Synthesis of Core-Shell Polyurethane-Polydimethylsiloxane Particles by Polyaddition in Organic Dispersant Media: Mechanism of Particle Formation

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Summary: Core-shell polyurethane (PUR)-polydimethylsiloxane (PDMS) particles were prepared by polyaddition between ethylene glycol and tolylene-2,4-diisocyanate in cyclohexane, used as the organic dispersant phase, in the presence of reactive hydroxy-terminated polydimethylsiloxane steric stabilizers. The reaction extent and the PUR particle size, monitored by FTIR, ^{1}H NMR, SEC, SEM and TEM techniques against time, were found a function of the PDMS concentration, functionality and molar mass. A mechanism of the polyurethane particle growth is proposed on the grounds of the kinetic investigation.

Keywords: core-shell particles; dispersion polymerization; polyaddition; polydimethylsiloxane, polyurethane

Introduction

The synthesis of polymers through an heterogeneous process is obviously of great interest as far as applications at an industrial scale are concerned. Due to the large number of materials that can be produced by radical polymerization, the latter method of polymerization was widely studied in heterogeneous conditions and the mechanisms of particle formation are relatively well-established. The more recent investigations in this field deal with the controlled radical polymerization of vinylic monomers through emulsion and miniemulsion processes for the production of well-defined polymers[1],[2].

While materials obtained by means of step-growth polymerization are of great importance due to their peculiar properties and functions, their synthesis in heterogeneous conditions is much less regarded, compared to free radical-synthesized polymers.[3] This fact pushed us to investigate the field of polyaddition and polycondensation reactions monitored in a dispersant medium with the objective to prepare well-defined core-shell materials that exhibit specific properties for large domains of applications.

As it is well-known, reactions in heterogeneous conditions usually require the use of a “so-called” surfactant -ionic and/or steric ; reactive or not- the role of which being to prevent the coagulation of the polymer thus to obtain a stable dispersion usually called "latex".

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Recently, Landfester et al. have reviewed that polyaddition and polycondensation reactions can be implemented in miniemulsion conditions[4].

The preparation of calibrated polyurethane particles in the size range 5-50 μm, by suspension technique in a non-aqueous medium, has been also reported by Nippon Paint[5]. 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(dodecyl methacrylate)s as reactive steric macromonomers for the preparation of polyurethane particles in a dispersant organic medium has also been reported by Sivaram *et al.*[6] Cramail et al. also explored the route to polyurethane particles with a core-shell structure by dispersion in organic medium[7],[8],[9]. A series of reactive steric stabilizers of the type ω-$(OH)_x$-poly(*n*-butyl acrylate) (P*n*BuA), -polystyrene (PS), or -polybutadiene (PBut) (x=1 or 2) and polydimethylsiloxane (PDMS) have been tested, leading to various core-shell polyurethane-based materials and exhibiting a large scope of properties with respect to the nature of the shell. We also recently demonstrated, for the first time, the possibility to synthesize core-shell polyurethane-polydimethylsiloxane materials in supercritical CO_2, used as the dispersant medium[10].

In this paper, we focus on the mechanism of polyurethane-polydimethylsiloxane core-shell particle formation, in cyclohexane used as the dispersant medium, in the presence of either hydroxy or isocyanate end-functionalized polydimethylsiloxane respectively noted PDMS-OH and PDMS-NCO. The aim of this study is to unveil the role of the reactive stabilizer depending on its functionality and to propose a mechanism for the particle formation.

Experimental

Materials

Tolylene-2,4-diisocyanate (Sigma-Aldrich) was purified by distillation under vacuum. Ethylene Glycol (Sigma-Aldrich, 99 %), monohydroxy-terminated PDMS 4670 g.mole^{-1} (Sigma-Aldrich, > 99 %), monohydroxy-terminated PDMS 1000 g.mole^{-1} (generously given by The Polymer Technology Group, > 99 %) and dibutyltin dilaurate (Sigma-Aldrich, 98 %) were used as received. Cyclohexane (Baker, 99 %) was distillated over CaH_2.

