Photostimulated Phase Separation Encapsulation

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ABSTRACT: Polymer capsules were prepared by photostimulated precipitation of azobenzene-functionalized poly(styrene-*alt*-maleimide) copolymers dissolved in an oil phase and dispersed in a continuous aqueous phase. The oil phase is selected to be a near Θ-solvent for the copolymers, such that the increasing polarity of the polymer due to the photochemical trans-to-cis isomerization induces polymer phase separation and migration to the interface. The resulting polymer walls are permanent even during storage in the dark or irradiation with visible light.

Introduction

The principle of the formation of hollow particles and microcapsules by phase separation of hydrophobic polymers has been well described in patents and publications.[1−4] The key element in these methods is the efficient phase separation of either a forming or a preformed polymer from the core oil, controlled by polymer/core oil interactions.

Two approaches dominate this field: polymerization-induced phase separation and solvent extraction and evaporation methods. The first approach, microencapsulation by in-situ polymerization, involves polymerization in an oil-in-water emulsion. The monomers are chosen to be soluble in the core phase while the forming polymer is not. This forming polymer hence phase separates from the core oil and typically deposits at the oil−water interface to form microcapsules. An efficient, early polymer phase separation is achieved either by using relatively polar monomers together with nonpolar core oils in which the monomers are barely soluble or by using a suitable mixture of nonpolar and very polar monomers.[1−3] In the second approach, an amphiphilic polymer dissolved in a core solvent mixture can be made to phase separate to the interface by selective evaporation of the low-boiling, good-solvent component. Other examples of this approach include selective liquid−liquid extraction of a good solvent from a corresponding solvent/nonsolvent mixed core oil.

In this paper, we describe the a new approach to phase separation encapsulation based on hydrophobic photoresponsive polymers. Here, the solubility of the wall-forming polymer in the oil phase is photochemically decreased, forcing it to precipitate at the oil−water interface. Polymers carrying photoionizable groups have previously been reported to offer photochemical control over properties including surface wettability,[5] viscosity,[6] pH,[7] and binding capacity.[8] A reversible photochemical phase separation of polystyrene carrying azobenzene pendant groups was first reported by Irie et al.[9] It was attributed to the azobenzene trans-to-cis isomerization which altered the balance of polymer−polymer and polymer−solvent interactions in favor of polymer−polymer interactions, likely due to the increased dipole moment of the *cis*-azobenzene.[10−12]

We report here the use of this concept in a heterogeneous environment. Specifically, azobenzene functional polymers that are soluble in their trans form are photochemically driven to phase separate from dispersed core oils to form remarkably stable, permanent polymer capsule walls. In addition, these walls should in principle show photochemically controlled release.[13] This new photochemical method to form hollow polymer particles should prove a useful addition to the area of microencapsulation.

Experimental Section

Polymerization (Typical Procedure). Preparation of poly(styrene (50%)-*co*-(4-phenylazomaleinanil (30%)−phenylmaleimide (20%))) (St50-PAMA30-PMI20). The copolymerization of styrene (1 g, 9.6 mmol) with 4-phenylazomaleinanil (1.6 g, 5.76 mmol) and phenylmaleimide (0.66 g, 3.84 mmol) was carried out at 70 °C in 20 mL of 1,4-dioxane in a 100 mL round-bottom flask fitted with a nitrogen bubbler, using AIBN as initiator (0.02 g, 0.12 mmol). After 24 h of polymerization the copolymer was isolated by precipitating the cooled reaction mixture into a 5-fold excess of cold methanol. The copolymer was filtered, washed with methanol, and dried at 40 °C under reduced pressure for 48 h. The yield of copolymer was 80%; M_w = 15 000, MWD = 1.62.

Typical Method for the Photochemical Preparation of Microcapsules. The following method describes the preparation of microcapsules from St50-PAMA50 copolymer in methyl isobutyl ketone. 100 mL of deionized water containing 1 g of poly(vinyl alcohol) (80% hydrolyzed, 9000−10 000 Da) was placed into a 200 mL Pyrex beaker and stirred at 450 rpm, and the oil phase consisting of 0.25 g of St50-PAMA50 copolymer dissolved in 10 mL of methyl isobutyl ketone was added dropwise over 60 s to form an oil-in-water emulsion. After an additional 20 min of stirring, the emulsion was transferred to a UV reactor containing five RPR 350 nm Rayonet photochemical reactor lamps positioned around the beaker at about 5 cm distance and irradiated for 1 h. A glass coldfinger with circulating cold water was submerged into the emulsion to keep its temperature near room temperature. Following irradiation, the resulting aqueous dispersion of microcapsules was stored at room temperature.

