Polymer Multilayer Particles: A Route to Spherical Dielectric Resonators

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ABSTRACT: Polymer multilayer particles with radial variation in refractive index can possess a photonic band gap and therefore can be used as spherical dielectric resonators (SDRs). We synthesized multilayer microspheres with morphology "predesigned" by modeling their scattering cross section. The particles had a polystyrene core and four 150 ± 20 nm thick alternating layers of polystyrene and poly(trifluoroethyl methacrylate) which were used as a high and a low refractive index counterpart, respectively. We confirmed the morphology of microspheres by transmission electron microscopy, energy dispersive X-ray analysis, and X-ray photoelectron spectroscopy. We undertook a further step in increasing refractive index contrast between the layers by copolymerizing styrene with vinylcarbazole.

Introduction

Polymer core−shell and multilayer particles have a broad range of applications in the production of impact-resistant polymers, composite materials, coatings, and adhesives.[1] Recently, multilayer latex particles labeled with fluorescent dyes have been used for high-density three-dimensional optical data storage[2] and security data encryption.[3] A new interesting application of polymer multilayer microspheres with periodic radial variation in refractive index was proposed by Sipe et al.[4] Such particles can be considered as spherical dielectric resonators (SDRs) which, due to their unique interactions with incident light, can be used in cavity quantum electrodynamics[5] and in new photonic devices such as optical switches and limiters.[6]

The synthesis of core−shell and multilayer spherical submicrometer-size particles with a well-defined layered morphology is not facile. Polymer multilayer particles can be obtained by using miniemulsion polymerization,[7] by layer-by-layer polyelectrolyte deposition,[8] or via the solvent-adsorbing/releasing method.[9] Typically, however, such particles are synthesized by using a multistage emulsion polymerization with a stepwise synthesis of each layer.[10] In this process, particle morphology is governed by the interfacial tension between constituent polymer layers,[11] the relationship between polymer glass transition temperatures (T_g's) and polymerization temperature,[12] and the type of initiator used.[13] The interplay of these factors can yield particles with raspberry, acorn, and Janus structures as well as particles with core−shell or multilayer morphologies.

Our first attempt toward polymer SDRs, reported elsewhere, involved the synthesis of polymer particles with alternating poly(heptafluorobutyl methacrylate)-rich and polystyrene-rich layers (used as the low and high refractive index counterparts, respectively).[14] We enhanced compatibilization between these polymers by copolymerizing styrene and heptafluorobutyl methacrylate (HFBMA) in different ratios in different layers and in this manner produced particles with a well-defined spherical shape and surface composition. In this stage, however, the multilayer morphology of the microbeads was not proved by imaging techniques.

In the present work, we report the synthesis of multilayer particles with morphology "predesigned" by modeling the scattering cross section. We used styrene and trifluoroethyl methacrylate for the synthesis of high and low refractive index layers, respectively. By contrast with our previous experiments,[14] we achieved good compatibilization between the alternating layers without copolymerization of these monomers. The multilayer structure of the polymer spheres was proved by using transmission electron microscopy (TEM) imaging of the microtomed particles, energy dispersive X-ray analysis, and X-ray photoelectron spectroscopy. Furthermore, in preliminary experiments we further increased the difference in refractive index between the layers by copolymerizing styrene with vinylcarbazole.

Background

Spherical dielectric resonators are multilayer particles with a periodic radial modulation in refractive index. Light confinement in SDRs occurs through Bragg reflection from the layers; thus, every spherical structure is analogous to a photonic crystal. For a particular composition of the layers and a particular wavelength of light one can either enhance or inhibit scattering of light (compared to the homogeneous microspheres) by tuning the diameter of the particle cores and the thickness of the layers. Moreover, it should be possible to design and synthesize polymer multilayer microspheres that will inhibit or enhance spontaneous emission of dyes or quantum dots embedded in the core of the particles.

