

High-Molecular-Weight Polyurethanes Prepared by One-Step Miniemulsion Polymerization

Chien-Yu Li,¹ Yuan-Hau Li,² Kuo-Huang Hsieh,^{2,3} Wen-Yen Chiu¹⁻³

¹Department of Material Science and Engineering, National Taiwan University, Taipei, Taiwan, Republic of China

²Department of Chemical Engineering, National Taiwan University, Taipei, Taiwan, Republic of China

³Institute of Polymer Science and Engineering, National Taiwan University, Taipei, Taiwan, Republic of China

Received 19 January 2006; accepted 25 July 2006

DOI 10.1002/app.25164

Published online 27 September 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Through one-step miniemulsion polymerization, hydrophobic polyurethane (PU) dispersions were prepared, with hexadecane (HD) as costabilizer in the oil phase and sodium dodecyl sulfate (SDS) as surfactant in the water phase. The oil phase, including isophorone diisocyanate, poly(oxytetramethylene) glycol, a costabilizer HD, a chain extender 1,4-butanediol, a crosslinking agent trimethylol propane, and a catalyst dibutyltin dilaurate (SnDBL), was dispersed in the water phase containing SDS. The influences of experimental parameters, such as SnDBL, NCO/OH equivalents, and concentrations of surfactant, were discussed. The particle size and the molecular weight of PU polymer were measured by light scattering and gel permeation chromatography, respectively. With the addition of

SnDBL and higher NCO/OH ratio, PU films with higher molecular weights were produced. The chemical structure of the PU polymer was identified by Fourier transform infrared spectrometer, and the adsorption of urethane group was observed. Thermal gravimetric analysis was used to characterize the thermal stability of PU. Furthermore, mechanical property was also investigated and characterized by tensile strength and elongation at break. With a higher NCO/OH ratio and the existence of SnDBL, the tensile strength of PU films was significantly increased. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 840–845, 2008

Key words: miniemulsion polymerization; one-step process; polyurethane dispersions

INTRODUCTION

Owing to environmental consideration and high prices of organic solvents, aqueous polyurethane (PU) dispersions were widely used and became more important during past years. They can be applied on coatings and adhesives without organic solvents. Their films could be prepared simply by evaporation of water even at ambient temperatures. Furthermore, their diversity of compositions is the most important advantage. Such aqueous PU dispersions had been discussed widely and were reviewed in many papers.^{1–3}

To disperse PU in water, ionic and nonionic hydrophilic^{4–10} segments were usually incorporated into PU structure. Kim and Suh⁵ prepared amphiphilic urethane acrylate hydrogels containing ionic group (dimethylpropionic acid, DMPA). These amphiphilic urethane acrylate hydrogels showed salt- and pH-dependent swelling properties. Cheong et al.⁶ synthesized a PU polymer with the incorporation of DMPA and showed that the aggregate sizes were strongly affected by solid content and total ionic strength in the aqueous phase. Kim and Lee⁸ synthesized DMPA-based PU ionomers and studied the influence of

DMPA on particle size and tensile modulus. Lee and Kim⁹ produced PU cationomers containing *N*-methyldiethanolamine (MDEA) and showed that tensile strength increased with the increase in the content of MDEA. The traditional way to prepare PU dispersions is as follows. NCO-terminated prepolymers are synthesized first from the reaction of polydiols, ionic segments, and excessive amount of diisocyanates in a bulk system or in organic solvents. Subsequently, prepolymers are neutralized with a base, typically triethylamine, and are chain-extended with diamines or diols in water phase to form aqueous PU dispersions. PU polymers which are modified by ionic groups are called PU ionomers. The traditional way to prepare aqueous PU dispersions always needs to incorporate hydrophilic segments in the PU backbone. Thus the properties of these PU polymers could not be as good as the hydrophobic ones prepared by solvent-based polymerization.

