Macromol. Symp. **2003**, *199*, 47-57

Polyaddition Reaction in a Dispersed Medium: Elaboration of New Core-Shell Polyurethane Particles

Pierre Chambon, Bindushree Radhakrishnan, Eric Cloutet,
*Eric Papon, Henri Cramail**

Laboratoire de Chimie des Polymères Organiques UMR 5629
ENSCPB – Université Bordeaux-1 – CNRS
16, Avenue Pey-Berland, F-33607 Pessac Cedex, France
E-mail: cramail@enscpb.fr

Summary: The elaboration in a dispersed organic medium of calibrated polyurethane particles with a core-shell structure is presented in this paper. The objective could be achieved by using a series of reactive steric stabilizers of the type ω-$(OH)_x$-poly(*n*-butyl acrylate), -polystyrene, -polysiloxane or -polybutadiene ($x=1$ or 2) that play the role of surfmers during the polyaddition reaction between ethylene glycol and tolylene-2,4-diisocyanate, in cyclohexane as a dispersant medium. The final size of the polyurethane particles (0,5-10 μm) was found to be a function of the steric stabilizer characteristics (nature, molar mass and concentration) and of the addition procedure of the different reactants. These novel particles constituted of a polyurethane core and various shells depending on the stabilizer used exhibit specific and original properties.

Keywords: core-shell particles, dispersion, polyurethane

Introduction

It is with the objective to find novel applications for polymers obtained by step polymerization that we investigate the field of polyaddition reaction in a dispersed medium. The need for numerous applications (coatings, adhesives, etc.) to have materials easy to handle and process led us to evaluate the possibility to elaborate, by an heterogeneous polymerization process, "polycondensates" as a form of calibrated particles. Usually such a preparation is made possible by the presence, in the dispersant phase, of an ionic or a steric stabilizer that avoid the coagulation of the precipitating polymer and maintains it as a stable dispersion ("latex").

Among the steric stabilizers generally tested, amphipathic block copolymers (PS-b-PEO as an example) and reactive polymers (surfmers or macromonomers) can be discriminated. While the former enable the stabilization of the growing particle by physical adsorption, the latter react

DOI: 10.1002/masy.200350905

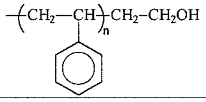
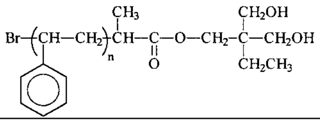
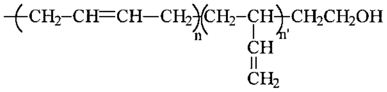
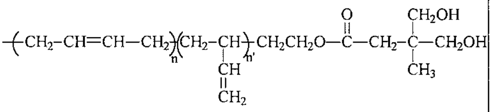
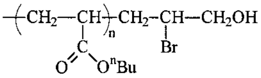
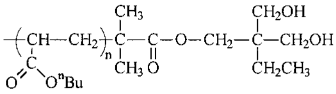
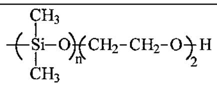
with the growing polymer and remain covalently bonded to the final particle. If the literature is well documented in the field of free radical polymerization of vinyl monomers in heterogeneous conditions, very few data are given concerning the preparation of polymer materials issued from a step polymerization *via* a controlled heterogeneous process. The preparation of calibrated polyurethane particles in the size range 5-50 µm, by suspension technique in a non-aqueous medium, has been reported by Nippon.[1] In this work, oligomeric glycols were condensed with diisocyanates in the presence of poly(ethylene oxide)-b-poly(dimethylsiloxane) block copolymer as a steric stabilizer. The use of dihydroxy-terminated poly(dodecylmethacrylate)s as reactive steric macromonomers for the preparation of polyurethane particles in a dispersed organic medium has been recently reported by Sivaram *et al.*[2] We also explored the possibility to prepare polyurethane particles with a core-shell structure by a dispersion technique.[3],[4] A series of reactive steric stabilizers of the type ω-$(OH)_x$-poly(*n*-butyl acrylate) (P*n*BuA), -polystyrene (PS), -polydimethylsiloxane (PDMS) or -polybutadiene (PBut) (x=1 or 2) have been tested, leading to various core-shell polyurethane-based materials and exhibiting a large scope of properties depending on the chemical nature of the shell. Results are discussed in terms of particle characteristics (size and size distribution) along with some properties.