The wavelength regime of Bragg reflection must be determined from detailed calculations of the scattering cross section of the SDR. Such calculations are performed by using a multipole expansion of the electromagnetic fields,[15] which in the case of a single isotropic sphere reduce to the classical Mie theory.[16] Certain guidance, however, can be provided by the

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Table 1. Recipes for Synthesis of PS/PTFEMA Particles

	precharge		monomer mixture				solution of ionic initiator		
sample	water (g)	seeds (g)	styrene (g)	TFEMA (g)	(g)	feeding rate (μL/s)	water (g)	KPS (g)	feeding rate (mL/min)
0	394.0		6.066		0.060			0.219	
2	25.0	15.0		4.613	0.049	0.29	10	0.050	0.14
3	25.0	25.0	4.507		0.046	0.27	45.5	0.051	0.62
4		50.0		4.002	0.044	0.29	46.0	0.060	0.73
5		50.0	3.026		0.039	0.26	97.0	0.062	0.75

Table 2. Recipes for Synthesis of PTFEMA/PS−PVC Particles

	precharge			monomer mixture					solution of ionic initiator		
sample	water (g)	seeds (g)	AIBN (g)	styrene (g)	VC (g)	TFMA (g)	EDGMA (g)	feeding rate (μL/s)	water (g)	V_{50} (g)	feeding rate (μL/s)
1	300.0			10.039			0.101			0.20	
2	30.0	6.356	0.030			5.625	0.055	0.82	50.3	0.05	19.8
3	40.2	24.214	0.043	2.030	1.3605			0.82	150.0	0.06	59.4
4	20.1	50.080	0.010			2.742	0.026	0.82	20.1	0.03	19.8
5		40.981	0.010	1.004	0.6814			0.82	60.0	0.03	19.8

Bragg condition for planar structures with weak refractive index modulation: the central wavelength of the confinement range is given by $\lambda = 2n\Lambda$, where λ is the wavelength of the light in a vacuum, n is the average refractive index of the sphere, and Λ is the period (typically two layers) of the modulation of refractive index.

In this paper we have chosen the targeted thickness of high- and low-refractive index layers to be 150 nm. This thickness of layers was obtained from the scattering analysis of multilayer spherical resonators embedded in an aqueous water solution with refractive index of 1.33, by using the formalism of Liang et al.[17] The formalism was based on the multipole expansion of the electromagnetic field, and it combined the classical Mie scattering theory with a transfer matrix method for multilayer particles. In our analysis the refractive indices of the polystyrene and poly(trifluoroethyl methacrylate) layers were 1.59 and 1.437, respectively.[18] For the refractive index contrast between these layers we predicted a large difference in the scattering pattern between the multilayer spheres and the uniform spheres (synthesized from the constituent polymers) with the same diameter, when examined at an incident wavelength of 400 nm.

Experimental Section

Materials. Styrene (99%), 2,2,2-trifluoroethyl methacrylate (TFEMA, 99%), 2,2′-azobis(2-methylpropionamidine) dihydrochloride (V_{50}, 97%), and ethylene glycol dimethacrylate (EGDMA, 98%) were purchased from Aldrich Canada and used without further purification. Potassium persulfate (KPS, >98%, BDH Chemicals Ltd.) and 2,2′-azobis(2-methylpropionitrile) (AIBN, VAZO 64, DuPont Canada) were used as received. *N*-Vinylcarbazole (Polysciences, Inc.) was recrystallized from hexane before use. Deionized water was purified by using a Millipore Milli-Q Plus purification system (Millipore Corp.).

