Colloid Polym Sci (2002) 280: 1122–1130
DOI 10.1007/s00396-002-0737-5

ORIGINAL CONTRIBUTION

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Synthesis of uniform polyurethane particles by step growth polymerization in a dispersed medium

Received: 12 April 2002
Accepted: 16 May 2002

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Abstract Polyurethane microspheres were prepared by polyaddition of ethylene glycol (EG) and tolylene-2,4-diisocyanate (TDI) at 60 °C in cyclohexane as the organic dispersion medium, in the presence of dibutyl tin dilaurate (DBTDL) as catalyst and poly(styrene)-*b*-poly(ethylene oxide) block copolymers or ω-hydroxypolystyrenes as the steric stabilizers. Different parameters such as the manner of addition of the reactants, the concentration, and length of the stabilizer were varied to tune the polyurethane particle size. When ω-OH polystyrenes of low molar mass ($\bar{M}_n = 2000$–3000 g mol^{-1}) were used as the reactive stabilizers of dispersion, polyurethane particles in a tunable size range of 0.2–5 μm with a narrow size distribution (span = 0.7) could be prepared.

Keywords Polyurethane microspheres · Reactive stabilizer · Dispersed medium

Introduction

Due to a growing industrial need for materials that are easy to process, the synthesis of polymer particles in the micron size range has been the subject of an intense research. Typically, these materials find applications in many domains [1] such as surface coatings, adhesives, encapsulants, etc. Polymeric materials with spherical shapes are usually prepared from emulsion, suspension, and dispersion polymerization techniques [2]. The polymerization in non-aqueous dispersions was found to be an effective alternative route for the preparation of uniform polymeric particles in a 1–10 μm size range [3].

Typically, polymerization in a dispersed medium starts with the monomers partially or totally soluble in the organic phase and results in the formation of an insoluble polymer in the form of stable colloidal dispersion. Polymer microspheres with very narrow size distribution may be prepared in appropriate conditions. The role of the steric stabilizer is crucial in this procedure as it not only provides stability to the resultant particles, but also affects the final particle size and size distribution as well as the polymer molar mass. Usually, amphipathic polymers – block or graft copolymers – are effective stabilizers [4]; these strongly adsorb onto the forming particle surface by virtue of the insolubility of one of their block units (also called the anchor part). Nevertheless, their desorption from the final material causing irreversible damages such as the loss of the stabilization of the particles may occur. One possibility to avoid this major drawback is to use reactive stabilizers or macro-monomers that remain attached to the final particle [5].

Although this polymerization technique has gained industrial importance for the production of major polycondensates, such as polyesters [6, 7], polyamides [8], polycarbonates, and polyurethanes [9, 10, 11], very few detailed studies have been published dealing with the preparation of such polymers in dispersed media.

The technology of aqueous suspension polyaddition was developed for polyurethanes by Bayer Co. This work has been reviewed by Dieterich [9]. Recently, Landfester et al. [12] have reported the preparation of polyurethane particles with diameters of about 200 nm by mini-emulsion in an aqueous medium.

Polyurethane particles formed by suspension polymerization in a non-aqueous medium have also been reported by Nippon [13]. According to this work, polyurethane microspheres in the size range of 5–50 µm were obtained by condensing oligomeric glycols with diisocyanates or isocyanate-terminated pre-polymer in an organic medium. Poly(ethylene oxide)-*b*-poly(dimethylsiloxane) block copolymer was used as the steric stabilizer in a 2–20 wt. % range.

Hoeschele [10] reported the preparation of thermoplastic polyurethane, directly in the form of powder, by reacting hydroxy telechelic polyether or polyester and low molar mass diols with diisocyanates in an organic solvent. The stabilizers used in this case contain reactive glycidyl groups and remain covalently bonded to the particles.

Sivaram et al. [14, 15] recently reported the use of a polycondensable macromonomer based on dihydroxy-terminated poly(dodecylmethacrylate) for the synthesis of polyurethane microspheres by dispersion as well as by suspension polymerization in aliphatic solvents.

The need to prepare novel materials based on "polycondensates" with specific properties (for instance as adhesives or reinforced materials) coupled with the lack of known research in this field led us to investigate polyaddition reactions in dispersed medium. Herein, we report our first data dealing with the preparation of polyurethane materials. A series of steric stabilizers either based on polystyrene-*b*-poly (ethylene oxide) or hydroxy-terminated polystyrene have been synthesized and tested for this purpose. In this paper, we discuss the parameters (time of addition of the reactants, nature and concentration of the stabilizer, etc.) that affect the particle size and the particle size distribution of the resultant polyurethane materials.