Recently, a new way to produce dispersions of hydrophobic PU via miniemulsion polymerization was shown in some papers.^{11–14} In miniemulsion polymerization,^{15–19} a pre-emulsion, which usually consisted of a hydrophobic monomer, a surfactant, a costabilizer, and water, had to be prepared by a ultrasonication process, in which the sizes of monomer droplets ranged from 50 to 500 nm. The choice of costabilizer is important for miniemulsion polymerization. An effective costabilizer, such as hexadecane (HD), should

Correspondence to: W.-Y. Chiu (ycchiu@ccms.ntu.edu.tw).

have low water solubility, and it will generate osmotic pressure in monomer droplets, so as to suppress the Ostwald ripening^{20,21} and maintain the stability of monomer droplets. In addition, the concentration of surfactant was usually controlled below its critical micelle concentration in the system to avoid micellar nucleation. Owing to the suppression of Ostwald ripening and reduction of micellar nucleation, monomer droplets can maintain their sizes without coagulation, and the polymerization is mainly proceeded in monomer droplets. So far, the technique of miniemulsion polymerization has been applied in many fields, such as free radical polymerization,^{22,23} encapsulation of inorganic particles within polymer colloids,²⁴ and polycondensation.^{25,26} According to the previous studies,²⁷ the molecular weight of PU prepared by miniemulsion polymerization in one step was always smaller than 10,000, because of the rapid side-reaction between diisocyanates and water. The NCO functional groups consumed by water were converted to urea segments, thus leading to the low molecular weight of PU.

In this article, high molecular weight of PU was successfully prepared by a one-step miniemulsion polymerization. The choice of polydiol was very important. Several experimental factors, such as the catalyst, concentration of surfactant, and NCO/OH equivalents, were studied, and the corresponding properties of PU polymers were also investigated.

EXPERIMENTAL

Materials

Isophorone diisocyanates (IPDI; Lancaster, Ward Hill, MA), 1,4-butanediol (BD; Tedia, Fairfield, OH), trimethylol propane (TMP; Acros, Geel, Belgium), dibutyltin dilaurate (SnDBL; TCI), sodium dodecyl sulfate (SDS; TCI, Tokyo, Japan), and hexadecane (HD; TCI) were used without further purification. Poly(tetramethylene oxide) (PTMO; Showa, Tokyo, Japan) with an average molecular weight of 1000 (g/mol) was dried under vacuum at 80°C for 24 h before use.

Preparation of PU dispersion

Figure 1 was the typical procedure for one-step miniemulsion. In an oil phase, IPDI, polydiol PTMO, chain extender BD, and TMP (molar ratio BD/TMP = 5), catalyst SnDBL, and costabilizer HD were stirred together for 5 min. Sodium dodecyl sulfate was dissolved in deionized water as the water phase. Then the oil and water phases were mixed and stirred for 10 min. Pre-emulsion was prepared by ultrasonifying the mixtures. All the aforementioned steps were proceeded in an ice bath, to prevent the premature polycondensation reaction. The pre-emulsion was then introduced into a 250-mL round-bottomed, four-

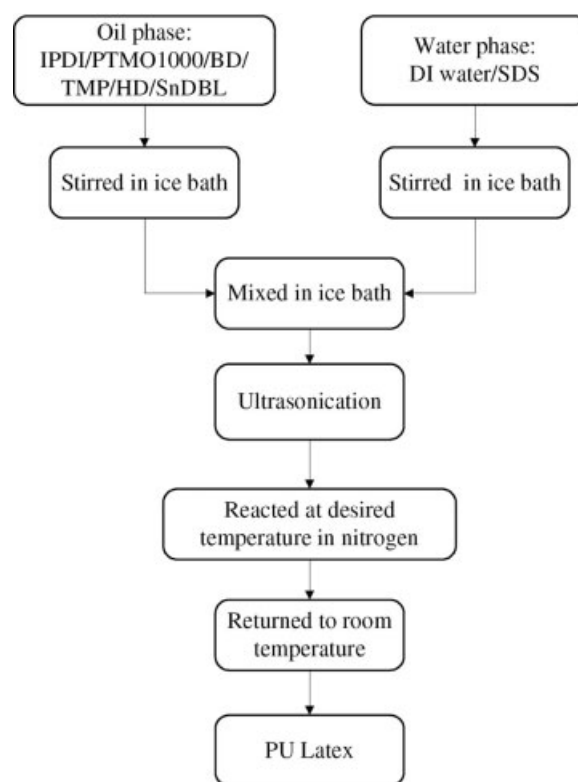


Figure 1 Polymerization scheme of one-step miniemulsion procedure.

