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Polymeric Nanocomposite Material with a Periodic Structure

O. Kalinina and E. Kumacheva*

Department of Chemistry, University of Toronto, 80 St. George Street,
Toronto, Ontario, Canada M5S 3H6

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A new approach to producing polymer nanocomposite materials with optically sensitive matrixes is developed. Core−shell latex particles with rigid cores and relatively soft shells are synthesized, packed into a three-dimensional array, and annealed at the temperature at which the shell-forming polymer (SFP) flows and forms a continuous phase, whereas the latex cores remain intact. During latex synthesis, low-molecular-weight species, such as a fluorescent dye, are incorporated into the SFP, thus leading do the polymer-based nanocomposite material with a fluorescent matrix. High modulation in composition and optical properties of the material is achieved by covalently attaching the dye to the SFP, which is accompanied by polymer cross-linking. Mixing of the dye in the SFP, especially when it is not followed by polymer cross-linking, results in a substantial reduction in optical contrast between the particles and the matrix.

Introduction

Studies of ordered arrays of submicrometer colloid particles have stimulated great interest in materials science. Generally, colloid crystals are employed either as templates for fabrication of materials with periodic structures[1] or in their own right as, e.g., chemical sensors[2] or devices for memory storage.[3] Recently, we have proposed a new approach to producing polymer-based nanocomposites, which employed monodisperse core−shell latex particles.[3−5] The strategy is demonstrated schematically in Figure 1. Monodisperse latex particles with hard cores and a somewhat softer shells are synthesized at stage A. The particles are assembled in a close-packed ordered three-dimensional array at stage B[5,6] and annealed at stage C at a temperature that is above the glass transition temperature, T_g, of the shell-forming polymer (SFP) and below the T_g of the core-forming polymer (CFP). As a result, the latex shells flow, fill interparticle gaps, and form a matrix, whereas the rigid cores remain intact and form a dispersed phase of the material. By variation of the dimensions of the cores, the shells, and the core−shell particles, nanocomposite materials with different morphologies and particle number density can be produced.

We showed that, at stage A, a fluorescent dye can be localized in the latex cores.[5] In this way, nanocomposite materials with a "direct" structure were fabricated, in which fluorescent particles were periodically embedded into an optically inert matrix. To obtain a material with a sharp modulation in composition and properties, diffusion of the chromophore between the CFP and the CFP was suppressed by (i) *covalently attaching* the dye to the CFP and by (ii) cross-linking of the CFP.

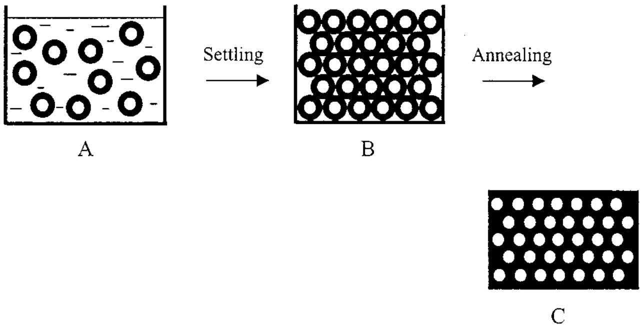

Figure 1. Schematics of the "core−shell" approach to producing polymer-based nanocomposites. Stage A: synthesis of the core−shell latex particles with hard cores and soft shells. Stage B: assembly of the latex particles in a 3-D close-packed structure. Stage C: annealing of the particle sediment at $T_{g,SFP} < T_{annealing} < T_{g,CFP}$.

However, the scope of the "core−shell" approach is broader. At stage A, different species, e.g., fluorescent dyes, can be incorporated into the shell-forming polymer; in this manner, materials with a "reverse" structure can be produced, i.e., optically inert particles embedded into a fluorescent matrix. Moreover, *different* functionalities, such as chromophores with different optical properties, can be incorporated into the CFP and the SFP, leading to nanocomposite materials with interesting and novel optical properties.