Results and Discussion

The preparation of polyurethane materials under the form of calibrated microspheres has been investigated in cyclohexane as the dispersant medium at 60°C in the presence of dibutyl tin dilaurate (DBTDL) as a catalyst. For this study, ethylene glycol (EG) and tolylene-2,4-di-isocyanate (TDI) were chosen as monomers at the ratio [NCO]/[OH] = 1,2. In order to prepare a series of novel core-shell polyurethane materials with specific properties, we designed a number of reactive stabilizers that differ by their chemical nature, molar mass, valence as well as solubility in the selected dispersant medium. The effect of each of the parameters indicated above were studied with respect to the ability to produce calibrated core-shell polyurethane particles with a tunable size and exhibiting specific properties.

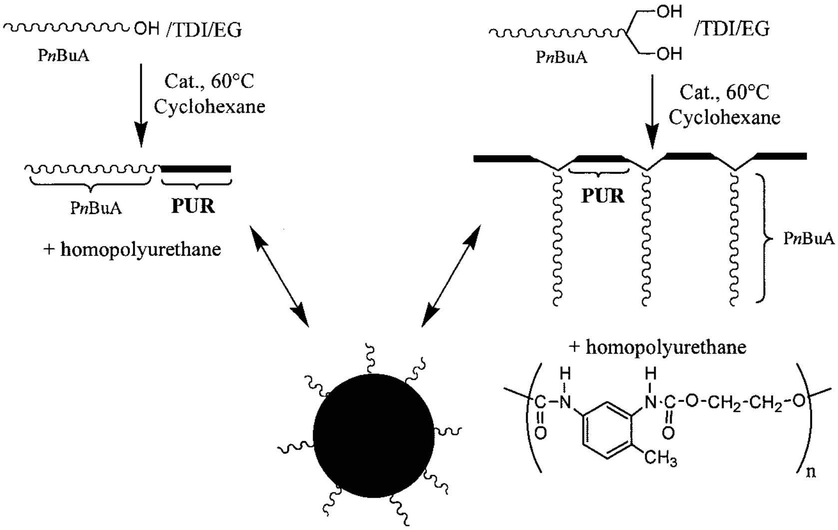
Unless PBut-OH and PDMS-OH that have been purchased, all the reactive stabilizers were synthesized either by "living" anionic or "controlled" radical polymerizations to insure a very good control of their molar mass and valence.[3],[4] A complete list of these different functional polymers is given in Table 1 together with their solubility parameter as well as the solubility parameter of cyclohexane (dispersant medium) for comparison. The knowledge of the solubility parameter of each component is of importance in regards to the nucleation process as well as to the stabilization and shelf life of the latex.

Table 1. List of the reactive stabilizers used for the preparation of polyurethane particles in cyclohexane as a dispersant medium at 60°C.

