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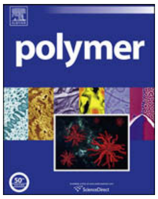

Polymer Communication

Synthesis of polyvinylpyrrolidone/silver nanoparticles hybrid latex in non-aqueous miniemulsion at high temperature

Daniel Crespy [a,*], Katharina Landfester [a,b]

[a] University of Ulm, Department of Macromolecular Chemistry and Organic Materials, Albert Einstein Allee 11, D-89069 Ulm, Germany
[b] Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany

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ABSTRACT

Since emulsions tend to become unstable with increasing temperature, reactions in emulsions are usually not performed at high temperatures. We show that non-aqueous inverse miniemulsions are relatively stable at temperatures higher than 150 °C. As an example of this remarkable stability, composite particles consisting of Ag nanoparticles and a polymer were synthesized via the polyol process in the monomer droplets to reduce silver ions to silver followed by the polymerization of the monomer. Silver nanoparticles were hence embedded in polyvinylpyrrolidone matrix particles. We showed here that non-aqueous miniemulsion nanodroplets are suitable loci for reactions performed at high temperature.

1. Introduction

Latexes synthesis is one of the most convenient technique in order to obtain nanostructured polymer materials [1]. There is hence an intensive search for the synthesis of nanomaterials derived from latexes to obtain new functionalities. These functionalities can be given by the chemical structure of the polymer and its physical properties, or the morphology of the dispersed phase, e.g. nanoparticles or nanocapsules. Among the dispersion techniques, the miniemulsion technique is very promising due to the flexibility allowed by this method [2]. It is possible to create latexes of different polymers from various types of polymerizations. The traditional free- or controlled-radical polymerization can be used in miniemulsion, but also unconventional reactions for heterophase systems such as polycondensation, ionic, oxidative, and enzymatic polymerizations. Thus, a wide range of polymer particles were synthesized including polyurethanes [3], epoxy [4], polyesters [5], polyamide-6 [6], polysiloxanes [7], and semi-conductor polymers [8]. It is also possible to fabricate nanocapsules via the miniemulsion polymerization process [9]. Though all the syntheses cited above were performed via the miniemulsification of the monomers, it is sometimes suitable to disperse directly the polymer instead of doing the polymerization. It is the case when a "ready-to-use" miniemulsion is needed without purification steps of the polymer to make semi-conductor polymer coatings [10], or if a miniemulsion/solvent displacement hybrid technique is employed to synthesize the nanoparticles and nanocapsules [11].

The miniemulsion technique is hence a suitable process in order to produce a wide range of functional organic or inorganic nanomaterials. However, the miniemulsion is still limited regarding its use at high temperature. Indeed, miniemulsions tend to become unstable at high temperature. Moreover, most of the dispersed and continuous phases used in miniemulsion and reported in the literature have a boiling point lower than 100 °C. Unfortunately a cornucopia of synthesis, especially in inorganic chemistry, require a high temperature to be proceeded. For instance, the polyol process can be used to produce metal nanoparticles with a controlled shape at 160 °C [12]. This solution phase process allows the reduction of silver salt to silver nanoparticles [12], or other structures such as silver nanowires [13], by ethylene glycol at temperature close to 200 °C in the presence of PVP as sole stabilizer. Thus it is suitable to extend the range of temperature used in miniemulsion to higher temperatures. Two approaches can be chosen in order to perform reactions in miniemulsion at high temperatures. The first approach to exceed the temperature above the boiling point of continuous phases is to use an autoclave and to apply some pressure in the miniemulsion reactor. Barrere and Landfester hence synthesized polyester in direct miniemulsion

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* Corresponding author. Present address: Empa, Laboratory for Protection and Physiology, Lerchenfeldstrasse 5, CH-9014 St. Gallen, Switzerland. Tel.: +41 71 274 7669; fax: +41 71 274 7762.

E-mail address: daniel.crespy@empa.ch (D. Crespy).

