Homogeneous polymer blend microparticles with a tunable refractive index

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We show that homogeneous polymer blend microparticles can be prepared *in situ* from droplets of dilute solution of codissolved polymers. Provided that the droplet of solution is small enough (<10 μm), solvent evaporation is rapid enough to inhibit phase separation. Thus the polymers that are being mixed need not be miscible, which greatly enhances the applicability of the technique. From analysis of two-dimensional Fraunhofer diffraction (angular scattering) patterns, we show that both the real and the imaginary parts of the refractive index can be tuned by adjustment of the relative weight fractions of polymers in solution. © 1999 Optical Society of America

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Recently, enormous commercial and scientific attention has been focused on multicomponent polymer systems as a means for producing new materials on the micrometer and nanometer scales. Composite polymer particles, or polymer alloys, with specifically tailored properties could find many novel uses such as electro-optic and luminescent devices,[1,2] thermoplastics and conducting materials,[3] hybrid inorganic–organic polymer alloys, and polymer-supported heterogeneous catalysis. The primary barrier to producing many commercially and scientifically relevant homogeneous polymer blends, however, is the problem of phase separation from bulk-immiscible components in solution, which has been studied in detail by several different groups.[4–7] In this Letter we show that this problem can be overcome by use of microdroplet techniques where the initial volume is sufficiently small that the solvent evaporation time scale is too short for the polymer components to achieve phase equilibrium. For spherical particles the small size also substantially increases the surface-area-to-volume ratio, thereby limiting the amount of space for polymer chain diffusion and further inhibiting phase separation. Thus, unlike solvent-cast or spin-coated thin films, in which molecular motion is restricted in only one degree of freedom, one can produce a particle of a two-component polymer blend in which the polymers typically do not possess enough energy at room temperature to overcome surface-energy constraints and segregate into separate phases.

We show by means of two-dimensional (2D) optical diffraction measurements that two bulk-immiscible polymers [poly(vinyl chloride) (PVC) and polystyrene (PS)] can be homogeneously blended within a single microparticle, provided that the initial droplet of solution is less than ~10 μm. This technique provides a means of tuning both the real and the imaginary parts of the refractive index of the microsphere. For larger droplets evaporation takes place too slowly to inhibit phase separation, and the resulting material inhomo-geneity is manifested in highly distorted 2D diffraction patterns. To our knowledge, this Letter describes the first observation of homogeneous blending of bulk-immiscible polymers (PVC and PS) in a spherical microparticle and should open new avenues for study and production of a new and interesting class of composite polymeric nanoscale and microscale materials.

Polymer blend particles were produced *in situ* by use of techniques originally developed for probing single molecules in small (≤ 10-μm-diameter) liquid droplets.[8] Briefly, droplets of dilute polymer solution (typically 1% w/w) were injected into a particle levitation device specifically designed for high-precision size and refractive-index measurements with Fraunhofer diffraction, or angle-resolved light scattering,[9] from spherical microparticles.[10] This nonimaging technique, well known in the aerosol particle community as a means of droplet sizing,[11] was also recently shown to be useful in characterizing nonspherical particles and clusters of small particles.[12] We showed recently[13] that a microdroplet approach can be used to produce polymer particles with 250-nm diameter and size dispersion of 1% to 2%. Using small droplets (5–10 μm) of solution offers the additional advantage of producing polymer blend microparticles and nanoparticles, since solvent evaporation is much faster than characteristic phase-separation time series.

The optical setup and the detector calibration are described in detail in Ref. 10. Electrodynamically trapped particles were illuminated with a vertically polarized He–Ne laser, and elastically scattered light from the particle was collimated with an $f/1.5$ achromat, spatially filtered, and detected with a cooled 16-bit CCD camera. Light was collected at $90° \pm 18°$ with respect to the direction of the He–Ne laser. Figure 1(A) shows a typical two-dimensional Fraunhofer diffraction pattern from a pure polyethylene glycol (PEG) particle (11.3 μm) produced from a 1% w/w aqueous solution. Figures 1(B) and 1(C) show the effect on the measured diffraction patterns of adding of

a small amount of 300-nm poly(methyl methacrylate) (PMMA) particles (0.5% and 5% PMMA:PEG weight fraction, respectively) to the aqueous solution. In this case the non-water-soluble PMMA already exists as a separate phase in aqueous solution. The resulting PEG–PMMA composite particles therefore exist as PEG hosts with 300-nm PMMA guest inclusions. The dry-particle sizes were all approximately the same (≈ 11-μm diameter), and the difference in refractive index for these two polymers is approximately 0.05. For a 0.5% PMMA–PEG relative weight fraction (≈ 250 PMMA particles within the PEG particle), some mild distortion in the optical diffraction is observed, whereas for the 5% PMMA–PEG particle a high degree of distortion in the diffraction pattern is observed. Thus these control experiments give some indication of the sensitivity of measured diffraction patterns to the domain size and number density of submicrometer phase-separated structures within the particle.