Latex Synthesis. All reactions were carried under nitrogen pressure in a double-walled three-neck flask equipped with a reflux condenser, a nitrogen inlet, and a mechanical stirrer. The reaction temperature was controlled by using a temperature-controlled water bath. Particle polymerization was conducted at 80 ± 0.1 °C. Homopolymer seeds (particle cores) were synthesized in batch reaction. The reactor was charged with water, the cross-linking agent EGDMA, and styrene and then purged with nitrogen for 30 min. The temperature of the mixture was then increased to 80 ± 0.1 °C. An aqueous solution of KPS or V_{50} was injected in the reactor with a syringe. The reaction was carried out for 3 h. The multilayer latex particles were prepared by using a multistage surfactant-free emulsion polymerization method.[19] The latex dispersion from the previous stage and water were mixed in the reaction flask. The monomer and EGDMA (0.5−1 wt %) were introduced into the reactor using a fluid-metering pump at a rate 0.0147 mL/min. An aqueous KPS solution was added with the monomer mixture at a rate 0.5 mL/min using the second fluid-metering pump. The reaction was carried out for 3 h after the feeding stage was complete. A five-stage polymerization series resulted in the preparation of particles with a core and four layers with alternating compositions. Table 1 gives the recipes for the synthesis of the seeds and the multilayer particles.

The synthesis of multilayer poly(trifluoroethyl methacrylate)/poly(styrene−vinylcarbazole) (PTFEMA/PS−PVC) particles was conducted in a similar way. Polystyrene seeds (particle cores) were synthesized in batch reaction. For each successive stage, the latex dispersion from the previous stage and water were mixed in the

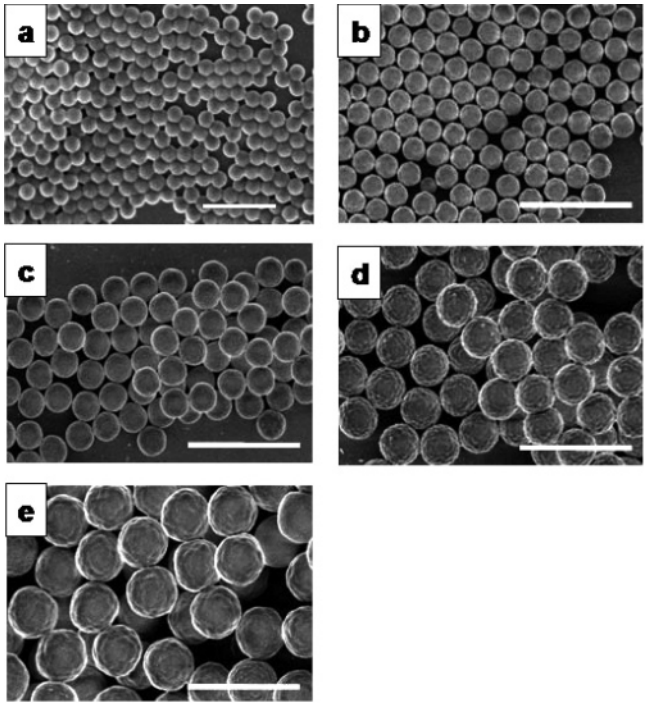

Figure 1. Scanning electron microscopy micrographs of latex particles synthesized in five successive stages. (a) Polystyrene particles. Scale bar is 1 μm. (b) Core−shell particles with PS core and PTFEMA shell. (c) Multilayer PS/PTFEMA/PS particles. (d) PS/PTFEMA/PS/PTFEMA particles. (e) PS/PTFEMA/PS/PTFEMA/PS particles. In (b−e) the scale bar is 3 μm.

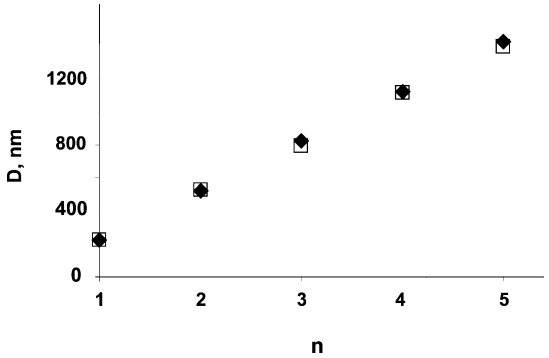

Figure 2. Increase in targeted (■) and experimentally measured (□) average particle diameter plotted as a function of the number of polymerization stages.