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(o/w) using water as continuous phase at a maximum temperature of 150 °C under pressure [5a]. Cunningham et al. reported the radical polymerization controlled by nitroxides also in direct miniemulsion with water at 135 °C in a pressurized reactor [14]. The second approach is to employ the combination of high boiling point dispersed and continuous phases, which can be performed preferably in, oil-in-oil miniemulsions so-called "non-aqueous inverse miniemulsions". An example of the latter method was demonstrated in the synthesis of polyamide-6 via ε-caprolactam/dimethyl sulfoxide in paraffin miniemulsifications [6]. The temperature of the system was raised to 150 °C for a short time since the activated anionic polymerization of ε-caprolactam is a fast reaction, and the miniemulsion system was therefore not significantly destabilized. We believe that this second approach is very promising for many reactions. In fact, the increase of pressure is less welcome in an industrial process than the increase of temperature owing to its higher cost. Therefore, we investigated the behavior of inverse non-aqueous miniemulsions at temperatures higher than 150 °C and their stability with different surfactants/stabilizers and dispersed phases. Finally the resulting stable miniemulsion droplets were used as nanoreactors to perform the reduction of silver nitrate in silver nanoparticles via the polyol process and to process the subsequent polymerization of the monomer present in the droplets.

2. Experimental

2.1. Materials

N-Vinylpyrrolidone or NVP (from Aldrich, 99%) was passed through a basic alumina column; Isopar M (Exxon), a mixture of branched saturated hydrocarbons with an average chain length close to 12.5, was dried and then distilled under reduced pressure. Ethylene glycol (water free, Aldrich), silver nitrate (Merck, p.a.), 2-pyrrolidone (Aldrich, 99%), dimethyl sulfoxide or DMSO (p.a., Merck), potassium carbonate (Aldrich, 99%), polyvinylpyrrolidone or PVP $M_w \sim 40\,000\ \mathrm{g\,mol^{-1}}$ (Aldrich), Brij 76 (Aldrich), Span 80 (Aldrich), xylene (p.a., Merck), and the initiator V-40 (Wako) were used as received. The block copolymer emulsifier P(B/E-*b*-EO), consisting of a poly(butylene-*co*-ethylene) block ($M_w = 3700\ \mathrm{g\,mol^{-1}}$) and a poly(ethylene oxide) block ($M_w = 3600\ \mathrm{g\,mol^{-1}}$), was synthesized starting from Kraton liquid (Shell), which was dissolved in toluene, by adding ethylene oxide under the typical conditions of anionic polymerization [15]. The chemical structures of the surfactants are shown in Fig. 1.

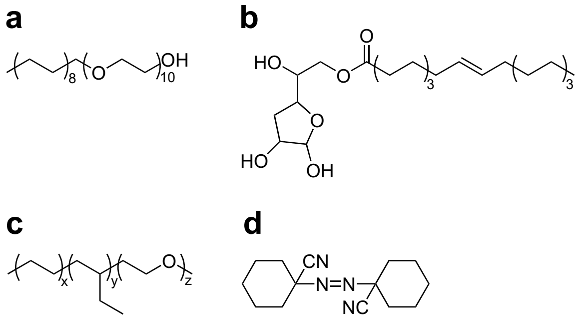

Fig. 1. Chemical structures of the surfactants and initiator. a: Brij 76 or polyethylene glycol octadecyl ether, b: Span 80 or sorbitan monooleate, c: P(B/E-*b*-EO) or poly [(butylene-*co*-ethylene)-*b*-(ethylene oxide)] with $M_{(x+y)} \sim 3700\ \mathrm{g\,mol^{-1}}$ and $M_z \sim 3600\ \mathrm{g\,mol^{-1}}$. d: V-40 or 1,1′-azobis(cyclohexane-1-carbonitrile).

Table 1
Boiling point of the different chemicals used to build the dispersed and continuous phases.

Chemical	Boiling point (°C)	Pressure
Isopar M	207–275	p_{atm}
DMSO	189	p_{atm}
Ethylene glycol	197	p_{atm}
2-Pyrrolidone	245	p_{atm}
1-Vinyl-2-pyrrolidone	94	11 mm Hg

2.2. Preparation of the miniemulsions

1.5 g of liquid polar disperse phase (NVP, ethylene glycol, 2-pyrrolidone, DMSO) was mixed either with 50 mg of PVP, or 25 mg of K_2CO_3. The polar phase was mixed with a solution of a controlled amount of P(B/E-*b*-EO) surfactant (75 mg for the hybrid latex) in 7.5 g of Isopar M. The mixture was pre-emulsified by magnetic stirring for 1 h, and then miniemulsified by ultrasonication for 180 s with a Branson sonifier W450 Digital at 70% amplitude (1/2 in. tip size). The mixture was cooled with an ice-bath during sonication. Then, the miniemulsion was purged with argon for 10 min and transferred in an oil-bath at 150 or 170 °C.