In separate experiments we used two non-water-soluble polymers, PVC [Aldrich 18,262-1; molecular weight (MW) = 90,000], and two PS's with different molecular weights (Aldrich Standard 32,782-4; $M_v = 687$; Aldrich 18,242-7; $M_w = 280,000$), which we observed to undergo micrometer-scale phase separation in solvent-cast thin films (M_v and M_w indicate viscosity-averaged and weight-averaged molecular weight, respectively). The polymers were used without further purification and codissolved in tetrahydro-furan (THF) at total polymer/solvent weight fractions of $\sim$1%, with variable droplet sizes from $\sim$10 to 40 μm. Figures 2(A) and 2(B) show measured diffraction patterns for particles prepared from single-component PVC and PS solutions, respectively; well-defined diffraction fringes can be seen. The real and the imaginary parts of the refractive indices for pure PVC and PS determined from analysis of the diffraction data were (1.4780 ± 0.0005, 10^{-3}) and (1.5908, 2×10^{-5}) respectively. Only a small difference in refractive index (≈ 2 parts in 1000) was observed for the two different molecular weight PS's.

Figures 2(C) and 2(D) show diffraction data obtained for two-component blends formed from 20:80 and 50:50 w/w mixtures of PVC with MW = 687 and MW = 280,000 PS, respectively. The domain-size resolution for these interferometric measurements (i.e., the smallest domain dimension required for distortion to be produced in the diffraction pattern) is approximately $L \approx \lambda/4\pi n_0$ (λ, 632.8-nm probe wavelength; n_0, refractive index), or $\sim$25 nm. That is, phase-separated domains smaller than L will not result in distortion of the 2D diffraction pattern; the absence of significant distortion in the diffraction data indicates that the mixed-polymer particles are homogeneous to a length scale of $\leq$25 nm. For the particle shown in Fig. 2(D), the critical length scale is comparable with the radius of gyration for the large-molecular-weight PS ($\approx$15 nm).[14] However, the polymer chains intercalate within the particle, so it is more appropriate to address the question of average A–B monomer composition within a subvolume with a diameter of L. From detailed molecular dynamics calculations with realistic interaction potentials, we found that the average A–B

monomer composition was very close to 50:50, even for subvolume dimensions as small as 5 nm.

Additional evidence for homogeneous blending comes from the excellent agreement between Mie theoretical calculations (solid curves) and 1D (center horizontal row) diffraction data (dots) beneath the 2D data.
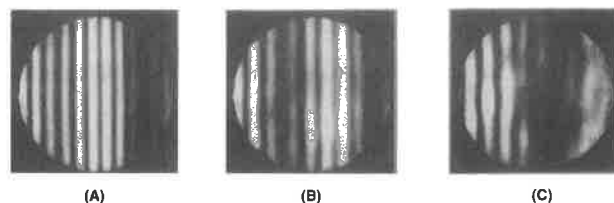

Fig. 1. 2D Fraunhofer diffraction patterns from PEG particles produced *in situ* from 1% w/w aqueous solution. (A) pure PEG, (B) 0.5% w/w PMMA–PEG, and (C) 5% w/w PMMA–PEG.
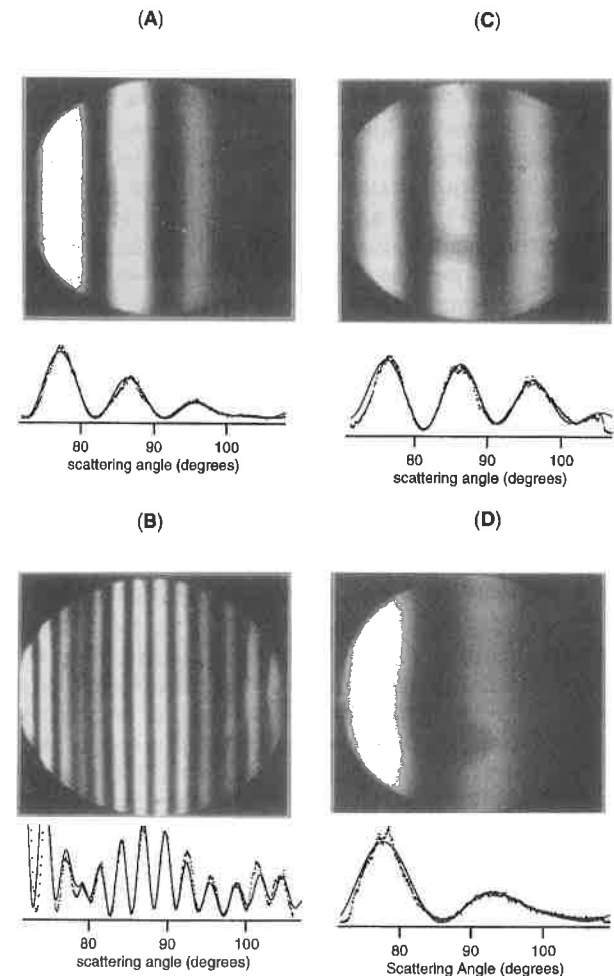