In this paper we address two issues. First, we demonstrate how incorporating a fluorescent dye into the SFP can lead to nanocomposite materials with the "reverse" structure. Second, we examine to what extent

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covalent attachment versus swelling of low-molecular species in the SFP is essential in providing sharp modulation in the composition of the material. The latter issue has great importance since mixing of low-molecular compounds with the corresponding polymer instead of their chemical attachment to the polymer provides a greater flexibility in the selection of suitable species. On the other hand, mixing should not reduce sharp modulation in the material composition and properties. The latter feature is important in various applications, e.g., in photonic crystals used in optical limiting and switching[7,8] or optical memory storage.[9]

Experimental Section

Methyl methacrylate (MMA) and butyl methacrylate (BMA) were purchased from Aldrich and purified by double distillation under reduced pressure. The nonionic initiator 2,2′-azobis-(2-methylpropionitrile) (AIBN, Kodak, 99%), the ionic initiator potassium persulfate (99%), the chain transfer agent dodecyl mercaptan (DDM, 98%), and the cross-linking agent ethylene glycol dimethacrylate (EGDMA) (all purchased from Aldrich) were used as received.

Core–shell latex particles with poly(methyl methacrylate) cores and poly(methyl methacrylate)–poly(butyl methacrylate) shells were synthesized by a multistage emulsion polymerization using ionic and nonionic initiators at different stages of synthesis.[5]

Fluorescent dye 2-[methyl(7-nitro-2,1,3-benzodiazol-4-yl)-amino]ethanol (NBD-OH) was synthesized using the recipe given elsewhere[5] and mixed with the SFP. To attach the dye chemically to the SFP, a fluorescent comonomer 4-amino-7-nitrobenzo-2-oxa-1,3-diazole–methyl methacrylate (NBD–MMA) was synthesized and copolymerized with the SFP. The chemical structure of the dyes is shown in Figure 2a.

The absorption and emission spectra of the chromophores dissolved in methanol to the concentration $c = 5 \times 10^{-3}$ mol % were measured using a fluorescence spectrometer SPEX Fluorolog with a double grating monochromator. Both NBD-OH and NBD–MMA had fluorescent properties demonstrated by their absorption and emission spectra shown in Figure 2b.

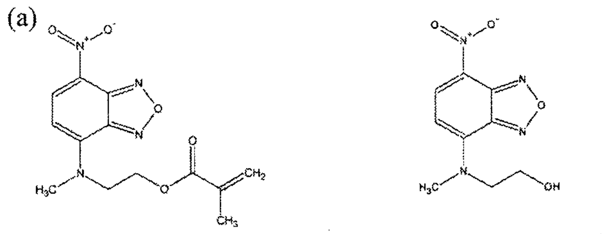
Particle dimensions and size distribution were measured after each stage of synthesis using a Hitachi S-570 scanning electron microscope at an accelerating voltage of 15 kV.

Latex dispersions were diluted to ca. 5 wt % and settled in Teflon containers. After removal of the water, dry sediments with the thickness of ca. 3 mm were annealed for 9 h at temperatures slowly increasing from 20 to 110 °C at a rate of ca. 10 °C/h.

The structure of the annealed samples was examined by laser confocal fluorescence microscopy (LCFM) using a Carl Zeiss LSM510 confocal microscope with a C-Apochromat 63×/1.2 W objective lens. The chromophores were excited using the 488 nm line of an argon ion laser. For this particular excitation wavelength and numerical aperture 1.3, the lateral and vertical resolutions were estimated to be 0.3 and 0.7 μm, respectively. The morphology of the polymer films was studied from the surface of the sample to 500 μm below the surface. The LCFM images were analyzed using Image Tool software (Health Science Center, University of Texas, San Antonio, TX). The contrast and brightness sliders functions and the enhancement filters were the same for all examined films.

Results and Discussion

Four latex dispersions were prepared shown in Table 1, in which the total dimensions of the particles, the core diameters, and the shell thicknesses were the same. In latexes a and b NBD–MMA was copolymerized with the SFP, whereas in samples c and d NBD-OH was mixed with the SFP. In latexes a and c the SFP was cross-linked.



