory which is applicable to adsorption of copolymers is based on the mean field theory^{29,30}. Most of these theories deal with adsorption properties such as surface density, block segment distribution profile, and thickness of adsorbed layers^{31–34}. The adsorption of block copolymers depends on the molecular characteristics of block copolymer, nature of the two blocks of the copolymer, the adsorbing surface and the solvent.

Micellization in selective solvents

Block copolymers aggregate in selective solvents (a good solvent for one block but precipitant for the other) analogous to conventional surfactants (Figure 6).

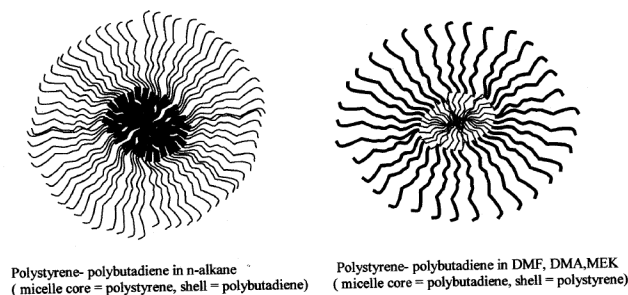


Figure 6. Block copolymer micelles in selective solvents.

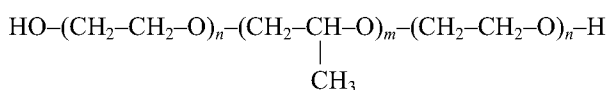
Several review articles^{35–40} deal with micellization of block copolymers. The self-assembly of block copolymer chains in solutions can usually be initiated either by increasing concentration (micelles do form at critical micelle concentration at a fixed temperature, CMC) or by changing the temperature (micelles do form at critical micelle temperature at fixed concentration, CMT). Both CMC and CMT are the fundamental parameters which characterize the solution behaviour of block copolymers. Copolymer micelles are formed through a closed association process and are often spherical in shape with low polydispersity, especially, near the CMC or CMT. The micelle shape (e.g. sphere, rod, etc.) depends on the concentration and molecular characteristics of copolymer and the nature of solvent. The aggregation of block copolymers has been treated as monomolecular micelles and multimolecular micelles, though the latter is generally favoured. Often the CMC of block copolymers is much less than that of conventional surfactants.

Polymeric micelles are made of a swollen core of the insoluble block surrounded by a flexible fringe of soluble blocks (Figure 6). Several different block copolymers with varying molecular characteristics have been examined for their micellization in a variety of solvents (pure and mixed solvents) by a large number of experimental techniques. Block copolymer micelles are characterized by critical micelle concentration, critical micelle temperature, aggregation number, core/shell size and micelle shape. Temperature induced sphere-rod transitions have also been observed in block copolymers⁴⁰. In some cases worm-like micelles have also been observed^{41,42}. The micelle size and shape as observed from above studies largely depend on the type (di-, tri-, multiblock copolymer), nature of the blocks, selectivity of solvents and temperature. There are cases of anomalous behaviour also. For example, one observes large particles with milky opalescence at the onset of micellization of a styrene-butadiene-styrene block copolymer in ethyl acetate⁴³ and isopropyl acetate⁴⁴. Such a behaviour has been attributed to transient formation of large unstable particles. Block copolymer micelles do solubilize substances, otherwise insoluble

in the selective solvent. Solubilization of various substances (both of low and high molecular weight) in copolymer micelles has been investigated^{45–48}.

EO/PO block copolymers

An interesting class of nonionic surface active agents is polyethylene oxide–polypropylene oxide–polyethylene oxide (PEO–PPO–PEO) block copolymers with structure shown below where polyethylene oxide forms the end blocks and polypropylene oxide forms the middle block. These were first introduced commercially by (BASF) under the trade name Pluronic[®]



The possibilities of large variation in total molecular weight and block composition in these copolymers have led to a large number of polymeric surfactants with varying hydrophilic–lipophilic balance (HLB) values. A brief account of surfactant properties of these polymers is also published by Schmolka^{49,50}. In the last decade, extensive studies on solution chemistry of these block copolymers have been made^{51–53}. Several physico-chemical and instrumental techniques, including different scattering and spectroscopic methods, have been used to understand the aggregation behaviour and thermorheological behaviour of solutions of block copolymers over wide temperature ranges and in the presence of various additives. In analogy to conventional surfactants, the micellization of EO/PO block copolymers is entropy driven, and results from structural changes in water on removal of the hydrophobic propylene oxide units. Important characteristic features of EO/PO copolymer aggregation are:

- (i) Strong temperature dependence of CMC (a hundred fold decrease in CMC with an increase in temperature from 20°C to 40°C) is a unique feature of block copolymers. Such a behaviour is accounted for by the fact that the hydrophilic nature of PPO depends on the temperature. This, along with the minor hydrophobic component (presumably diblock copolymer) present as impurity in commercial copolymer samples has been responsible for erratic CMC data reported in literature. Chu and Zhou³⁸ have recently compiled CMCs of several commercially available copolymers. The critical micelle temperature (CMT) may be a better choice than CMC for copolymer micelles.
- (ii) It is generally believed that the dehydration of PPO block with increasing concentration is responsible for micelle formation. CMC of co-

polymers shows a large decrease with PPO block length. The influence of the PEO block length is less pronounced than that of PPO block. For a constant PPO/PEO ratio, the CMC and CMT decrease with increasing molecular weight of copolymer. The micellization of PEO–PPO–PEO in water is achieved at lower concentration than that of reverse pluronics (PPO–PEO–PPO) of similar composition.

- (iii) The micellization of prominently hydrophilic copolymer (e.g. $\text{EO}_{76}\text{PO}_{30}\text{EO}_{76}$) can be achieved at much lower concentration of the copolymer in the presence of a salt like NaCl. Further it is seen that micelle size increases with increase in salt concentration. The micelle growth is seen at temperatures close to the cloud point also. However, no substantial micelle growth is seen for highly hydrophilic copolymer (e.g. $\text{EO}_{103}\text{PO}_{39}\text{EP}_{103}$) with increase in temperature or with addition of salts⁵⁴. It has also been seen that for the above highly hydrophilic copolymer, the water of dehydration from the hydrophilic PEO shell is not uniform unlike the other copolymers. Only a part of PEO adjacent to PPO core of the micelle loses water with increasing temperature or salt concentration.

- (iv) Concentrated solutions of pluronics undergo reversible gelation on warming. The gels have been characterized by X-ray diffraction, thermal polarizing microscopy and differential scanning calorimetry (DSC). It is observed that they consist of cubic structures of micellar subunits. Phase diagrams of some of the pluronics are known. For example, the phase diagram of Pluronic P 85 ($\text{EO}_{26}\text{PO}_{39}\text{EO}_{26}$) is shown in Figure 7. At low concentration and low temperature, the copolymer molecules are present as fully dissolved Gaussian chains. At critical micellization concentration/temperature, spherical micelles are formed. These spherical micelles undergo a hard-sphere crystallization at higher concentrations or temperature. A sphere-to-rod transition in the micellar shape of this pluronic occurs at around 70°C in dilute solutions. This is supported by the observation that the neutron scattering profile of $\text{EO}_{26}\text{PO}_{39}\text{EO}_{26}$ in D_2O shows a significant change. For concentrated solutions, an increase in temperature leads to appearance of another crystalline mesophase consisting of hexagonally ordered rod-like micelles. The two crystalline phases in P85 Pluronic are separated by a liquid phase of prolate or rod-like micelles. On the lower temperature side, P85 exhibits the bcc crystalline phase and at high temperatures it exists in hexagonal mesophase. At temperatures above 80°C, the latter phase melts and a new liquid phase appears.

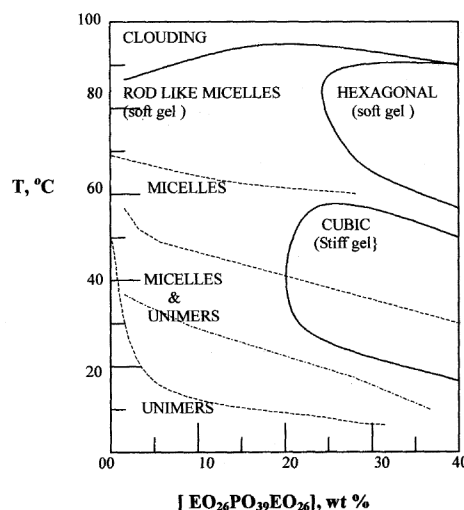


Figure 7. Phase diagram for Pluronic P 85 ($\text{EO}_{26}\text{PO}_{39}\text{EO}_{26}$).

The different ordered (cubic, hexagonal and lamellar) phases of P 85 are schematically shown in Figure 8.

Alexandridis *et al.*⁵⁵ reported the ternary isothermal study of $\text{EO}_{19}\text{PO}_{43}\text{EO}_{19}$ -*p*-xylene- D_2O at 25°C. A record nine different phases, namely, normal (oil-in-water), micellar cubic (I_1), normal hexagonal (H_1), normal bicontinuous cubic (V_1), lamellar (L_α), reverse bicontinuous cubic (V_2), reverse hexagonal (H_2), reverse micellar cubic (I_2) lyotropic liquid crystalline phases, in addition to water-rich (normal micellar, i.e. L_1) and water-lean/oil-rich (reverse micellar solutions, i.e. L_1) solutions have been shown. The ability of EO/PO block copolymers to attain diverse microstructures can be used for numerous practical applications.

