Convenient Synthesis of Fluorinated Latexes and Core−Shell Structures by Miniemulsion Polymerization

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ABSTRACT: Fluorinated latexes in the size range of 100−250 nm are made by the polymerization of miniemulsions of fluoroalkyl acrylates as fluorinated monomers under employment of rather low doses of protonated surfactants. In addition, it is shown that miniemulsifaction of mixed monomer species allows efficient copolymerization reactions to be performed with standard hydrophobic and hydrophilic monomers in a joint heterophase situation, resulting either in core−shell latexes or in statistical copolymers. Contrary to the pure fluorinated polymers, those copolymers dissolve in organic solvents but still show the profitable interface properties of the fluorinated species.

Introduction

Acrylate copolymers with fluorinated side chains possess a whole range of very interesting material properties, such as a very low refractive index, very good tribological properties, ultralow surface tensions and the related nonwettability, very high oxygen permeation at a simultaneously low water uptake, CO_2 solubility, and a potentially high chemical resistance, just to name a few.[1] On the other hand, they are often very difficult to handle and rely many times on rather uncommon solvents (except for using CO_2 as solvent)[2] for processing and application. Therefore, it is a well-known solution to prepare polymer dispersions of those fluorinated polymers in water which allow synthesis and handling via the dispersed state.

Making a fluorinated dispersion by classical emulsion polymerization is however not trivial. This technique relies on monomer transport from the monomer droplets to the growing particles, and the solubility of fluorinated monomer in water is usually extraordinarily low. This is why classical industrial recipes using fluorinated acrylate monomers add large amounts of an organic solvent to the continuous phase, for instance acetone.[3−5] Linemann et al. used emulsion polymerization to prepare fluorine-containing polymer latex particles.[6] The synthesis using only water as continuous phase led to low monomer conversion accompanied by substantial losses of the fluorine-containing acrylate monomer due to severe coagulation during polymerization and during storage. Only the synthesis with the addition of acetone and butyl acrylate led to coagulation-free dispersions. Another serious problem is the choice of the surfactant which has to be compatible with the fluoropolymer and is preferentially a fluorinated surfactant in itself. Those surfactants are however very expensive and environmentally questionable. In the case of excellent surfactant packing, also long-chain hydrophobic surfactants can be employed, e.g., cetyltrimethylammonium bromide,[6] which again is coupled to a serious restriction of processing and parameter space; i.e., those recipes are very sensitive toward changes.

Another general possibility to incorporate fluoropolymers into polymer dispersions is swelling of a first stage polymer dispersion with the fluoromonomer, followed by second stage polymerization. Marion et al. used a semicontinuous emulsion polymerization process to synthesize core−shell particles containing a fluoropolymer in the shell.[7] This technique however relies on a compatibility between the first stage polymer and the monomer and is therefore restricted to monomers with low fluorine content, e.g., single trifluoromethyl groups.

A third general possibility is given by the polymerization from fluorinated microemulsions.[8,9] Here, the polymerization is carried out in the presence of larger amounts of a perfluoropolyether and fluorinated surfactants. Although the control of particle size and particle morphology is very good, the employed components make such procedures appropriate for the generation of model particles but less useful for the above-mentioned applications.

It is therefore promising to employ the newly developed technique of polymerization in miniemulsion to the heterophase polymerization of fluorinated monomers. In a first step of the miniemulsion process, small stable droplets in a size range between 30 and 500 nm are formed by shearing a system containing the dispersed phase, the continuous phase, a surfactant, and an osmotic pressure agent. In a second step, these droplets are polymerized without changing their identity.[10−12] Shortly, polymerization in miniemulsion does not rely on monomer transport through the water phase, but droplet nucleation of the minidroplets is the predominant initiation mechanism.[13,14] This enables the polymerization of the as-prepared miniemulsions, and the problem of polymerization and copolymerization of fluorinated monomers reduces to the question of the preparation of stable miniemulsions, whereas solubility questions have been avoided. Fluorinated monomers have already been tried in miniemulsion polymerization, but in previous work latexes with only 1.4% fluorinated polymer were obtained, even though it was started with 25% fluorinated monomer.[15]

It will be shown that improved miniemulsion procedures indeed allow complete polymerization and stabilization of pure fluorinated monomers with sodium dodecyl sulfate (SDS) as a simple surfactant. This is done using perfluoromethyldecalin or heptadecafluorodecyl methacrylate as a fluorophilic (ultra)hydrophobe for the buildup of an osmotic pressure control, as it was

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also described for fluorocarbon emulsions stabilized by lecithin as surfactant and perfluorodimorphinopropane as an ultrahydrophobe.[16]

In addition, copolymerization reactions with standard comonomers by common miniemulsification of both fluorocarbon and hydrocarbon comonomers will be attempted. It will be shown that, depending on reaction conditions, both homogeneous latexes composed of statistical copolymers as well as core−shell latexes composed of block copolymers can be made.