Characterization. A Phillips-2020 environmental scanning electron microscope (ESEM) was used to obtain electron microscopy images. Dilute aqueous dispersions of microcapsules were deposited on aluminum stubs, dried at room temperature, and sputter-coated with a 5 nm gold layer. Optical microscopy was performed using a Olympus BH-2 microscope equipped with a Kodak DC 120 digital camera.

^{1}H NMR spectra were measured in acetone-d_6 on a Bruker AF 300 NMR spectrometer. Quantitative ^{13}C NMR spectra using inverse gated decoupling were measured in $CDCl_3$ on a Bruker AF 300 and on a Bruker DRX 500 NMR spectrometer. UV/vis spectrometry was carried out in DMF solution on a

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Table 1. Azobenzene Group Content and Molecular Weights of the Copolymers

polymer	PAMA content[a]	M_n (GPC)
St50-PAMA40[b]-PMI10[c]	38	16 000
St50-PAMA30-PMI20	29.5	15 000
St50-PAMA20-PMI30	20.6	17 000
St50-PAMA10-PMI40	11.8	15 000

[a] Measured using the absorption of the St50-PAMA50 copolymer at 353 nm as a standard. [b] PAMA40 = 40 mol % of 4-phenylazomaleinanil in polymerization feed. [c] PMI10 = 10 mol % of phenylmaleimide in polymerization feed.

Table 2. Elemental Composition of Three Copolymers

polymer	C_{found}(theo)	H_{found}(theo)	N_{found}(theo)
St50-PAMA50	74.34 (75.57)	4.99 (5.02)	10.8 (11.02)
St50-PAMA30-PMI20	75.29 (76.28)	5.10 (5.08)	9.42 (9.14)
St50-PAMA10-PMI40	76.63 (77.11)	5.65 (5.08)	5.49 (6.77)

Cary 100 UV/vis spectrometer, using the azobenzene absorption band at 353 nm to confirm the compositions of the ternary copolymers, assuming similar molar absorptivities for the azobenzene groups in the ternary copolymers. Elemental analysis was carried out by Guelph Chemical Laboratories.

Results and Discussion

The copolymers used in this study were prepared by free radical solution copolymerization of 4-phenylazomaleinanil (PAMA), phenylmaleimide (PMI), and styrene (St). Styrene and maleimides copolymerize in an strongly alternating sequence,[14] and the use of PMI allowed us to vary the content of photochemically active PAMA while maintaining a stoichiometric styrene/maleimide ratio. The azobenzene content in the final copolymer was estimated by UV/vis spectroscopy, using the absorption of the alternating St50-PAMA50 copolymer at 353 nm in DMF solution as a calibration standard for the other, ternary copolymers. The composition of the azo-aromatic polymers thus obtained from UV/vis is shown in Table 1. They are in general agreement with the results obtained from elemental analysis, shown in Table 2, especially for the copolymers containing larger amounts of PAMA. The copolymer compositions were further confirmed by ^{1}H NMR and quantitative inverse gated decoupling ^{13}C NMR analysis of the carbonyl peaks at 176.3 and 177.1 ppm and the aromatic carbons adjacent to the azo group at 152.7 and 152.1 ppm.

The magnitude of the change in the physical properties of photoresponsive polymers and their solutions depends on the relative stability of the system.[11] For example, when a polymer solution is already close to the point of polymer phase separation, small polarity changes caused by irradiation may cause a large effect, such as polymer precipitation. Thus, the solvent or solvent mixture from which polymer may precipitate out upon irradiation should be a Θ-solvent for the polymer, where the polymer−solvent interactions are just balanced by the polymer−polymer and the solvent−solvent interactions.[15] The solvent should also have a low dielectric constant to enhance the mutual attraction between the dipolar cis-azo groups.[6] Finally, to be used in heterogeneous systems such as encapsulations, the organic solvent should be water immisible and have a relatively high boiling point.