Reactive stabilizer		Synthesis method	Solubility parameter δ (MPa)$^{1/2}$
PS-OH		Anionic [3]	18,6
PS-(OH)$_2$		Anionic[6]	18,6
PBut-OH	 $-\!\left(CH_2-CH=CH-CH_2\right)_n\!\left(CH_2-\underset{\underset{\underset{CH_2}{\|}}{CH}}{|}{CH}\right)_{n'}\!-CH_2CH_2OH$	Anionic [6]	17,2
PBut-(OH)$_2$	 $-\!\left(CH_2-CH=CH-CH_2\right)_n\!\left(CH_2-\underset{\underset{\underset{CH_2}{\|}}{CH}}{|}{CH}\right)_{n'}\!CH_2CH_2O-\overset{\overset{O}{\|}}{C}-CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_2OH}{|}}{C}}-CH_2OH$	Anionic [6]	17,2
P*n*BuA-OH	 $-\!\left(CH_2-\underset{\underset{C(=O)O^nBu}{|}}{CH}\right)_n\!CH_2-\underset{\underset{Br}{|}}{CH}-CH_2OH$	ATRP [3],[5]	20,4
P*n*BuA-(OH)$_2$	 $-\!\left(\underset{\underset{C(=O)O^nBu}{|}}{CH}-CH_2\right)_n\!\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-\underset{\underset{O}{\|}}{C}-O-CH_2-\underset{\underset{CH_2CH_3}{|}}{\overset{\overset{CH_2OH}{|}}{C}}-CH_2OH$	ATRP [5]	20,4
PDMS-OH	 $-\!\left(\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-O\right)_n\!\left(CH_2-CH_2-O\right)_2\!H$	commercial	7,4
cyclohexane			16,8

In addition to the chemical nature and valence of the steric and reactive stabilizer that govern the formation of a stable dispersion of the growing polyurethane chains, numerous other parameters such as the wt % concentration of the stabilizer, the kinetic and order of addition of the reactants, the concentration of the monomers (solid content), the stirring speed in the reactor, etc. may be tuned to enable the preparation of calibrated particles with a very narrow size distribution.

As shown in Scheme 1, the growing particles are constituted of homo-polyurethane chains together with either block- or graft- copolymers - depending on the valence (1 or 2) of the surfmer used - that play the role of steric stabilizers in the dispersion process.



Scheme 1. synthetic route to core-shell polyurethane particles.

Influence of the Procedure

The order of addition of the reactants was found to be crucial in the procedure. Indeed, it was observed that ω-(di)hydroxyl steric stabilizers have to be pre-reacted first with a slight excess of tolylene-2,4-diisocyanate (TDI) leading to the formation of ω-(di)NCO-terminated polymers, considered as the true reactive stabilizers. EG is then added over a 30' period giving rise to a turbid medium due to the insolubility of this monomer and of growing PUR oligomers in cyclohexane. TDI, totally soluble in cyclohexane, was then added drop-wise over variable time periods. The time of TDI addition was also found to be important with respect to the size of the particles ; the longer the time of TDI addition, the lower the particle size. As an example in the specific case of PS-OH used as a stabilizer ($\overline{M}_n$=2100 g/mole; 10 wt%), the particle size goes from 2 μm to 0,5 μm while TDI is added over 1 or 6 hours.

The procedure of addition described above was followed in all the cases, whatever the reactive stabilizer used. Different parameters discussed in the next sections were then varied to compare the efficiency and behavior of each reactive stabilizer.

Influence of the wt% Concentration of the Reactive Stabilizer

The effect of the stabilizer concentration on the average size of the polyurethane particles has been evaluated for the various mono-hydroxy reactive stabilizers (see Figure 1).

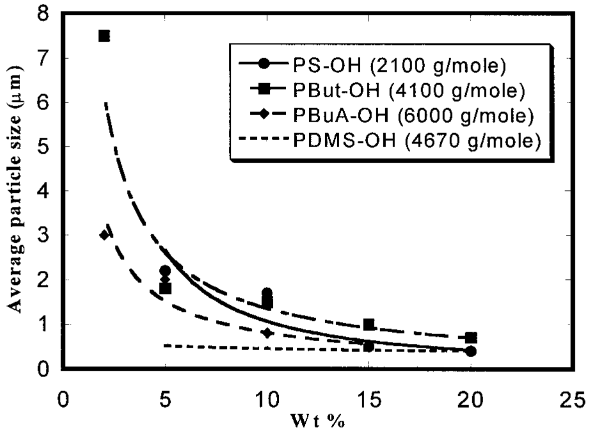


Fig. 1. Influence of the wt % concentration of the monovalent stabilizers on the PUR particle size.

