Macromolecules

Volume 41, Number 14 July 22, 2008

Communications to the Editor

Nonaqueous Emulsions as a Tool for Particles with Unique Core−Shell Topologies

Robert Haschick, Kevin Mueller, Markus Klapper,* and Klaus Muellen

Max-Planck Institute for Polymer Research, Ackermannweg 10, D-55128 Mainz, Germany

Received March 11, 2008
Revised Manuscript Received April 27, 2008

Introduction. The formation of latex particles represents an important field in academic and industrial research.[1] There is a wide range of industrial applications for such particles, e.g. as composites, film-forming materials, or additives for inks.[2] The direct synthesis of such particles in aqueous emulsions or suspensions is almost exclusively limited to radical polymerization.[3] Other polymerization techniques allowing the use of non-vinylic monomers suffer from limited stability either from the monomers or from the catalyst and undergo side reactions with the continuous phase.[4] There is thus a strong need for practical and versatile techniques allowing the synthesis of various polymers in emulsions. This becomes even more pressing when considering core−shell structures wherein one wishes to combine the properties of different polymers to obtain particles with superior properties. Prominent examples are polystyrene−polybutadiene or polystyrene−poly(butyl acrylate)−latices.[5]

Many different synthetic routes to generate core−shell particles have already been presented. In particular, aqueous emulsions were used to form hybrid particles by such techniques as miniemulsion polymerization,[6,7] seeded emulsion polymerization, preparation of cross-linking, and graft copolymerization.[8,9] A major drawback of these aqueous methods, however, is their poor applicability for water-sensitive reactions. Catalytic polymerization of olefins tends to result in low molecular weight polymers as polyaddition reactions performed with isocyanates and diols lead to the formation of urea as a side product and to decreased molecular weights, compromising both the mechanical and thermal properties.[10] To overcome these drawbacks associated with water-sensitive compounds, novel nonaqueous emulsions have been developed by us.[11−13] These emulsions avoid the presence of not only water but also any protic solvent and offer the possibility to carry out water-sensitive reactions in emulsions. This method allows the fabrication of high molecular weight PU or polyesters by a one-step synthesis without using a prepolymer. Furthermore, side reactions, which would lead to the formation of ureas, are suppressed, and catalytic polymerizations using metallocenes result in remarkably high molecular weight polymers when performed in nonaqueous emulsions.[14] Mechanistically, the process can be considered as a mixture of a miniemulsion and an emulsion polymerization depending on the solubility of monomers and catalysts.[12] Because of this versatility, it then becomes possible to combine different polymerization procedures and monomers when forming core−shell particles.

PU plays a particularly important role in polymer composites due to its favorable mechanical (toughness, impact, and abrasion resistance) and thermal (service temperature and dimensional stability under heat) properties.[15] The fabrication of composite materials from methacrylates, acrylates, alkyds, or polyesters with PU enhances the toughness, abrasion resistance, and film-forming properties of the polymer matrix.[16] The first synthesis of PU particles which can be used for the incorporation into composite materials was performed in 2000 and 2001 via miniemulsion.[17,18] But this system resulted also in side reactions with water as it was mentioned before. However, since PU is immiscible with many polymer matrices, a compatibilization of the PU with the polymer matrix is mandatory to prevent phase separation, gel formation, or discoloration.[19] This can be achieved by preparing PU particles having a matrix-compatible polymeric shell.

Therefore, we have chosen to demonstrate the efficiency, simplicity, and versatility of the nonaqueous emulsions by the formation of PU/polymethacrylate core−shell particles. To optimize these particles by increasing their molecular weights, a method is described which avoids the presence of protic solvents. In this paper *N,N*-dimethylformamide (DMF) was used to generate *nanoreactors* in *n*-hexane, by which particles of high molecular weight PU cores and surrounded by a polymethacrylate shells were synthesized.

---

* To whom correspondence should be addressed. E-mail: klapper@mpip-mainz.mpg.de.