On the basis of these requirements, methyl isobutyl ketone and toluene were evaluated as core solvents for the photoinduced encapsulation procedure, using a series of poly(styrene-*alt*-maleimide) copolymers containing between 10 and 50% azobenzene groups. Only the St50-PAMA50 copolymer dissolved in these single solvents, while the ternary copolymers, in which some or all of the PAMA had been replaced with the more polar PMI, required the presence of polar cosolvents such as dichloromethane or aniline in order to dissolve. For example, the St50-PAMA10-PMI40 copolymer dissolved homogeneously in a toluene/aniline 1:1 volume ratio to form a yellow solution. Upon irradation at 350 nm, the polymer precipitated from this solution, indicating that 10 mol % of the azobenzene units in the copolymer chain are sufficient to cause a solubility change of the polymer dissolved in a near-Θ-solvent system. These results are also in good agreement with literature observations.[11] Similar photochemical copolymer precipitation was observed for all copolymers, from appropriate solvents.

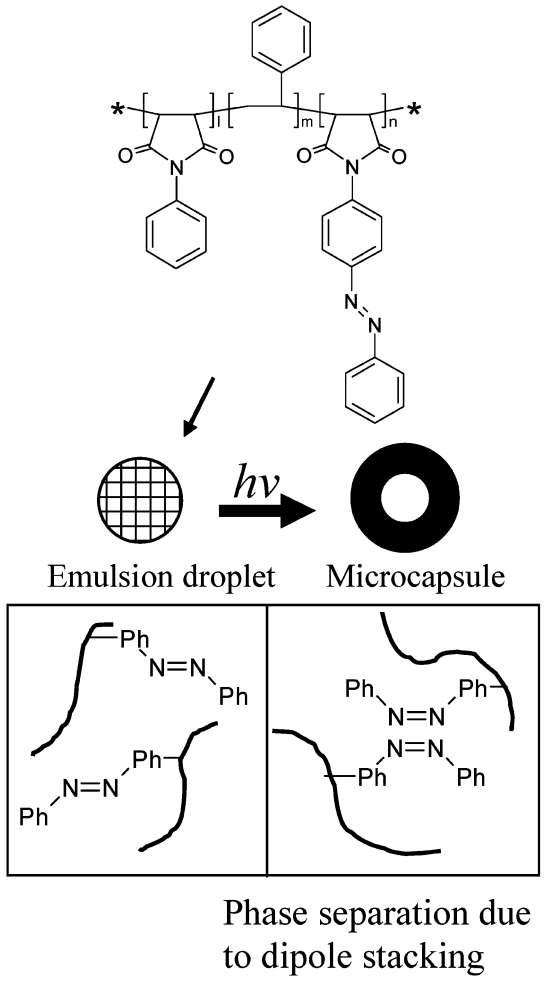

Figure 1. Mechanism of capsule formation by photochemically induced precipitation encapsulation.

In principle, one should be able to compensate for the higher polarity of the PMI comonomer by replacing an appropriate amount of styrene with the more lipophilic 4-*tert*-butylstyrene and thus maintain single solvent solubility throughout a range of PAMA contents. For the present report, we focused our attempts to use photoresponsive copolymers for capsule formation on the St50-PAMA50 copolymer in methyl isobutyl ketone.

Homogeneous solutions of St50-PAMA50 copolymer in methyl isobutyl ketone (1 g/100 mL) showed phase separation upon irradiation at 350 nm for 60 min. The yellow solutions of the azobenzene functional polymer