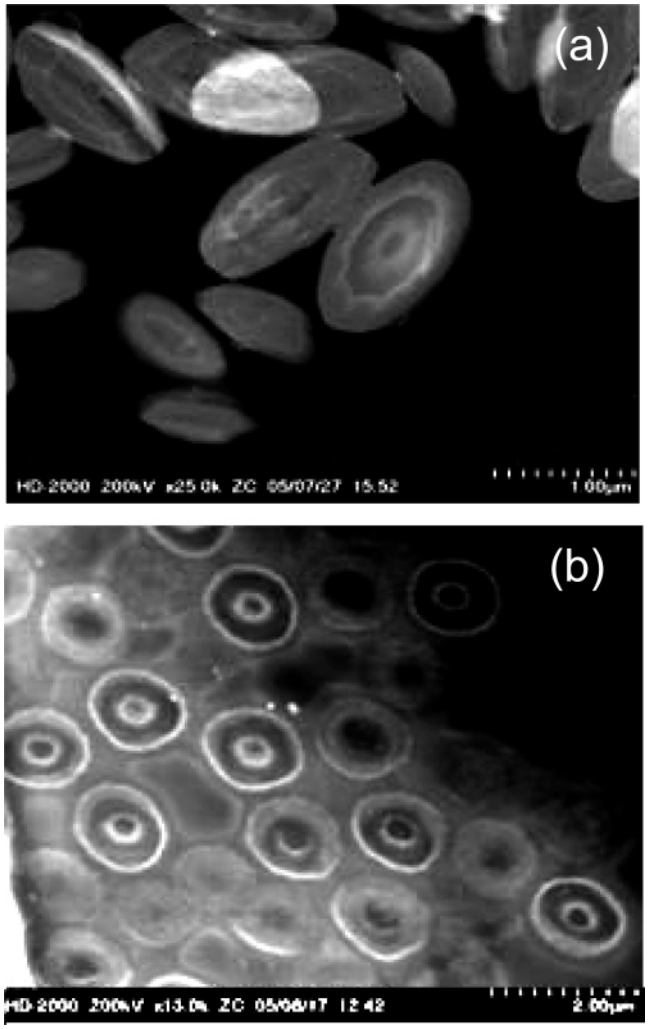

Figure 3. TEM micrographs of multilayer latex particles synthesized in five polymerization stages. The particles were cryotomed at −160 °C (a) and at room temperature (b). In (b) the particles were embedded in epoxy resin (low-viscosity resin kit, Canemco Inc., standard recipe). PTFEMA and PS layers appear as bright and dark rings, respectively. Scale bar is 1 and 2 μm in (a) and (b), respectively.

reaction flask. The mixture of monomer, EGDMA, and AIBN was introduced into the reactor using a fluid-metering pump at a rate of 0.0147 mL/min. The monomer mixture for the synthesis of polystyrene layer included vinylcarbazole as a comonomer. An aqueous solution of V-50 was added with the monomer mixture at a rate of 0.5 mL/min using the second fluid-metering pump. The reaction was carried out for 3 h after the feeding stage was complete. Table 2 shows the recipes for the synthesis of the seeds and the multilayer PTFEMA/PS−PVC particles.

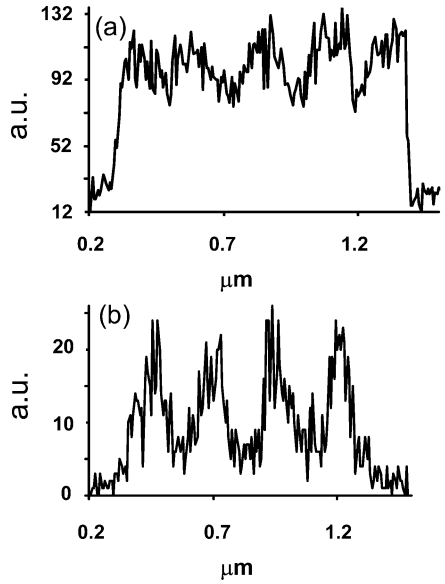

Figure 4. Line profile of carbon (a) and fluorine (b) content in PS/PTFEMA/PS/PTFEMA/PS particles cryotomed at −160 °C.

