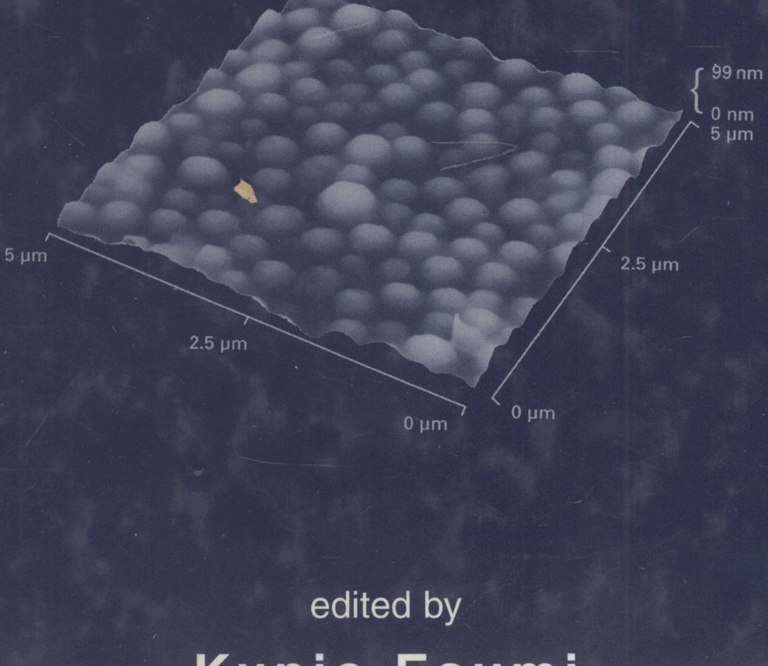
Polymer Interfaces and Emulsions



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To Setsuko with thanks for her patience and love

Preface

Polymeric materials are used for many applications in a wide array of technological areas, and their surface/interface characteristics as well as solution properties are of great importance for their application. Considerable theoretical and experimental work has been carried out to understand the properties and performance of polymeric materials in solution and at various interfaces. In addition, polymer latexes produced by emulsion polymerization have a large and still growing importance as model colloids and industrial products. It is obvious that these polymer colloids will find further use in microdevices and micromachines.

The volume has 14 chapters. K. Ishizu outlines the structural ordering in polymer solutions such as the $(AB)_n$ star, core-shell polymer microsphere, and block copolymer in Chapter 1. In Chapter 2, S.-B. Lee deals with the influence of polymer surface structure on polymer surface behavior for polymer systems including block copolymers and graft copolymers. G. H. Ma reviews the advances in preparations of polymeric microspheres and gives examples for their application in Chapter 3. Some new methodologies for latex particle chemical heterogeneity as well as the fundamentals of each relevant methodology are discussed in Chapter 4, by F. Galembeck and E. Fátima de Souza. Chapter 5, by F. J. de las Nieves, A. Fernández-Barbero, and R. Hildago-Alvarez, outlines the electrokinetic behavior of polymer colloids and discusses the anomalous electrokinetic behavior. K. Furusawa focuses on the preparation of composite particles consisting of polymer latices and inorganic colloids and their physicochemical properties in Chapter 6.

Chapter 7 by H. D. Ou-Yang and M. M. Santore, reviews the current approaches used to understand polymer-bridging of colloids both thermodynamically and kinetically. T. Miyajima presents the polyelectrolytic nature and metal complexation of polyelectrolyte systems in Chapter 8. In Chapter 9, by S. G. Dixit and A. K. Vanjara, the adsorption of quaternary ammonium compounds at polymer surfaces is described. In Chapter 10, W. Loh, J. R. Lopes, and A. C. S. Ramos review adsorption onto poly(tetrafluoroethylene) from aqueous solutions. Chapter 11, by Yu. S. Lipatov, T. T. Todosijchuk, and V. N. Chornaya, deals with the analysis of the data on the adsorption of polymer mixtures at solid interfaces from semidiluted and concentrated solutions. K. Esumi discusses polymer adsorption as well as the simultaneous adsorption of polymer and surfactant at oxide surfaces in Chapter 12. In Chapter 13, Y. Gushikem and E. A. Toledo describe the preparation of oxide-coated cellulose and some physicochemical characteristics of the oxide particles dispersed onto the polymer in the form of a fiber or membrane. M. Morra, C. D. Volpe, and S. Siboni outline the basic concepts and definitions related to acid–base properties and discuss some problems estimated with different methods.