As expected, the higher the stabilizer concentration, the lower the particle size. Indeed, the higher the concentration, the higher the surface coverage of the nuclei that are formed at the earliest stage of the polymerization, therefore preventing their coalescence. It is also interesting to note that the variation of the particle size with the stabilizer concentration is very much dependent to the chemical nature of the latter. While a pronounced effect on the particle size is found with PBut-OH concentration, no change was observed in the case of PDMS-OH used as a steric stabilizer. Whatever the wt % of PDMS-OH, PUR particles in the range 400-500 nm were systematically obtained.

Influence of the Molar Mass of the Reactive Stabilizer

The molar mass of the reactive stabilizer was found to have a dramatic effect on the formation of a stable latex. Indeed, a critical length of the stabilizer is required to control the nucleation step and thus to avoid coagulation of the growing particles. The domain of molar masses required to get a stable latex constituted of particles with a controlled size was observed to be very much dependent to the chemical nature (as well as to the valence, see next chapter) of the reactive stabilizer. As illustrated in Figure 2, the comparison of PS-OH and PBuA-OH allowed us to define $\overline{DP}_n$ intervals (20-40 and 40-200 respectively) where these polymers are efficient in the PUR particles stabilization process, in these experimental conditions. Outside these intervals, partial or complete coagulation of the latex was observed.

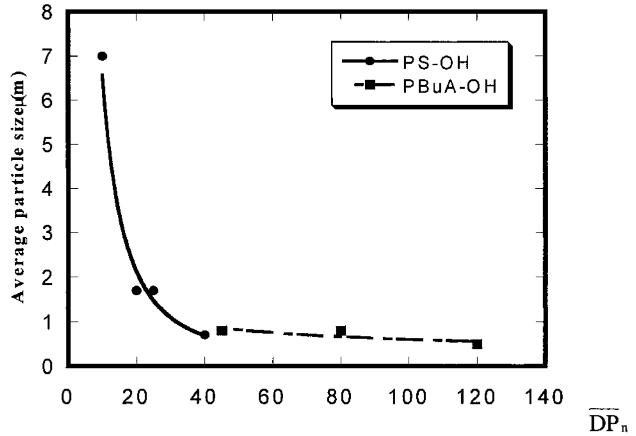


Fig. 2. Influence of the stabilizer molar mass on the PUR particle size.

Influence of the Valence of the Reactive Stabilizer

The valence of the stabilizer has an important effect on the formation of stable latex. Depending on the valence of the stabilizer (one or two), block or graft copolymers are formed during the polymerization (see Scheme 1). The ability of these block or graft copolymers to initiate the nucleation step and to stabilize the final latex may be different. Indeed, this behaviour is exemplified here (Figure 3) in the case of acrylate-based stabilizers (PBuA-OH and $PBuA(OH)_2$ respectively).

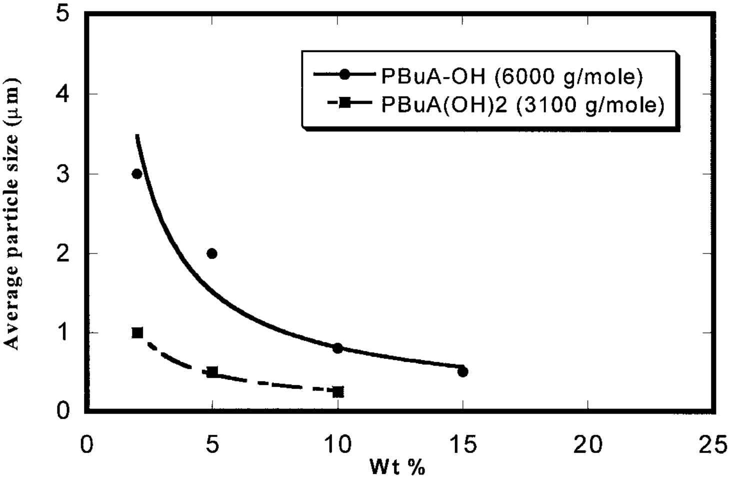


Fig. 3. Influence of the valence of the reactive stabilizer on the PUR particle size in thecase of mono- and divalent poly(*n*-butyl acrylate)s (PBuA-OH & $PBuA(OH)_2$).

