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Hydroxy and Di-Hydroxy End-Capped Polybutadiene as Reactive Steric Stabilizers for the Synthesis of Polyurethane Particles in Organic Dispersant Media

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Summary: The synthesis of polyurethane particles by polyaddition of ethylene glycol (EG) and tolylene-2,4-diisocyanate (TDI) in cyclohexane at 60 °C was investigated in the presence of ω-hydroxy and ω,ω'-dihydroxy polybutadiene, used as reactive steric stabilizers. The effect of the functionality and concentration of the reactive polybutadiene, as well as the monomer addition procedure, onto the polyurethane particle formation was studied. Calibrated PUR particles with an average diameter in the range 1–2 μm could be readily obtained.

Keywords: macromonomers; particles; polyaddition; polybutadiene; polyurethanes

Introduction

One of the criteria for novel polymers to have potential applications in domains such as cosmetics, diagnostic tests, drug delivery systems, etc., concerns their synthesis that must be undertaken through a heterogeneous polymerization process.[1] The classical techniques to prepare dispersed solid materials include emulsion, mini-emulsion, dispersion, suspension, as well as emulsification of preformed polymers.[2,3]

The production of stable latexes is conditioned by the chemical nature and physico-chemical characteristics of the stabilizer used. If well selected, amphipathic block copolymers may play efficiently the role of steric stabilizers by adsorbing at the surface of the particles and forming a repulsive protecting shell. Since the latter are not covalently bonded to the core of the particles, they may desorb and their stabilizing properties lost under the influence of high shear stress. Typically, in coating applications, the stabilizers can migrate through the film and segregate,[4] leading to the loss of the film properties. For example, a stabilizer migration to a ''film-air'' or to a ''film-substrate'' interface can affect the gloss of a film [5] or reduce adhesion phenomenon, respectively.

In order to avoid such drawbacks, one strategy consists of using a reactive stabilizer such as functionalized homo- and copolymer, also called macromonomer. Since the latter participates in the polymerization reaction by forming block or graft copolymers, it finally remains covalently bonded to the polymer particles, leading to an increased stability of the resultant latexes.[6] For instance, homopolymers such as poly(vinylpyrollidone), poly(acrylic acid), hydroxy propyl cellulose, or thiol end-capped polyethylene oxide were used as stabilizers for the free-radical polymerization of styrene in aqueous dispersion.[7–11]

If there is sufficient literature concerning the production of latexes via controlled free-radical polymerization,[12] it is less documented when dealing with polyaddition and polycondensation reactions. Sivaram et al. reported the use of amphiphilic block copolymers, poly(1,4-isoprene)-*b*-poly(ethylene oxide)s, as well as a

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polycondensable macromonomer based on dihydroxy-poly(dodecylmethacrylate) for the preparation of polyurethane microspheres by dispersion and suspension polymerizations in organic media.[13–15] The preparation under dispersion conditions of polyurethane micro-gels has also been described by Graham[16] and Clark.[17] We have also investigated the polyaddition reaction between ethylene glycol (EG) and tolylene-2,4-diisocyanate (TDI) in a dispersant organic medium (cyclohexane) in the presence of hydroxy-functionalized macromonomers (ω-OH polystyrene,[18] ω-OH poly(*n*-butyl acrylate),[19] and ω-OH polydimethylsiloxane[20,21]) as steric reactive stabilizers. This technique allowed us to synthesize a series of calibrated core-shell polyurethane particles with a large palette of properties depending on the macromonomer used, which finally constitutes the shell of the particles. We have also shown that difunctional ω,ω'-di-OH poly(*n*-butyl acrylate)s –that may lead to the in situ formation of grafted copolymers– are more effective reactive stabilizers compared to monofunctional ω-OH poly(*n*-butyl acrylate), in terms of particle size control.[22]

It is with the objective to extend the type of reactive stabilizer and also to focus on the effect of the macromonomer functionality, onto the final latex characteristics, that we compared ω-OH polybutadiene and ω,ω'-di-OH polybutadiene as reactive steric stabilizers, for the preparation of PUR latexes. A first comparison of the solubility parameters of polybutadiene ($\delta = 17.2$ $MPa^{1/2}$) with the one of the dispersant medium (cyclohexane, $\delta = 16.8$ $MPa^{1/2}$), argues for the affinity of polybutadiene towards cyclohexane. Therefore, it may be anticipated that the behavior of hydroxy functionalized polybutadiene could be different than those of ω-hydroxy polystyrene ($\delta = 18.6$ $MPa^{1/2}$), ω-hydroxy poly(*n*-butyl acrylate) ($\delta = 20.4$ $MPa^{1/2}$), or ω-hydroxy polydimethylsiloxane ($\delta = 14.9$ $MPa^{1/2}$), in regard to the nucleation step and to the final characteristics of the PUR particles formed.