2.3. Preparation of the miniemulsion polymerizations

The polar phase was composed of 50 mg of PVP and 1.5 g of NVP for the preparation of the latex or 0.1 g of ethylene glycol, 30 mg of $AgNO_3$, 50 mg of PVP and 1.4 g of NVP for the hybrid latex. The polar phase was mixed with a solution of a controlled amount of P(B/E-*b*-EO) surfactant (75 mg for the hybrid latex) in 7.5 g of Isopar M. The mixture was pre-emulsified by magnetic stirring for 1 h in the dark, and then miniemulsified by ultrasonication for 180 s with a Branson sonifier W450 Digital at 70% amplitude (1/2 in. tip size). The mixture was cooled with an ice-bath during sonication. Then, the miniemulsion was purged with argon for 10 min and transferred in an oil-bath at 160 °C. 30 mg of the initiator V-40 dissolved in 1 g of xylene was added immediately to the miniemulsion to perform the polymerization of NVP to form the latex, or after 30 min if silver nitrate was present in the dispersed phase to form the hybrid latex. The reaction was then stopped 3 h after the addition of the initiator.

Table 2
Characteristics of the miniemulsions at high temperature.

Entry	T (°C)	Stabilizer		Dispersed phase	Diameter (nm)[a]	
		Nature	Amount (mg)		t_{10}	t_{1200}
M1	170	P(B/E-*b*-EO)	25	NVP	640	1500
M2	170	P(B/E-*b*-EO)	50	NVP	350	790
M3	170	P(B/E-*b*-EO)	75	NVP	330	690
M4	150	P(B/E-*b*-EO)	75	DMSO	480	1170
M5	150	P(B/E-*b*-EO)	75	NVP	220	510
M6	170	P(B/E-*b*-EO)	75	2-Pyrrolidone	450	420
M7	150	P(B/E-*b*-EO) K_2CO_3	75 25	NVP	150	180
M8	170	P(B/E-*b*-EO) K_2CO_3	75 25	NVP	180	410
M9	150	P(B/E-*b*-EO) PVP	75 50	DMSO	330	330
M10	150	P(B/E-*b*-EO) PVP	75 50	2-Pyrrolidone	140	180
M11	170	P(B/E-*b*-EO) PVP	75 50	2-Pyrrolidone	180	180
M12	150	P(B/E-*b*-EO) PVP	75 50	NVP	190	410
M13	170	P(B/E-*b*-EO) PVP	75 50	NVP	440	690

[a] Hydrodynamic diameters determined by DLS after 10 min (t_{10}) and after 1200 min (t_{1200}), u = unstable.

2.4. Analytical methods

The droplet and particle sizes were measured by dynamic light scattering using a Nicomp particle sizer (model 370, PSS Santa Barbara, CA) at a fixed scattering angle of 90°. The droplet size of the miniemulsion was measured at room temperature on cooled samples at different times between 10 min (t_{10}) and 1200 min (t_{1200}). The data were processed using the cumulants method. Electron microscopy was performed with a Phillips 400T transmission electron microscope operating at 80 kV. The dispersion was diluted in cyclohexane and then applied to a 400 mesh carbon-coated copper grid and left to dry. No further contrasting was applied.