As shown in Figure 3, gemini-type $PBuA\text{-}(OH)_2$ macromonomer is much more efficient than its monovalent analog with respect to the formation of polyurethane particle with a controlled size. Low concentration of $PBuA\text{-}(OH)_2$ are sufficient to form a stable dispersion and the corresponding polyurethane particles are systematically smaller than the ones obtained with PBuA-OH. In addition it was observed that the required critical $\overline{DP_n}$ of $PBuA\text{-}(OH)_2$ to form a stable latex is much lower than the one needed with PBuA-OH.

These trends were also observed with the other reactive stabilizers used. These general observations show that the formation of first nuclei occurs more easily when divalent reactive stabilizers are used. A better repartition of the stabilizer chains at the surface of the PUR particles may explain this phenomenon.

Characterization of the PUR Particles

The characterizations of these new materials have been performed to check the true participation of the reactive stabilizer in the polyaddition reaction and thus to prove the core-shell structure of the particles. ^1H NMR, SEC and mechanical tests were systematically realized. The ^1H NMR characterization was implemented in DMSO at 50°C to permit the solubilization of all the chains packed in the particle. As shown in Figure 4 with poly(*n*-butyl acrylate) used as a stabilizer, the integration of the different peaks allowed us to estimate that more than 90% of the stabilizer initially introduced in the reactor vessel, do participate in the polyaddition reaction and is covalently bonded to urethane segments.

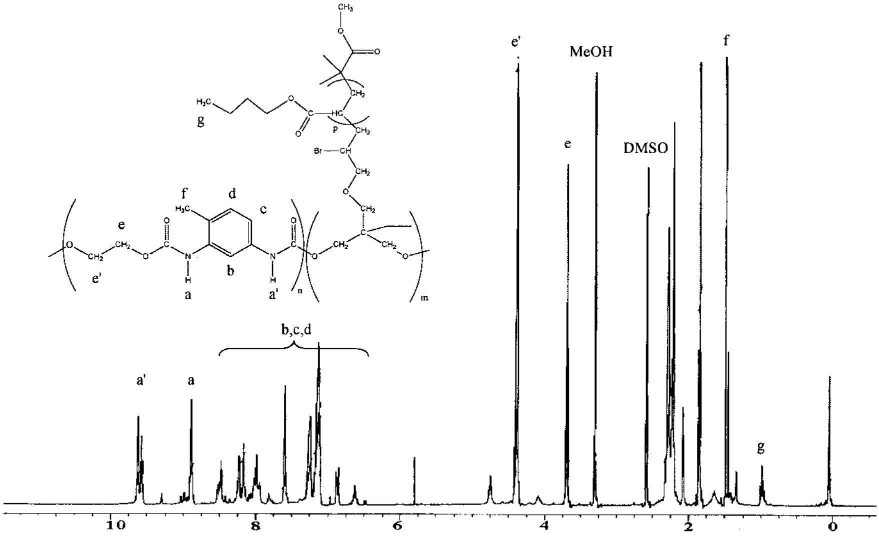


Fig. 4. ^1H NMR spectrum (DMSO-d_6, 200 MHz) of core-shell PUR-PBuA particles.

The SEC characterization of these materials was realized in DMF. The experimental molar masses based on polystyrene calibration were systematically found around 5000-8000 g/mole with a multimodal distribution. These values are rather low in agreement with the experimental conditions. No real correlation between the molar mass and the particle size was observed.

It is also worth noting that dynamic mechanical analyses of the PUR particles reveal two glass transition temperatures corresponding to the core and the shell moieties of the particles. An illustration of this is given in Figure 5, with polystyrene-OH used as a stabilizer.