2- [methyl(7-nitro-2,1,3-benzoxadiazol-4-yl)amino]ethyl 2-methyl methacrylate]

2- [methyl(7-nitro-2,1,3-benzoxadiazol-4-yl)amino]ethanol

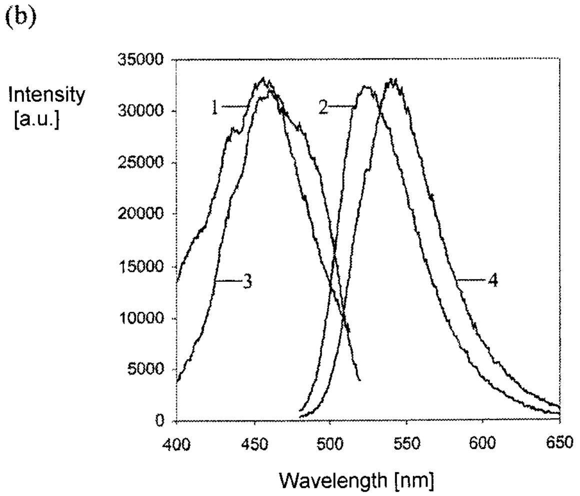


Figure 2. Chemical structure of the fluorescent species incorporated into the shell-forming polymer (a) and their absorption and emission spectra (b). NBD-OH: (1) absorption spectrum; (2) emission spectrum. NBD-MMA: (3) absorption spectrum; (4) emission spectrum.

The recipes of the latex synthesis are given in Table 2. Cross-linked poly(methyl methacrylate) cores were synthesized in three stages using a combination of ionic and nonionic initiators. At the end of stage 3, the latex shells composed of a copolymer of MMA and BMA were synthesized on the surface of the core particles. For the weight ratio poly(methyl methacrylate)/poly(butyl methacrylate) 1:1 the glass transition temperatures of the SFP was 74 °C in latexes a and c and 67 °C in latexes b and d. Figure 3 shows two typical micrographs of the core (a) and of the core–shell particles (b) obtained in stage 3 in latexes a–d (Table 2). In all dispersions, the average diameters of the core and core–shell particles were 0.7 and 0.95 μm, respectively, and the thickness of the shells was 0.125 μm. The polydispersity index of the particles after each stage of polymerization did not exceed 1.03.

After the latex dispersions settled and the sediments of the core–shell particles were annealed, the morphology of the composite films was examined using laser confocal fluorescent microscopy. In Figure 4 the LCFM images show the morphology of the polymeric films obtained from dispersions a–d (Table 1). All films exhibit a similar morphology, i.e., a fluorescent matrix formed by the SFP and dark inclusions formed by the CFP. No difference in the 2D structure was noticed for the films obtained from latex dispersions a–d.

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Table 1. Core−Shell Latex Particles Used for Fabrication of the Polymer Nanocomposite

sample	dye	cross-linking of the CFP	diameter of the latex core/ tot. diameter of core−shell latex particle (μm)
a	covalently attached to the SFP	yes	0.7/0.95
b	covalently attached to the SFP	no	0.7/0.95
c	mixed with the SFP	yes	0.7/0.95
d	mixed with the SFP	no	0.7/0.95

Table 2. Recipes for the Three-Stage Emulsion Polymerization of the Core−Shell Particles with Fluorescent Shells

	flask content	pumping	diameter (μm)
stage 1: synthesis of cores	70 g of H_2O, 0.18 g of $K_2S_2O_8$	30 g of MMA, 0.088 g of DDM	0.45
stage 2: synthesis of cores	30 mL of seed from stage 1, 90 g of H_2O	7.5 g of MMA, 7.5 g of BMA, 0.044 g of DDM, 0.375 g of EGDMA, 0.1 g of AIBN	0.63
stage 3:			
step 1, synthesis of latex cores	20 mL of seed from stage 2, 50 g of H_2O	1.5 g of 0.1% $K_2S_2O_8$ in water, 2 g of MMA, 2 g of BMA, 0.0117 g of DDM, 0.1 g of EGDMA, 0.027 g of AIBN	0.7
step 2, synthesis of latex shells		2 g of 0.1% $K_2S_2O_8$ in water 4 g of monomer mixture 1, 2, 3, or 4[a], 0.025 g of AIBN	0.87
step 3, synthesis of latex shells		2 g of 0.1% $K_2S_2O_8$ in water 4 g of monomer mixture 1, 2, 3, or 4[a], 0.025 g of AIBN	0.95

