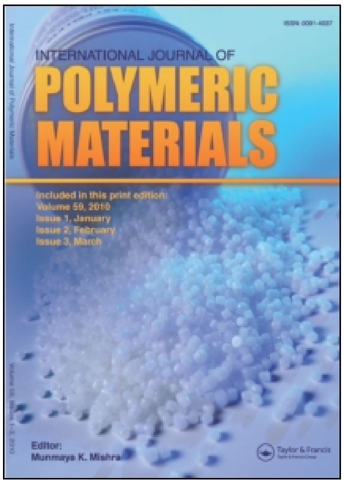

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POLYMERS IN SOLUTIONS AND BLENDS

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This review covers the sessions of "Solution Properties" and "Polymer Gels". The five special subjects have been reviewed; (1) multicomponent solution system, (2) polymer blend, (3) kinetics of emulsion polymerization, (4) micelle, and (5) interaction of polyelectrolyte particles.

Multicomponent solution system

Thermodynamic properties of the three component system composed of solvent (1) + solvent (2) + polymer (3) were discussed by Y. Ishitaka and M. Nakata (838, E257) using the second virial coefficient A_2 observed by static light scattering measurements. In this system the Gibbs free energy of mixing can be described by the generalized Flory-Huggins equation with an extra term $g_T\ (u_2, \pi_3) = \alpha(u_2) + \beta(u_2)\pi_3$, where u_2 is the volume fraction of solvent (2) in the mixed solvent and π_3 is the volume fraction of polymer.

Based on the analysis of experimental data the interaction parameter $g_{12}(u_2)$ for the mixed solvent is closely connected with g_T. It is well known that the cosolvency may be observed when g_{12} becomes a larger positive value.

In this report the authors were interested in studying the ternary system [poly(methyl methacrylate) + 1,4 dioxan + dichloromethane] in order to obtain the relation between g_T and g_{12} since g_{12} is negative and each solvent is a good solvent for PMMA. The A_2 values observed by light scattering were plotted against u_2. The A_2 values were positive and slightly lower level than the straight line connecting between A_2 at $u_2 = 0$ and 1.

In conclusion, if the function of g_T could be described as $g_T = ag_{12} + bg_{12}\pi_3$, the A_2 values predicted by the Flory-Huggins equation agreed with the experimental values of A_2 when one put $a = 1.04$ and $b = 1.09$.

K. Kawate and M. Nakata (839, E258) measured the cloud-point temperature for the dilute solution of polystyrene (3) + nitroethane(1) + cyclohexane(2). This mixed solvent has a critical temperature at 22.9°C.

The Gibbs free energy of mixing for the solvent was initially determined as a function of temperature by vapor pressure measurements.

When polystyrene($M_w = 5 \times 10^4$) was dissolved in the mixed solvent the cloud-point decreased with decreasing polystyrene concentration. The A_2 values observed in the mixed solvent of the critical composition were almost independent of temperature and were as large as that in good solvent over the range from 25° to 60°C.

N. Nemoto, T. Kojima *et al.* (855, E266; 1971, E243) studied self-diffusion coefficient(D_s) and steady viscosity(η) of linear polystyrenes in the concentrated regime. Seven polystyrene samples(PS) with weight-average molecular weight from 43,900 to 2,890,000 were labelled with a photobleachable dye and were dissolved in 40 wt% dibutylphthalate(DBP) solutions. The D_s for homopolymers and also the tracer diffusion coefficient (D_{tr}) in the 40 wt% DBP solution of PS with $M = 43{,}900$ were measured by using the forced Rayleigh scattering technique[1]. The viscosity were measured by a cone-plate type Rheometer in the 40 wt% DBP solution. The molecular weight dependence of D_s thus obtained was expressed as $D_s \propto \alpha$ $M^{-2.6 \pm 0.2}$ over the whole molecular weight range investigated.