Fig. 2. 2D diffraction data for (A) pure PVC, (B) pure polystyrene, (C) 20:80 w/w PVC–PS (MW = 687) blend, and (D) 50:50 w/w PVC–PS (MW = 280,000) blend. For (C) and (D) the total polymer weight fraction in THF was 1%, and the initial droplet sizes were 9–10 μm. The particle size, d, and the refractive index (Re, Im) above each panel define the Mie theory fit (solid lines) to 1D slices (symbols) in the plot below each panel.
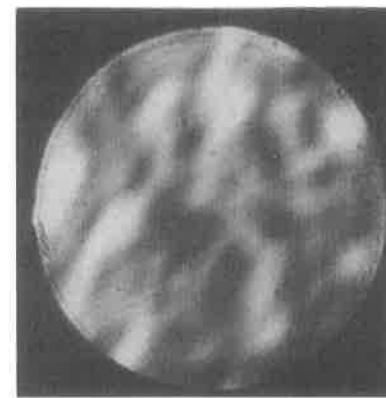

Fig. 3. Observed 2D diffraction pattern for 50:50 w/w PVC–PS (MW = 280,000) blend produced from a 35-μm droplet of 1% polymer–THF solution.

Interestingly, the refractive indices for the blend particles are in very good agreement with values calculated simply as a mass- (density-) weighted average of the two components. For the 80:20 PS–PVC blend the refractive index of the particle was determined to be (1.5635, 0.0001), and for the 50:50 PS–PVC blend the refractive index was (1.5285, 0.0008). The combined qualitative evidence of high fringe contrast in the 2D diffraction data and quantitative agreement with Mie theory for 1D slices is conclusive evidence that the polymers are homogeneously blended in the particle.

An additional observation is that homogeneous blend particles are not formed for droplets with initial sizes much larger than approximately 15–20 μm. Figure 3 shows the highly distorted 2D diffraction pattern obtained from the 50:50 PVC–PS blend in THF with an initial droplet size of $\sim$35 μm. These patterns are not analyzable with our analysis program, but they show island features similar to those reported in Ref. 12 for a cluster of particles. Our results show that for large droplets the time scale for solvent evaporation is too long to inhibit phase separation, and the different components segregate to (presumably) spheroidal domains. This observation also supports the conclusion that the small ($<$5-μm) mixed-polymer particles are homogeneous, as opposed to layered sphere-within-a-sphere structures. Such spherically symmetric phase-separated structures would also present well-defined diffraction fringes. However, since this obviously does not occur for large droplets (where conditions favor phase separation), it seems very unlikely that sphere-within-a-sphere structures are formed in the smaller droplets. Furthermore, for the relatively large-molecular-weight polymers considered here, the chain diffusion is much too slow for molecules to form such structures on the 2–3-ms time scale for solvent evaporation from a 5- or 6-μm THF droplet.

In summary, we have shown that stable, homogeneously blended (bulk-immiscible) mixed-polymer composites can be formed in a single microparticle of

variable size with a tunable refractive index (both the real and the imaginary parts). For small droplets of solution ($<$10 μm), solvent evaporation takes place on a time scale short enough to inhibit phase separation, producing dry polymer blend particles that are homogeneous to within molecular dimensions. This capability allows production of polymer-alloy microspheres with a tunable refractive index (both the real and the imaginary parts) simply by adjustment of the relative weight fractions of the polymers in solution. To our knowledge, the method reported here represents a new tool for probing phase-separation behavior at nanometer-length scales as well as for making and characterizing polymer particles and plastic alloys. A wide range of electronic, optical, physical, and mechanical properties of single-component and multicomponent polymer nanoparticles remains to be explored.

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