10.1021/ma800550z CCC: $40.75

Table 1. Experimental Conditions and Results of the Preparation of PU/Polymethacrylate Core−Shell Particles in Nonaqueous Emulsion[a]

sample	HMDI (core)/mmol	BHC (core)/mmol	M_n[b] (core)/g mol^{-1}	PDI[b] (core)	av diam[c] std dev[d] (core)/nm	methacrylate (shell)/mmol		av diam[c] std dev[d] (core−shell)/nm
1	1.60	1.5	6800	2.06	110 ± 40	5.0	MMA	150 ± 140
2	1.60	1.5	13900	1.60	120 ± 90	5.0	MMA	420 ± 120
3	1.60	1.5	8700	1.30	350 ± 200	4.0	MMA	670 ± 140
4	1.60	1.5	10100	1.69	70 ± 30	3.5	*t*BMA	240 ± 110
5	1.60	1.5	14800	1.55	90 ± 30	3.5	*t*BMA	130 ± 90
6	1.60	1.5	6700	1.35	500 ± 140	2.8	*t*BMA	920 ± 370
7	1.60	1.5	8600	1.31	120 ± 100	3.8	HEMA	330 ± 80
8	1.28	1.2	8100	1.66	500 ± 80	3.1	HEMA	600 ± 130
9	1.60	1.5	7500	1.36	240 ± 50	3.1	HEMA	260 ± 60

[a] In 12 g of *n*-hexane, 210 mg of PI-*b*-PMMA, and 1,2 g of DMF, after 10 min ultrasonification, at 40 °C. [b] Determined by SEC in DMF vs PS standard. [c] Determined by SEM by measuring the diameter of 100 particles. [d] $\pm\sigma = (\sum(x - \bar{x})(n-1)^{-1})^{0.5}$.

Experimental Part. Chemicals. N,N′-Dimethylformamide (DMF, Aldrich, anhydrous) and *n*-hexane (Aldrich, anhydrous) were used as received. Polyisoprene-*block*-poly(methyl methacrylate) (PI-*b*-PMMA) copolymer was prepared using a sequential anionic polymerization technique described elsewhere.[13] 4,4′-Methylenebis(cyclohexyl isocyanate) (HMDI, Aldrich, 95% purity), 1,4-bis(hydroxymethyl)cyclohexane (BHC, Aldrich, 99% purity), dibutyltin diacetate (DBDA, Aldrich), 2,2′-azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70, Wako Pure Chemical Industries), phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide (Irgacure 819, Ciba Specialty Chemicals Inc.), and *N,N′*-methylenebisacrylamide (MBAA, Aldrich) were used as received without further purification. 2-Hydroxyethyl methacrylate (HEMA, Aldrich), methyl methacrylate (MMA, Acros), and *tert*-butyl methacrylate (*t*BMA, Acros) were dried over CaH_2 and distilled under reduced pressure prior to use.

Preparation of Polyurethane Polymethacrylate Nanoparticles. PI-*b*-PMMA copolymer (M_n = 33 700 g/mol, PDI = 1.1, 71 wt % PI and of 29 wt % PMMA) (0.210 g) was dispersed in *n*-hexane (12.0 g, 139 mmol) at room temperature. BHC (0.144 g, 1.00 mmol) and DBDA (0.050 g, 0.14 mmol) were dissolved in DMF (1.2 g, 20 mmol) and added dropwise to the hexane/copolymer dispersion. The emulsion was formed at room temperature by stirring the mixture for 2 h and ultrasonification of the solution for 10 min using a Bandelin Sonorex RK255H ultrasonic bath, operating at 640 W. Subsequently, HMDI (0.289 g, 1.10 mmol) was added dropwise to the emulsion within 1 h. The polyaddition reaction proceeded under stirring for 16 h at room temperature. A sample of this emulsion was taken to analyze the PU core particles. For the preparation of the shell a second amount of DMF (0.3 g, 4.1 mmol) was then added, containing the initiator (2.5 mol % V-70 or Irgacure 819) and the cross-linking agent (2.5 mol % MBAA). The dispersed phases were combined and stirred for 2 h at room temperature, followed by ultrasonification for 10 min. Subsequently, methacrylate (400 mg of HEMA, MMA, or *t*BMA) was added dropwise to the emulsion. The radical polymerization was carried out at 30 °C for 16 h. The reaction mixture was placed in a separating funnel, and ethanol was added to remove the emulsifier. The particles, remained in ethanol, were precipitated in *n*-hexane, filtered, and washed twice with *n*-hexane to yield 0.5 g (50%) of a colorless residue which was either dried under vacuum overnight or directly redispersed in ethanol.