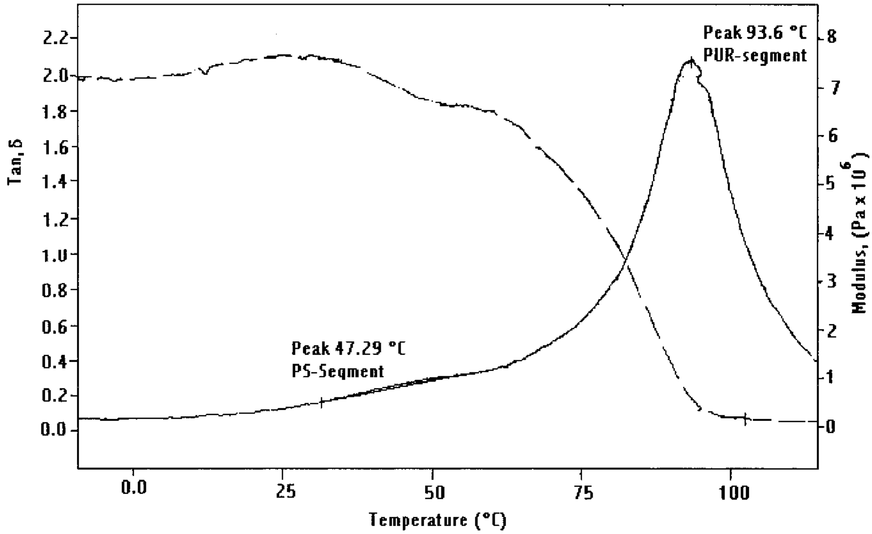


Fig. 5. DMA characterization of core-shell PUR-PS particles.

Adhesive Properties of the PUR Films

Films of PUR latexes prepared using poly(*n*-butyl acrylate) as the stabilizer were coated on different substrates (glass, aluminium, PET) to check their thermo-dynamical surface properties and their tacky behavior. After evaporation of the solvent, the particles aggregate to form hexagonal structures like a "bee-hive", as shown in Figure 6.

Contact angle measurements as well as tack tests clearly show that the coating conditions govern the surface properties. Interestingly, a PBuA-like behavior of the film is observed at room temperature due to a contribution on the surface properties of the PBuA chains. In addition, an increase of the poly(*n*-butyl acrylate) molar mass yields higher tack property. Conversely, a PUR-like behavior was found on heating above Tg at 120°C, due to a coalescence of the PUR core.

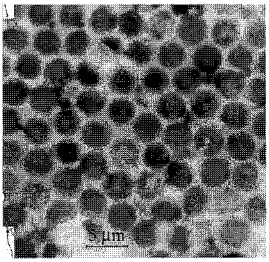
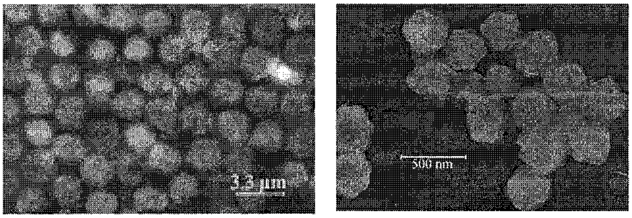


Fig. 6. TEM micrograph of a PUR latex film.

Derivatization of the PUR Particle Surface

The controlled character of the atom transfer radical polymerization of n-alkyl acrylates allowed us to prepare new stabilizers of the type P*t*BuA-b-P*n*BuA-OH with various compositions. Following the same procedure as described above, such block copolymers were then used as reactive polymers for the preparation of polyurethane particles in a dispersed medium. The derivatization of the *t*-butyl ester groups, located at the shell of the particle, into acrylic acid functions after treatment of the latex with trifluoro-acetic acid rendered the PUR particles re-dispersible in water. Typical TEM microscopy of PUR organic and aqueous latexes are shown in Figure 7.



(a) **(b)**

Fig. 7. TEM micrographs negatives of PUR particles obtained using (a) P*n*BuA$(OH)_2$, and (b) P*t*BuA-b-P*n*BuA-OH (particles redispersed in water after conversion of the P*t*BuA block in PAA block).

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