necked separable flask with a mechanical stirrer, thermometer, condenser, and a nitrogen inlet and an outlet. Completion of reaction was monitored by Fourier-transform infrared spectrometer (FTIR) analysis, according to the disappearance of NCO absorbance.

Analysis

Particle size measurement

PU latex was first diluted by SDS solution (8.6 mM) and the size of latex particles was measured by using a particle size analyzer (Beckman Coulter, LS230).

Structure analysis

FTIR spectrum of PU polymer was obtained by a FTIR spectrometer (Bio-red, FTS3000). The latex samples were casted on CaF₂ before measurement.

Preparation of PU films

PU dispersions were poured into aluminum molds and were heated to 40°C for 24 h in the air to obtain the PU films. Then the films were heated to 110°C for 8 h in the vacuum and underwent the following characterizations.

Molecular weights of PU films

Molecular weights of PU polymers were measured by gel permeation chromatography (Perkin-Elmer,

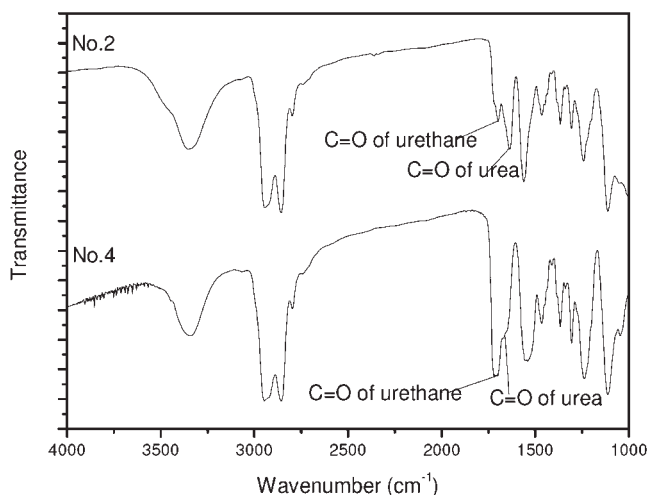


Figure 2 FTIR spectra of PU polymers; No. 2 (without SnDBL), No. 4 (with SnDBL).

Spectroflow 400) with a RI detector (Shodex RI-71) and heat chamber in a THF solvent, with a flow rate of 1 mL/min at 40°C. Average molecular weights were calculated based on polystyrene standards.

Mechanical properties of PU films

Mechanical properties (Orientec, RTM-IT) of PU polymers were performed by elongation (%) and tensile stress at break (kg/cm²). The preparation of sample specimens was according to ASTM D 638. Each test was performed on five specimens with a crosshead speed of 10 mm/min, and the average value was recorded.

Thermal gravimetric analysis

Thermal degradation behavior of PU polymers was recorded by thermal gravimetric analysis (TGA, Perkin-Elmer, TGA-7), with a heating rate of 10°C/min under nitrogen atmosphere.

RESULTS AND DISCUSSION

Influence of SnDBL on chemical structure of PU

The effect of SnDBL on the chemical structure of the thus-synthesized PU was investigated through FTIR spectra. In Figure 2 for the sample No. 2, without SnDBL, the FTIR spectrum showed two absorbance peaks at 1635 and 1698 cm⁻¹. The one at 1635 cm⁻¹ was assigned as the peak of carbonyl group of urea, and 1698 cm⁻¹ was that of urethane absorbance. The large intensity at 1635 cm⁻¹ indicated that the formation of urea segments occurred rapidly because of the relatively slow urethane reaction in the absence of the catalyst. However, when SnDBL was added (No. 4), the absorbance at 1635 cm⁻¹ for urea group decreased, whereas the intensity at 1698 cm⁻¹ for urethane group

increased obviously, which revealed the fact that urethane formation dominated over urea formation when the catalyst, SnDBL, was involved in the reaction. This result showed that SnDBL accelerated the urethane reaction effectively and was efficient to retard the urea formation.