Typical synthesis of isocyanate-terminated polydimethylsiloxane (PDMS-NCO)

A three-neck round bottom flask equipped with a condenser and a nitrogen inlet was loaded with 19 mg of TDI (1.04×10^{-4} mole) and 5 mL of cyclohexane, heated at 60°C and stirred at 500 rpm. Then 0.2536 g of mono-hydroxy-terminated polydimethylsiloxane (4670 g/mole,

5.43×10^{-5} mole) dissolved in 15 mL of cyclohexane were added drop-wise through an addition funnel and let to react under stirring over a period of 4 hours. After evaporation of the cyclohexane, the excess of TDI was removed by precipitation in pentane (three times). The PDMS-NCO in pentane solution was dried under vacuum and characterized by SEC, MALDI-TOF and NMR. Less than 5 % of coupled product (*i.e.* PDMS-TDI-PDMS) could be detected by SEC. Similar procedure was followed with PDMS-OH precursor with Mn = 1000g/mol.

Typical polymerization procedure in cyclohexane [7-9]

The reactor was loaded with x wt % (x = 4.7, 9.1, 13, 16.7) vs. the monomers of the reactive stabilizer (either PDMS-OH or PDMS-NCO), dibutyl tin dilaurate (DBTDL) as the catalyst (0.1 g of 1 wt% solution in paraffin) and all the solvent (cyclohexane, 20 g). The temperature and the stirring speed were respectively set-up at 60°C and 500 rpm. EG (0.6207 g, 0.01 mole) non soluble in cyclohexane was then added in one lot and the mixture let under stirring for 30 minutes. Then, TDI (1.9158 g, 0.011 mole) was added drop-wise over 4 hours (0.4 mL/hour).

After 7 hours, the latex was removed by the sampling outlet and then washed three times by centrifugation/re-dispersion in cyclohexane.

After drying under vacuum, the samples were characterized by ^{1}H NMR, SEC and TEM or SEM.

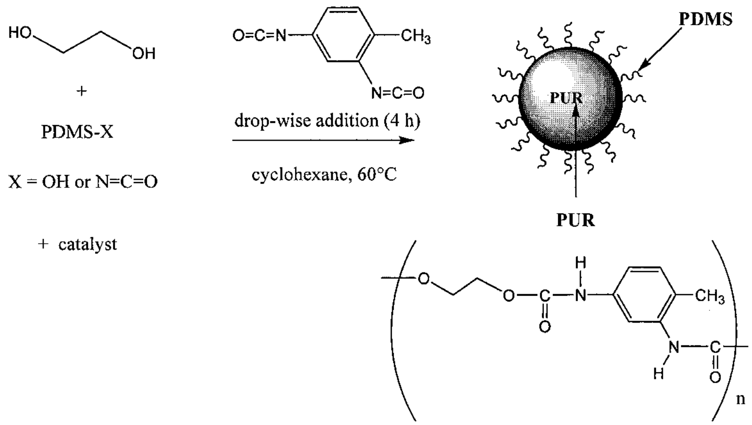
Characterization

The molar masses of the polymers were determined by size exclusion chromatography (SEC) in dimethyl formamide (DMF) at room temperature (flow rate 0.7 mL/min) on a Varian apparatus equipped with a refractive index detector and 3 TOSOHAAS TSK gel columns in series calibrated by means of narrow polystyrene standards. ^{1}H NMR spectra were recorded using a Bruker Avance 400 NMR spectrometer (400MHz). Infrared (FTIR) spectroscopy experiments of polyurethane samples were performed on a Bruker Tensor 27 apparatus using ATR technique. Scanning electronic microscopy (SEM) analysis were carried out on a JEOL JSM 2500 apparatus and transmission electronic microscopy (TEM) was performed on a JOEL JEM-100S electronic microscope.

Results and discussion

Step-growth polymerizations between ethylene glycol (EG) and tolylene-2,4-diisocyanate (TDI) were implemented in cyclohexane (at 60°C and 500 rpm) in the presence of either

PDMS-OH or PDMS-NCO-, used as a steric reactive stabilizer. A typical experimental procedure consists in the drop-wise addition of the di-isocyanate, TDI, over a cyclohexane solution containing the reactive polydimethylsiloxane stabilizer and all the diol, EG, present as dispersed droplets[7-9]. The general synthetic pathway is given in Scheme 1.