Characterization of the Surface Composition of the Layers. Surface composition of the alternating layers in the multilayer particles was performed by X-ray photoelectron spectroscopy (XPS) using a Leybold "MAX200" apparatus. Prior to the experiments, the aqueous suspensions were centrifuged and redispersed three times. The latex dispersion was deposited on a glass slide, and the water was allowed for evaporation at room temperature. The relative amount of fluorine-to-carbon was determined by employing a dual-anode Mg radiation source and an aperture of 4 × 7 mm^2. When vinylcarbazole was used as a comonomer for the synthesis of high refractive index layers, we determined the content of nitrogen in the layers, converted it into the molar ratio of nitrogen-to-carbon, and calculated the mole fraction of poly(vinylcarbazole) in the layer.

Characterization of Particle Shape and Morphology. The morphology and shape of the multilayer particles were examined by scanning electron microscopy (SEM, Hitachi S-5200 scanning electron microscope) at an accelerating voltage of 1.0 kV and a current of 10 mA. A droplet of a dilute latex dispersion was dried on a carbon-coated copper TEM grid. Prior to imaging the dispersion was centrifuged, redispersed in a 10% aqueous glycerol solution and frozen at −160 °C. The particles were cryotomed with a diamond/glass knife using Leica Ultracut UCT microtome using a cryochamber. The slices were then placed onto a carbon-coated TEM grid and imaged by using a Hitachi HD-2000 scanning transmission electron microscope (STEM) equipped with energy-dispersive X-ray spectrometer (EDX) Inca X-sight (Oxford Instruments Inc.) at an accelerating voltage of 200.0 kV and the current of 30 mA. The morphology of PTFEMA/PS−PVC particles was accessed at accelerating voltage of 200 kV without microtoming.

Determination of Polymer Refractive Indices. Dispersions of non-cross-linked microspheres were dried at 80 °C and subsequently dissolved in ethyl acetate or chlorobenzene to concentration of ca. 5 wt %. The polymer solutions were spin-coated on single-side polished silicon wafers. A Sopra GES-5 spectroscopic ellipsometer was used to acquire Ψ and Δ from 0.62 to 4.9 eV at angles of incidence of 65°, 70°, and 75°. The Levenberg−Marquardt regression algorithm was used to find the minimum difference between the acquired Ψ and Δ curves and the data generated from an optical model. The model consisted of three layers: a homogeneous crystalline silicone substrate, a 2 nm SiO_2 layer, and the polymer layer. The refractive index and the absorptivity of the polymer layer were modeled using a Cauchy dispersion law.

Results and Discussion

The polymer spherical dielectric resonators required a spherical shape of the microbeads, a periodic modulation in the