Influence of SDS concentration on size of latex particles and molecular weight of PU

As shown in Table I, latex particles showed slightly smaller sizes when the concentration of SDS increased. Because of the protection of SDS, the extent of coagulation between particles can be reduced. Besides, the molecular weight of PU increased as the concentration of SDS increased. The formation of urea between NCO group and H₂O was effectively reduced by the protection of SDS over latex particles. Therefore, the equivalent ratio of NCO/OH remained closer to 1.0 when the concentration of SDS was high, which resulted in higher molecular weight of PU polymers to be synthesized.

Influence of NCO/OH ratio on molecular weight of PU

In the earlier research,^{11,12,27} one-step miniemulsion for preparing PU always provided a low-molecular-weight PU, from which the molecular weight was below 10,000. Owing to the rapid urea formation, NCO groups were greatly consumed by water. Hence, to avoid a large amount of urea formation, the urethane reaction should be accelerated quickly. In this work, as shown in Table II, high molecular weight of PU from one-step miniemulsion was prepared successfully. Because the sizes of latex particles (Nos. 4, 5, 6) were all similar, the size effect on molecular weight of PU could be ignored. When NCO/OH ratio was increased, both M_w and M_n of PU polymers increased obviously. With the help of SnDBL and excessive amount of NCO groups, the urethane reaction happened more rapidly. Although some NCO groups were consumed by water in the beginning of polymerization, the urethane reaction also occurred at the same

TABLE I
Influence of SDS Concentration

No. ^a	SDS ^b (phr)	D_n^c (nm)	D_m^c (nm)	M_n (g/mol)	PDI (M_w/M_n)
1	2	900	715	5490	1.45
2	4	889	699	5720	1.64
3	6	872	685	6600	1.47

^a Experimental condition: without adding SnDBL, solid content = 20%; temperature = 60°C; NCO/OH = 1.0; HD = 4 phr.

^b Based on total oil phase.

^c D_n , number-average diameter, D_m , median diameter.

TABLE II
Influence of NCO/OH Ratio on the Properties of PU Films

No. ^a	NCO/OH	D_n^b (nm)	D_m^b (nm)	M_n (g/mol)	PDI	Tensile strength (kg/cm ²)	Elongation (%)	T_g (°C)
4 ^c	1.00	889	712	21,500	2.11	92.9	306	-70.9
5 ^c	1.25	854	696	23,500	2.12	210.9	255	-66.0
6 ^c	1.45	879	680	25,900	2.15	305.6	231	-63.1
2 ^d	1.00	889	699	5720	1.64	36.4	35	-65.3
7 ^d	1.25	941	742	6250	1.50	51.4	26	-63.6
8 ^d	1.45	932	759	6980	1.38	67.8	19	-60.1

^a Experimental condition: without adding SnDBL, solid content = 20%; temperature = 60°C; HD = 4 phr; SDS = 4 phr.

^b With SnDBL.

^c Without SnDBL.

^d D_n , number-average diameter, D_m , median diameter.

time, which led to an increase of viscosity inside the droplets. Therefore, urea formation was hindered due to the raising viscosity. Another major reason of obtaining a higher molecular weight of PU was the choice of polydiol. The reactivity of polydiol to react with diisocyanates must be considered. Some polydiols, which had low reactivity, were not suitable for one-step miniemulsion polymerization, such as polypropylene glycol (PPG). In our work, PTMO1000 was chosen as the polydiol. The reaction between IPDI and PTMO1000 was very fast when added with SnDBL and could compete with the urea reaction. Hence, high-molecular-weight PU could be obtained.

The usage of SnDBL was worth mentioning. Without the addition of SnDBL, the molecular weight of PU was still small and below 10,000 even if the NCO/OH ratio was increased. Therefore, from this result, both the usage of SnDBL and proper polydiol were necessary for the one-step procedure to obtain high molecular weight of PU polymers.