Experimental Part

Chemicals. The fluorinated monomers tridecafluorooctyl methacrylate ($CH_2{=}C(CH_3)CO_2(CH_2)_2(CF_2)_6F$), heptadecafluorodecyl methacrylate ($CH_2{=}C(CH_3)CO_2(CH_2)_2(CF_2)_8F$), and heineicosafluorododecyl acrylate ($CH_2{=}CHCO_2(CH_2)_2(CF_2)_{10})F$ purchased from Aldrich were used as received. The protonated monomers styrene (Aldrich), methyl methacrylate (Fluka), acylic acid (AA, from Aldrich), and methacryloxyethyltrimethylammonium chloride (MADQUAT, from Aldrich) were freshly distilled under reduced pressure and stored at −10 °C. The initiator V59 (2,2′-azobis(2,4-dimethylbutyronitrile)) from Wako-Chemicals Japan was used as received. The hydrophobes hexadecane, perfluoromethyldecalin, and perfluorohexane and the surfactants sodium dodecyl sulfate (SDS) and cetyltrimethylammonium chloride (CTMA-Cl) (as 25% solution) were purchased from Aldrich and used as received.

Synthesis of the Latexes. 3 g of the monomer (or the monomer mixture), 125 mg of the (ultra)hydrophobe, and 80 mg of V59 were added to a solution of a controlled amount of surfactant in 15 g of water. After stirring 1 h for preemulsification, the miniemulsion was prepared by ultrasonicating the mixture for 120 s at 90% amplitude (Branson sonifier W450 Digital) at 0 °C in order to prevent polymerization. For polymerization, the temperature was increased to 60 °C. Completion of reaction was observed after 2 h, as checked by NMR by the absence of vinylic protons. In all cases, the solid content was close to the expected 16.7%. The full incorporation of the fluorinated monomer was determined by evaluating the peak intensities in the ^1H spectra.

Analysis. The particle sizes (intensity average) were measured using a Nicomp particle sizer (model 370, PSS Santa Barbara, CA) at a fixed scattering angle of 90°.

The polymer molecular weights were determined by GPC analysis performed on a P1000 pump with UV1000 detector ($\lambda = 260$ nm) (both from Thermo Separation Products) with 5 μm 8 × 300 mm SDV columns with 10^6, 10^5, and 10^3 Å from Polymer Standard Service in THF with a flow rate of 1 mL min^{-1} at 30 °C. The molecular weights were estimated from a calibration relative to PS or PMMA standard.

Electron microscopy was performed with a Zeiss 912 Omega electron microscope operating at 100 kV. The diluted colloidal solutions were applied to a 400 mesh carbon-coated copper grid and left to dry; no further contrasting was applied.

Liquid ^1H and ^{13}C NMR spectra were recorded with a Bruker DPX400 using $CDCl_3$ as solvent.

Contact angle measurements were performed on a Krüss G10 contact angle goniometer; and the static contact angle was obtained from a droplet (ca. 5 μL) on the surface.

Results and Discussion

In a first set of experiments, the fluorine-containing monomer tridecafluorooctyl methacrylate ($CH_2{=}C(CH_3)$-$CO_2(CH_2)_2(CF_2)_6F$) was used for the miniemulsion procedure. Indeed, this monomer could be miniemulsified using perfluormethyldecalin as hydrophobe and the standard hydrocarbon surfactant sodium dodecyl sulfate (SDS). The use of this simple standard surfactant is worth mentioning, since most other recipes relied on fluorinated surfactants or long chain alkyl surfactants (densely packing). The analytical characteristics of the resulting latexes are summarized in Table 1.