Scheme 1. Synthesis of polyurethane particles by polyaddition between ethylene glycol and tolylene diisocyanate in cyclohexane as the dispersant medium and using (NCO or OH) end-functionalized polydimethylsiloxane reactive stabilizers.

In most cases, latexes constituted of well-calibrated particles have been obtained, as illustrated by the Scanning Electron Micrograph shown in Figure 1.

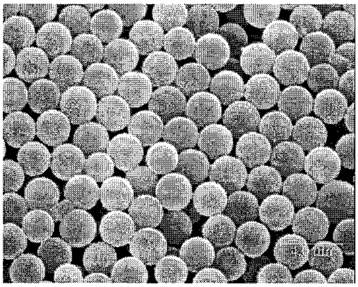


Figure 1. Scanning Electron Microscopy (SEM) picture of polyurethane-polydimethylsiloxane particles obtained in cyclohexane at 60 °C (500 rpm) using TDI and EG as monomers and PDMS-OH (9 wt%) as reactive stabilizer (entry c11, Table 1).

The influence of the polydimethylsiloxane molar mass, weight percentage and type of functionality (OH or NCO) on the resulting polyurethane (PUR) latex has been investigated. Data are collected in Table 1.

Table 1. Data of dispersion step-growth polymerization between tolylene-2,4-diisocyanate and ethylene glycol carried out in cyclohexane (20 g) in the presence of functional PDMS surfmer, at 60°C and for 7 hours (cat. DBTDL, 500 rpm, [NCO]/[OH] = 1.1).

Run	**Reactive stabilizer**	**M_n of PDMS-OH (g/mole)**	**Wt % of PDMS introduced**	**Wt % of PDMS incorporated^a**	**Yield (%)^b**	**Particle average size (μm)^c**	**$\overline{M_W}$ (g/mole)^d**	**PDI**
c1	**No**	**-**	**-**	**-**	***90***	**No particle**		
c2	**PDMS-NCO**	**4670**	**4.8**	**-**	***86***	**0.45 ± 0.10**	**2800**	**1.9**
c3	**"**	**4670**	**9**	**3.5**	***89***	**0.5 ± 0.10**	**4100**	**1.4**
c4	**"**	**4670**	**13**	**5.3**	***85***	**0.37 ± 0.05**	**4200**	**2.7**
c5	**"**	**4670**	**16.7**	**8.7**	***80***	**0.4 ± 0.05**	**3400**	**2.1**
c6^e	PDMS-NCO	4670	9	7.1	80	No particle	1080	1.3
c7	**"**	**1000**	**4.8**	**4.2**	***88***	**0.9 ± 0.10**	**5600**	**2.4**
c8	**"**	**1000**	**9**	**2.8**	***91***	**1.1 ± 0.10**	**3200**	**2.8**
c9	**"**	**1000**	**16.7**	**2.2**	***82***	**1.0 ± 0.20**	**2070**	**1.6**
c10	**PDMS-OH**	**4670**	**4.8**	**5**	***65***	**4.2 ± 1.00**	**1700**	**1.7**
c11	**"**	**4670**	**9**	**6**	***68***	**2.5 ± 0.10**	**2400**	**2.0**
c12	**"**	**4670**	**16.7**	**6.5**	***73***	**2.2 ± 0.20**	**1750**	**1.7**
c13	**"**	**1000**	**9**	**8.5**	***67***	**3.5 ± 1.00**	**1800**	**1.7**

(a) Determined by ^{1}H NMR relative integration from the final particles (*i.e.* after 3 centrifugation/re-dispersion cycles in cyclohexane)

(b) PUR particles recovered after 3 centrifugation/re-dispersion cycles in cyclohexane (yield = weight of washed product *vs.* weight of monomers + surfmer)

(c) Determined by SEM and TEM analysis; average values estimated over 100 particles