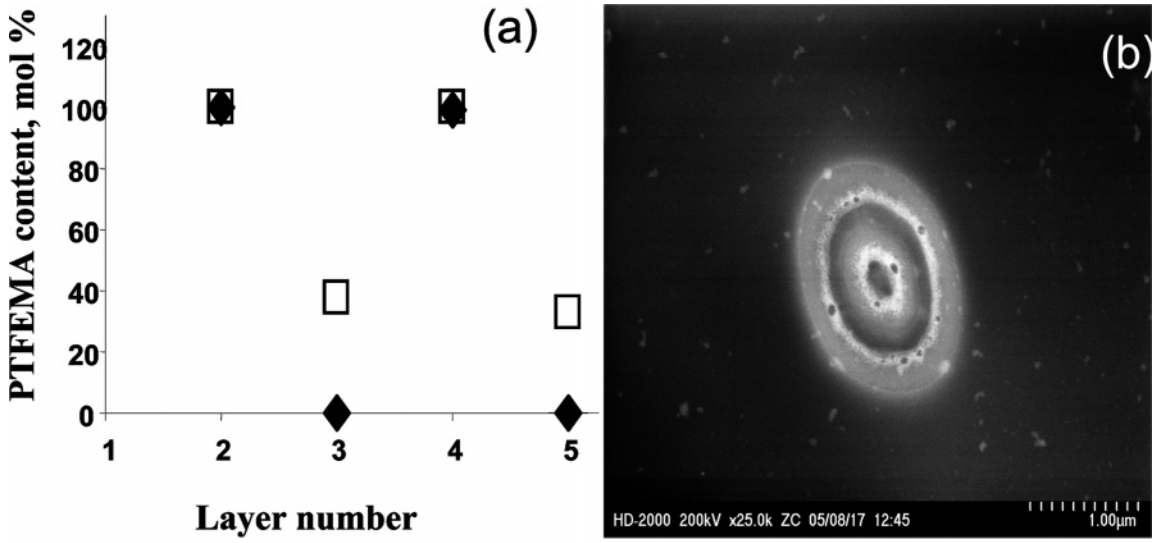

Figure 5. (a) Expected (■) and measured (□) content of PTFEMA in different layers of multilayer particles (number "1" corresponds to the particle cores). Calculation of expected content of PTFEMA was based on the molar ratio of monomers in the mixture fed to the reactor. (b) High-magnification TEM image of PS/PTFEMA particle. Scale bar is 1 μm.

composition of the constituent layers of the particles (leading to refractive index modulation), and a targeted thickness of the layers. Our objective was to synthesize multilayer particles with a PS core and alternating layers of PS and PTFEMA. We used a five-stage polymerization procedure to obtain particles with polystyrene cores, two polystyrene layers, and two layers of PTFEMA. The core and each layer were synthesized in separate stages. The targeted thickness of the layers of 150 nm was achieved by controlling either the number of particles (used as seeds) in the system or the amount of monomer fed in the reaction mixture in a particular stage.

Figure 1 shows typical SEM micrographs of the polymer particles synthesized in five polymerization stages. Figure 1a shows polystyrene latex microbeads (particle cores) (sample 1, Table 1). These particles were engulfed with PTFEMA shells in the second stage (Figure 1b). Figure 1c shows the SEM image of PS/PTFEMA/PS microbeads synthesized in the third stage. Similarly, Figure 1c,e shows typical SEM images of PS/PTFEMA/PS/PTFEMA and PS/PTFEMA/PS/PTFEMA/PS multilayer particles, respectively (samples 4 and 5, Table 1). The microbeads had a spherical shape and monodispersity of ca. 1.2. Notable roughness of microsphere surface was acquired after the fourth polymerization stage; however, the lateral size of protrusions was smaller than the wavelength in the visible spectral range.

After each stage we conducted image analysis of the corresponding SEM images to determine particle dimensions and hence the thickness of layers. Figure 2 shows the variation in average dimensions of the microsphere as a function of the number of polymerization stages (stage "1" corresponded to the synthesis of latex cores). In each stage the mean particle size increased by 300 ± 40 nm, yielding the thickness of the layers of 150 ± 20 nm, very close to the targeted 150 nm.

The multilayer morphology of the microspheres was confirmed by transmission electron microscopy (TEM) experiments. Figure 3 shows typical TEM micrographs of the PS/PTFEMA particles synthesized in the five-stage polymerization process and microtomed at -160 °C and at room temperature (Figure 3, a and b, respectively). In the dark field mode used for TEM imaging PTFEMA and PS layers appeared as bright and dark rings, respectively (Figure 3a).

Periodic modulation in composition of the microspheres was confirmed by conducting energy-dispersive X-ray analysis of the four-layer particles cryotomed at ca -160 °C. Figure 4a shows the variation in carbon content in the different layers of the particles. Since the PS layers contained mostly carbon and hydrogen (by contrast with the neighboring PTFEMA phases), in Figure 4a we observed five carbon peaks, corresponding to the PS core and the third and fifth layers (two for each layer). Similarly, Figure 4b shows the four fluorine peaks corresponding to the second and fourth PTFEMA layers.

