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Notes

Small-Angle X-ray Scattering Studies of Polymer Colloids: Nonaqueous Dispersions of Poly(isobutylene)-Stabilized Poly(methyl methacrylate) Particles

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Several years ago, we began an investigation into the internal structure of colloidal polymer particles thought to be of the core-shell type.[1] The core-shell model for a particle composed of two different and incompatible polymers pictures a structure with one material in the center forming the core and the other as a spherical exterior shell. This model treats the system as though minimization of surface energy were the controlling factor in determining particle structure during its synthesis.

Our studies focused on nonaqueous dispersions of poly(methyl methacrylate) (PMMA) particles, sterically stabilized by poly(isobutylene) (PIB).[1] These materials were prepared in a two-step process where MMA was polymerized to low conversion in the presence of PIB (degraded butyl rubber) containing 2% unsaturation. This process produces a graft copolymer stabilizer, which is then added to a large excess of MMA plus initiator in an aliphatic hydrocarbon solvent (here isooctane). Free radical polymerization leads to the formation of spherical particles.[2] Alternatively, the same particles can be produced in a one-pot synthesis where, presumably, the graft copolymer stabilizer is generated in situ. These recipes produce particles with a fairly narrow size distribution. The mean particle diameters range from 0.3 to 2 μm, depending upon the ratio of reactants. The particles prepared for the experiments reported here had a mean diameter of 0.6 μm and a composition of approximately 90 mol % MMA. According to the core-shell model, these particles should consist of a sphere of (glassy) PMMA coated with a shell of PIB. Problems with the core-shell model for these materials first became apparent during fluorescence energy-transfer studies on particles containing naphthalene (N) groups as fluorescent labels.[3,4] These groups were incorporated covalently into the PMMA phase of the particles by adding a comonomer, 1-naphthalmethyl methacrylate, to the particle synthesis step. When dispersions of these particles in cyclohexane were exposed to low concentrations of anthracene, efficient energy transfer could be observed. This process

$$\underset{\substack{\text{emits at}\\ 340\text{ nm}}}{N^*} + A \rightarrow N + \underset{\substack{\text{emits at}\\ 400\text{ nm}}}{A^*} \qquad (1)$$

requires the A molecules to approach to within 20–40 Å of the N* species. Analysis of the data indicated that most, if not all, of the N in the particle were able to transfer energy to A.

Since the N groups are statistically distributed throughout the particles and the light penetrates into them to a depth of at least its wavelength, these observations require that the A molecules have access to a pathway to penetrate rapidly (seconds or minutes) into the deepest reaches of the particle core.

As a consequence, we rejected the core-shell model for this system and replaced it with an alternative model that presumes extensive grafting between PMMA and PIB during particle synthesis.[4] These covalent bonds oppose macroscopic separation of phases but permit local phase separation. Under such circumstances, much of the PIB would be located in the particle interior where it might form an interconnecting network of channels. These could be swollen by hydrocarbon solvents and thereby permit rapid diffusion of certain substances into and out of the particles. We call this the *microphase model* of polymer colloid structure.[4] One might note similarities between this model and the traditional view of the morphology of interpenetrating networks.[5]

Since this is a new model, it would be particularly useful to see if the structure it suggests would be consistent with experiments involving other analytical techniques. Light scattering techniques, in view of the particle size, would be well suited for differentiating between these two models. However, quantitative use of light scattering is somewhat difficult due to the large amount of scattering arising from the surface. Small-angle X-ray scattering (SAXS), on the other hand, probes a much smaller size scale. Evaluation of the structure factor of the core-shell model or of the microphase model by SAXS is not possible. However, the two models differ dramatically in the homogeneity of the phases within the particles. In the core-shell model, the particle consists of two homogeneous phases, whereas in the microphase model, the structure is heterogeneous. This difference should give rise to a discernible difference in the SAXS profiles. In order to enhance the contrast, we chose to treat the particles with a small amount of tetraphenyllead, a hydrocarbon-soluble heavy metal derivative. We assumed that under mild conditions this derivative would diffuse rapidly into the PIB regions of the particle, whereas the time scale for diffusion into the glassy PMMA phase would be very long. For tetraphenyllead with a molecular diameter of ca. 10 Å, the diffusion constant in PMMA at room temperature would be quite small and would take years to fully saturate the particles.[6]