Characterization Methods. The molecular weights of the PU cores were determined by size exclusion chromatography (SEC) vs polystyrene standard in DMF at 60 °C, using MZ-Gel SDplus 10E6, 10E4, and 500 columns and a ERC RI-101 differential refractometer detector. The composition of the PU/methacrylate core−shell particles was investigated by ^{1}H NMR spectroscopy in DMF-d_7 using a Bruker Avance spectrometer operating at 250 MHz. SEM images were taken using a Zeiss Gemini 912 microscope. For SEM sample preparation, the nanoparticles were dispersed in methanol and drop-cast on a silica wafer. The preparation of the samples for TEM imaging was carried out in methanol. A drop of the particle dispersion was given on a TEM grid, and images were obtained using a FEI Tecnai F20 microscope operating at 200 kV.

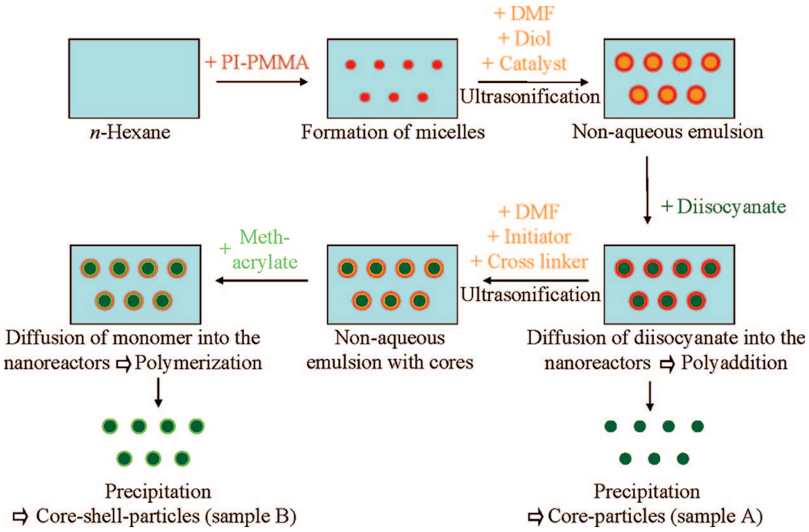
Results and Discussion. For the formation of a nonaqueous emulsion, DMF and *n*-hexane were used as an almost nonmiscible solvent pair (miscibility below 3%, studied by NMR spectroscopy). DMF served as the dispersed phase, and *n*-hexane was used as the continuous phase. These solvents were selected to ensure that the reaction took place exclusively in the dispersed phase (DMF) due to the solubility of all monomers therein and the insolubility of the diol (for polyaddition) and the initiator (for radical polymerization) in the continuous phase (*n*-hexane). A polyisoprene-*block*-poly(methyl methacrylate) copolymer (PI-*b*-PMMA) was used as an emulsifier to suppress the separation of the solvents yielding stable droplets. The applied emulsifier showed an average molecular weight (M_n) of 33 700 g/mol (PDI = 1.1) and a block composition of 71 wt % PI and of 29 wt % PMMA. The PMMA block was exclusively soluble in the dispersed phase while the PI block stabilized the micelles for steric reasons in the continuous phase.