Experimental Part

Cyclohexane (J. T. Baker, 99%) for dispersion polymerization was used as received. Tetrahydrofuran (THF, J. T. Baker, 99%), was first distilled over CaH_2 and then distilled over sodium-benzophenone. Acetone was cryo-distilled over magnesium sulfate. Dry dichloromethane was obtained by cryo-distillation over calcium hydride.

Ethylene glycol (Aldrich, 99%) and TDI (Aldrich, 98%) were used as received. Dibutyl tin dilaurate (DBTDL, Aldrich, 98%) was used as received. A 1% (mol/wt) stock solution was prepared by dissolving 2.48×10^{-3} mol of DBTDL in 25 g of paraffin.

Trimethylol propane (TMP) (Aldrich, 99%), bis-(hydroxymethyl) propionic acid (Aldrich, 99%), 1,3-dicyclohexylcarbodiimide (DCC, Aldrich, 99%), 2,2′-dimethoxy propane (Lancaster, 98%), and triethylamine (Lancaster, 99%) were used as received. 4-(Dimethylamino)pyridinium 4-toluenesulfonate (DPTS) was synthesized using reported procedure.[23]

ω-Hydroxy polybutadiene ($\overline{M}_n = 4\,000$ g · mol^{-1}) was provided by Polymer Expert S. A. (France).

Synthesis of ω,ω'-Dihydroxy Polybutadiene (see Scheme 2)

Step 1: Esterification of Polybutadiene (Acetal-terminated Polybutadiene)

0.12 g (0.73 mmol) of isopropylidene-2,2′-bis(methoxy) propionic acid, protected using reported procedure,[24] 3 g (0.73 mmol) of ω-hydroxy polybutadiene, and 0.025 g (0.087 mmol) of DPTS were mixed with 15 mL of CH_2Cl_2. The reaction flask was flushed with nitrogen and 0.18 g (0.87 mmol) of DCC was added. The reaction mixture was stirred at room temperature for 15 h under nitrogen atmosphere. Once the reaction was complete, the DCC-urea formed was filtered off in a glass filter and washed with a small volume of CH_2Cl_2. The solvent was then evaporated at room temperature and the

protected polybutadiene was precipitated in acetone. The polymer was characterized by ^{1}H NMR. Yield: 2.5 g (82%). ^{1}H NMR ($CDCl_3$): δ in ppm 0.9 (m, 3H, $-CH_3$), 1.20–1.30 (m, 6H, $-CH_3$), 1.60 (m, 3H, $-CH_3$), 2.1 (m, 2H, $-CH_2$, $-CH{=}CH-C\underline{H}_2$), 3.65 (d, 2H, $-CH_2O$), 4.1 (t, 2H, $-CH_2-O-CO$), 4.18 (d, 2H, $-CH_2O$), 5.0 (m, 2H, $C\underline{H}_2{=}C$), 5.5 (m, 3H, $-C\underline{H}{=}C\underline{H}-$, $-C\underline{H}{=}CH_2$).

Step 2: Cleavage of the Acetal Group of the Polybutadiene

2 g of protected polybutadiene was dissolved in 5 mL (50/50, v/v) solution of THF/HCl-water mixture. The mixture was stirred overnight at room temperature. The ω,ω'-dihydroxy polybutadiene $PB(OH)_2$ was recovered by precipitation in acetone. The polymer was characterized by size exclusion chromatography (SEC) and ^{1}H NMR. ^{1}H NMR ($CDCl_3$): δ in ppm 0.9 (m, 3H, $-CH_3$), 1.6 (m, 3H, $-CH_3$), 3.7 (d, 2H, $-C\underline{H}_2OH$), 3.9 (d, 2H, $-C\underline{H}_2OH$), 4.1 (t, 2H, $-CH_2-O-CO$), 5.0 (m, 2H, $C\underline{H}_2{=}C$), 5.5 (m, 3H, $-C\underline{H}{=}C\underline{H}-$, $-C\underline{H}{=}CH_2$).