3. Results and discussion

Non-aqueous miniemulsions were performed as an inverse system. Owing to the absence of water in the formulations, these miniemulsions can also be denominated as oil-in-oil emulsions. Isopar M was chosen as the continuous phase in all experiments owing to its high boiling point (Table 1), a low viscosity, and its apolarity. DMSO, ethylene glycol, 2-pyrrolidone, and 1-vinyl-2-pyrrolidone as disperse phases were selected owing to their polar nature, and their relatively high boiling points as shown in Table 1. The temperature of auto-polymerization of NVP is as high as 200 °C. The surfactants used in the study have a low hydrophilic–lipophilic balance (HLB), enabling the stabilization of inverse miniemulsions. Especially the non-ionic amphiphilic poly (ethylene-*co*-butylene-*b*-ethylene oxide) was already found to be a suitable surfactant to stabilize inverse miniemulsion droplets [6,9g,14]. The block copolymer, with either sodium chloride or sodium hydroxide as costabilizer, was used to stabilize miniemulsions for the radical polymerization of hydroxyethyl(meth)acrylate, acrylic acid, and acrylamide [16]. It was also used to stabilize DMSO droplets in paraffin with sodium hydride and sodium caprolactamate as costabilizers [6], and water or formamide droplets in cyclohexane with sodium chloride or silver nitrate being the costabilizers [9g]. PVP or K_2CO_3 was chosen as lipophobes or costabilizers for the study of the miniemulsions. They build an osmotic pressure in the droplets to suppress (or at least limit) the Ostwald ripening in our system.

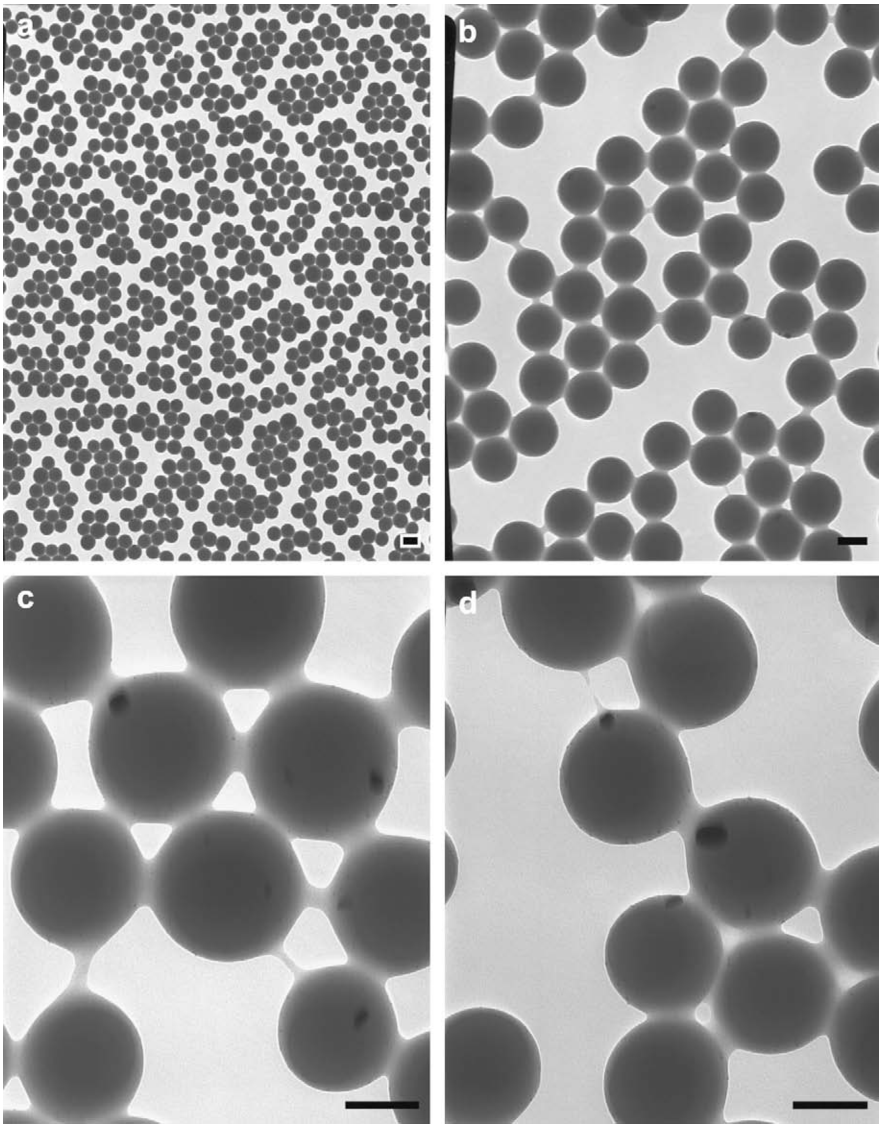

Fig. 2. a–d. TEM micrographs of a: the PVP particles, b–d: the silver nanoparticles/PVP hybrid particles. The bar represents 200 nm.