Experimental

Materials

Cyclohexane (J.T. Baker, 99%) for anionic polymerization was first distilled over CaH_2 and then cryodistilled over polystyryl lithium, 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.

Styrene (Aldrich, 99%) was distilled over CaH_2 and stored over dibutyl magnesium. It was then cryodistilled just before polymerization. Ethylene oxide (Fluka, purity 99.8%) was transferred from its steel tank into a three-neck flask in which it was stirred over sodium at –30 °C for 3 h and then cryodistilled. 1,1-Diphenyl ethylene (Aldrich, 97%) was stored over CaH_2 and cryodistilled. Ethylene glycol (EG) (Aldrich, 99 %) and tolylene-2,4-diisocyanate (TDI) (Aldrich, 98%), were used as received. A THF solution of the deprotonating agent, diphenylmethyl potassium (Ph_2CHK or DPMK) was prepared according to a reported procedure [16].

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

Synthesis of the stabilizers

All anionic polymerizations used for the synthesis of the stabilizers were performed under an inert atmosphere using a reactor equipped with a nitrogen inlet, magnetic stirrer, burettes meant to introduce solvents, monomers etc.

PS-b-PEO block copolymer

A series of PS-*b*-PEO block copolymers were synthesized using anionic techniques according to the well-known reported procedure [17]. The molar mass of the PS block was determined by SEC and that of the second PEO block was determined by ^1H NMR spectroscopy. SEC of the block copolymers was then performed to determine their molar mass distribution, which remained close to 1.02. The characteristics of the block copolymer are given in Table 1.

ω-Hydroxypolystyrene

The end-functionalization of the polystyrenes synthesized by anionic polymerization was performed by end-capping with ethylene

Table 1

Stabilizer $\overline{DP_n}$(PS)/ $\overline{DP_n}$(PEO)	Stabilizer (wt %)	Particle size[b], $d_{(0.5)}$, (µm)	Span[c], $\frac{d(0.9)-d(0.1)}{d(0.5)}$	Observations
none	–	–	–	coagulation
S1 120 / 245	5,10,15,20	–	–	coagulation
S2 120 / 115	5,10,15	–	–	coagulation
	20	2.75	14.1	broad distribution
S3 25 / 5	1,2	–	–	coagulation
	5	120	9.5	broad distribution
	10	51	2.0	broad distribution
	15	27	2.8	broad distribution
	20	11	1.7	broad distribution

[a] Monomer / solvent ratio = 1/6

[b] Particle size obtained by performing light scattering measurements on a Malvern Master sizer 2000 (Hydro 2000S) apparatus

[c] 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

oxide followed by terminating with methanol. ω-Hydroxypolystyrenes were characterized by SEC and by ^{1}H NMR spectroscopy. The characteristics of the polymers are given in Table 4.

Synthesis of polyurethane microspheres

Polyurethane synthesis was carried out in a 250 mL jacketed glass reactor fitted with a reflux condenser, a stainless steel half-moon type stirrer, a sampling device, and nitrogen inlet tube. Different procedures were followed according to the stabilizer used.

Typical procedure using ω-hydroxypolystyrenes as stabilizers

The reactor was charged with the stabilizer (0.288 g, 10 wt % vs monomers), 2 equiv. (x mol) of TDI with respect to the OH functions and all of the solvent (20 g). This was allowed to react in the presence of DBTDL as the catalyst (0.1 g of 1% solution in paraffin) for 2 h at 60 °C at a stirring speed of 500 rpm. EG (0.635 g, 0.010 mol) was then added in one portion and left to react for 30 min. Then, (0.012–x) mol of TDI was added over a variable time period.

Polymerization kinetics

Aliquots were removed at regular intervals to monitor the kinetics of the reaction. The kinetics was followed by solid content measurements to determine the conversion. Conversion for the polymerization reaction was calculated using the following equation:

$$\text{Conversion\%} = \frac{\text{experimentalSC\%}}{\text{theoriticalSC\%}} \times 100 \tag{a}$$

where SC% is the solid content.

The theoretical SC% is calculated using the equation:

$$\text{Theoretical SC\%} = \frac{\text{monomer(g)} + \text{stabilizer(g)}}{\text{monomer(g)} + \text{stabilizer(g)} + \text{solvent(g)}} \times 100 \tag{b}$$

The experimental solid content is the mass of solid obtained after evaporation of the solvent and monomers.

Growth of the particles with time was observed by various microscopy techniques.

Characterization

^{1}H and ^{13}C NMR spectra were recorded using Brüker AC-200 and AC-400 NMR spectrometers.