Applications of block copolymers

The unique architecture of block copolymers allows them to possess some interesting and novel properties for industrial applications. The use of styrene–butadiene and styrene–isoprene block copolymer as thermoplastic elastomers in footwear is well known. The other thermoplastic elastomers are polyether–polyester and polyether–polyamide. Styrene–diene and styrene–hydrogenated diene triblock copolymers are reportedly good pressure sensitive adhesives and are used for bitumen modification. The interfacial characteristics make block copolymers useful materials as adhesives, sealants, binders for laminates, constituent of coating materials, surface modifiers for fillers and fibers. Blending of block copolymers with other polymers provides new polymeric materials with desired properties. Some grades of high impact polystyrene are such systems. Block copolymer blends with homo- or copolymers of different kinds (elastomers, thermoplasts

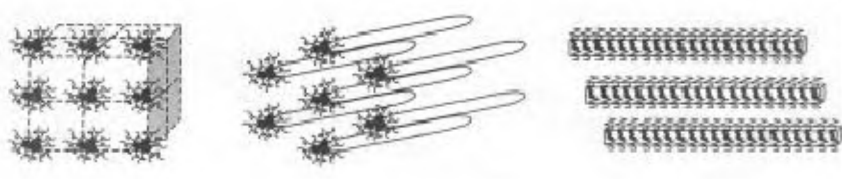


Figure 8. Organized copolymer structures in concentrated aqueous solutions.

and thermosets) lead to interesting mechanical properties. Surfactant-based applications of block copolymers are as colloid stabilizers in dispersion polymerization in aqueous and nonaqueous media (particularly in the latter case where the conventional surfactants fail to perform satisfactorily), in emulsion stabilization, microemulsion polymerization and polymeric emulsions. EO/PO block copolymers find numerous applications in medical, pharmaceutical, textile, cosmetic, detergents and pesticidal formulations.