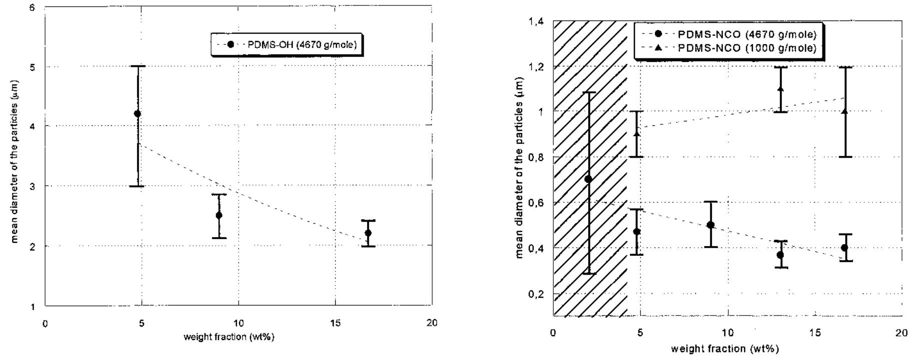
(d) $\overline{M_W}$ values of the chains constituting the PUR-PDMS particles (*i.e.* after 3 centrifugation/re-dispersion cycles in cyclohexane); SEC in DMF (0.7 mL/min; calibration PS)

(e) "Reversed process" : PDMS-NCO + TDI (1 lot), then addition of EG dropwise (5 hours addition)

It is worth mentioning that dispersion conducted in absence of reactive stabilizer (entry c1) leads to the formation of coagulum. Similar results are obtained while changing the experimental procedure (drop-wise addition of EG over a TDI solution, entry c6). These two experiments underline the major role of the reactive PDMS as well as the dramatic effect of the experimental procedure onto the particle formation. A mechanism of the particle formation, taking into account these data, is proposed later in the paper.

Influence of the wt% concentration of PDMS-OH and PDMS-NCO on the particle size.

Whatever the functionality (*i.e.* hydroxyl or isocyanate) of PDMS 4670 g/mole, it is observed that the average size of the particles as well as their size distribution slightly decrease with an increase of PDMS weight fraction (entries c2-c4 and c10-c12). Such a trend, illustrated in Figures 2(a,b) argues for the statement that a higher steric stabilizer concentration yields a higher surface coverage of the polymer nuclei, formed at the very beginning of the reaction. In addition, it is worth noting that the final PUR particle size is larger while using PDMS-OH instead of PDMS-NCO. This phenomenon can be attributed to a lower affinity of PDMS-OH, compared to PDMS-NCO, with the growing polyurethane chains at the early stage of the reaction.



(a) **(b)**

Figure 2. Influence of the weight percentage of reactive stabilizer on the polyurethane particle size, (a) : PDMS-OH, (b) : PDMS-NCO.

In the case of PDMS 1000 g/mole, there is no clear effect of the reactive stabilizer concentration on the PUR particle size ; the latter remains nearly constant around 1 µm. As expected, bigger particles are obtained when using a reactive stabilizer of smaller molar mass.

SEC and MALDI-TOF Analysis

The $\overline{M}_w$ values of the polymer chains, constituting the particles, were determined by SEC in DMF, on the basis of a polystyrene calibration. Data are collected in Table 1. A typical SEC trace is also given in Figure 3. $\overline{M}_w$ values as well as polydispersity index (PDI) are in agreement with a polyaddition mechanism. The theoretical $\overline{DP}_n$ =(1+r+2q)/(1+r+2q-2rp) was calculated close to 19 (p=1), taking into account the OH/NCO ratio (r=0.91) and the presence of monofunctional surfmer (q=($OH_{monofunctional}$/OH)=0.0054). A further characterization of the polyurethane chains was undertaken by MALDI-TOF technique using dithranol as a matrix. As shown in Figure 4, only oligourethanes could be detected in the tested experimental procedure. It was checked that the difference between each peak corresponds to the repeating unit (EG + TDI). The reasons why the block copolymers PUR-PDMS are not detected in such experimental conditions is not fully understood yet and is currently under investigation.

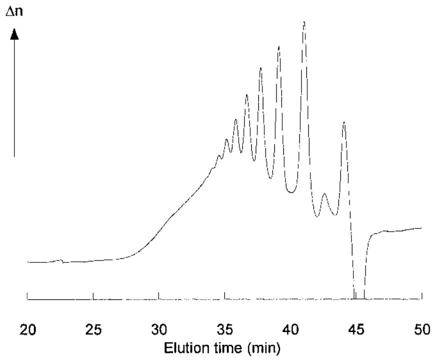


Figure 3. SEC trace of PUR samples obtained in cyclohexane at 60 °C from the system : EG/TDI/PDMS (10 wt %) over 7 h.