3.1. Stability of the miniemulsions

Here also, the P(B/E-*b*-EO) was found to be the best stabilizer at room temperature among the tested ones. Indeed, the use of Span 80 (75 mg), Span 80 or Brij 76 and K_2CO_3 (75 and 25 mg), Span 80 or Brij 76 and PVP (75 and 50 mg) was not sufficient to effectively stabilize the miniemulsions. However the P(B/E-*b*-EO) only was found not to be efficient enough to stabilize the miniemulsions of NVP at 170 °C. In fact, the particles' size increased from 640 nm after 10 min at 170 °C to 1500 nm after 1200 min with a concentration of ~1.7 wt.% of P(B/E-*b*-EO) compared to the NVP (M1 in Table 1). The droplet size decreased as expected to 350 nm (M2) and 327 nm (M3) after 10 min with 3.3 wt.% and 5 wt.% of P(B/E-*b*-EO) respectively. However, the droplets were not stable since the size increased to 790 (M2) and 690 nm (M3) after 1200 min. Even at 150 °C with the sole P(B/E-*b*-EO), the particles size increased from 480 nm for DMSO (M4), and 220 nm for NVP (M5) after 10 min to 1170 nm for DMSO, and 510 nm for NVP after 1200 min. The increase of droplet size is probably due to the absence of osmotic pressure agent (or lipophobe) in the droplets and hence the presence of Ostwald ripening, which is enhanced by the high temperature. We believe that the efficiency of the P(B/E-*b*-EO) is also reduced at high temperature since the poly(ethylene oxide) block becomes more lipophilic. On the contrary, the miniemulsion of 2-pyrrolidone at 170 °C stabilized by the sole P(B/E-*b*-EO) was stable even after 1200 min as shown in Table 2 (M6).

In a second step, the P(B/E-*b*-EO) was used in combination with K_2CO_3 or PVP. We investigated the influence of an inorganic salt (K_2CO_3) as osmotic pressure agent on the stability of the miniemulsions. It is known that osmotic pressure agent stabilizes the miniemulsion droplets against Ostwald ripening due to the building of an osmotic pressure that counteracts the Laplace pressure on the droplets [2]. Indeed, K_2CO_3 could stabilize the miniemulsion of NVP at up to 150 °C (M7), higher temperature showed a decrease in stability, e.g. at 170 °C (M8), the particle size increases from 180 nm after 10 min to 413 nm after a long waiting time of 1200 min. However, it can be seen that the increase of the particle size is significantly less with the addition of K_2CO_3 than without.

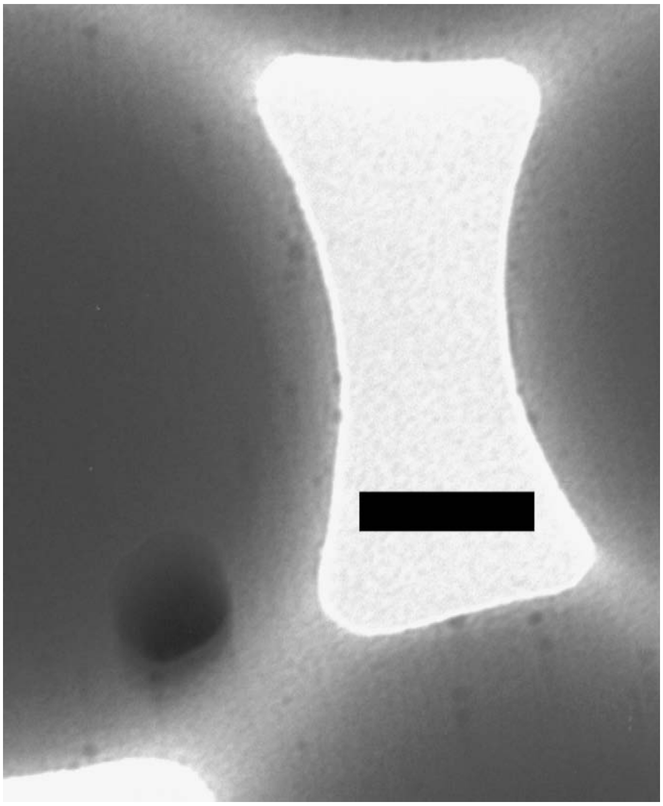

Fig. 3. TEM micrograph of the composite particles (the bar represents 50 nm).