The aliphatic diol 1,4-bis(hydroxymethyl)cyclohexane (BHC) and the aliphatic diisocyanate 4,4′-methylenebis(cyclohexyl isocyanate) (HMDI) were used for the synthesis of the PU core particles, as shown in Table 1. MMA, *t*BMA, and HEMA were used to prepare the shell structures.

The synthesis of the core−shell particles was carried out according to Scheme 1. BHC was dissolved in DMF with 2.5 mol % catalyst and added to the *n*-hexane/copolymer dispersion. The emulsion was formed by ultrasonification of this mixture. The polyaddition was started by a dropwise addition of HMDI to the emulsion. Since the diol is insoluble in the *n*-hexane phase, it is assumed that the diffusion of HMDI into the droplets starts the reaction. Dibutyltin diacetate (DBDA) was applied as a catalyst for promoting the polyaddition and achieving high molecular weights.

The highest molecular weight was achieved not by direct mixing both components in an equimolar ratio, but by adding HMDI slowly to the emulsion of the corresponding diol. This slow addition of HMDI, as it is used in industrial polycondensations or polyaddition reactions,[20] makes sure that one finally reaches the exact equimolar ratio of the two reactants, which is necessary to achieve high molecular weights. Excessive addition of the component beyond the equimolar ratio leads to no decrease of the molecular weight due to the irreversibility of the polyaddition reaction.

Scheme 1. Preparation of PU/Polymethacrylate Core−Shell Particles in Nonaqueous Emulsion



To prepare the shell structures, a second amount of DMF containing the radical initiator and a cross-linking agent was added. After ultrasonication, the methacrylate was added to the mixture. Since the initiator is almost insoluble in the *n*-hexane phase, it was assumed that the polymerization, initiated by an increase of the temperature to 30 °C, takes mainly place inside of the droplets and is controlled by the diffusion of the methacrylate into the droplets. Even in the case of a small amount of initiator soluble in the continuous phase an initiation herein should lead similar to an emulsion polymerization in aqueous phase to the diffusion of oligomeric radicals into the existing droplets and therefore not to the formation of pure PMMA particles.

To investigate the formation of core−shell particles by measuring the increase of the particle size, 2 mL samples of the emulsion were taken out before and after the radical polymerization. This procedure and its results are illustrated in the following for the PU/PMMA particles. Similarly, the corresponding PU/HEMA and PU/*t*BMA (experiments 4−9) were studied.

The composition of the samples was investigated by NMR spectroscopy after removal of the emulsifier. Comparison of the spectra of sample A (taken before shell polymerization) and sample B (taken after shell polymerization) clearly indicates the formation of methacrylic polymers other than PU. Figure 1 shows the NMR spectra of sample 1A and 1B. The peak at about 3.65 ppm represents the protons in α-position with respect to the ester group ($-COO-CH_3$) of the PMMA in sample B. The signals at 0.83 and 1.87 ppm are due to the methyl and the methylene protons of PMMA, which are overlapped by those of the PU ring protons. Therefore, one can safely assume that sample 1B contains both PU and PMMA. The spectra of the other samples led to comparable results.

The presence of both polymers in the samples, however, does not necessarily indicate the formation of core−shell structures because pure PMMA particles and pure PU particles may coexist in the sample. To exclude this possibility, the particle size was investigated. Dynamic light scattering (DLS) could not be used for the direct determination of particle size due to the formation of aggregates after the removal of the emulsifier. Therefore, the untreated emulsion was diluted and analyzed by DLS to compare the diameter of the droplets before and after the shell preparation. Alternatively, the mean particle size was determined by SEM, thereby measuring the diameter of 100 particles and calculating their average value. In all cases, monomodal curves were obtained and the identified values of both methods were comparable. The achieved diameters of the particles are shown in Table 1. It is obvious that the particles show an increase in size after the addition of the methacrylates and their radical polymerization. For example, the particle size of sample 1A (PU core particle) is about 110 nm while the diameter of sample 1B (PU/PMMA core−shell particle) is about 150 nm. This firmly indicates the formation of a shell structure around the cores.