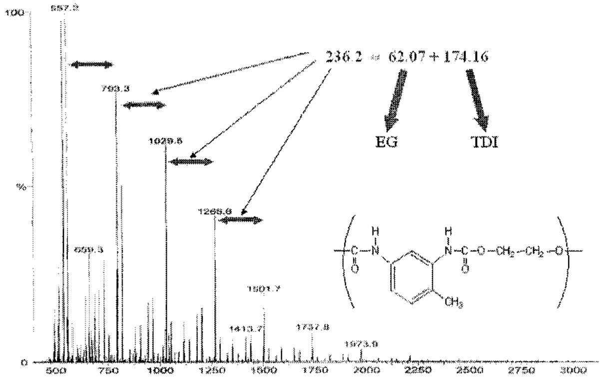


Figure 4. MALDI-TOF (dithranol, Na^+) spectrum of a PUR-PDMS sample (Table 1, c3).

Polymerization Kinetics

The growth of the polymer chains with time was followed by sampling out aliquots for SEC. As indicated in Figure 5, a plateau is reached after 7-8 hours reaction time corresponding to the complete consumption of alcohol functions.

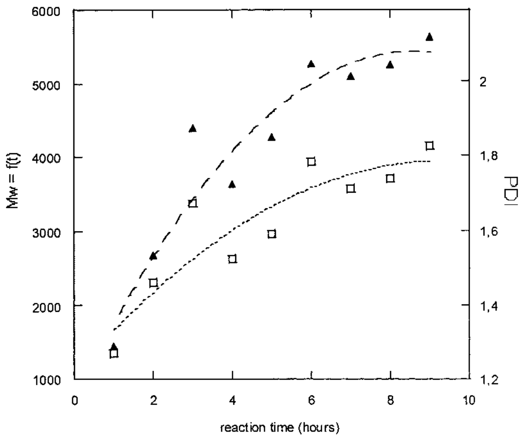


Figure 5. $\overline{M}w$ (□) and PDI (▲) evolution *vs.* time of PUR-PDMS samples obtained from the system TDI/EG/PDMS-OH (9 wt%) in cyclohexane at 60°C (results obtained before centrifugation).

The polymerization kinetic was also followed by means of FTIR analysis using an ATR technique (see for example FTIR spectra recorded in the case of PDMS-NCO on Figure 6). The increase with time of the signal characteristic of the -N-H vibration mode located at 3300 cm^{-1} which corresponds to the formation of urethane linkages, allowed us to determine the reaction extent, p, against time (p is considered equal to 1 when there is no more evolution of the -N-H signal intensity). The kinetic curves given in Figure 7 for polyadditions carried out in the presence of PDMS-OH or PDMS-NCO are comparable and argue for a complete formation of urethane units after 7-8 hours. It is worth noting that the curves exhibit a plateau between 3 and 5 hours, plateau that corresponds to the end of the drop-wise addition of TDI. As illustrated in Figure 7, it can be noticed that the initial rate of polymerization is affected by the functionality of the PDMS reactive stabilizer. The polymeriztions carried out in the presence of PDMS-OH starts faster than the ones with PDMS-NCO. This phenomenon can be ascribed to a better solubility of PDMS-OH in cyclohexane vs. PDMS-NCO. [11]

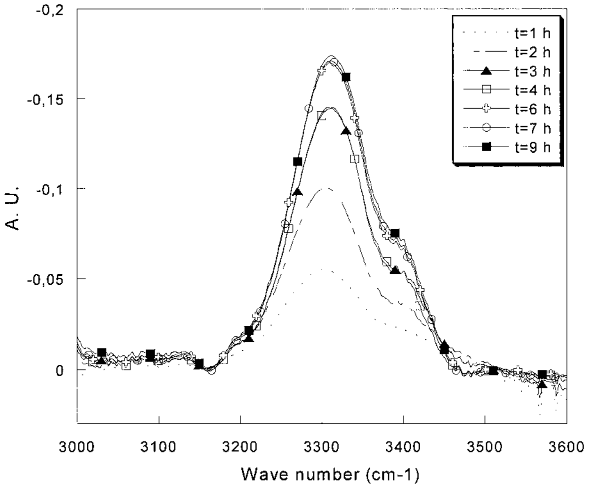


Figure 6. FTIR spectra recorded using ATR technique during the step-growth polymerization in cyclohexane between EG and TDI in the presence of PDMS-NCO as the surfmer at 60°C.