[a] Monomer mixtures 1, 2, 3, and 4 were pumped into the flask to obtain latexes *a*−*d*, respectively. Monomer mixture 1: 5 g of MMA; 5 g of BMA; 0.029 g of DDM; 0.006 g of NBD−MMA; 0.25 g of EGDMA. Monomer mixture 2: 5 g of MMA; 5 g of BMA; 0.029 g of DDM; 0.006 g of NBD−MMA. Monomer mixture 3: 5 g of MMA; 5 g of BMA; 0.029 g of DDM; 0.0045 g of NBD-OH; 0.25 g of EGDMA. Monomer mixture 4: 5 g of MMA; 5 g of BMA; 0.029 g of DDM; 0.0045 g of NBD-OH.

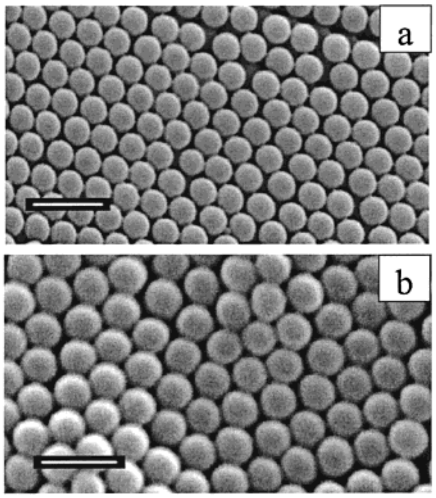

Figure 3. SEM images of the latex cores (a) and the core−shell particles (b). The scale bar is 2 μm.

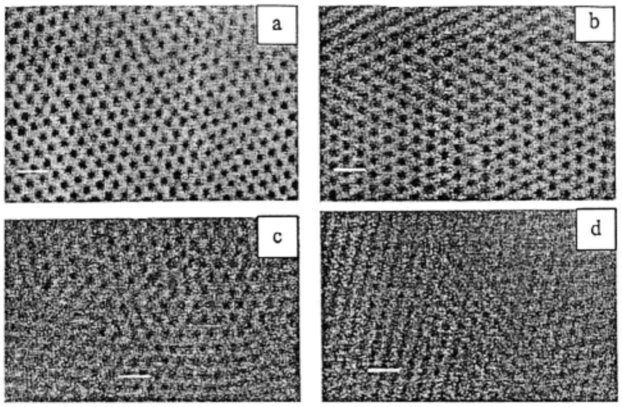

Figure 4. LCFM images of the composite films obtained from the corresponding latex dispersions a−d shown in Table 1. The fluorescent matrix formed by the SFP appears bright. Images are taken at the distance 10 μm from the film surface. The scale bar is 2 μm.

While in this work we did not examine a 3D structure of the films, it is known that latex microsheres slowly sedimenting from their dilute dispersions undergo a disorder−order transition, i.e., crystallization,[10] and assemble in either hexagonal close-packed (HCP) or face-centered cubic (FCC) lattices.[11] In both lattices, the structure of the 2D planes perpendicular to the direction of sedimentation is represented by a hexagonal pattern, as is shown in Figure 4.

A distinct feature of the images shown in Figure 4 is the variation in contrast between the fluorescent matrix and the optically inert particles. The highest contrast between the matrix and the particles, i.e., the highest signal-to-noise-ratio, STNR, is achieved in Figure 4a for the films formed from system a (cross-linked CFP carrying covalently attached NBD−MMA). The optical contrast between the CFP and the SFP domains in the film displayed in Figure 4b (chemically attached dye; the SFP is not cross-linked) is lower but still comparable with that obtained in Figure 1a. Swelling of the dye in the SFP (Figure 4c,d) led to a substantial reduction of the STNR. The lowest contrast between the particles and the matrix was achieved in films obtained from latex d (mixing of NBD-OH with the SFP; SFP is not cross-linked).