Size exclusion chromatography (SEC) of the stabilizers was performed by 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 a same manner, we performed SEC measurements for the PUR samples in dimethylformamide (DMF) as the mobile phase.

IR spectra of the PUR samples were recorded on a Perkin-Elmer 16 PC-FT-IR spectrometer.

Dynamic light scattering (DLS) measurements were performed on a Malvern Zetasizer 3000HS$_{A}$ instrument to observe the formation of micelles. The analyses were performed at 25 °C in cyclohexane at an angle of 90°.

PUR particle size and particle size distribution or 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 2100 rpm.

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

Dynamic mechanical analysis (DMA) was conducted on a Perkin-Elmer System in flowing nitrogen.

Results and discussion

Polyurethane particles synthesis using PS-*b*-PEO block copolymers as the stabilizers

For the present study, the monomers ethylene glycol (EG) and tolylene-2,4-diisocyanate (TDI) have been selected. The polyaddition was performed at 60 °C in cyclohexane to comply with the requirements of insolubility of the resultant polyurethane formed. Dibutyl tin dilaurate (DBTDL) was chosen as the polymerization catalyst. It is important to indicate that EG is not soluble in cyclohexane unlike TDI. On the basis of literature data [13], PS-*b*-PEO block copolymers were first tested as stabilizers for the synthesis of polyurethane in a dispersed medium; the polystyrene block provided the solvated moiety, and the poly(ethylene oxide) block, which is insoluble in cyclohexane, provided the anchoring moiety to the growing polyurethane.

Since the stability and the size of the latexes depend both on the nature and concentration of the stabilizer, we tested a series of PS-*b*-PEO block copolymers by varying the molar mass of each block. Their characteristics are given in Table 1.

As generally realized for polymerization using steric stabilizers in dispersed media, all the reactants were added together, at the start of the reaction. For the study, we used 0.01 mol of EG (0.635 g) and 0.012 mol of TDI (2.088 g) in 20 g of cyclohexane. The amount of added stabilizer was varied from 1 to 20 wt % with respect to the total amount of monomers. The monomer/solvent ratio (m/s) was kept around 1/6. Results of the dispersion in terms of the polyurethane particle formation in the presence of PS-*b*-PEO block copolymers as stabilizers are reported in Table 1.

Influence of the PS-b-PEO length

As may be seen in Table 1, coagulation occurs in the absence of stabilizer. In addition, while S1 is soluble in cyclohexane at 60 °C, it does not participate in the stabilization process and coagulation also occurs whatever S1 concentration. Indeed, it has been shown by Walbridge that the growth of the particles without the continued provision of stabilizer from the medium resulted in coagulation [18].

The balance between PS and PEO blocks was further reduced to a 1:1 ratio (S2) and 5:1 ratio (S3). In these cases, large amounts of stabilizer (10–20 wt %) are needed to avoid coagulation, but the particle size distribution remains very broad. These behaviors stress a bad control of the nucleation step in the presence of PS-*b*-PEO block copolymers. The poor stabilization ability of these block copolymers was speculated to come from the formation of stable micelles in cyclohexane. Indeed, it has already been noted that the dissociation rates of such micelles to free polymer may be very low in organic solvents. Therefore, the ability of S3 to form micelles in cyclohexane have been examined by light scattering measurements at 25 °C. The hydrodynamic radius R_H (nm) versus concentration (mmol L^{-1}) of the micelle formed was plotted in Fig. 1. A critical micellar concentration (CMC) value was estimated at around 3 mmol L^{-1} with an R_H value of around 3.5 nm. When S3 is used as a stabilizer at a 10 wt % concentration with respect to the monomers, its concentration in the reactor is close to 6.25 mmol L^{-1}, a value twice that of the CMC. This clearly indicates that micelles are present under our experimental conditions. The micelle formation would be enhanced with increasing the length of the block copolymers. This would also have contributed to the poor stabilization in the cases in which S1 and S2 were used as stabilizers.

Influence of the stabilizer concentration

The influence of the stabilizer concentration on the particle size was checked in the specific case of S3 used as the stabilizer. S3 concentration was varied of 1–20 wt %. The data are given in Table 1.

As expected, the higher the stabilizer concentration, the lower the particle size. A variation of stabilizer concentration of 5–20 wt % leads to a particle size decrease from around 100 µm to 10 µm. Indeed, the occurrence of the nucleation step at the earliest stage leads to a maximum number of particles at the very beginning of the polymerization. Once the nuclei are formed, they may aggregate and form bigger particles. This feature is more probable at lower stabilizer concentration than at a higher one because of a more pronounced steric barrier effect in the latter situation. Moreover, a 1 wt % stabilizer concentration is not effective and coagulation of the polymer chains occurs. This is sustained by the work reported by El Aasser et al. and is in agreement with the mechanism of dispersion polymerization they have proposed [19].