Besides the increase in size of the particles, in most cases the size distribution of the core−shell particles is broader than that of the initial core particles (e.g., sample 1A: 40 nm; sample 1B: 150 nm). This might indicate a inhomogeneous coverage of the core particles by methacrylate shells. This was supported by the TEM.

In Figure 2 TEM images of sample 1B are shown. Figure 2B shows a particle after the formation of the shell. The area of high contrast (black), caused by the polyurethane due to the urea groups, is surrounded by a ring of low contrast. Since methacrylates possess a low contrast in TEM micrographs,[21] Figure 2B supports the assumption that PMMA shell structures were generated around the PU cores. The TEM images also reveal that the shells are partially discontinuous. A similar effect is known when silica particles are surrounded by a polymer shell in emulsion.[22] One may assume that the PU particle is not in the center of the micelles when MMA is added, and therefore the shell has a different thickness in certain areas. Before the synthesis of the shell structures and after the core-particle synthesis, a relatively narrow and monomodal size distribution of the droplets was determined by dynamic light scattering. After adding the dissolved initiator and the methacrylate monomer, a growth of the particles caused by the diffusion of the monomers into the particles was observed. Since the size distribution obtained from DLS was still monomodal, we assume that the monomer has been almost quantitatively diffused inside the PU-containing droplets. A second species of particles formed by a part of the added MMA was not observed by DLS and also TEM revealed them only in a very limited amount (especially considering the volume fraction). This lead to the assumption that the number of pure PMMA particles formed by secondary nucleation was negligible.

Furthermore, the molecular weights of the PU core particles were investigated by means of SEC (Table 1). The determined molecular weights showed values up to 14 800 g/mol (M_n).