Table 1. Characteristics of Poly(tridecafluorooctyl methacrylate) Latex Particles Using Different Amounts of SDS and Different Types of Hydrophobes

sample	hydrophobe	SDS [rel%]	diameter [nm]
1	perfluoromethyldecalin	0.66	206
2	perfluoromethyldecalin	1.0	139
3	perfluoromethyldecalin	1.33	132
4	perfluoromethyldecalin	2.66	111
5	perfluoromethyldecalin	4.0	103
6	perfluoromethyldecalin	5.33	98
7	hexadecane	1.33	178
8	heptadecafluorodecyl methacrylate	1.33	135
9	perfluorohexane	1.33	139

Already at surfactants loads as low as 0.66 rel % (weight percent SDS with respect to the disperse phase), a stable miniemulsion could be obtained. Because of low water solubility, it was not possible to perform initiation from the water phase, and the polymerization was started inside the droplets by using V59 as a hydrophobic initiator. With 0.66 rel % SDS, after polymerization, a coagulate-free and long-time stable latex with a particle diameter of about 200 nm was obtained. The size of the final particles could be easily decreased by increasing the amount of surfactant from about 200 nm (0.66%) to 100 nm (5.33%) (see Table 1), having a size distribution of less than 20%. As compared to polystyrene latexes made under similar conditions, all fluoromethacrylate latexes are slightly larger, thus expressing the more hydrophobic surface and therefore the higher interfacial tension and the connected higher packing density of surfactant required for stabilization. On the other hand, the latexes are smaller than those made from lauryl methacrylate,[11] which we interpret with an higher average surface energy for the fluoromethacrylate due to the fact that mainly methacryloyl units are pointing to the water phase.

At a constant SDS content of 1.33 rel %, the type of hydrophobes was varied. Perfluorohexane could be used also to obtain osmotic stability of the miniemulsion, and the final particle size after polymerization was similar to the particle sizes obtained with other fluorinated components. Beside perfluormethyldecalin, also the polymerizable heptadecafluorodecyl methacrylate ($CH_2{=}C(CH_3)CO_2(CH_2)_2(CF_2)_8F$) with its lower water solubility can act as osmotic pressure agent. During the polymerization, it is consumed by incorporation in the polymer, which is important because of possible environmental considerations. Employment of hexadecane did not result in stable miniemulsions, since at 1.33 rel % of surfactant an increase of the particle size after polymerization to 180 nm (instead of 130−140 nm for the fluorinated hydrophobes) was observed.

By drying the dispersions onto solid glass supports at elevated temperatures (50 °C), polymer films can be formed. The contact angles of water droplets on the film were determined to be higher than 130°, indicating that the hydrophobic character of the fluoropolymer is not affected by the small amounts of SDS. The contact angles of hexadecane droplets on the film were determined to be about 100° (receding), with a very pronounced hysteresis. This is due to a comparably rough surface due to a caterpillar-like self-dewetting, as was described by Sheiko et al.[17] This is also the reason why adhering ultrahydrophobic coatings rely on the presence of appropriately designed copolymers.