Based on the molecular theories of polymer dynamics, the authors assumed that friction properties both in the concentrated solution and in melts might be described by the multiplication of two terms with different molecular interaction; the first term contained the segment friction coefficient(ζ_0) and its temperature dependence and the other was the topological constraint associated with entanglement, which changed as a function of polymer concentration(c) and molecular weight(M). The product of D_s and η could be related to the extent of entanglement per diffusing polymer, since both values were described by the same segment frictional motion with the same characteristic relaxation time. Therefore, the reduced form of $D_s\ \eta$ divided by the theoretical value for the free-draining Rouse chain ($cRT\ R_g^2/6M$) may be dependent only on the entangled number (M/M_e); where c is a constant, R_g is the radius of gyration and M_e is the molecular weight between entangled points.

Using experimentally estimated values from the concentrated solution and melts, the plots of $D_s\eta/(cRT\ T_g^2/6M)$ against M/M_e appeared to be valid, qualitatively.

In order to compare D_s in the concentrated solution with that in melts, the reduced form of $\log\{D_s(M)/D_s(M_e)\}$ was plotted against $\log(M/M_e)$, where M_e values were estimated as 42,000 and 18,000 in the 40wt% solution and in melts, respectively.

The reduced data make one master curve in the range of $10 > M/M_e > 1$. For $M/M_c > 10$, i.e., in the highly entangled region, they could not compose one master curve but the data in the concentrated solution showed the stronger molecular weight dependence, while the data in melts satisfied the functional relation of the molecular weight dependence of D_s predicted by the tube model: $D_s \propto M^{-2}$.

The tracer diffusion coefficient (D_{tr}) for homopolystyrene(PS) dissolved in an imhomogeneous matrix solution produced from a microdomain structure of tri-block copolymer was measured by T. Inoue, N. Nemoto *et al.* (856, E266; 1974, E244) using the forced Rayleigh scattering technique. The copolymer sample was styrene-ethylenebutylene-styrene tri-block copolymer(SEBS, $M_w = 1.04 \times 10^5$, PS wt% = 29.8). Concentrations of labelled PS was 1 wt% and the matrix solution was 29 wt% DPB solution of SEBS, DBP is a preferential solvent for the styrene block and SEBS dissolved in DBP as a micelle. The spatial structure of micelle particles packed in solution was analyzed by small angle X-ray scattering experiments and modelled using the paracrystal theory.

The spherical particles of 16 nm in radius composed from ethylenebutylene block chains are dispersed in the form of the face centred cubic lattice with lattice size of 64nm. The decay curves of diffracted light can be analyzed with a single exponential type over the molecular weight ranging from 6,000 to 102,000. For $M_w > 102{,}000$, the decay curves have been decomposed in two modes(D_1 and D_2) because of the appearance of one peak in the curve.

Plotting D_{tr}, D_1 and D_2 against molecular weight of PS with double-logarithmic scale, the molecular weight dependence of Rouse-type, $D_s \propto M_w^{-1}$, was found in the low molecular weight region and also agreed with the tendency for the molecular weight dependence of D_s estimated in the entangled matrix solution composed by 13 wt% DBP solution of PS with infinite molecular weight.

Polymer Blend

T. Nose (848, E262) theoretically studied the concentration flucation dynamics in ternary polymer blend by using the random phase approximation. The blend consisted of volume fraction π_1 of polymer A with degree of polymerization P_1, π_2 of polymer B with P_2 and π_3 of polymer B with P_3.

The dynamic structure factor in ternary blend

$$S_{i,j}(q;t,\tau) = \langle|\delta\pi_1(q;t)\delta\pi_1(-q;t+\tau)|\rangle$$

were obtained by solving the diffusion equation under the assumption of incompressibility of the system.

Near the spinodal point the time correlation function of concentration fluctuation $S(q,\tau)$ in the stable region can express the following form:

$$S(q,\tau) = S(q,O)\exp(R\tau)$$

where R are explicitly given by functions of polymerization index (P_i) and Onsager's phenomenological coefficient of each component and interaction parameter between the polymer A and B. The interesting result is that the ternary system can be regarded as a quasi-binary system in dynamics of concentration fluctuations near the spinodal point.