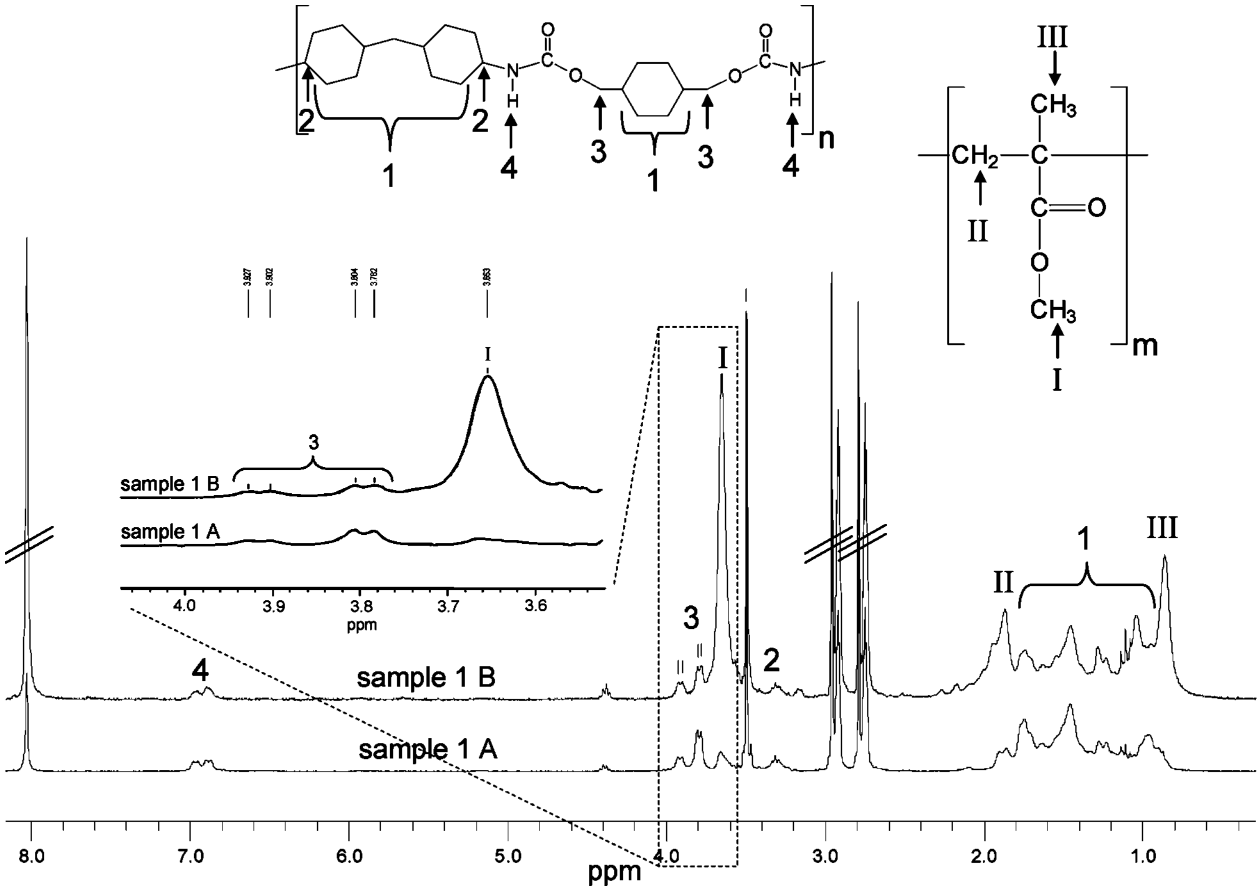


Figure 1. Comparison of the proton (250 MHz) NMR spectra of samples 1A and 1B in DMF-d_7 at room temperature.

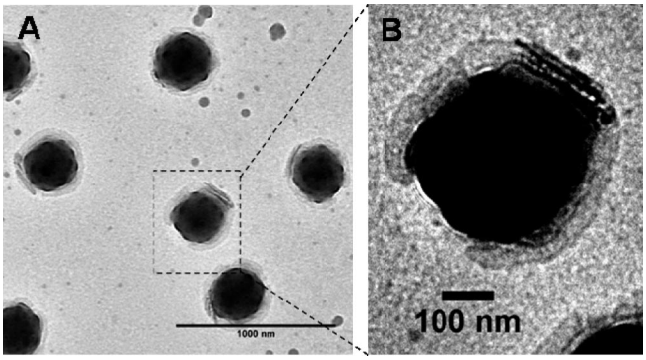


Figure 2. TEM images of sample 1B.

These remarkably high molecular weights are caused by the absence of water, which leads to higher conversions for polyadditions; urea formation is thus suppressed, which would otherwise cause deviations from the ideal stochiometry of diol and disocyanate.[13] The preparation of high molecular weight cores offers the possibility to generate particles with very rigid cores and soft shells. In comparison to the literature[4] where PU cores show molecular weights (M_n) up to a maximum of 13 500 g/mol with a high content of urea, the described method affords higher molecular weights without the need of multipot synthesis, prepolymers, or special conditions. In addition to the high molecular weight, another advantage of the described method is the quantitative reaction of the isocyanate groups with the hydroxy groups and the absence of side reactions with water.[3] This would result in a loss of starting material and urea derivates would be formed influencing the properties of the PU core.

Because of the increased size of the particles after radical polymerization, in combination with the observed shell around the dark PU cores in the TEM images, one can safely assume that the preparation of core–shell particles by water-sensitive monomers in nonaqueous emulsion proceeds successfully.

Conclusion. Through the use of nonaqueous emulsions, a simple and versatile method to form polymer core–shell particles has been described. This concept was demonstrated in detail for PU/PMMA core–shell particles. The prepared particles showed diameters as small as 125 nm and molecular weights up to 14 000 g/mol. This approach documents the advantage of nonaqueous emulsions to form core–shell particles with water-sensitive reactions. No prepolymer formation is necessary to generate high molecular weight polymers, as in classical emulsions, which shows the ease of this method. Also, no multistep synthesis or demanding synthetic setups are needed since the formation of the core and the shell are carried out in one pot.