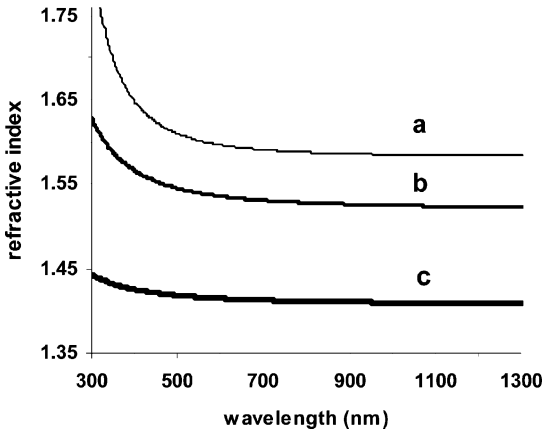

Figure 6. Variation in refractive index as a function of wavelength for PS (a), a copolymer of PS and PTFEMA comprising 33 mol % of PTFEMA (b), and PTFEMA (c).

We quantified the composition of alternating layers by conducting X-ray photoelectron spectroscopy (XPS) experiments. Figure 5 shows the variation in PTFEMA content in the different layers of microsphere (number "1" corresponds to the particle cores). The variation in PTFEMA content confirmed the layered structure of the microspheres, yet it showed a significant (35 ± 3 mol %) content of PTFEMA in the PS layers. We note that XPS experiments provide information about a thin (up to ca. 10 nm) surface layer, and the surface composition of these PS layers may not reflect their bulk composition, where the average content of PTFEMA may be lower.

Figure 5b shows a high-magnification TEM image of PS/PTFEMA multilayer particle. A close inspection of this image reveals that the interface between the layers was sharper when PTFEMA was synthesized on the PS surface than when PS was polymerized on the PTFEMA layer. This phenomenon was

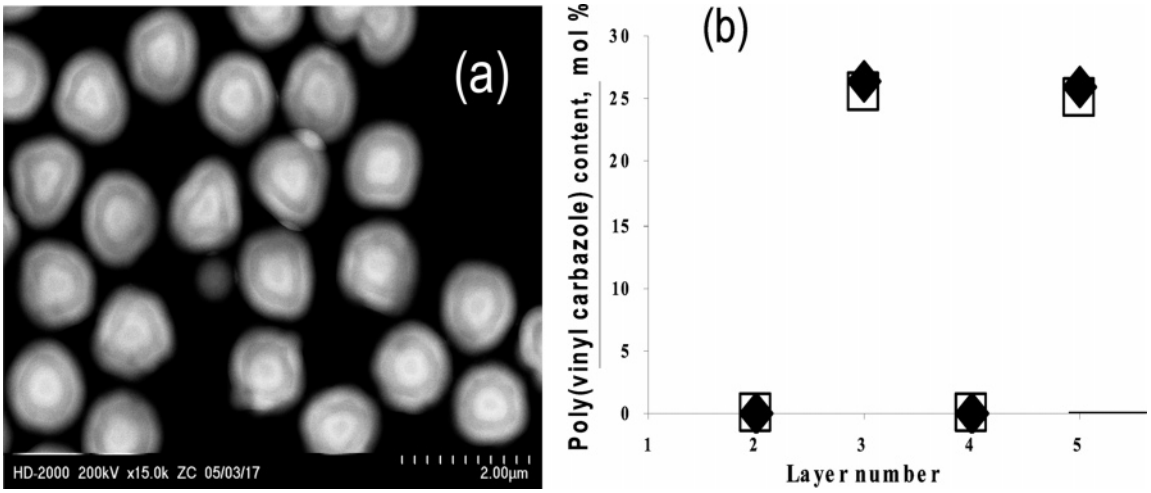

Figure 7. (a) TEM micrograph of microbeads comprising a PS core and alternating PTFEMA and poly(styrene-*co*-vinylcarbazole) layers. To improve contrast between layers TEM was used in the dark field mode. Scale bar is 2 μm. (b) Expected (■) and measured (□) content of poly(vinylcarbazole) plotted as a function of the number of layers (number "1" is assigned to the PS particle cores). Calculation of expected poly(vinylcarbazole) content was based on the molar concentration of vinylcarbazole in the monomer mixture.