Phase separation behaviour of poly(methylethylsiloxane) (PMES) with bimodal molecular weight distribution/poly(dimethylsiloxane)(PDMS) ternary blend system was studied by H. Horiuchi and T. Nose (849, E263) by using static and time-resolved light scattering technique. Here, polymer A(species 1) was PDMS with high molecular weight enough for entanglement and polymer B(species 2 and 3) were two fractions of PMES having $M_2 = 3.14 \times 10^3$ and $M_3 = 6.10 \times 10^3$, respectively. Cloud-point curves were measured by intensity changes of scattered light as a function of π_1 at the prescribed τ values ($\tau = \pi_2/(\pi_2 + \pi_3)$). The upper critical solution temperature increased with decreasing τ in the total PMES component. From this result, the temperature dependence of χ for PMES was determined as $\chi = 4.07/T - 0.0020$.

In the early stage of phase separation, the wave length of a dominant concentration fluctuation was in disagreement with the predicted values estimated from the temperature dependence of χ using the linear theory.

(3) Kinetics of Emulsion Polymerization

T. Matsuo and S. Hashiya (861, E269; 1950, E236) studied the emulsion polymerization kinetics of methyl methacrylate using a photoionization initiation reaction technique. A homemade rapid angular scanning photometer used in this work was improved for these experiments. The photometer could measure the intensity of scattered light on scanning the scattering angle from 20° to 160° in a cycle of one second. The dynamic range of intensity level observed was extended to a value of 10^6 by using a computer control of the high voltage used to control the photomultiplier tube. Therefore, one could observe the time-dependent change of scattered light intensity at the early stage of surfactant-free emulsion polymerization.

Mixed aqueous solutions of methyl methacrylate monomer and 4,4′-azobis-4-pentanoic acid poured directly in a light scattering cell through the Millipore filter were irradiated at 30°C with mercury lamp under N_2 atmosphere. After a prescribed period of irradiation the number of particles arisen in the cell increases with increasing the scattered light intensity and with continuous decrease of the monomer concentration, indicating progress of successive coagulation. The initial rate constant of coagulation(k) was estimated by the Smoluchowski equation.

It is concluded that the rate increases rapidly at the initial stage and the polymer particles become more stable with the elapse of time because of the increase of their charge on a particle.

(4) Micelle

H. Urakawa, K. Kajiwara *et al.* (871, 872, E274) investigated the micellar structure of polyoxyethylene-mono-n-alkyl ether (C14E8) in aqueous solutions. The small-angle X-ray scattering (SAXS) measurements for C14E8 were carried out using the SOR instrument of "Photon Factory" in Tsukuba over the scattering vector ranging from 0.013 to 0.335 A^{-1} as a function of temperature and concentration of C14E8.

From the scattering curve thus observed the phases of the micellar solution, which were previously assigned as isotropic, cubic, hexagonal and lamellar, were confirmed by reference to the phase diagrams proposed by Jahns and Finkellmann[2]. For the isotropic phase at low concentration of C14E8 Fourier-transformation of SAXS intensities was used to obtain the radial distribution function P(r). P(r) of the 5% C14E8 solution at 20°C exhibits two maxima and one minimum. The negative minimum of P(r) suggests the inhomogeneous electron density distribution in the micelle, i.e., a skin-core structure. Moreover, a number of maxima and minima suggest the ordered intermicellar structure in the isotropic phase at high concentrations.

T. Shikata (1968, E242) investigated the static and dynamic light scattering of thread-like micelles of 3×10^{-7} cm in radius which were composed from cationic surfactant cetyltrimethylammonium bromide (CTAB) in sodium salicylate (NaSal) aqueous solution. Under the condition of $C_D D_A^{-1} = 1$ the pronounced vioscoelastic properties of the micelle solutions manifested as C_D increased because of the chain entanglement between thread-like micelles; where C_D was the CTAB concentration and C_A was the NaSal concentration as added-salt[3].

The concentrations of CTAB used were 1.75, 5.0 and 10.0mM, respectively. The solutions were prepared by dissolution in water contained the equimolar concentration of NaSal and were allowed to stand for two days before measurements. The correlation lengths ξ were obtained from the q^2 dependence of scattered light intensity, where q is the scattering vector. The relationship of ξ with C_D as ξ $C_D^{-0.9}$ corresponded to that in semi-dilute regime of polymer solution at the theta temperature.