While water-sensitive polymerizations cannot be performed in classical emulsions, this approach allows the use of sensitive monomers or catalysts. It can safely be assumed that by this method core–shell particles based on totally new combinations of polymers will be accessible. Other than radically polymerizable monomers can now easily be combined to new polymer topologies. Shell or core structures can be formed for example also by polycondensates or polyolefins. Polymers obtained from catalytic polymerizations such as acyclic diene metathesis (ADMET) or ring-opening metathesis polymerization (ROMP) can be also incorporated in core–shell structures. By this new technology, it is expected that a large number of new particles with special material properties can be designed which have for example optimized film-forming abilities or adhesion behavior on surfaces necessary for coatings or paints.

Acknowledgment. The authors acknowledge Thomas Wagner and Jürgen Thiel for the synthesis of the PI-*b*-PMMA copolymers as well as Gunnar Glasser, Ingo Lieberwirth, and Katrin Kirchhoff for the SEM and TEM measurements.

References and Notes

(1) Antonietti, M.; Landfester, K. *Prog. Polym. Sci.* **2002**, *27*, 689–757.
(2) Hirose, M.; Zhou, J.; Katsutoshi, N. *Prog. Org. Coat.* **1997**, *31*, 157–169.
(3) Guyot, A.; Landfester, K.; Schork, F. J.; Wang, C. *Prog. Polym. Sci.* **2007**, *32*, 1439–1461.
(4) Barrere, M.; Landfester, K. *Macromolecules* **2003**, *36*, 5119–5125.
(5) Parka, C.; Yoonb, J.; Thomas, E. L. *Polymer* **2003**, *44*, 6725–6760.
(6) Musyanovych, A.; Landfester, K. *Macromolecular Engineering*; Wiley-VCH: New York, 2007; Vol. *2*, Chapter 13.
(7) Tiarks, F.; Landfester, K.; Antonietti, M. *Langmuir* **2001**, *17*, 908–918.
(8) Kukanja, D.; Golob, J.; Zupancic-Valant, A.; Krajnc, M. *J. Appl. Polym. Sci.* **1999**, *78*, 67–80.
(9) Chen, G.-N.; Chen, K.-N. *J. Appl. Polym. Sci.* **1999**, *71*, 903–913.
(10) Li, C.-Y.; Chiu, W.-Y.; Lee, C.-F. *e-Polym.* **2007**, *15*, 1–17.
(11) Mueller, K.; Klapper, M.; Muellen, K. *Macromol. Rapid Commun.* **2006**, *27*, 586–593.
(12) Mueller, K.; Klapper, M.; Muellen, K. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 1101–1108.
(13) Mueller, K.; Klapper, M.; Muellen, K. *Colloid Polym. Sci.* **2007**, *285*, 1157–1161.
(14) Nenov, S.; Clark, C. G., Jr.; Klapper, M.; Muellen, K. *Macromol. Chem. Phys.* **2007**, *208*, 1362–1369.
(15) Cheremisnoff, N. P. *Handbook of Ceramics and Composites*; CRC: Boca Raton, FL, 1990; Vol. *2*, Chapter 5.
(16) Allen, G.; Bowden, M. J.; Blundell, D. J. *Polymer* **1973**, *14*, 597–603.
(17) Landfester, K.; Tiarks, F.; Hentze, H.-P.; Antonietti, M. *Macromol. Chem. Phys.* **2000**, *201*, 1–5.
(18) Tiarks, F.; Landfester, K.; Antonietti, M. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 2520–2524.
(19) Li, M.; Daniels, E. S.; Dimonie, V.; Sudol, E. D.; El-Aasser, M. S. *Macromolecules* **2005**, *38*, 4183–4192.
(20) Kumar, A.; Gupta, R. *Fundamentals of Polymer Engineering*, 2nd ed.; Marcel Dekker: New York, 1997; Chapter 4.
(21) Janik, H. *Macromol. Rapid Commun.* **2004**, *25*, 1167–1170.
(22) Wang, H.; Shi, T.; Zhai, L. *J. Appl. Polym. Sci.* **2006**, *102*, 1729–1733.

MA800550Z