I would like to thank Professor A. T. Hubbard for his advice and help, as well as the authors who participated in this effort. I am indebted to Mr. Joseph Stubenrauch and Ms. Anita Lekhwani of Marcel Dekker, Inc., for their assistance in preparing this volume.

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1

Structural Ordering in Polymer Solutions

Koji Ishizu
Tokyo Institute of Technology, Tokyo, Japan

I. INTRODUCTION

The star-branched, or radial, polymers have the structure of linked-together linear polymers with a low-molecular-weight core. Generally, the star polymer has smaller hydrodynamic dimensions than that of a linear polymer with an identical molecular weight. The interest in star polymers arises not only from the fact that they are model branched polymers but also from their enhanced segment densities. Zimm and Stockmayer were the first to study the conformation of star-shaped polymers [1]. Recently, Daoud and Cotton [2] have studied the conformation and dimension of a star polymer consisting of three regions: a central core, a shell with semidilute density in which the arms have unperturbed chain conformation, and an outer shell in which the arms of the star assume a self-avoiding conformation. Stars with multiarms (the critical number of arms is estimated to be of order 10^2) are expected to form a crystalline array near the overlap threshold (C^*) [3].

Leibler [4] has developed a Landau-type mean-field theory on the microphase-separation transition in diblock copolymers and has presented the phase diagram for the microdomain morphologies in the weak-segregation limits as a function of segregation power and composition of the block copolymer. Ohta and Kawasaki [5] have generalized Leibler's theory to the strong-segregation limit by taking into account a long-range interaction of the local order parameter on the basis of the Ginzburg–Landau-type mean-field theory. More recently, Fredrickson and Helfand [6] have corrected Leibler's mean-field theory to take into account the effect of composition fluctuations on the microphase-separation transition. These theories expect that the morphologies are changed with the segregation power. Because the segregation power is a function of temperature, morphology may be reversibly controlled and, hence, the transition between the different kinds of morphology may occur by changing temperature.

The star-block copolymers have a molecular conformation similar to star polymers. De la Cruz and Sanchez [7] have calculated the phase-stability criteria and static structure factors in the weak-segregation limits for an n-arm diblock copolymer [$(AB)_n$ star]. According to their results, as the arm number (n) becomes large, the $(AB)_n$ star begins to develop a "core and shell"-type structure. This self-segregation or self-micellization tends to create significant concentration fluctuations at the core–shell interface.

Four ordered microphases for block copolymers are well known; they consist of alternating layers, cylinders on a hexagonal lattice, spheres on a body-centered-cubic (BCC) lattice, and a bicontinuous double-diamond structure [8,9]. The spherical, cylindrical, and lamellar structures are all stable in the strong-segregation limits [10]. The stable phases are considered to be spherical microdomains for the volume fraction of either diblock, $f = \sim 0.17$. If the structure of the self-assemblies can be fixed by cross-linking of the spherical parts (the spherical microdomains in the solid state and the core in solution), the cross-linked products can form core–shell polymer microspheres (see Fig. 1). In fact, polystyrene (PS)–*block*—polybutadiene(PB)–*block*–PS triblock copolymer micelles with cores of PB blocks in dilute solution were stabilized by cross-linking the chains in the micellar cores by ultraviolet (UV) irradiation in the presence of a photoinitiator and by fast electrons [11–13]. The irradiated, stabilized micelles, examined by light scattering, sedimentation, and gel permeation chromatography (GPC), did not decompose upon heating or when placed in good solvents for both blocks. Others have obtained the core–shell polymer microspheres by cross-linking of the core domains in micelles formed in selective solvents for several different block and graft copolymers [14–21]. It was concluded from these results that the reaction rate of intra micelle cross-linking and the lifetime of the polymer micelle were both important for successful cross-linking of the polymer micelle. A core–shell polymer microsphere could be synthesized when intra micelle cross-linking occurred before the breakup of the micelle.