Effect of NCO/OH equivalent ratio on mechanical property of PU

As shown in Table II, while NCO/OH equivalent ratio was increased (Nos. 4, 5, and 6), the tensile strength was improved significantly under the existence of SnDBL. With higher NCO/OH ratio, relatively larger amount of urea linkage and hard segments were formed in PU polymers because of the rapid reaction of diisocyanates and water, although the molecular weight of PU also increased. These factors, urea linkage, hard segments, and higher molecular weight, resulted in higher tensile strength of PU. On the contrary, larger amount of urea linkage and hard segments resulted in poorer elongation because of its rigid structure. Without the addition of SnDBL (Nos. 2, 7, and 8) in reaction, the tensile strength and elongation of PU polymers were much smaller. The tensile strength was increased, whereas the elongation was decreased by increasing the NCO/OH ratio.

Effect of NCO/OH ratio on thermal property of PU

The T_g of PU increased with increasing NCO/OH ratio as shown, from the DSC analysis in Table II, whether the catalyst SnDBL was added or not. It was

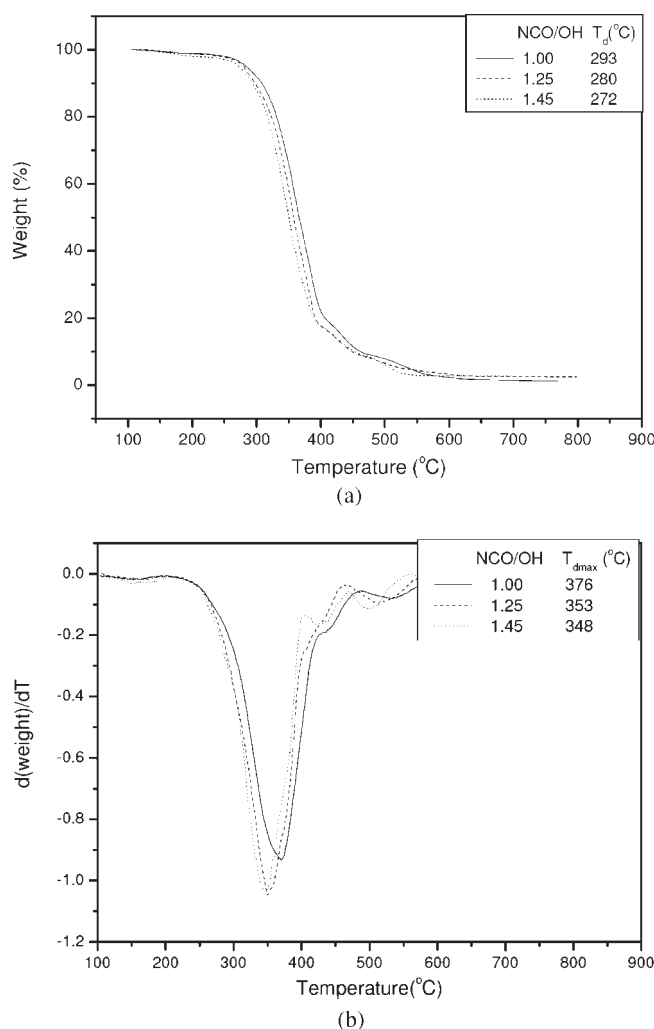


Figure 3 (a) TGA and (b) DTA analysis of PU synthesized at different NCO/OH ratios with SnDBL; 1.00 (No. 4), 1.25 (No. 5), 1.45 (No. 6).