ascribed to the swelling of the PTFEMA layer with styrene.[20] The temperature of polymerization of ca. 80 °C exceeded the glass transition temperature of PTFEMA of 60 °C, which resulted in the decreased viscosity of this layer and allowed for the diffusion of oligoradicals of styrene inside the PTFEMA layer.[21,22] In the PTFEMA layer PS underwent phase separation and formed small inclusions that are clearly seen in Figure 5b. We conducted preliminary experiments for polymerization of PTFEMA layers at 50−55 °C (that is, below the glass transition temperature of PTFEMA). The resulting particles had a sharper interface between the PS and the PTFEMA layers.

We estimated the difference in refractive indexes for the alternating layers by forming the films with compositions determined in the XPS experiments. In the spectral range from 400 to 1300 nm the average difference in refractive index between a copolymer of poly(TFEMA−PS) and PTFEMA was ca. 0.125 (Figure 6, lines b and c, respectively). We note that refractive index measured for poly(TFEMA−PS) at $\lambda = 589$ nm was very close to the calculated refractive index contrast for PTFEMA and poly(TFEMA−PS) obtained by using the equation

$$n^2 = \phi_{PS} n_{PS}^2 + \phi_{PTFEMA} n_{PTFEMA}^2$$

where ϕ_{PS} and ϕ_{PTFEMA} are the volume fractions and n_{PS} and n_{PTFEMA} are the refractive indices at $\lambda = 589$ nm for PS and PTFEMA, respectively.[18]

For comparison, we plotted the variation in refractive index for polystyrene (Figure 6, line a): at $\lambda = 589$ nm the loss in refractive index difference between the high and low refractive index polymers due to the swelling of PTFEMA with styrene was ca. 0.025, comparison with the pure PS and PTFEMA phases. We admit that a lower than expected refractive index difference would require a slight increase in the thickness of both high and low refractive index layers, in order for the particles to perform as SDRs.

To compensate for the loss of refractive index contrast caused by partial mixing between the PS and PTFEMA, we attempted to increase the refractive index of high refractive index layers by copolymerizing styrene with vinylcarbazole (poly(vinylcarbazole) has refractive index of 1.68).[18] We used a styrene/vinylcarbazole mixture comprising 40 wt % (26 mol %) of vinylcarbazole.

Figure 7 shows preliminary results on characterization of the structure and composition of the multilayer particles. Figure 7a shows a TEM micrograph of four layer particles with a PS core and four alternating layers of PTFEMA and poly(styrene-*co*-vinylcarbazole) (the latter phases appear dark). This image confirms a multilayer particle morphology. Figure 7b shows the variation in molar concentration of poly(vinylcarbazole) as a function of the number of the layer (number "1" was assigned to the PS cores). The experimentally measured molar content of poly(vinylcarbazole) in the third and fifth layers was remarkably close to its expected content calculated from the molar concentration of vinylcarbazole in the monomer mixture. We conclude that this approach can be used for the synthesis of multilayer particles with enhanced high refractive index contrast between the layers. Assuming that partial mixing between PS-*co*-PVK and PTFEMA occurs in a manner similar to that described above for PS and PTFEMA (that is, the high refractive index layers contain 35 mol % of PTFEMA), we estimated the refractive index of these layers to be ca. 1.57, bringing thereby refractive index contrast between the layers to 0.15.

In summary, we have prepared polymer particles with 150 nm thick alternating high and low refractive index layers, which were synthesized from polystyrene and poly(trifluoroethyl methacrylate), respectively. The multilayer morphology of the particles was proved by transmission electron microscopy, energy dispersive X-ray analysis, and X-ray photoelectron spectroscopy. The results of XPS indicate limited mixing of the polymers; however, the resulting the refractive index contrast of 0.125 was achieved. This refractive index contrast was increased to ca. 0.15 by copolymerizing styrene and vinylcarbazole for the synthesis of high refractive index layers.

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