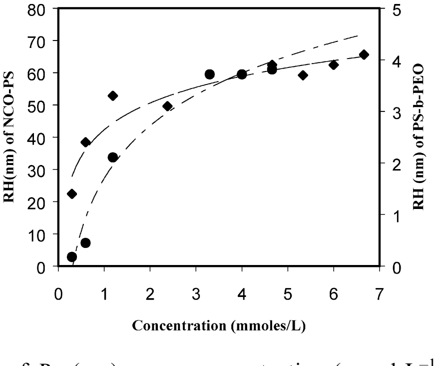


Fig. 1 Plot of R_H (nm) versus concentration (mmol L^{-1}) for PS-*b*-PEO block copolymer ($\overline{DP_n}$(PS block) = 25; $\overline{DP_n}$(PEO block) = 5) (◆), and for *ω*-NCO polystyrene ($\overline{DP_n}$ = 20) (●) in cyclohexane at 25 °C

Experiments performed in the presence of PS-*b*-PEO block copolymers as stabilizers reveal that such block copolymers are not well suited for the purpose. While PEO and PUR have rather close solubility parameters (δ_{PEO} = 9–11 $MPa^{1/2}$ and δ_{PUR} = 10 $MPa^{1/2}$), it is observed that the PEO moiety has a relatively poor affinity towards the polyurethane particles and therefore cannot play its anchor role. This observation prompted us to check the efficiency of functionalized homopolymers such as *ω*-hydroxypolystyrene as the steric stabilizer for polyurethane synthesis. Indeed, it is known from the literature that functionalized homopolymers mainly based on poly(ethylene oxide) can behave as efficient stabilizers as they form, in situ, amphipathic block or graft copolymers [20, 21, 22]. Similarly, we anticipated that *ω*-hydroxypolystyrenes could participate through the hydroxy-end groups to the urethanization reaction with the isocyanate functions.

Polyurethane particles synthesis using *ω*-hydroxypolystyrene as the reactive stabilizer:

A series of well-defined hydroxy-terminated polystyrenes (PS-OH) of different molar masses were prepared by conventional anionic polymerization followed by end-capping the polystyryl lithium chains using ethylene oxide. The characteristics of these polymers are given in Table 2.

Manner of addition of the reactants

We first studied the effect of the reactants addition manner towards the particle formation and their

Table 2

Stabilizer	$\overline{DP_n}$[a]	$Ip = \overline{M_w}/\overline{M_n}$[a]	Functionality[b] (%)
S4	10	1.05	98
S5	20	1.04	96
S6	25	1.05	97
S7	40	1.06	99

[a] Determined by SEC

[b] Determined by ^1H NMR spectroscopy, calculating the ratio of the area of the signal corresponding to the protons of the methylene group adjacent to the hydroxyl chain ends (I_1, δCH_2-OH = 3.5 ppm) to that of the peak arising from the protons of methyl group of the initiator (I_2, δCH_3 = 0.9 ppm); functionality (%) = $\frac{I_1}{2/3 I_2} \times 100$

characteristics. PS-OH (S5, 10 wt %) was added together with TDI and EG at the start of the polymerization. As could be expected, coagulation occurs demonstrating that when this functional homopolymer is added as such, it cannot play the role of a stabilizer. This phenomenon clearly underlines the lesser reactivity of hydroxy functions from the polystyrene chain ends compared to the ones of EG monomer.

Therefore, to enhance the efficiency of PS-OH as a reactive stabilizer, the reaction between PS-OH and isocyanate functions was carried out in a first stage. PS-OH (1 equiv.) was pre-reacted with TDI (2 equiv.) in the presence of DBTDL at 60 °C in cyclohexane. The reaction was monitored by FTIR spectroscopy, which revealed that complete derivatization of the OH groups occurs within two hours. The resultant polymer was isolated by precipitation in MeOH and then characterized by ^{1}H NMR spectroscopy and SEC. The ^{1}H NMR spectrum of the reaction product is shown in Fig. 2. The assignment of the peak at 4.4 ppm corresponding to the proton of the N-H group as well as the absence of a signal at 3.5 ppm (that would correspond to the protons of $-CH_2$-OH group from PS-OH) provide evidence for the complete derivatization of the hydroxy function. SEC traces of the isolated polymer shown in Fig. 3a, reveals a bimodal feature. The shoulder corresponding to nearly 20 % in weight of the whole sample was logically attributed to coupling product **B** along with the formation of the expected main product **A**, as presented in Scheme 1.