The microphase-separated structures in bulk films are more stable than micelles in solution. The cross-linking of spherical microdomains in films is often a superior method for the preparation of core–shell polymer microspheres. A well-defined PS–*block*—poly(4-vinylpyridine) (P4VP) diblock copolymer (P4VP block, 24 wt%) was prepared by a sequential anionic polymerization [22]. The microdomain structure in this specimen showed a texture of discrete P4VP spheres in a PS matrix. These segregated P4VP chains in a sphere were cross-linked by using quaternization with 1,4-dibromobutane (DBB) vapor in the solid state. These microsphere particles had a narrow size distribution. The micelle of core–shell polymer microsphere moved like the pseudo-latex in solution. The particles of core–shell microspheres were well aligned in a hexagonal array on the

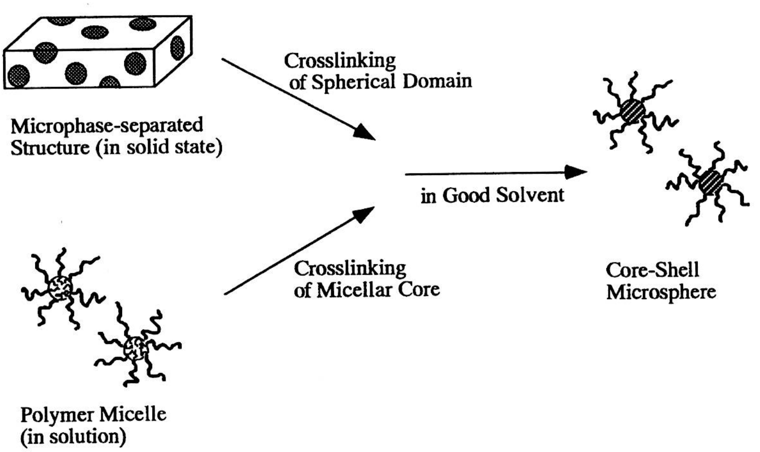

Figure 1 Schematic presentation of synthesis routes on core–shell polymer microspheres.

carbon substrate from two-dimensional observation [23,24]. It was expected that in the core–shell microspheres, such crystalline order in solution appeared close to the C^*.

In this chapter, we outline the structural ordering in polymer solutions such as the star, $(AB)_n$ star, core–shell polymer microsphere, and block copolymer. The ordering mechanisms of these polymers are also mentioned in detail. We also discuss the architecture of polymeric superstructures by locking cubic lattices formed by core–shell microspheres.

II. STRUCTURAL ORDERING IN STAR POLYMER SOLUTIONS

As mentioned in Sec. I, the stars with multiarms are expected to form a crystalline array near the C^*. Several groups [25–27] investigated the ordering phenomena of stars [$8 <$ arm number(n) < 20] around the C^* by means of small-angle neutron scattering (SANS) and small-angle x-ray scattering (SAXS). They showed that ordering was very weak for 8- and 18-arm stars but became stronger with increasing arm numbers.

Star polymers are best prepared by coupling anionic living polymers with multifunctional electrophilic coupling agents. The coupling agents are either multifunctional chloromethylated benzene derivatives or multifunctional chlorosilane compounds. In general, it is difficult to extend the functionality of the stars with these compounds. Roovers et al. [28,29] have reported a new synthesis method of regular PB star molecules and their dilute-solution properties. These 64- and 128-arm stars were prepared by coupling of living PB–lithium with dendrimers having chlorosilane groups at the surface. At present, the most convenient way of preparing star polymers possessing more than 10 arms is by cross-linking monocarbanioic chains with divinylbenzene (DVB) [30–33]. More recently, we synthesized polyisoprene (PI) stars by the free-radical cross-linking of the vinylbenzyl-terminated PI macromonomers with DVB in *n*-heptane that dissolved PI but precipitated DVB [34]. The radical copolymerization of PI macromonomer with DVB led to microgelation in micelles formed by the primary copolymer radicals in the selective solvent (organized polymerization).

This idea could be applied to the PI star synthesis by anionic cross-linking of PI monoanions with DVB in *n*-heptane [35]. The anionic copolymerization of PI–lithium with DVB led to microgelation in micelles formed by the primary copolymer anions in the selective solvent. All of the PI stars prepared had an apparently narrow molecular-weight distribution ($\overline{M}_w/\overline{M}_n = 1.03–1.07$) from GPC profiles.

Table 1 lists the characteristics of PI stars. For example, the $(SI42)_{43}$ sample in Table 1, which shows the star structure having an arm molecular weight of 4.2×10^4 and arm number $n = 43$. All of the feed DVB was consumed in the core formation of star polymers. It was possible to estimate the core radius (R_0) of PI stars,

Table 1 Characteristics of PI Stars

	Molecular weight						
Code	Arm[a] ($10^{-4}\ M_n$)	Star[b] ($10^{-6}\ M_w$)	Arm number (number/ molecules)	R_g[c] (nm)	R_h[d] (nm)	R_0[e] (nm)	C^*[f] (wt%)
$(SI33)_4$	3.3	0.12	4	16.0	10.7	—	3.9
$(SI42)_{43}$	4.2	1.87	43	30.1	24.7	2.7	4.9
$(SI27)_{91}$	2.7	2.79	91	29.2	22.2	4.4	10.1
$(SI42)_{111}$	4.2	5.00	111	41.3	33.0	4.7	5.5
$(SI08)_{237}$	0.8	2.09	237	19.1	18.1	3.9	14.1

[a] Determined by GPC using PI standard samples.