The correlation function observed in three different C_D were analyzed by using two different exponential decays decomposed to two modes and two diffusion coefficients were estimated as D_1 and D_2 ($D_1 > D_2$). The D_1 values thus estimated were independent of q at 10 mM of C_D, while at 1.75mM and also at 5 mM, the unique stepwise increase of D_1 with the scattering angle was observed as reflecting intramicellar motion such as bending with nodes at the entangled points.

In the region of $q\xi < 1$ the D_2 values were the constants predicted by the cooperative diffusion constant as $D_{coop} = kT/6\pi\eta\xi$). For $q\xi > 1$ the q dependence of D_2 agreed with the proportionality of $D_{app} = (kT/16\eta)q$. These observations suggest that the micellar systems of CTAB in an aqueous NaSal solution behave like a semi-dilute polymer solution.

(5) Interaction between polyelectrolyte particles

The ordered structure formation of deionized monodisperse colloidal sphere has been studied by many authors. In the higher particle concentration, i.e. when the average distance between particles is shorter than a hundred nanometer, it is well known that the disorder-order phase transition of colloid particles can be explained by the DLVO theory based only on the electrostatic repulsive interaction.

Recently, in the very dilute region where the particle distance becomes more than several micrometer, some extra-ordinary behaviour has been investigated using experiments with microscopes, light scattering, SAXS and spectroscopy. In the SPSJ meeting of this year there were three groups of researchers concerning the studies of interaction between polyelectrolyte particles which fall into this category. Although some topics have been previously reviewed in Polymer Yearbook 5 the following additional remarks can be made.

T. Okubo (818–820, E247–248; 824–826; E250–251; 2061–2069, E275–277) studied the extraordinary behaviour by using microscopic observation, reflection spectroscopy, and reological measurements[4]. On the basis of a large number of his experimental results, the author proposed the following view. The deionization by using ion exchange resins was a surprisingly time-consuming process and sometimes it took over a week. Therefore, if the deionizing was completed, all the extra-ordinary behaviour observed in this system could be explained satisfactorily only by the repulsive interaction due to the Debye screening length. Moreover, the strength of the repulsive force between particles was directly proportional to the number of changes on the particle. For highly charged particles the force became effective at short range. On the contrary, for slightly charged particles these forces prevail to long range.

K. Ito and N. Ise (835–837, E256–257; 2046–2051, E270–271) have often emphasized the existence of the interparticle attractive interaction for the following reasons; (1) the spacing between solute particles ($2D_{exp}$) observed by SAXS and light scattering measurements was smaller than the average spacing ($2d_0$) at low concentration, (2) the decrease of the $2D_{exp}$ with decreasing dielectric constant of the dispersion media was supported the concept of an electrostatic attraction[5].

Polymethylmethacrylate lattices with fluorescences dye were observed directly by an inverted fluorescent microscope and followed 2D-Fourier transformation by the image processing system, indicated the coexistence of ordered structure and disordered regions was found. The size of local structure in polymer latex suspension became larger with time and finally grew to a huge regular lattice. The authors concluded that the growth of the ordered structure obeyed the Ostwald ripening and the attraction interaction created by the counterion in-between colloidal particle in a similar way to hydrogen bonding interactions.

S. Yoshino (815, E246) claimed that a colloid particle appeared to have a long-range attractive interaction of tens micrometer distance on the basis of the direct observations by using an optical microscope[6]. The colloid particles used in this work were a suspension of paraffin liquid oil drop, purple membrane, biological vesicles, and charged polystyrenesulphate latex of 0.4 μm in diameter.

A lot of colloid particles within a field in the microscopic eye-piece formed a pair with a constant distance of a micron, several microns or several tens micrometer and in some cases each particle pair moved around for several seconds or more. Since these observations could not be explained by the DLVO theory, the author proposed the hypothesis as follows; (1) the Brownian motion of the colloid particle makes the random disturbance of the ion atmosphere caused by a flow of solvent around the particle, (2) the resulting deformation of the charge distribution forms electric multipoles with rather long lifetime, (3) a long-range attractive potential around a colloid particle derives from the interaction between multipoles thus created.

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