Synthesis of Polyurethane Particles

The synthesis has been performed according to the procedure previously described in ref.[18–22]

Characterization

^{1}H NMR spectra were recorded using a Bruker AC 400 MHz NMR spectrometer. SEC of the stabilizers was performed using a JASCO HPLC pump type 880-PU, TOSOHAAS TSK gel columns, a Varian (series RI-3) refractive index detector and a JASCO 875 UV/Vis absorption detector, with THF as the mobile phase. The system was calibrated by means of narrow polystyrene standards. In the same manner, we performed SEC measurements for the PUR samples in dimethylformamide (DMF) as the eluant.

PUR particle size and particle size distribution (span) were measured using a Malvern Master sizer 2000 (Hydro 2000S) fitted with a flow cell that passes the sample/dispersant beam of the optical unit. The solvent used was cyclohexane and the measurements were performed at 25 °C at a stirring speed of 2 100 rpm.

Optical microscopy data were collected on an Olympus BX 50 microscope equipped with a Sony Power Had camcorder.

Transmission electron microscopy (TEM) was performed on a JEOL, JEM-100S electron microscope. The sample was placed on a carbon-coated copper grid and was let to dry at room temperature.

Scanning electron microscopy (SEM) was performed on a JEOL JSM 2500 electron microscope. The sample was let to dry on a metal support and then treated with gold.

Dynamic mechanical analysis (DMA) was performed with a Perkin-Elmer apparatus in flowing nitrogen (1 Hz frequency).

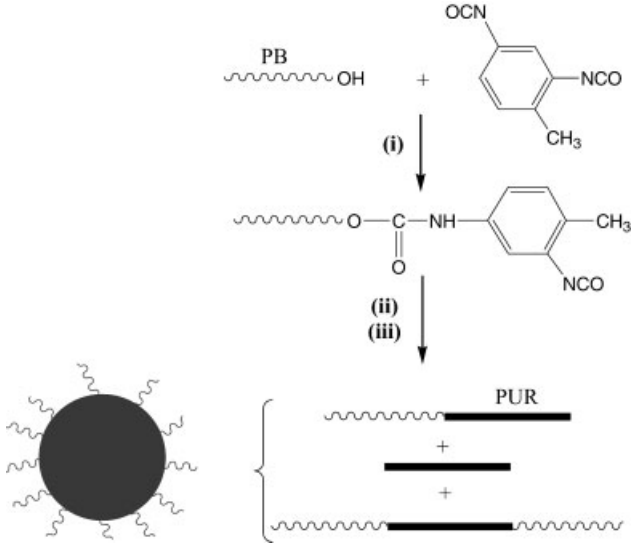
Results and Discussion

Polyurethane Particles Synthesis Using ω-Hydroxy Polybutadiene as a Stabilizer

The precedent studies dealing with the synthesis of PUR particles in the dispersant cyclohexane phase have clearly shown that the procedure of macromonomer and monomers addition is essential in order to get uniform particles and to avoid coalescence phenomenon.[18–22] Indeed, the hydroxy-terminated stabilizer had to be pre-reacted first with a slight excess of the diisocyanate (TDI, 2 eq.) to form in situ ω-NCO reactive stabilizer, previous to the addition of EG and the rest of TDI, respectively (see Scheme 1).

We performed a series of polyaddition reactions between TDI and EG –molar ratio [NCO]/[OH] = 1.1- in cyclohexane in the presence of ω-OH polybutadiene (PB-OH), following the three-stage experimental procedure (see Scheme 1), i.e.:

(i) a 2 h pre-reaction of ω-OH polybutadiene with TDI (2 mol eq.) in cyclohexane at 60 °C in the presence of DBTDL to form in situ ω-NCO polybutadiene,
(ii) addition of the whole amount of EG; it is worth noting that EG is not soluble



Scheme 1.
Core-shell PUR-PB particle synthesis.

in cyclohexane and is present as monomer droplets,

(iii) drop-wise addition of TDI over a variable time period.

The particle characteristics with respect to experimental parameters such as the concentration of PB-OH as well as the time of TDI addition are presented thereafter.