The relative concentration of the fluorescent species in the CFP and the SFP was further characterized by analyzing the variation in fluorescence intensity in the nanocomposite films. Such comparison is possible because NBD−MMA and NBD-OH incorporated into the latex shells have similar fluorescence properties (see Figure 2b).

The nanocomposite films were studied in LCFM experiments in which the microscope settings such as brightness, contrast, intensity of sample irradiation, the number of scans, and the position of the examined 2D plane were fixed for all films.

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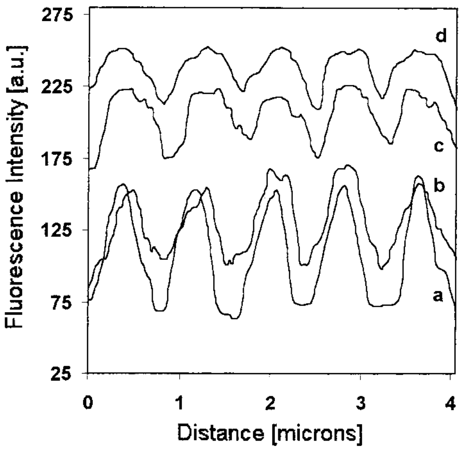

Figure 5. Variation in the fluorescence intensity for the nanocomposite films shown in Figure 4. The position of the examined 2D slice is 10 μm below the top surface of the film.

The fluorescence line profiles for the polymer films obtained from samples a–d are shown in Figure 5. In these profiles, the peak-to-well height characterizes the STNR. Two features are indicative. First, the average STNR's of the films obtained from latexes b–d are 84%, 56%, and 44%, respectively, of the STNR measured for the films prepared from dispersion a. This result suggests that (i) even for the worst scenario corresponding to mixing of NBD-OH with the SFP without cross-linking of the polymer (Figure 5, profile d), the dye resides mostly in the SFP and (ii) the chemical attachment of the dye to the SFP has a greater effect on suppression of its diffusion than cross-linking of the SFP (Figure 5, profile b versus profile d).

Second, a gradual change in the width of the wells on the STNR profiles is observed in Figure 5 (the wells correspond to the nonfluorescent core particles). Although precise measurement of the dimensions of the fluorescent and nonfluorescent domains in the film is limited by the resolution of the LCFM, qualitative conclusions can be made by comparing the width of the humps and wells in Figure 5 with the dimensions of the latex cores and shells given in Table 2. The average ratio of the well-to-hump width measured in the middle of the peaks, decreases from 1.3 in profile a to 1.15, 0.74, and 0.68 in profiles b–d, respectively. The wells on the STNR curves should appear broader than the humps, since the diameter of the nonfluorescent cores is substantially larger than the thickness of the fluorescent shells. The gradual broadening of the fluorescent domains, especially in profiles c and d, is a consequence of diffusion of the fluorescent species into the CFP, which characterizes the distribution of the chromophores between the CFP and the SFP.

The STNR is determined by the concentration of the fluorescent species in the particles and the matrix of the composite film, which, in turn, depends on diffusion of the molecules of NBD-OH or macromolecules of the CFP bearing covalently attached NBD–MMA between the cores and shells of the latex particles. On the basis of the results presented in Figures 4 and 5, it can be concluded that chemical attachment of the dye to the shell-forming polymer accompanied by its cross-linking gives the best effect in achieving sharp modulation in composition of the nanocomposite film. Incorporation of NBD–MMA into the SFP by mixing leads to a substantial reduction in the optical contrast between the particles and the matrix, even when the shell-forming polymer is cross-linked.

In summary, we have extended a “core–shell” approach to producing periodic polymer nanocomposite materials with the optically sensitive matrix. We demonstrated that chemical attachment of the dye to the shell-forming polymer is a critical condition for the preparation of nanocomposites materials with sharp periodic modulation of their optical properties; whereas cross-linking of the shell-forming polymer plays a less significant role. It should be admitted, however, that in this work we used core–shell particles with a similar composition of the CFP and SFP. For the latex cores and shells synthesized from dissimilar monomers, diffusion of low-molecular-weight species between the CFP and the SFP can be suppressed by selecting species with a strong affinity to a particular polymer.

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