We succeeded in eliminating the formation of **B** by changing the manner of mixing the two reactants, that is, PS-OH (1 equiv.) was added dropwise over a TDI (2 equiv.) solution in cyclohexane in the presence of

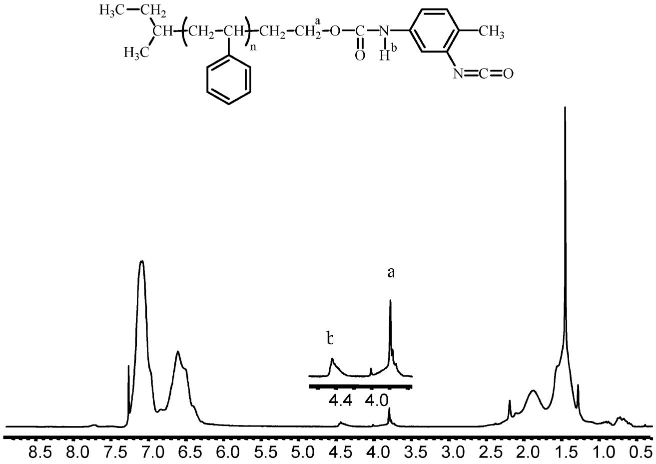
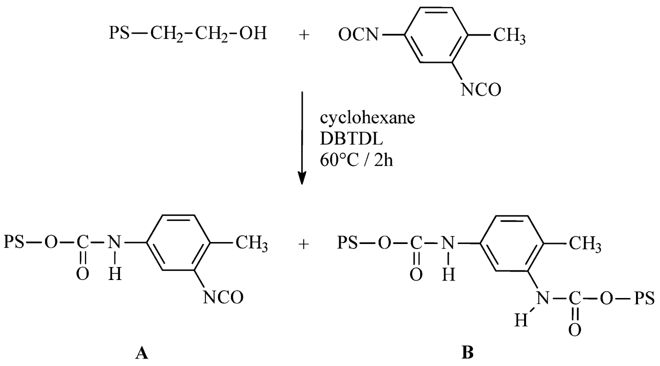


Fig. 2 ^{1}H NMR spectrum (200 MHz) of ω-NCO polystyrene (S5, $\overline{DP_n}$ = 20) in CDC^{13}



Scheme 1

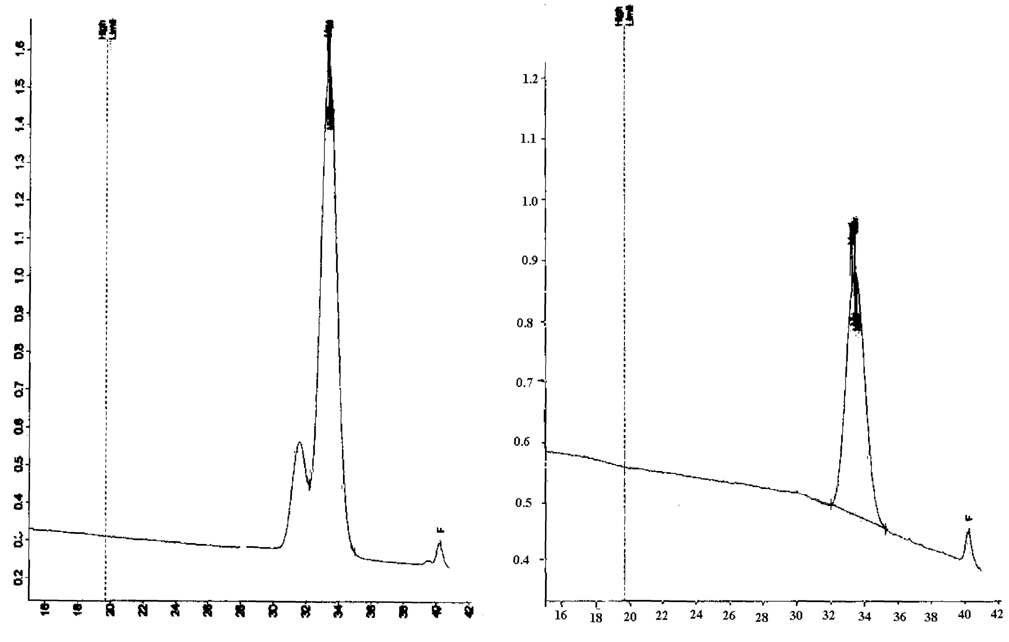


Fig. 3a,b SEC of ω-NCO polystyrene (S5, $\overline{DP_n}$ = 20) as a function of the experimental procedure: **a** PS-OH and TDI added in one portion (left), **b** dropwise addition of PS-OH onto TDI (right)

DBTDL. The total formation of the mono-adduct **A** has notably been confirmed by SEC (see Fig. 3b). These preliminary investigations finally allowed us to prepare ω-NCO polystyrene (**A**) with an efficiency close to 1. The latter has to be considered as the true reactive stabilizer of the dispersion.