Effect of ω-OH Polybutadiene Concentration

The wt.-% versus monomers of ω-OH polybutadiene ($\overline{M}_n = 4\ 000\ g \cdot mol^{-1}$) used as a steric stabilizer was varied from 1 to 20. As it is shown in Table 1, polyurethane particles are readily formed, without coalescence, provided that the concentration of ω-OH polybutadiene is higher than 2 wt.-%. The expected trend, i.e., a diminution of the particle size with an increase in steric stabilizer concentration is observed; the average particle size varied from 7.5 to 0.70 μm when ω-OH polybutadiene concentration was increased from 2 to 20 wt.-%. Indeed, larger amount of steric stabilizers used enable a higher

Table 1.
Effect of the stabilizer concentration, ω-OH polybutadiene (PB-OH), on the PUR particle size (TDI addition time = 1 h).

Entry	wt.-% of PB-OH introduced	wt.-% of PB incorporated	$d_{(0.5)}$[a] / μm	Span[b] $\frac{d(0.9)-d(0.1)}{d(0.5)}$	SEC[c] $\overline{M}_n$ / g · mol^{-1}	SEC[c] PDI $= \frac{\overline{M}_w}{\overline{M}_n}$	Observation
Exp1	1	ND	-	-	-	-	Coagulation
Exp2	2	ND	7.4	2.1	4 500	1.8	Bimodal size distribution
Exp3	5	ND	1.8	0.8	11 400	1.5	Monodisperse
Exp4	10	3	1.2	0.6	10 600	1.1	Monodisperse
Exp5	15	ND	1.1	0.6	13 800	2.1	Monodisperse
Exp6	20	7	0.7	0.7	15 100	2.0	Monodisperse

[a] Particle size obtained by performing light scattering measurements on a Malvern Master sizer 2000 (Hydro 2000S) apparatus. $d_{(0.5)}$ = 50% particles have size lower than the given value.

[b] Particle size distribution or "span" $= \frac{d(0.9)-d(0.1)}{d(0.5)}$, where, $d_{(0.9)}$ = 90% particles have size lower than the given value, $d_{(0.5)}$ = 50% particles have size lower than the given value, $d_{(0.1)}$ = 10% particles have size lower than the given value.

[c] Determined by SEC using *N*,*N*-dimethylformamide (DMF) as eluant. ND = not determined.

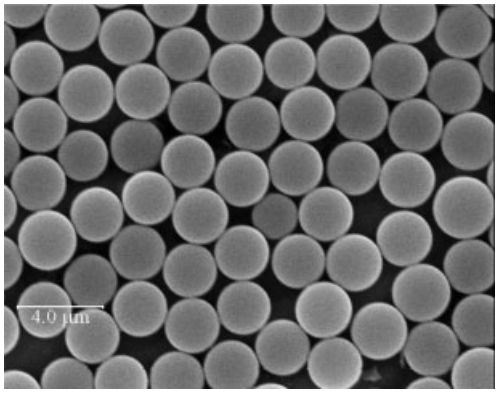


Figure 1.
SEM picture of PUR particles synthesized using PB-OH (5 wt.-%), as the stabilizer.

surface to be covered thus leading to a larger number of smaller particles to be formed. In addition, the size distribution of the PUR particle remains very narrow as indicated by the span value (span $\cong$ 0.6–0.8), nearly irrespective of the stabilizer concentration, above 5 wt.-%. This trend indicates that ω-hydroxy polybutadiene plays very efficiently its stabilizer role as it is confirmed further in the paper. A typical SEM microscopy picture of the PUR particles synthesized using ω-hydroxy polybutadiene as the stabilizer at a 5 wt.-% concentration is shown in Figure 1. The average particle size was measured close to 2.0 µm, in agreement with data obtained from light scattering measurements.

A comparison with experiments run in the presence of ω-OH polystyrene ($\overline{M}_n = 2\ 100\ g \cdot mol^{-1}$) used as a reactive stabilizer shows a similar trend as illustrated in Figure 2. In both cases, the particle size decreases while the stabilizer concentration increases and reaches a plateau (average diameter $\approx$ 0.5 µm) at high stabilizer weight concentration.