Finally, we studied the influence of PVP for the stabilization of the miniemulsions. It has first to be noticed that the use of PVP as sole stabilizer (8.3 wt.%), i.e. without P(B/E-*b*-EO), for miniemulsion of 2-pyrrolidone does not lead to stable particles. Thus it was used in combination with the P(B/E-*b*-EO) surfactant. The combination PVP/P(B/E-*b*-EO) was found to stabilize the miniemulsion of DMSO at 150 °C (M9). Remarkably this combination of stabilizers was efficient to stabilize the miniemulsions of 2-pyrrolidone performed at 150, and 170 °C (M10, and M11 respectively). The system PVP/P(B/E-*b*-EO) was less efficient than K_2CO_3/P(B/E-*b*-EO) to stabilize the miniemulsions of NVP. Indeed the particle size grows from 190 nm at 150 °C (M12, t_{10}) and 441 nm at 170 °C (M13, t_{10}), to 410 nm at 150 °C (M11, t_{1200}) and 670 nm at 170 °C (M13, t_{1200}). Thus, the miniemulsions of 2-pyrrolidone are better stabilized with the PVP/P(B/E-*b*-EO) whereas K_2CO_3/P(B/E-*b*-EO) is more suitable for the miniemulsions of NVP. This is due to the fact that NVP is less hydrophilic and hence more soluble in the continuous phase than 2-pyrrolidone. The Ostwald ripening effect is then more pronounced with NVP and better counterbalanced by an efficient osmotic pressure agent such as K_2CO_3.

Please note that for a polymerization, such long-time stable system is not required, here a stability of the miniemulsion within the course of the polymerization is required.

3.2. Polymerization of NVP and synthesis of silver/PVP hybrid latexes

In order to illustrate the principle of reactions in miniemulsion at high temperature, we polymerized the NVP at high temperature. Miniemulsion polymerizations of NVP performed at 160 °C led to high conversion of the monomer (>99% determined by gravimetry) and to stable monodisperse particles as shown in Fig. 2a (200 nm with 8% size distribution). The formation of the polymer stabilized the miniemulsion even during polymerization compared to the non-polymerized miniemulsion of NVP (M12 and M13 at 150 and 170 °C respectively) since it additionally acts as a lipophobe with a very limited (if not zero) solubility in the continuous phase.

The reaction in miniemulsion at high temperature can be pushed one step further: the droplets of NVP can be used as nanoreactors for a reduction reaction of metal ions and the subsequent polymerization can lead to hybrid polymer particles. The miniemulsion process is particularly suitable to produce composite latex when the inorganic part is soluble in the monomer dispersed phase since the size is almost conserved from the monomer droplet to the polymer particle, which is not the case in emulsion polymerization with micellar nucleation. Thus, silver nitrate was dissolved in the dispersed phase composed of ethylene glycol and NVP and then reduced to silver nanoparticles by the so-called "polyol process". In a second step, we polymerized the NVP droplets. The end product is a latex composed of hybrid particles where silver nanoparticles are embedded in polyvinylpyrrolidone matrix particles as shown in Fig. 2. The silver nanoparticles could be identified since they displayed darker spots in the TEM micrographs due to the higher electronic density of the silver compared to the polymer (Figs. 2c,d and 3). Such latex can further be used to produce antimicrobial paints or films.