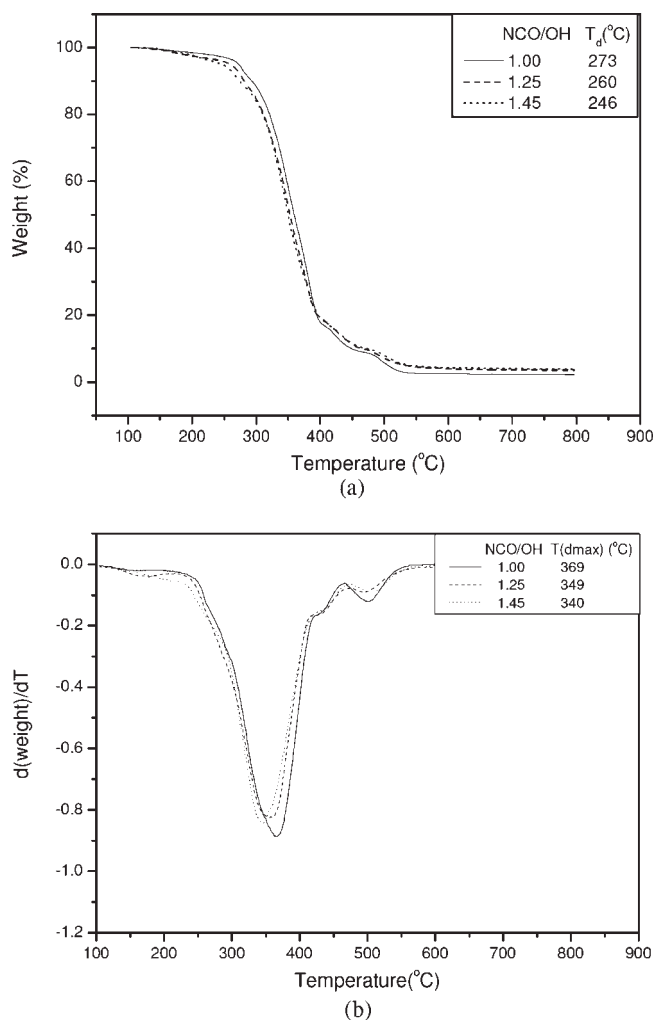


Figure 4 (a) TGA and (b) DTA analysis of PU synthesized at different NCO/OH ratios without SnDBL; 1.00 (No. 2), 1.25 (No. 7), 1.45 (No. 8).

due to the reason that higher NCO/OH ratio increased the amount of both urea linkage and hard segments, as mentioned earlier. As a result, more rigid structure in PU polymers was obtained. On the other hand, from TGA analysis, PU polymer with larger portion of hard segments showed poorer thermal stability. It was reported that degradation of PU chains started from the linkage of hard segments.^{28,29} Figure 3 showed the TGA and DTA curves of PU polymers synthesized at different NCO/OH ratios, with SnDBL as a catalyst. The data of thermal degradation temperatures (T_d) at 5% weight loss and ($T_{d\max}$) at maximum degradation rate were listed in figures, which were reduced with increasing the NCO/OH ratio. Similarly, Figure 4 showed the same result if SnDBL was not added. The thermal stability decreased as the NCO/OH ratio increased. When Figures 3 and 4 were compared, both T_d and $T_{d\max}$ of PU prepared without adding SnDBL were obviously lower than those with the SnDBL. The decrease

of thermal stability was mainly due to lower molecular weight of polymer formed in the absence of SnDBL.

CONCLUSIONS

In this work, higher molecular weight of PU was successfully prepared by one-step miniemulsion polymerization. The experimental factors, such as catalyst, concentration of surfactant, and NCO/OH equivalents, were discussed. With the addition of the catalyst and proper polydiol, such as PTMO1000 in this work, the urea formation was hindered, which was evidenced by the characterization of FTIR spectra. Smaller latex particles and higher molecular weight of PU were obtained, when the concentration of SDS increased. Both SnDBL and polydiol played important roles in the preparation of high-molecular-weight PU. Without adding SnDBL, high molecular weight of PU could not be obtained. As for the mechanical property, NCO/OH ratio resulted in larger amount of urea linkage and hard segments in the PU backbone, which decreased the elongation, but increased the tensile strength of PU. High molecular weight of PU prepared with SnDBL as a catalyst exhibited much better mechanical properties than low molecular weight of PU prepared without SnDBL. The T_g of PU increased, but the thermal stability decreased as the NCO/OH ratio increased. It was attributed to the amount of urea linkage and hard segment.