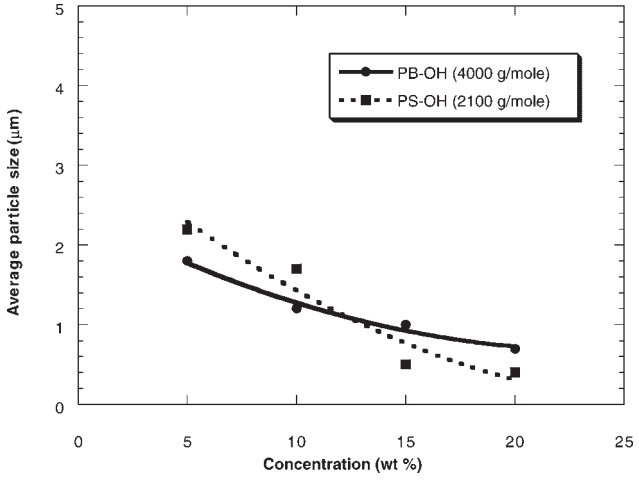


Figure 2.
Influence of the stabilizer wt.-% concentration on the PUR particle size: comparison between PS-OH ($\overline{M}_n = 2\ 100\ g \cdot mol^{-1}$) and PB-OH ($\overline{M}_n = 4\ 000\ g \cdot mol^{-1}$).

Table 2.
Effect of TDI addition time on the PUR particle size (PB-OH: 5 wt.-%).

Entry	Time of TDI addition	$d_{(0.5)}$[a)] / μm	Span[b)]	Observation
Exp1	1 lot	-	-	Coagulation
Exp2	1 h	1.0 and 4.8	1.4	Bimodal size distribution
Exp3	3 h	1.2	0.6	Monodisperse
Exp4	6 h	1.9	0.9	Monodisperse

[a)] Particle size obtained by performing light scattering measurements on a Malvern Master sizer 2000 (Hydro 2000S) apparatus. $d_{(0.5)} = 50\%$ particles have size lower than the given value.

[b)] Particle size distribution or span $= \frac{d(0.9)-d(0.1)}{d(0.5)}$, where, $d_{(0.9)} = 90\%$ particles have size lower than the given value, $d_{(0.5)} = 50\%$ particles have size lower than the given value, $d_{(0.1)} = 10\%$ particles have size lower than the given value.

Effect of TDI Addition Time on the Dispersion Process

As shown in Table 2, a variation of TDI addition time, at a constant ω-hydroxy polybutadiene concentration of 5 wt.-%, affects the final particle size. Indeed, a drop-wise TDI addition over a time period ranging from 3 to 6 h is required to produce calibrated PUR particles (span ≤ 0.9). Faster TDI addition (in one lot or over 1 h time) leads to coagulation or to the formation of two particle populations, respectively, sign of a bad control of the nucleation step. Conversely to results obtained with ω-OH polystyrene used as a reactive stabilizer, a slight variation of the particle size with TDI addition time was noticed. This phenomenon may be explained by a better affinity of ω-hydroxy polybutadiene towards cyclohexane compared to ω-hydroxy polystyrene.

PUR Particles Characterization

Before analysis, the samples were washed several times with cyclohexane by centrifugation in order to remove residual unreacted ω-OH polybutadiene. The characterization of the polyurethane samples was first performed by means of SEC measurements in DMF (good solvent for PUR). As it is shown in Table 1, the experimental molar masses—based on a polystyrene calibration—increase from 5×10^3 to 15×10^3 g · mol^{-1} when the concentration of ω-OH polybutadiene increases from 2 to 20 wt.-%. In the mean time, the PDI index remains close to 2, as it is logically expected for a polyaddition reaction. This observation argues for a participation of the steric stabilizer in the polyaddition process. A typical SEC trace is given in Figure 3.

The polyurethane samples were also analyzed by ^{1}H NMR spectroscopy. The ^{1}H NMR spectrum in DMF of PUR sample prepared in the presence of 10 wt.-% of PB-OH ($\overline{M}_n = 4\,000$ g · mol^{-1}) is shown in Figure 4. The assignment as well as the intensity of the signals located at around 2.1 ppm (aliphatic protons of the PB moiety δ_{-CH_2-}) and at 6.6–7.9 ppm (aromatic protons of the PUR backbone) enable us to estimate that 3 wt.-% of PB are present within the sample. This result is in agreement with a participation of PB-OH in the polyaddition reaction with efficiency close to 30%.

We further explored the evidence of the polybutadiene stabilizer anchorage on the PUR particles by performing thermomechanical analysis (DMA). As it is shown in Figure 5, the DMA traces show two transition temperatures −75 °C and 95 °C, attributed to the polybutadiene moiety (shell) and to the polyurethane segment (core), respectively. This analysis supports that the stabilizer is covalently linked to the PUR particle and has taken part in the polyaddition reaction.