Experimental Section

PMMA–PIB particles were prepared in isooctane according to the one-pot recipe previously reported.[2] In order that the same batch of material could be analyzed by several different methods, the recipe included ca. 2 mol % 1-naphthylmethyl methacrylate in the methyl methacrylate feed. The dispersions were purified

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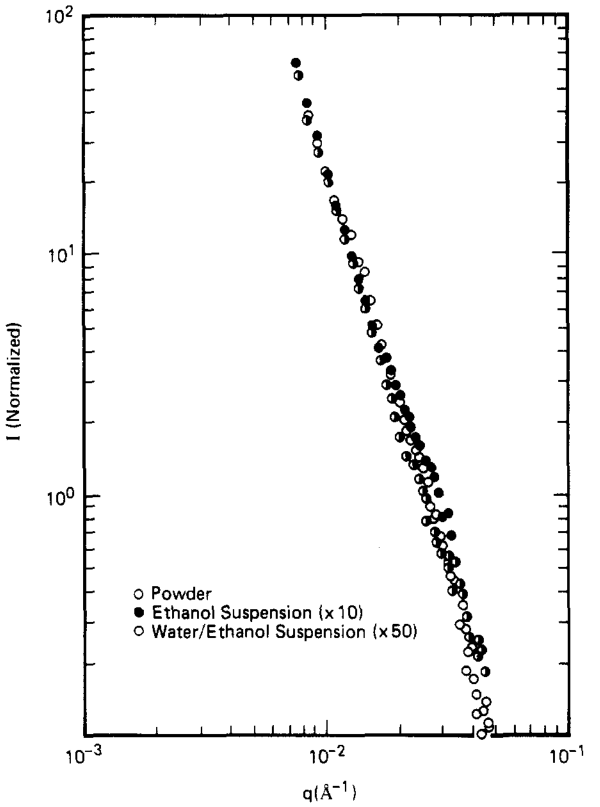

Figure 1. Small-angle X-ray scattering profiles of PIB/PMMA particles synthesized from a 9/91 mole ratio of IB/MMA, respectively. Three scattering profiles of the particles are shown where the particles are a dry powder (○); a suspension in ethanol (●), and a suspension in a 50/50 mixture of ethanol/water (◑), respectively. Measurements were performed at room temperature in the same scattering cell.

and transferred into cyclohexane by five successive centrifugation redispersion steps and subsequently freeze-dried. Analysis of a solution of the material in $CDCl_3$ by ^1H NMR indicated that the mole ratio of IB/MMA is 9/91. Further analysis, by UV spectroscopy, indicated that the particles contained 1.8 mol % N groups in the PMMA phase. Particle diameters (scanning electron microscopy) ranged from 0.5–0.7 μm.

Dyeing the Particles. Half-gram samples of the freeze-dried powder were dispersed in 50 mL of cyclohexane. To this was added a solution of tetraphenyllead in cyclohexane, with the amount of lead derivative corresponding to 0.1%, 0.5%, and 1.0% by weight of the polymer particles. The dispersions were placed in a rotary evaporator and the solvent was removed at reduced pressure (ca. 10 Torr) at approximately 25 °C.

Scattering Experiments. X-ray scattering experiments were performed at Stanford Synchrotron Radiation Laboratory on Beamline I-4 with X-rays of wavelength 1.429 Å. The experiments performed consisted of examining the following preparations for each specimen: (1) dry powder, (2) suspension of the powder in ethanol, (3) suspension of the particle in a 1/1 ethanol/water mixture. Experiments were conducted with the different suspension fluids to avoid problems associated with porosity at the surface of the particles. In addition, the different suspension fluids varied the average electron density of the sample.

Results and Discussion

All the scattering profiles measured in these experiments are monotonically decreasing functions of the scattering vector q ($q = (4\pi/\lambda)\sin(\epsilon/2)$), where λ is the wavelength and ϵ is the scattering angle. An example is shown in Figure 1 for a series of samples containing 1% $(C_6H_5)_4Pb$. In these data, it is important to note that the overall shapes of the scattering profiles are independent of the suspension fluid. Similarly, the shape of the scattering profiles were independent of the concentration of the $Ph(C_6H_5)_4Pb$ used. Therefore, it is apparent that only the contrast factor is being varied in these experiments and the structure factor is remaining constant.