4. Conclusion

The stability of the non-aqueous miniemulsions against temperature was shown for high temperatures up to 170 °C. Experiments performed at temperatures superior to 150 °C showed that miniemulsions stabilized by the block copolymer P(B/E-*b*-EO) are usually getting unstable with time (>10 h) due to coalescence facilitated at high temperature. When the additional stabilizer PVP was used in the miniemulsions containing DMSO or 2-pyrrolidone as the dispersed phase, the miniemulsion was relatively stable at high temperature even for periods of at least 20 h. Two applications of the high temperature non-aqueous miniemulsions were successfully carried out to demonstrate the versatility of the technique: the polymerization of NVP by free-radical polymerization resulted in very monodisperse polymer nanoparticles; and the reduction of silver nitrate by ethylene glycol in miniemulsion droplets which requires such high temperatures. A combination of both reactions gave hybrid metal/polymer latexes. These results broaden the use of the miniemulsion technique to non-aqueous miniemulsions at higher temperatures, thus allowing new nanomaterials to be synthesized in the miniemulsion droplets which are difficult to be obtained at lower temperatures.

References

[1] Antonietti M, Tauer K. Macromol Chem Phys 2003;204:207.
[2] Landfester K. Annu Rev Mater Res 2006;36:231.
[3] (a) Tiarks F, Landfester K, Antonietti M. J Polym Sci Part A: Polym Chem 2001;39:2520;
(b) Barrere M, Landfester K. Macromolecules 2003;36:5119.
[4] (a) Landfester K, Tiarks F, Hentze HP, Antonietti M. Macromol Chem Phys 2000;201:1;
(b) Kawahara H, Goto T, Ohnishi K, Ogura H, Kage H. J Appl Polym Sci 2001;91:128;
(c) Taira S, Du YZ, Kodaka M. Biotechnol Bioeng 2006;93:396.
[5] (a) Barrere M, Landfester K. Polymer 2003;44:2833;
(b) Taden A, Antonietti M, Landfester K. Macromol Rapid Commun 2003; 24:512.
[6] Crespy D, Landfester K. Macromolecules 2005;38:6882.
[7] (a) Barrere M, Maitre C, Dourges MA, Hemery P. Macromolecules 2001; 34:7276;
(b) Barrere M, Ganachaud F, Bendejacq D, Dourges MA, Maitre C, Hemery P. Polymer 2001;42:7239;
(c) Landfester K, Pawelzik U, Antonietti M. Polymer 2005;46:9892;
(d) Palaprat G, Ganachaud F, Mauzac M, Hemery P. Polymer 2005;46:11213.
[8] (a) Marie E, Rothe R, Antonietti M, Landfester K. Macromolecules 2003; 36:3967;
(b) Cho SH, Kim WY, Jeong GK, Lee YS. Colloids Surf A 2005;255:79;
(c) Ham HT, Choi YS, Jeong N, Chung IJ. Polymer 2005;46:6308.
[9] (a) Tiarks F, Landfester K, Antonietti M. Langmuir 2001;17:5775;
(b) Rajot I, Bone S, Graillat C, Hamaide Th. Macromolecules 2003;35:7484;
(c) Luo Y, Zhou X. J Polym Sci Part A: Polym Chem 2004;42:2145;
(d) Torini L, Argillier JF, Zydowicz N. Macromolecules 2005;38:3225;
(e) Paiphansiri U, Tangboriboonrat P, Landfester K. Macromol Biosci 2006;6:33;
(f) Crespy D, Musyanovych A, Landfester K. Colloid Polym Sci 2006;284:780;
(g) Crespy D, Stark M, Hoffmann-Richter C, Ziener U, Landfester K. Macromolecules 2007;40:3122.
[10] Landfester K, Montenegro R, Scherf U, Güntner R, Asawapirom U, Patil S, et al. Adv Mater 2002;14:651.
[11] Crespy D, Landfester K. Macromol Chem Phys 2007;208:457.
[12] Sun Y, Xia Y. Science 2002;298:2176.
[13] Sun Y, Yin Y, Mayers BT, Herricks T, Xia Y. Chem Mater 2002;14:4736.
[14] Cunningham MF, Xie M, McAuley KB, Keoshkerian B, Georges MK. Macromolecules 2002;35:59.
[15] Schlaad H, Kukula H, Rudloff J, Below I. Macromolecules 2001;34:4302.
[16] Landfester K, Willert M, Antonietti M. Macromolecules 2000;33:2370.