In this first part, we have demonstrated that ω-hydroxy polybutadiene is an efficient reactive stabilizer for the preparation of uniform ''core-shell'' PUR particles in

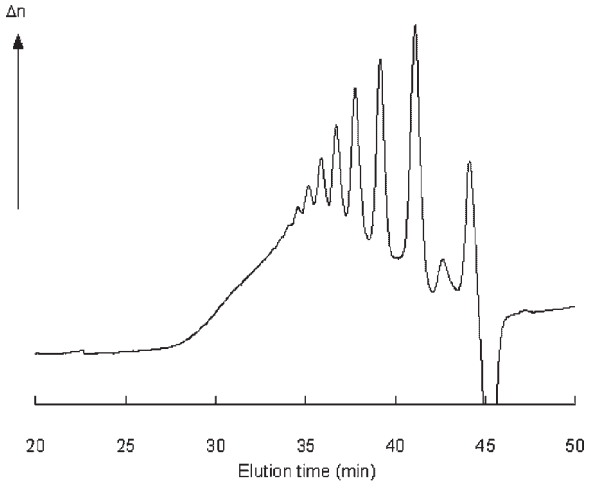


Figure 3.
Typical SEC trace of PUR-PB particles redissolved in DMF.

cyclohexane used as a dispersant organic medium. Similarly to previous studies with poly(butyl acrylate)s,[22] we investigated the effect of the –OH functionality of polybutadiene onto the PUR particle synthesis. For that purpose, we synthesized

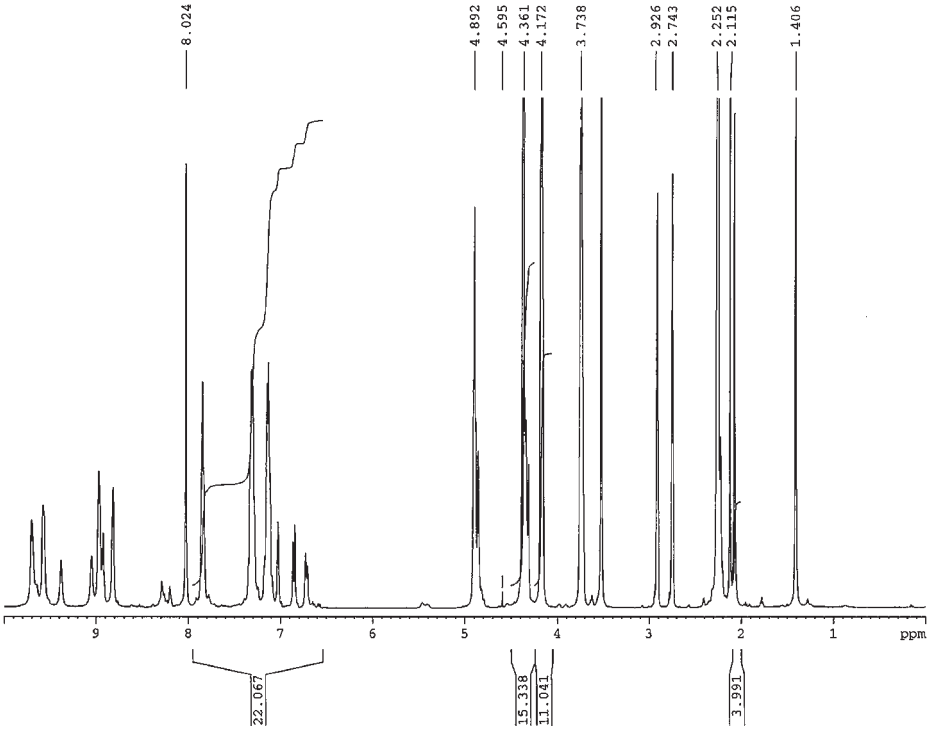


Figure 4.
^{1}H NMR spectrum of PUR-PB core-shell particles dissolved in DMF-d7.