The procedure depicted above was thus applied in the following to prepare **A** in situ, that is, in the experimental dispersion conditions before addition of the monomers. Therefore, after the formation of **A** is complete within two hours, EG (insoluble in cyclohexane) was first added in one portion (0.010 mol) and the turbid mixture was allowed to react for 30 min. TDI (0.012 mol) was then added dropwise over a variable time period. The manner and time of TDI addition was found to be very crucial to avoid coagulation and also to control the particle size and the particle size distribution, as shown in Fig. 4.

It is worth noting that addition of TDI in one portion yields two populations of particles while a dropwise addition leads to a single population. In addition, the longer the time of TDI addition, the lower the particle size. The formation of two populations may be the consequence of two nucleation processes, that is, homogeneous and micellar nucleations. The formation of micelles by ω-NCO polystyrene (**A**) was demonstrated by dynamic light scattering (DLS) measurements; a critical micellar concentration (CMC) value was estimated at around 3.5 mmol L^{-1} and large micelles with an R_{H} value close to 55 nm could be measured as shown in Fig. 1. It is important to underline that the stabilizer concentrations used (5–8 mmol L^{-1}) are systematically higher than the CMC value, clearly indicating that the micelles are formed and must play a role in our experimental dispersion conditions.

Surprisingly, it was also observed that when ω-NCO polystyrene (**A**) –synthesized in a separate experiment then isolated – was added as such into the reactor before EG and TDI, a bimodal particle size distribution was systematically obtained. However, the intensity of the peak corresponding to bigger particles could be lowered and even suppressed by either increasing the time of TDI addition or by pre-mixing **A** with one equivalent of TDI.

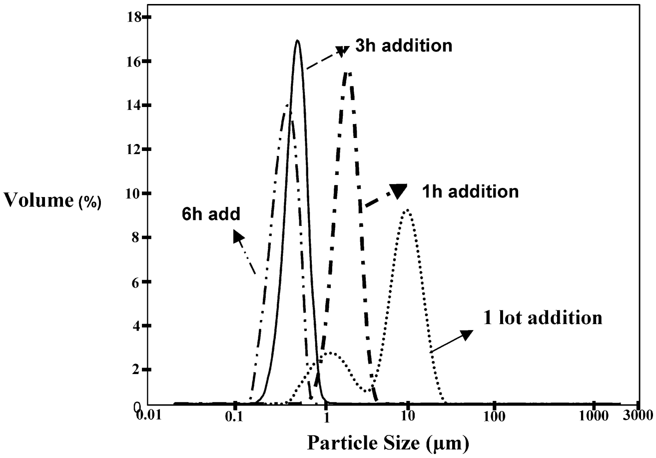


Fig. 4 Effect of TDI addition time on the average size of the PUR particles in the presence of 10 wt % S5 ($\overline{DP_n}$ = 20)

Typical optical micrograph of polyurethane particles obtained in the presence of S5 stabilizer and for a 1 h addition of TDI is shown in Fig. 5. It reveals the narrow size distribution of the particles.

Many other parameters can influence the main characteristics of the particles. Among them, we mainly investigated the effect attributable to the reactive stabilizer itself, that is, its molar mass and concentration. Indeed, such features have already been described in the literature to drastically govern the formation and stability of the growing particles [19, 21, 23].

Effect of the stabilizer molar mass

For this study, we varied the molar mass of the stabilizer between 1000 and 4000 g mol^{-1}. The results are given in Table 3.

As may be observed in Table 3, the dispersion results are very sensitive to the stabilizer size. While keeping the stabilizer concentration constant (10 wt %), a small change of the stabilizer molar mass can cause a dramatic effect such as the flocculation of the polymer. Only polystyrene with a molar mass in the range 2000–3000 g mol^{-1} (S5; S6) give monodisperse latexes, while lower and higher molar mass PS are less efficient using this experimental procedure. We may assume that S4 cannot properly adsorb onto the resultant particles leading to coagulation, except in the case when the addition of TDI is performed over 6 h. In the case of S7, it leads to about 20 % coagulation and the resultant latexes show a broad span of particle size. The low efficiency of S7 could be explained on the basis of the restricted mobility of the rigid aromatic polystyrene chains thereby affecting the stabilization process. This phenomenon has already been described in the literature