- Riess, G., Hurtrez, G. and Bahadur, P., in *Encyclopaedia of Polymer Science Engineering*, Wiley, NY, 1985, vol. 2, pp. 324–434.
- Szwarc, M., Levy, V. and Milkovich, R., *J. Am. Chem. Soc.*, 1956, **78**, 2656.
- Gallot, B. R. M., *Adv. Polym. Sci.*, 1978, **29**, 85.
- Meier, D. J., in *Block and Graft Copolymers* (eds Burke, J. J. and Weiss, V.), Syracuse University Press, Syracuse, NY, 1973.
- Helfand, E., *Macromolecules*, 1975, **8**, 552.
- Sanchez, I. C., *J. Macromol. Sci. Phys.*, 1980, **17**, 565.
- Mortensen, K. and Talmon, Y., *Macromolecules*, 1995, **28**, 8829.
- Mortensen, K., *J. Phys.: Condens Matter*, 1996, **8**, A103.
- Napper, D. H., *Polymer Stabilization of Colloidal Dispersions*, Academic Press, New York, 1983.
- Cosgrove, T., *J. Chem. Soc. Faraday Trans. 1*, 1990, **86**, 1323.
- Cosgrove, T., Heath, T. G., Ryan, K. and Crowley, T. L., *Macromolecules*, 1987, **20**, 2879.
- Cosgrove, T. and Ryan, K., *Langmuir*, 1990, **6**, 136.
- Taunton, H. J., Toprakcioglu, C. and Klein, J., *Macromolecules*, 1988, **21**, 3333.
- Luckham, P. F., *Adv. Colloid Interface Sci.*, 1991, **34**, 191.
- Hadziioannou, G., Patel, S. and Tirrell, M., *J. Am. Chem. Soc.*, 1986, **108**, 2896.
- Koopal, L. K., Hlady, V. and Lyklema, J., *J. Colloid Interface Sci.*, 1988, **121**, 49.
- Cohen-Stuart, M. A., Waajen, F. H. W. H., Cosgrove, T., Vincent, B. and Crowley, T. L., *Macromolecules*, 1984, **17**, 1825.
- Pefferkorn, E., Carroy, A. and Varoqui, R., *J. Polym. Sci., Polym. Phys. Ed.*, 1985, **23**, 1997.
- Lok, B. R., Cheng, Y.-L. and Robertson, C. R., *J. Colloid Interface Sci.*, 1983, **91**, 104.
- Cosgrove, T., Prestidge, C. A. and Vincent, B., *J. Chem. Soc. Faraday Trans.*, 1990, **86**, 1377.
- Dijt, J. C., Cohen-Stuart, M. A., Hofman, J. E. and Fleer, G., *J. Colloids Surf.*, 1990, **51**, 141.
- Stronberg, R. R., Passaglia, E., Tutas, D. J., *J. Res. Natl. Bur. Stand. Sect. A.*, 1964, **68**, 601.
- Takahashi, A., Kawaguchi, M., Hirota, H. and Kato, T., *Macromolecules*, 1980, **13**, 884.
- Israelchavilli, J. N. and Adams, G. E., *J. Chem. Soc. Faraday Trans. 1*, 1978, **74**, 975.
- Tirrell, M., Patel, S. and Hadziioannou, G., *Proc. Natl. Acad. Sci.*, 1987, **84**, 4725.
- Hadziioannou, G., Patel, S., Granick, S. and Tirrell, M., *J. Am. Chem. Soc.*, 1986, **108**, 2869.
- Alexander, S., *J. Phys.*, 1977, **38**, 983.
- De Gennes, P. G., *Macromolecules*, 1986, **19**, 686.
- Scheutjens, J. M. H. M. and Fleer, G. J., *J. Phys. Chem.*, 1979, **83**, 1619.
- Scheutjens, J. M. H. M. and Fleer, G. J., *J. Phys. Chem.*, 1980, **84**, 178.
- van Lent, B. and Scheutjens, J. M. H. M., *Macromolecules*, 1989, **22**, 1931.
- Evers, O. A., Scheutjens, J. M. H. M. and Fleer, G. J., *Macromolecules*, 1990, **23**, 5221.
- Griffiths, P. C., Cosgrove, T., Shar, J., King, S. M., Yu, G.-E., Booth, C. and Malmsten, M., *Langmuir*, 1998, **14**, 1779.
- Munch, M. R., Gast, A. P., *Macromolecules*, 1988, **21**, 1366.
- Tuzar, Z. and Kratochvil, P., *Adv. Colloid Interface Sci.*, 1976, **6**, 201.
- Tuzar, Z. and Kratochvil, P., in *Surface and Colloid Science* (ed. Matijevic, E.), Plenum Press, New York, 1993, vol. 15, pp. 1–83.
- Price, C., in *Developments in Block Copolymers* (ed. Goodman, I.), Applied Science Publishers, London, 1982, vol. 1, pp. 39–80.
- Chu, B. and Zhou, Z., in *Nonionic Surfactants, Surfactant Science Series* (ed. Nace, V. M.), 1996, vol. 60, p. 67.
- Bahadur, P. and Riess, G., *Tenside Surf. Deterg.*, 1991, **28**, 173.
- Price, C., *Pure Appl. Chem.*, 1983, **55**, 1563.
- Mortensen, K., Talman, Y., Gao, B. and Kops, J., *Macromolecules*, 1997, **30**, 6764.
- Canham, P. A., Lally, T. P., Price, C. and Stubbersfield, R. B., *J. Chem. Soc. Faraday I*, 1980, **76**, 1857–1867.
- Lally, T. P. and Price, C., *Polymer*, 1974, **15**, 325.
- Tuzar, Z., Sikora, A., Petrus, V. and Kratochvil, P., *Makromol. Chem.*, 1977, **178**, 2743.
- Tuzar, Z. and Kratochvil, P., *Makromol. Chem.*, 1973, **170**, 177.
- Tuzar, Z., Bahadur, P. and Kratochvil, P., *Makromol. Chem.*, 1981, **182**, 1751.
- Nagarajan, R., Barry, M. and Ruckenstein, E., *Langmuir*, 1986, **2**, 21.
- Oranli, L., Bahadur, P. and Riess, G., *Can. J. Chem.*, 1985, **63**, 2691–2696.
- Schmolka, I. R., *J. Am. Oil Chemists' Soc.*, 1977, **54**, 110.
- Lundsted, L. G. and Schmolka, I. R., in *Block and Graft Copolymerization* (ed. Ceresa, R. J.), Wiley, New York, 1976, vol. 2.
- Chu, B., *Langmuir*, 1995, **11**, 414.
- Almgren, M., Brown, W. and Hvidt, S., *Colloid Polym. Sci.*, 1995, **273**.
- Alexandridis, P. and Hatton, T. A., *Colloids and Surfaces A*, 1995, **1**, 96.
- Jain, N., Aswal, V. K., Goyal, P. S. and Bahadur, P., *J. Phys. Chem. B*, 1998, **102**, 8452.
- Alexandridis, P., Olsson, U. and Lindman, B., *Langmuir*, 1998, **14**, 2627.