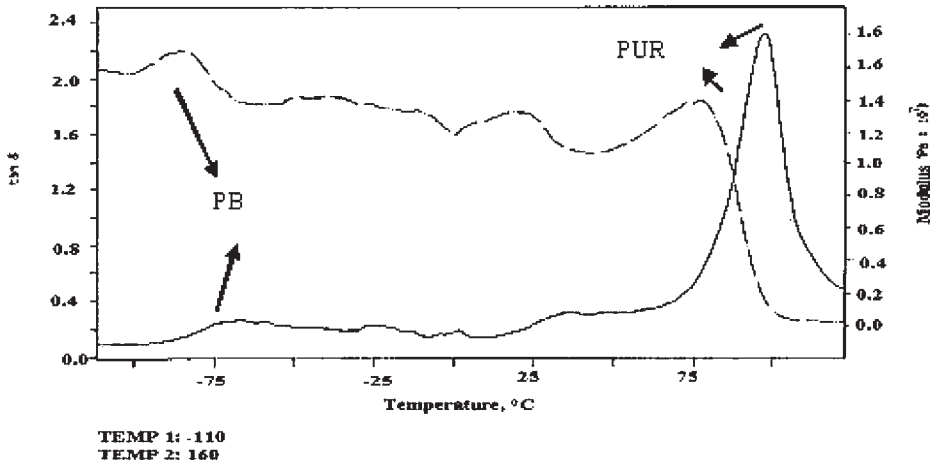


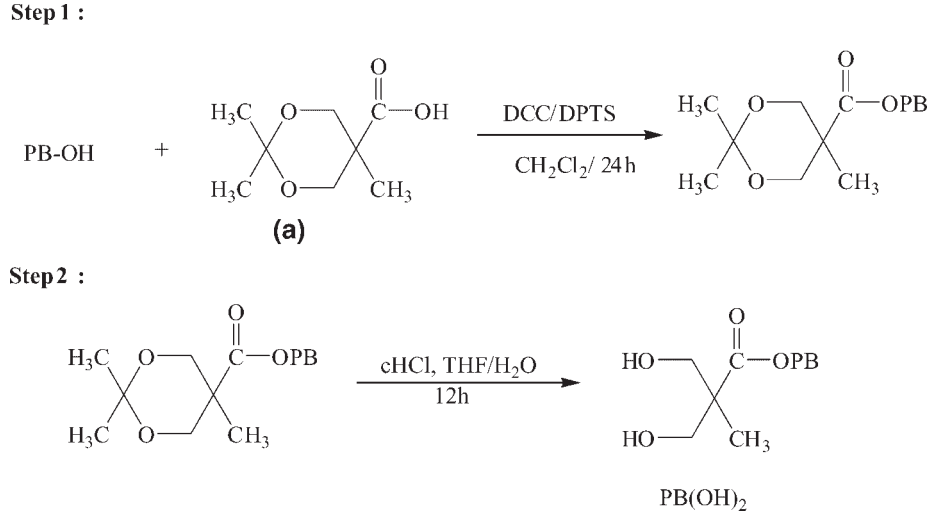
Figure 5.
DMA of PUR sample prepared using PB-OH as the stabilizer.

ω,ω'-dihydroxy polybutadiene and tested the latter for the preparation of core-shell PUR particles.

PUR Particle Synthesis Using ω,ω'-Dihydroxy Polybutadiene, $PB(OH)_2$, as Reactive Steric Stabilizer

Synthesis of ω,ω'-Dihydroxy Polybutadiene

The ω,ω'-dihydroxy polybutadiene was synthesized by esterification of the ω-hydroxy polybutadiene ($\overline{M}_n = 4\,000$ g · mol^{-1}) with the bis-hydroxymethyl propionic acid in the presence of DPTS and DCC at room temperature (see Scheme 2). The protected polymer obtained was thereafter deprotected by acidic treatment in water/THF mixture to give $PB(OH)_2$. The presence of two primary alcohol functions at the end of the polybutadiene has been checked by ^{1}H NMR or by reacting with trichloroacetyl isocyanate. In this latter



Scheme 2.
Synthetic pathway to ω,ω'-dihydroxy polybutadiene, $PB(OH)_2$. (a) = isopropylidene-2,2′-bis(methoxy) propionic acid.

Table 3.
Effect of the stabilizer concentration [PB-$(OH)_2$] and TDI addition time on the PUR particle size.