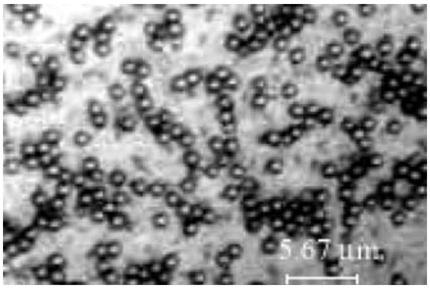


Fig. 5 Optical microscopy picture of PUR particles synthesized using S5 as the stabilizer (particle size: 1.70 μm)

Table 3

Stabilizer 10 wt %	Time of addition[a] of TDI (h)	Particle size[b] $d_{(0.5)}$, (µm)	Span[b] $\frac{d(0.9)-d(0.1)}{d(0.5)}$	Observations
S4	1	–	–	coagulation
	3	7.30	9.82	multimode
	6	6.70	2.86	multimode
S5	1	1.70	0.70	monodisperse
S6	1	1.70	0.77	monodisperse
S7	1	0.70	2.61	20% coagulation

[a] TDI is added dropwise
[b] Refer to footnote of Table 1

by El Aasser and co-workers [19]. These authors observed that polymeric surfactants were unable to stabilize the growing particles if their molar mass was too low, while too high a molar mass polymer resulted in diminishing the reactivity of the homopolymers thereby hindering the formation of in situ block copolymers that would have helped in the particle stabilization.

Effect of the stabilizer concentration

As predicted, the higher the stabilizer concentration, the lower the PUR particle size (Table 4). This is in agreement with the theories of particle formation proposed, for example, by Barett in the case of free radical polymerization [3]. Moreover, it is worth noting that the span values of the polyurethane latexes remain narrow indicating the high efficiency of S5 to give monodisperse particles.

Kinetic study and characterization of the particles

Kinetics and particle growth

The polymerization kinetic was followed by sampling out at regular intervals of 30 min for 6 h and determining the solid content using the equation given in the Experimental. Whatever the stabilizer used – the block copolymers or the reactive homopolymers – the conversion goes to completion after 6 h.

The particle growth with time was followed by optical microscopy in the case of S5. It was found that a steady growth in particle size took place until a conversion of about 80 %, after which there was only a slight increase as shown in Fig. 6.

Table 4

S5[a] wt %	$d_{(0.5)}$[b] (µm)	Span[b]	$\bar{M}_n$[c,d]	$Ip=\overline{M_w}/\overline{M_n}$[b]
2	–	–	–	–
5	2.20	2.61	8400	1.59
10	1.70	0.70	11,500	1.50
15	0.50	0.64	11,600	1.81
20	0.40	0.96	nd	nd

[a] TDI added at 1 h
[b] Refer to footnote of Table 2
[c] Determined by SEC using *N,N*-dimethylformamide (DMF) as eluent
[d] $\overline{DP}_n^{theo} = \frac{1+r+2q}{1+r+2q-2rp} \cong 10$ with $q = \frac{[\text{PS-OH}]}{[\text{EG}]}$ and $r = \frac{[\text{EG}]+[\text{PS-OH}]}{[\text{TDI}]}$

Structural characterization and molar mass determination

The PUR samples were totally soluble in DMF, and this solvent was chosen as eluent for SEC characterization (see Table 4). As shown in Table 4, the experimental molar masses – based on polystyrene calibration – slightly increases with the wt % of stabilizer used, while in the mean time, the particle size decreases. The observed trend may be explained if we consider that the contribution of the reactive stabilizer with respect to the global molar mass of the PUR sample is quite high. Indeed, the calculated theoretical average number of urethane units could be estimated to be close to ten, taking into account the non-stoichiometry between OH and NCO functions as well as the presence of PS-OH as a chain stopper (valence = 1). These PUR experimental molar masses also indicate that PS-OH is an effective reactive stabilizer.