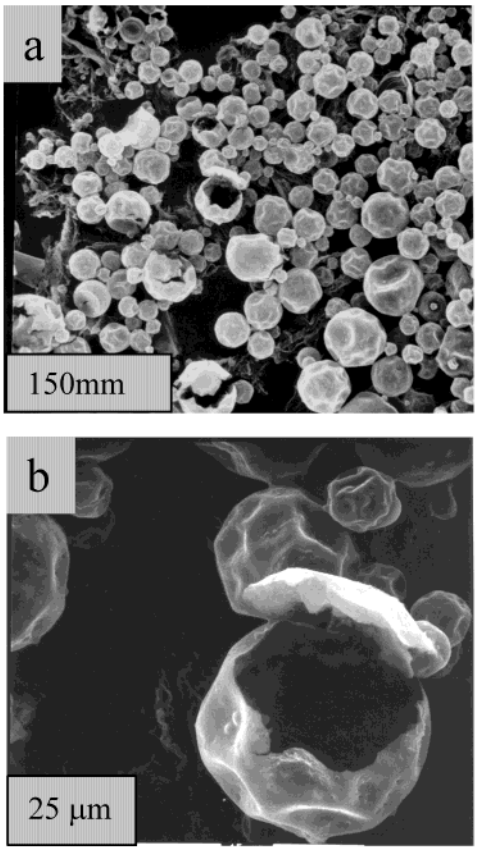

Figure 2. ESEM image of microcapsules produced by irradiation of an aqueous emulsion of methyl isobutyl ketone containing 5% St-PAMA50.

became almost clear following the irradiation, with the polymer precipitating as an orange solid.

For the photoinduced encapsulations, a solution of 5% w/v of poly(styrene-*alt*-PAMA) in methyl isobutyl ketone was dispersed in an aqueous phase containing poly(vinyl alcohol) as colloidal stabilizer. The resulting emulsion was irradiated at 350 nm at room temperature for about an hour, after which time the emulsion droplets had turned into liquid-filled polymer microcapsules. Apparently, the polymer phase separated from the MIK during irradiation and migrated to the o/w interface to form the capsule wall. This encapsulation process is illustrated in Figure 1.

Figure 2a,b shows environmental scanning electron microscope (ESEM) images of the resulting microcapsules. The polymer capsule walls are thin, on the order of 200 nm. They show indentations on their surface, which are likely due to partial fill release and wall collapse at the shell thin spots under the high vacuum required for SEM sample preparation.[16]

The enlarged area shown in Figure 2b illustrates how some of the capsules have burst during ESEM processing. Optical microscopy gave further insight into the morphology and the release properties of these microcapsules. Thus, the capsules were clearly spherical and had smooth surfaces while wet (Figure 3a). However, after drying on the glass slide for 15 min surface indentations were observed, indicating the release of the MIK core solvent (Figure 3b). This result suggests a high permeability or porosity of the capsule walls.

The analogous encapsulation, using an emulsion of methyl isobutyl ketone containing 10 wt % of the same copolymer, led to much thicker capsule shells (Figure

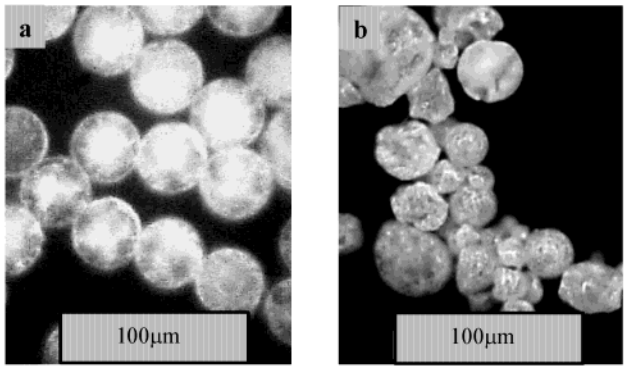

Figure 3. Optical microscope images of microcapsules produced by irradiation of an aqueous emulsion of methyl isobutyl ketone containing 5% St-PAMA50: (a**)** wet microcapsules on the glass slide; (b**)** dry microcapsules, 15 min on the glass slide.