The intensity in a small-angle X-ray scattering experiment will be given by[7,8]

$$I(q) = KV\overline{(\Delta\eta)^2}\int_0^\infty \gamma(r)\frac{\sin qr}{qr}4\pi r^2\,dr \qquad (2)$$

where $\overline{(\Delta\eta)^2}$ is the mean-square fluctuation of the electron density, K is a constant, V is the volume, and $\gamma(r)$ is the spatial correlation function having a value of 1 at $r = 0$ and 0 as $r \to \infty$. $\gamma(r)$ describes the spatial correlations of the electron density or the spatial organization of scattering centers in the specimen and gives rise to the angular dependence of the scattering. If the scattering centers are completely uncorrelated then $\gamma(r) = 0$ and the scattering, in excess of thermal density fluctuations, would be zero.

Let us now consider the type of scattering profiles that would be observed from the two different models under consideration. For the core-shell model, the structure factor related to the size and shape of the individual particles cannot be resolved by the instrumentation used and cannot contribute significantly to the observed scattering. If the core and the shell contain pure PMMA and PIB, respectively, then the only scattering that should be observed would be that arising from thermal density fluctuations. This scattering is independent of the scattering angle. The data shown in Figure 1 is the scattering in excess of that due to thermal density fluctuations, and, consequently, the core-shell model does not provide a suitable description of the observed scattering.

For the microphase model, on the other hand, the individual particles are spherical and contain randomly dispersed and, most likely, interconnected phases of PIB in PMMA. As with the core-shell model, the structure factor of the individual particles would not contribute to the observed scattering. There is an additional contribution to the scattering arising from the phase separation within the particle. If we assume that the correlation function in eq 2 can be given by an exponential, i.e., $\gamma(r) = \exp(-r/a)$, where a is the correlation length defining the average size of the heterogeneities in the system, then we find that[7,8]

$$I(q) = KV(\Delta\eta)^2a^3/(1 + q^2a^2)^2 \qquad (3)$$

Therefore, plotting $I(q)^{1/2}$ vs. q^2 (so-called Debye–Bueche plots) should produce a straight line with a slope-to-intercept ratio of a^2. Debye–Bueche plots for a 0.5% $(C_6H_5)_4Pb$-doped particle and a 1% $(C_6H_5)_4Pb$-doped particle suspended in ethanol/water mixtures are shown in Figures 2 and 3. From these plots, it is evident that two different straight line regions are observed. Similar results were found for all specimens regardless of dopant concentration or suspension fluid. The correlation distances obtained from the high scattering vector portion of the scattering profiles was ca. 50 Å, whereas from the smaller scattering vectors values ranging from 150 to 300 Å were found.

The different correlation lengths observed can be related to an average size of the phases if and only if the volume fractions of the phases are known.[9] Unfortunately, these are not known precisely. If we make the assumption that the volume fractions of the phases are equal to the volume fractions of the two components, i.e., 0.1 for PIB and 0.9 for PMMA, then we can calculate average domain sizes of 500 and 2200 Å for the PMMA and 55 and 250 Å for the PIB. This assumption is equivalent to the assumption that the domains within the particle are pure PMMA and

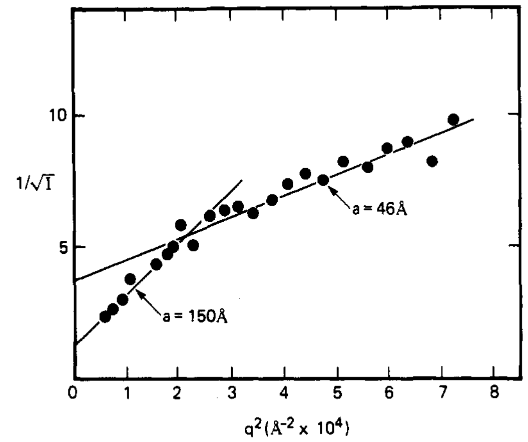

Figure 2. Plot of $I^{-1/2}$ vs. q^2 for PIB/PMMA particles doped with 0.5% $(C_65H_5)_4$Pb and suspended in an ethanol/water mixture. The data plotted are those in excess of thermal density fluctuation scattering.