The experimental results highlight that ω-hydroxypolystyrene took part in the stabilization process through formation of an in situ block copolymer. We tried to explore the evidence of the true covalent linkage between the stabilizer and the PUR moiety by performing ^{1}H NMR and thermomechanical analysis. Samples in the form of powders were recovered after several washing with cyclohexane and filtration, and then characterized by using both ^{1}H NMR and DMA techniques. The ^{1}H NMR spectrum (in DMSO at 50 °C)

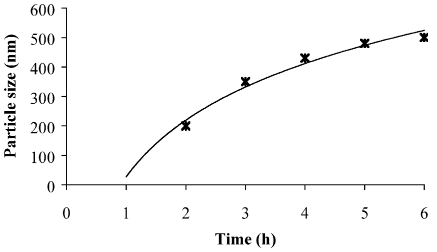


Fig. 6 Plot of PUR particle size (µm) versus time (h); (stabilizer = S5 ($\overline{DP_n}$= 20), 10 wt %; time of TDI addition = 6 h)

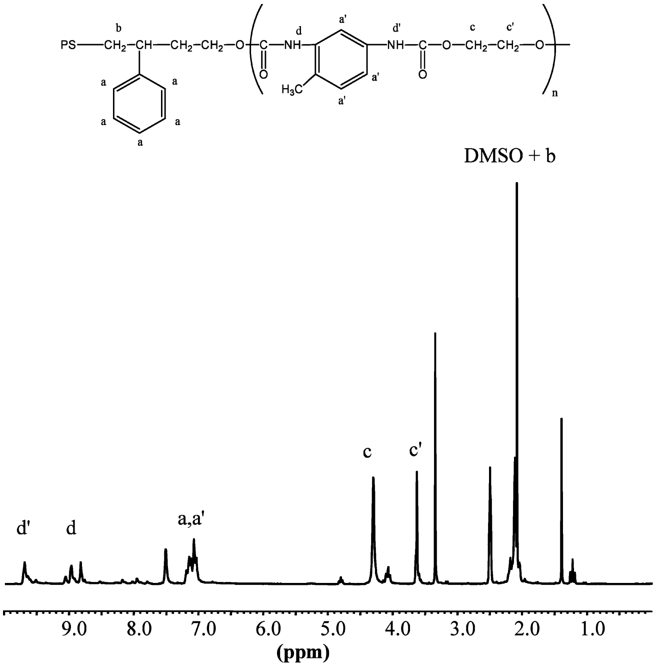


Fig. 7 ^{1}H NMR (400 MHz, DMSO) spectrum of PUR synthesized using PS-OH (S5; $\overline{DP_n}$ = 20/10 wt %) as the stabilizer

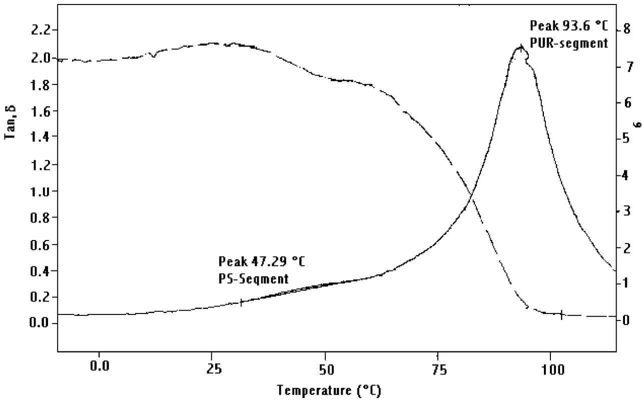


Fig. 8 DMA curve of PUR synthesized using PS-OH (S5; $\overline{DP_n}$ = 20) as the stabilizer

of one PUR sample, prepared in the presence of 10 wt % of PS-OH (S5) is shown in Fig. 7.

The assignment of signals located at around 7 ppm to the aromatic protons of styrene and TDI units, and at 8.8–9.7 ppm to the proton of the NH groups, allowed us to estimate that the amount of grafted stabilizer onto the particle was close to 100%. This characterization is in agreement with the participation of the stabilizer as a reactive molecule in the process. To further confirm the core-shell type of these materials, DMA analysis were implemented.

PUR thermomechanical analysis

As expected, DMA traces show the presence of two transitions as shown in Fig. 8. The two glass transition temperatures that could be attributed to polystyrene and polyurethane parts were found at 47 °C and 94 °C respectively. These results also confirm that hydroxy-polystyrene has taken part in the PUR synthesis.

Conclusion

The preparation of polyurethane particles could be achieved in a dispersed medium. We have demonstrated, for the first time, that polyurethane synthesis in organic dispersed media could be readily carried out using functional homopolymers such as ω-hydroxy-polystyrene. The ability of the hydroxy-terminated PS to play the role of steric reactive stabilizer depends not only on its concentration and size, but also on the method of monomer addition. The stabilization of the particles was obtained by in situ formation of block copolymers PS-*b*-PUR insoluble in the reaction medium. The exact mechanism of particle formation could not be completely elucidated, since we could not discriminate between homogeneous and micellar nucleations to explain the experimental results. Further experiments as well as characterizations of the particles (number of grafted stabilizer per particle, etc.) are currently under investigation to elucidate the pending questions. Data will be published in forthcoming papers.

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