It is concluded from this work, that the role of catalyst and choice of polydiol are the key factors to obtain a high molecular weight of PU by one-step miniemulsion polymerization.

References

- Kim, B. K. *Colloid Polym Sci* 1996, 274, 599.
- Cho, G.; Natansohn, A.; Ho, T.; Wynne, K. J. *Macromolecules* 1996, 29, 2563.
- Kim, C. K.; Kim, B. K. *J Appl Polym Sci* 1991, 43, 2295.
- Consolati, G.; Levi, M.; Turri, S. *Polymer* 2001, 42, 9723.
- Kim, J. W.; Suh, K. D. *Colloid Polym Sci* 1998, 276, 342.
- Cheong, I. W.; Nomura, M.; Kim, J. H. *Macromol Chem Phys* 2000, 201, 2221.
- Coutinho, M. B.; Delpech, M. C.; Alves, L. S. *J Appl Polym Sci* 2001, 80, 566.
- Kim, B. K.; Lee, Y. M. *J Macromol Sci Pure Appl Chem A* 1992, 29, 1207.
- Lee, J. S.; Kim, B. K. *Prog Org Coat* 1995, 25, 311.
- Lan, P. N.; Corneille, S.; Schacht, E.; Davies, M.; Shard, A. *Biomaterials* 1996, 17, 2273.
- Tiarks, F.; Landfester, K.; Antinietti, M. *J Polym Sci Part A: Polym Chem* 2001, 39, 2520.
- Barrere, M.; Landfester, K. *Macromolecules* 2003, 36, 5119.
- Wang, C.; Chu, F.; Graillat, C.; Guyot, A. *Polym React Eng* 2003, 11, 541.
- Li, M.; Daniels, E. S.; Dimonie, V.; Sudol, E. D.; El-Aasser, M. S. *Macromolecules* 2005, 38, 4138.
- Tang, L.; Sudol, E. D.; Silebi, A. A.; El-Aasser, M. S. *J Appl Polym Sci* 1991, 43, 1059.

16. Miller, C. M.; Blythe, P. J.; Sudol, E. D.; Silebi, C. A.; El-Aasser, M. S. *J Polym Sci Part A: Polym Chem* 1994, 32, 2365.
17. Alduncin, J. A.; Forcada, J.; Barandiaran, M. J.; Asua, J. M. *J Polym Sci Part A: Polym Chem* 1991, 29, 1265.
18. Alduncin, J. A.; Forcada, J.; Asua, J. M. *Macromolecules* 1994, 27, 2256.
19. Landfester, K.; Bechthold, N.; Tiarks, F.; Antinietti, M. *Macromolecules* 1999, 32, 2679.
20. Landfester, K.; Bechthold, N.; Tiarks, F.; Antinietti, M. *Macromolecules* 1999, 32, 5222.
21. Blythe, P. J.; Morrison, B. R.; Mathauer, K. A.; Sudol, E. D.; El-Aasser, M. S. *Langmuir* 2000, 16, 898.
22. Reimers, J.; Schork, F. J. *J Appl Polym Sci* 1996, 59, 1833.
23. Schork, F. J.; Poehlein, G. W.; Wang, S.; Reimers, J.; Rodrigues, J.; Samer, C. *Colloid Surf A* 1999, 153, 39.
24. Yang, Z.; Qiu, D.; Li, J. *Macromol Rapid Comm* 2002, 23, 479.
25. Barrere, M.; Landfester, K. *Polymer* 2003, 44, 2833.
26. Landfester, K.; Tiarks, F.; Hentze, H. P.; Antinietti, M. *Macromol Chem Phys* 2000, 201, 1.
27. Li, C. Y.; Chiu, W. Y.; Don, T. M. *J Polym Sci Part A: Polym Chem* 2005, 43, 4870.
28. Chang, W. L. *J Appl Polym Sci* 1994, 53, 1759.
29. Chiu, W. Y.; Wang, P. S.; Don, T. M. *Polym Degrad Stab* 1999, 66, 233.