Entry	wt.-% of $PB(OH)_2$	wt.-% of PB incorporated	Time of TDI addition	$d_{(0.5)}$ [a] μm	Span[b]	Observation
Exp1	10	ND	1 lot	-	-	Coagulation
Exp2	10	ND	1 h	3.2	6.7	Bimodal size distribution
Exp3	10	5	3 h	1.3	1.0	Monodisperse
Exp4	10	5	6 h	1.1	1.0	Monodisperse
Exp5	5	-	6 h	0.9	1.0	Monodisperse
Exp6	1	-	6 h	13.2	3.4	15% coagulation bimodal size distribution

[a] Particle size obtained by performing light scattering measurements on a Malvern Master sizer 2000 (Hydro 2000S) apparatus. $d_{(0.5)} = 50\%$ particles have size lower than the given value.
[b] Particle size distribution or span $= \frac{d(0.9)-d(0.1)}{d(0.5)}$, where, $d_{(0.9)} = 90\%$ particles have size lower than the given value, $d_{(0.5)} = 50\%$ particles have size lower than the given value, $d_{(0.1)} = 10\%$ particles have size lower than the given value.

case, the ester peak corresponding to two $-CH_2-O-CO-NH-CO-CCl_3$ is visible at 4.5 ppm on the ^1H NMR spectrum. This allowed us to confirm the isoreactivity of the two hydroxy functions.

The procedure described above for the preparation of core-shell PUR particles was therefore undertaken in the presence of $PB(OH)_2$ as the stabilizer. Parameters such as the concentration of $PB(OH)_2$ and the time of TDI addition were varied to achieve efficient dispersions.

Effect of TDI Addition Time

For the purpose, the concentration of ω,ω'-dihydroxy polybutadiene was maintained at 10 wt.-% and TDI was added over a variable time period. Data are collected in Table 3. As already observed with ω-hydroxy polybutadiene, a fast addition of TDI (one lot or in 1 h) leads to either coagulation phenomenon or PUR particles with a bimodal size distribution. Conversely, monodisperse PUR particles (span values lower than 1) with an average size diameter around 1 μm are obtained for longer time of TDI addition (3 and 6 h). As it is shown in Table 3, best results in terms of particle size distribution are obtained for longer TDI addition time.

Effect of the Stabilizer Concentration and Comparison With PB-OH

A series of polyaddition at different concentrations of ω,ω'-dihydroxy polybutadiene was carried out. As it is shown in Table 3, calibrated PUR particle with an average diameter slightly lower than 1 μm could be readily

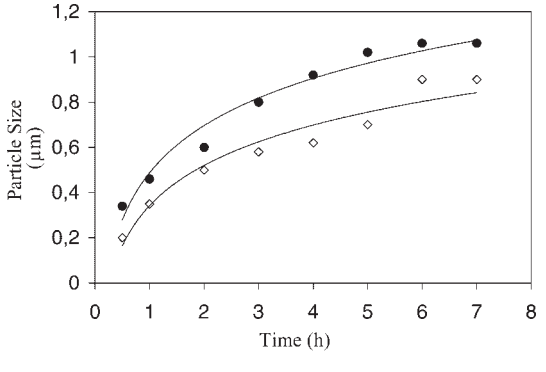


Figure 6.
Plot of particle size (μm) versus time (h); PB-OH (●) and PB-$(OH)_2$ (◇) as the stabilizers (5 wt.-% vs. monomers), and time of TDI addition: 6 h.

prepared for a ω,ω'-dihydroxy polybutadiene concentration up to 10 wt.-%.

In agreement with data obtained with poly(*n*-butyl acrylate)[22] used as a reactive stabilizer, $PB(OH)_2$ yields slightly smaller particles (0.9 μm as diameter) than PB-OH does at the same weight concentration (5 wt.-%) and TDI addition time (6 h). This is confirmed by the kinetic of particle growth monitored by optical microscopy (see Figure 6). These results prove that a larger number of nuclei are formed in the presence of ω,ω'-dihydroxy polybutadiene compared to mono-hydroxy polybutadiene.

The PUR samples were analyzed by SEC in DMF. The experimental molar masses, based on a polystyrene calibration, remain close to 10^4 g · mol^{-1}, whatever the experimental conditions, as already observed with ω-OH polybutadiene. Thermo-mechanical analyses of the PUR samples also reveal the presence of two glass transition temperatures at −70 °C and at 95 °C corresponding to the shell and the core of the particle.

Conclusion

The synthesis of novel polyurethane particles with soft polybutadiene shell could be easily prepared by polyaddition in an organic dispersant medium. ω-Hydroxy polybutadiene and gemini-type ω,ω'-dihydroxy polybutadiene used as reactive stabilizers were both found very efficient in regard to the formation of well-calibrated PUR particles.

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