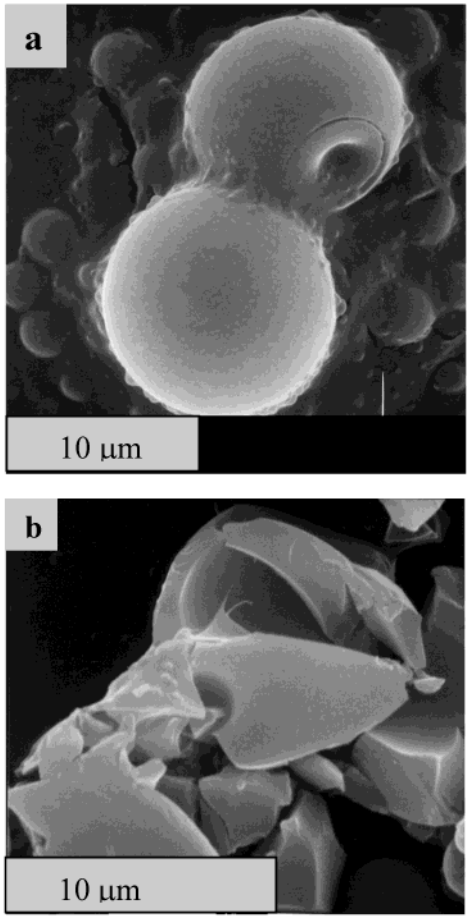

Figure 4. ESEM images of microcapsules produced by irradiation of an aqueous emulsion of methyl isobutyl ketone containing 10% St-PAMA50: (a) whole capsules; (b) capsule wall fragments.

4a,b). Figure 4a shows a representative section of the electron micrograph image of the capsules obtained after 90 min irradiation at 350 nm. These capsules were stable during ESEM processing and were manually fractured in order to investigate their internal structure (Figure 4b). The shell thickness of the microcapsules is related to the concentration of copolymer in the organic phase. Increasing the polymer content in the oil phase should produce proportionally thicker shells. However, the thickness of the capsule walls prepared from 10 wt % polymer solutions is about 1−2 μm for a 10 μm diameter capsule. This wall thickness is more than can

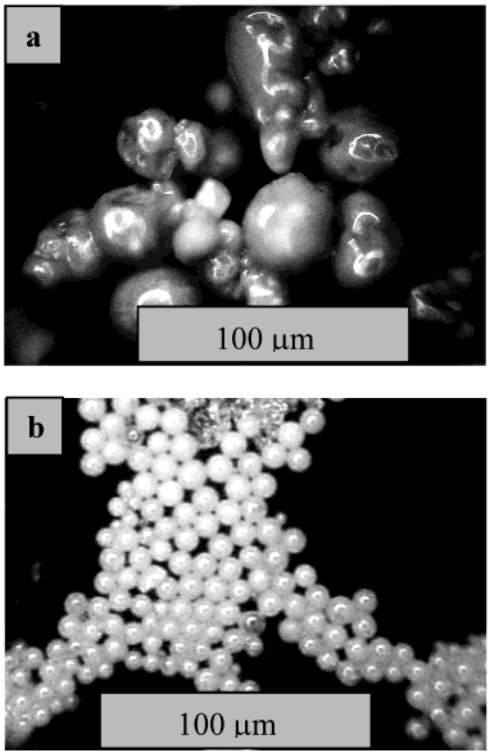

Figure 5. Optical microscope images of microcapsules produced by irradiation of aqueous emulsions of (a**)** toluene/aniline 5:1 volume ratio containing 5% St50-PAMA20-PMI30 and (b**)** toluene/CH_2Cl_2 1:1 v/v containing 5% St50-PAMA20-PMI30.

be expected from a bulk wall at 10 wt % wall-former loading and suggests a high porosity of the capsule wall. This result correlates well with the observed relatively fast fill release rate from these microcapsules.

Capsules were also prepared from copolymers having less than 50 mol % azobenzene groups. For example, St50-PAMA20-PMI30 capsules prepared from a 5/1 toluene/aniline mixture had a very broad size distribution. This may be due to the fact that the density of aniline is higher than the density of water, making it difficult to disperse the aniline containing oil phase in water (Figure 5a). The resulting microcapsules were also very brittle and fell apart upon being transferred to a glass slide. However, microcapsules prepared with toluene/dichloromethane as a core mixture were smaller in size with narrow size distribution (Figure 5b).

These precipitations of the present polymers are due to the photochemical trans−cis conversion and should hence be reversible. Redissolution by thermal back-isomerization was in fact observed in all homogeneous polymer solutions. However, the capsules formed by irradiation in heterogeneous emulsion systems did not redissolve upon standing in the dark for several weeks. We assume that this permanence may be due to the presence of a small amount of water in the core oil of the microcapsules prepared by photoinduced phase separation encapsulation, which prevents the shell polymer from redissolving even after heating or a long dark period. Water can diffuse into the capsules through the pores of the relatively polar shells during the encapsulation process or/and upon storage. As well, the permanence may be due to a kinetic entrapment of the polymer chains, perhaps due to entanglement, after having been precipitated at the oil−water interface.

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