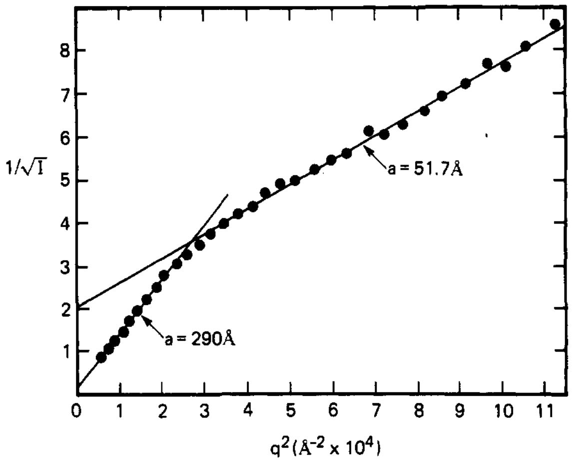

Figure 3. Plot of $I^{-1/2}$ vs. q^2 for PIB/PMMA particles doped with 1% $(C_6H_5)_4$Pb and suspended in an ethanol/water mixture.

pure PIB. This, however, is not correct since grafting between the PMMA and PIB chains would lead to a diffuse interface between the phases. It is clear though that small-angle X-ray scattering shows evidence of the formation of microphases and, in fact, two different size scales are observed. What is not clear, at present, is the precise meaning of these size scales.

Up to this point, attention has been focused on the angular dependence of the scattering, and, as shown in eq 4, the mean square fluctuation of the election density difference should provide information on the actual densities of the phases giving rise to the observed scattering. While measurements were performed on an absolute level, evaluation of the electron density difference between the phases was not reliable for several reasons. First, it is necessary to know the volume fractions of the phases giving rise to the scattering. This, as mentioned before, is not possible with any degree of precision. Second, it is clear from the results presented that the phases are not monodisperse in size and a significant proportion of the scattering occurs at scattering angles that are not accessible experimentally. Thus, the total integrated scattering from which $\overline{(\Delta\eta)^2}$ is obtained would be low due to truncation effects. Finally, it would be necessary to assume that the distribution of the $(C_6H_5)_4$Pb in the PIB phase is uniform and that the extent of penetration of the $(C_6H_5)_4$Pb into the PIB is small. Thus, while measurement of the total integrated scattering could yield, in principle, the electron density difference between the individual phases, too many assumptions and restrictions were encountered to make even qualitative use of this quantity.

In conclusion, small-angle scattering measurements on PIB-stabilized PMMA particles doped with $(C_6H_5)_4$Pb show clearly that there are microphase-separated regions within the particles. This is consistent with our previous hypothesis.[4] The size scales of the heterogeneities are consistent with our previous fluorescence energy-transfer studies in further support of our model.

Registry No. (IB)(MMA) (copolymer), 30971-07-4.

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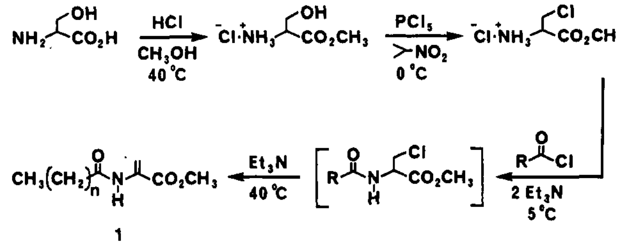
Communications to the Editor

Monolayer Polymerization of Methyl 2-(Octadecanamido)propenoate: An Amphiphilic Captodative Monomer Based on Dehydroalanine

We recently began exploring the polymerizability of a new family of dehydroalanine monomers 1 available in high yield from DL-serine.[1] The common dehydroalanine structure offers enormous potential as a basic building block for functional polymers. First, it offers *two* sites for derivatization: a carboxyl moiety capable of existing as a free acid, carboxylate anion, and a wide range of ester and amide derivatives; and an enamine nitrogen which may be converted to a host of amide or amine derivatives. Second, dehydroalanines are unusually active in free radical polymerizations. In our work, for example, one sample of the decanamide derivative (1, n = 8) spontaneously formed polymer of over 15 million molecular weight.[1]



Captodative stabilization of the propagating radical