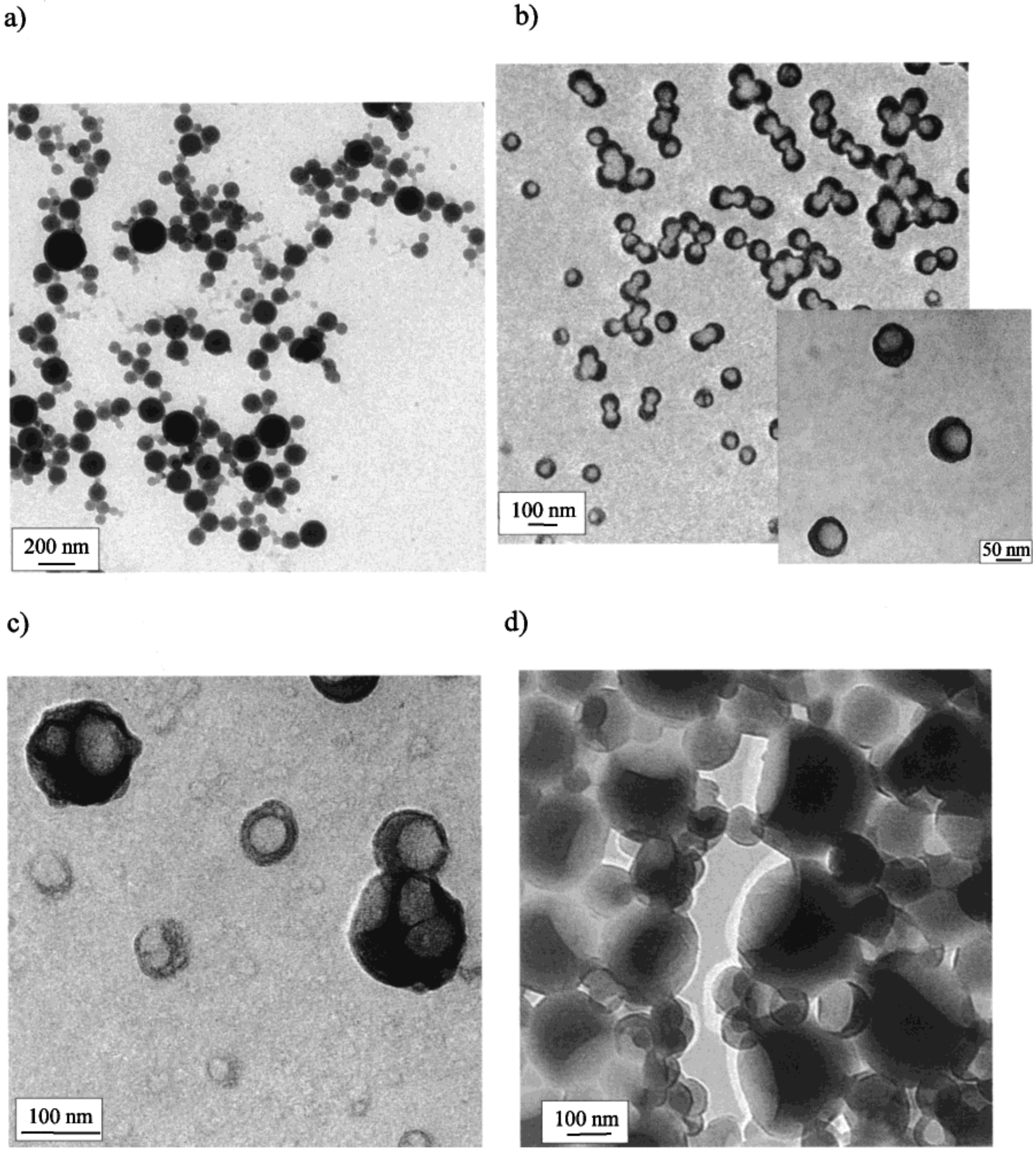

Figure 1. (a) $C_8F_{13}H_4$-MA/styrene/MADQUAT with CTMA-Cl as surfactant (sample 13); (b) $C_8F_{13}H_4$-MA/MMA/AA with SDS as surfactant (sample 15); (c) $C_8F_{13}H_4$-MA/MMA with SDS as surfactant (sample 14); (d) $C_8F_{13}H_4$-MA/MMA/MADQUAT with CTMA-Cl as surfactant (sample 18).

Copolymerization with Hydrocarbon Monomers. One of the most prominent advantages of miniemulsion polymerization is that it allows copolymerization of monomers with very different polarities in heterophase situations. Therefore, in a next set of experiments, fluorine-containing monomers were copolymerized with some hydrocarbon monomers, such as methyl methacrylate and styrene. The technical reason behind these experiments is to “dilute” the expensive fluoromonomer by simple hydrocarbon monomers under preservation of the advantageous low surface tensions of the films and to stop the auto-dewetting. The additional incorporation of a minor amount of charged monomers allows promotion of tack toward the lower substrate of the film.

To obtain negatively charged sticker groups, the surfactant SDS and small amounts of acrylic acid were used, whereas positively charged particles were made with cetyltrimethylammonium chloride as surfactant and MADQUAT as a polymerizable comonomer. In all cases, coagulum-free and stable polymer latexes were obtained. It could also be shown that the use of acrylic acid or MADQUAT did not significantly affect the particle size. For some unknown reason, the size distribution of all these copolymer latexes is broader than for the pure fluorinated polymer particles. As the increase in the surfactant amount leads often to bimodal distributions for those monomer mixtures, the experiments were restricted to 1.3 rel % surfactant.