[b] Determined by static light scattering (SLS).

[c] Radius of gyration (R_G) was determined by SLS.

[d] Hydrodynamic radius (R_H) was determined by dynamic light scattering (DLS; scattering angle = 90°).

[e] Core radius (R_0) was calculated from the equation $n = (4\pi/3P_E)R_0^3\rho N_A$, assuming that the core was of spherical form. ρ-density of DVB core; N_A-Avogadro's number; P_E-the number of monomer units (mixture of DVB and ethylstyrene) at the arm PI terminal end.

[f] Overlap threshold (C^*) was calculated from the equation $C^* = 3M_w/4\pi N_A R_H^3$.

because the yield of the star and the feed amounts of DVB were known. The values of R_0 were very small compared to the corresponding radii of gyration (R_G) for PI stars. For dendrimers used as coupling agents, R_0 was estimated to be 2.4–2.5 nm for the generation $m = 3–4$ [36]. Therefore, the core size of such PI stars seemed to correspond to the size of dendrimer with m somewhat larger than $m = 4$.

The hydrodynamic radius (R_H) was measured by dynamic light scattering (DLS) at 90° of scattering angles. The values of R_H are also listed in Table 1. The value of R_G/R_H is a sensitive fingerprint of the inner density profile of star and polymer micelle. The observed values of R_G/R_H approached unity as n became large. Even the stars with multiarm behaved not as neat hard spheres ($R_G/R_H = 0.775$) but as soft spheres that were penetrable near the outer edge in a good solvent.

We studied structural ordering of PI stars in cyclohexane [37]. According to the theoretical results of Witten et al. [3], a crystalline structure of the stars should appear near the C^*. The calculated C^* for each PI star is also listed in Table 1. Below C^*, the star polymers remain isolated, as any arrangement of stars in solution is expected near or above C^*. First, the SAXS intensity profiles of the $(\mathrm{SI42})_{43}$ star were measured at 6 and 13 wt% cyclohexane polymer solutions. Both polymer concentrations were higher than C^* (4.9 wt%). However, no regular scattering peaks appeared at these concentrations. As a matter of course, the structural ordering had never been observed in the $(\mathrm{SI33})_4$ star.

Figure 2 shows typical SAXS intensity profiles for the $(\mathrm{SI08})_{237}$ star in the small-angle region, where $q\ [= (4\pi/\lambda)\sin\theta]$ is the magnitude of the scattering maxima and values in parentheses indicate the interplaner spacings (d_1/d_n) calculated from Bragg reflections. Below 8 wt% of polymer concentration ($C^* = 14.1$ wt%), no regular scattering peaks appeared due to disordering. At 11 wt% of polymer concentration (Fig. 2a), the first four peaks appear close together at the relative q positions of $1 : \sqrt{2} : \sqrt{3} : 2$ as shown in parentheses. The interplaner spacing (d_1/d_n) at the scattering angles is relative to the angle of the first maximum according to Bragg's equation: $2d \sin\theta = n\lambda$ (where θ is one-half the scattering angle and $\lambda = 1.5418$ Å). In general, this packing pattern appears in the lattice of not only simple cubic (SC) but also body-centered-cubic (BCC) structures. As mentioned, in the section of $(\mathrm{AB})_n$ stars, the $(\mathrm{AB})_n$ stars with a multiarm were packed in the lattice of a BCC structure near C^* [38,39]. The conformation of stars can be regarded as similar to one of $(\mathrm{AB})_n$ stars in solution. It is reasonable that these values correspond to the packing pattern of (110), (200), (211), and (220) planes in a BCC structure.

In the SAXS intensity profile at 33 wt% of the polymer concentration, the complicated scattering peaks appear as shown in Fig. 2b. The first five peaks appear at the relative q positions of $1 : \sqrt{4/3} : \sqrt{2} : \sqrt{8/3} : \sqrt{3}$. In general, the relative q positions of $1 : \sqrt{4/3} : \sqrt{8/3}$ correspond to a packing pattern of (111), (200), and (220) planes in a face-centered-cubic (FCC) structure. Therefore, it is concluded that the stars are packed in the mixed lattice of BCC and FCC structures