Whereas the pure fluorinated polymers are not soluble at all in protonated solvents, the 1:1 copolymers are all entirely soluble in standard solvents, e.g., chloroform and THF. This is already a very good indication for the fact that indeed copolymers were formed; i.e., the latexes are not a mixture of pure fluorocarbon and hydrocarbon chains. The GPC of those samples was also apparently

Table 2. Composition and Properties of Latexes Made by Copolymerization of Hydrocarbon and Fluorocarbon Monomers[a]

latex	fluorinated monomer	protonated monomers	surfactant	diameter [nm]	morphology
sample 10	$C_8F_{13}H_4$-MA[b]	Sty, 2% AA	SDS	125	homogeneous
sample 11	$C_{10}F_{17}H_4$-MA[c]	Sty, 2% AA	SDS	228	homogeneous
sample 12	$C_{12}F_{21}H_4$-A[d]	Sty, 2% AA	SDS	239	homogeneous
sample 13	$C_8F_{13}H_4$-MA	Sty, 2% MADQUAT	CTMA-Cl	164	homogeneous
sample 14	$C_8F_{13}H_4$-MA	MMA	SDS	120	multiblobs
sample 15	$C_8F_{13}H_4$-MA	MMA, 2% AA	SDS	128	core−shell
sample 16	$C_{10}F_{17}H_4$-MA	MMA, 2% AA	SDS	122	homogeneous + core−shell
sample 17	$C_8F_{13}H_4$-MA	MMA	CTMA-Cl	170	cups
sample 18	$C_8F_{13}H_4$-MA	MMA, 2% MADQUAT	CTMA-Cl	156	cups
sample 19	$C_{10}F_{17}H_4$-MA	MMA, 2% MADQUAT	CTMA-Cl	192	cups
sample 20	$C_8F_{13}H_4$-MA	BMA	SDS	120	homogeneous

[a] The ratio of fluorinated to protonated monomer was 1:1 weight; 1.33 rel % surfactants was used. [b] Tridecafluorooctyl methacrylate. [c] Heptadecafluorodecyl methacrylate. [d] Heineicosafluorododecyl acrylate.

simple and revealed apparent molecular weights on the order of 10^5 g mol^{-1}. However, intrapolymer hydrophobic interaction and a coupled distortion of the molecular weight determination cannot be excluded. (In this case, the real molecular weights would be significantly higher.)

^{1}H and ^{13}C NMR measurements in $CDCl_3$ showed the presence of all relevant groups for all copolymers with MMA and styrene; that is, they are mobile and therefore statistically copolymerized. From the intensity of the signals in the ^{1}H spectra, full incorporation of the fluorinated monomer is clearly determined. Indeed, in all copolymers, about 50 wt % of the polymer was found to be fluorinated. This NMR experiment however does not exclude the presence of a minor amount of homopolymer which would be simply not seen. Also, DSC is suited to judge the homogeneity of the copolymerization process. In all cases with styrene as a monomer, one single glass transition at 50 °C was found, indicating indeed a statistical copolymerization. With the more polar methyl methacrylate, one melting point at 18 °C indicating side-chain crystallized perfluoroalkyl groups which have to be close to each other and one glass transition at about 50 °C were found, which are however typical for a statistical copolymer. Both facts clearly indicate that the copolymerization with MMA is more heterogeneous. It is possible that the very first chains formed are still generated from a homogeneous state, resulting in a statistical copolymer, whereas demixing by the polymer might result in a three-phase polymerization situation at later stages (two oil phases in each droplet) and the coupled formation of block copolymers or homopolymers.[18]

Those interpretations are strongly supported by TEM of the final polymer dispersions, shown in Figure 1a−d.

The particles consisting of styrene and fluorinated methacrylate show a broad size distribution but are homogeneous in morphology (Figure 1a). This goes very well with a statistical copolymerization and no demixing throughout the polymerization reaction.

Contrary to that, the particles consisting of MMA and fluorinated methacrylate showed a variety of internal structures, such as core−shell morphology (Figure 1b, sample 15), multiblobs (Figure 1c, sample 14), or cuplike structures (Figure 1d, sample 18). Here, the morphology depends on the reaction conditions, such as type and amount of initiator, amount of surfactant, and comonomer, as was already described for the generation of capsules from miniemulsions.[19]

Obviously, we obtain in the MMA case a phase separation throughout polymerization, and composite particles result. For geometric reasons (low interface area), core−shell structures and cup structures point toward the formation of homopolymers in coexistence with block copolymers, whereas the multiblob structure is indicative of block copolymer formation. This goes well with solubility experiments in THF or chloroform where the presence of block copolymers is indicated by the formation of completely dissolved, but opaque and therefore micellar, solutions.

For the formation of films with low surface energy, blocking and the formation of pure fluorocarbon phases are expected to be positive. The copolymers presented in Table 2 were applied under slightly elevated temperatures to glass supports, and the contact angle was measured. Indeed, sample 20 showed an excellent film topography and very low contact angles, e.g., 61° against cyclohexane and 105° against water. For all other samples, still a more or less distorted and rough topography is found with very high contact angles and large hystereses, indicating a variety of three-dimensional surface morphology effects which are out of the scope of the present paper.

Conclusion

Latexes consisting of fluorinated polymers in the size range of 100−250 nm stabilized by low doses of protonated surfactants can be obtained by using the miniemulsion polymerization process. The miniemulsifaction of mixed monomer systems allows efficient copolymerization reactions to be performed using a fluorinated monomer with standard hydrophobic or hydrophilic protonated monomers. Depending on the reaction conditions, such as type and amount of initiator, amount of surfactant, and comonomer, homogeneous particles, but also different particle morphologies such as core−shell, multiblobs, and cups, can be obtained. Contrary to the pure fluorinated polymers, those copolymers dissolve in organic solvents but still show the profitable interface properties of the fluorinated species.

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References and Notes

(1) Ameduri, B.; Boutevin, B. *Actual. Chim.* **2000**, *2*, 23−32.
(2) Huang, Z. H.; Shi, C. M.; Xu, J. H.; Kilic, S.; Enick, R. M.; Beckman, E. J. *Macromolecules* **2000**, *33*, 5437−5442.
(3) Fasick, R. W.; Johnson, E., Jr.; Raynolds, S. US Patent 3,378,609, E.I. du Pont de Nemours Co., 1968.
(4) Raynolds, S.; Tandy, T. K., Jr. US Patent 3,462,296, E.I. du Pont de Nemours Co., 1969.

(5) Fasick, R. W.; Raynolds, S. US Patent 3,282,905, E.I. du Pont de Nemours Co., 1966.
(6) Linemann, R. F.; Malner, T. E.; Brandsch, R.; Bar, G.; Ritter, W.; Mülhaupt, R. *Macromolecules* **1999**, *32*, 1715−1721.
(7) Marion, P.; Beinert, G.; Juhue, D.; Lang, J. *J. Appl. Polym. Sci.* **1997**, *64*, 2409−2419.
(8) Giannetti, E.; Visca, M. US Patent 4,864,006, 1989.
(9) Degiorgio, V.; Piazza, R.; Bellini, T. *Adv. Colloid Interface Sci.* **1994**, *48*, 61−91.
(10) Landfester, K. *Adv. Mater.* **2001**, *10*, 765−768.
(11) Landfester, K. *Macromol. Rapid Commun.* **2001**, 896−936.
(12) Landfester, K.; Bechthold, N.; Förster, S.; Antonietti, M. *Macromol. Rapid Commun.* **1999**, *20*, 81−84.
(13) Reimers, J. L.; Schork, F. J. *J. Appl. Polym. Sci.* **1996**, *60*, 251−262.
(14) Bechthold, N.; Landfester, K. *Macromolecules* **2000**, *33*, 4682−4689.
(15) Thomas, R. R.; Lloyd, K.G.; Stika, K. M.; Stephans, L. E.; Magallanes, G. S.; Dimonie, V. L.; Sudol, E. D.; El-Aasser, M. S. *Macromolecules* **2000**, *33*, 8828−8841.
(16) Lowe, K. C. *Artif. Cells, Blood Subtitutes, Immobilization Biotechnol.* **2000**, *28*, 25−38.
(17) Sheiko, S.; Lermann, E.; Möller, M. *Langmuir* **1996**, *12*, 4015−4024.
(18) Willert, M.; Landfester, K. *Macromol. Chem. Phys.*, in press.
(19) Tiarks, F.; Landfester, K.; Antonietti, M. *Langmuir* **2001**, *17*, 908−917.

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