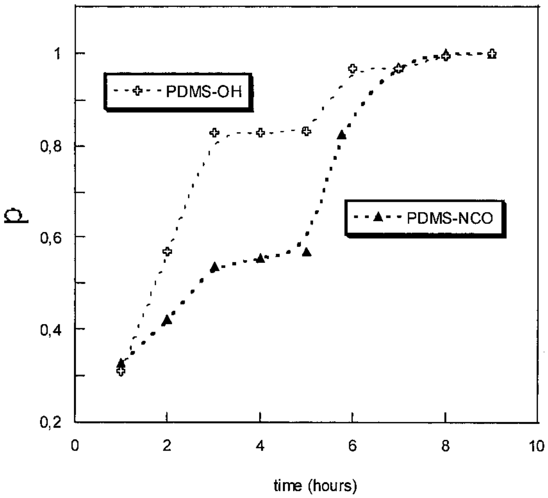
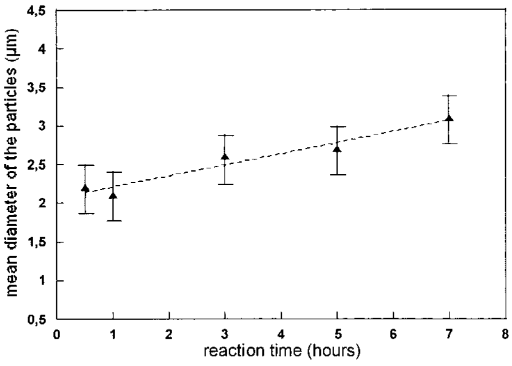


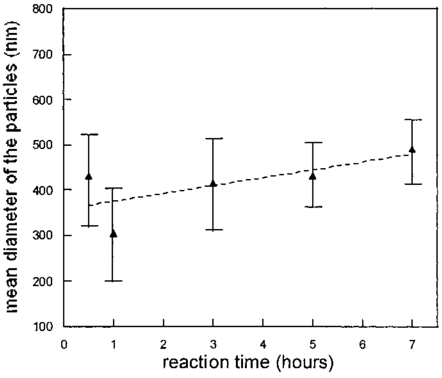
Figure 7. Reaction extent, p, versus polymerization time for step-growth polymerizations between EG and TDI in the presence of PDMS-OH or PDMS-NCO (9.1 wt %) in cyclohexane at 60°C.

Kinetic of Particle Growth

The growth of the polyurethane particles was quantified all along the reaction time by means of SEM analysis while using polydimethylsiloxane of 4670 g/mole as the reactive stabilizer (see Figure 8).



PDMS-OH



PDMS-NCO

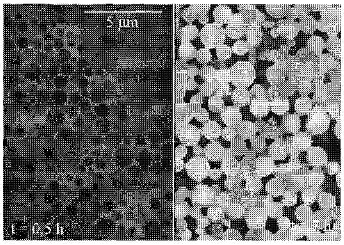
Figure 8. Polyurethane particle growth with reaction time : comparison between PDMS-OH and PDMS-NCO.

As can be seen in Figure 8, the increase in the particle size with time is more pronounced with PDMS-OH compared to PDMS-NCO. Indeed, the PUR particles grow continuously from 2 µm to 3 µm with PDMS-OH while the average size diameter increases from 300 nm to ~500 nm with PDMS-NCO. As already discussed, the discrepancy in particle size when comparing the two reactive stabilizers can be attributed to a better solubility in cyclohexane of

PDMS-OH compared to PDMS-NCO, at the early stage of the reaction. The fact that very little variation of polyurethane particles is observed after the first 30 minutes supports the idea that all events occurring during the initial stage of the polymerization are crucial. A mechanism is proposed which tries to explain the obtained data (Scheme 2).

Proposed Mechanism

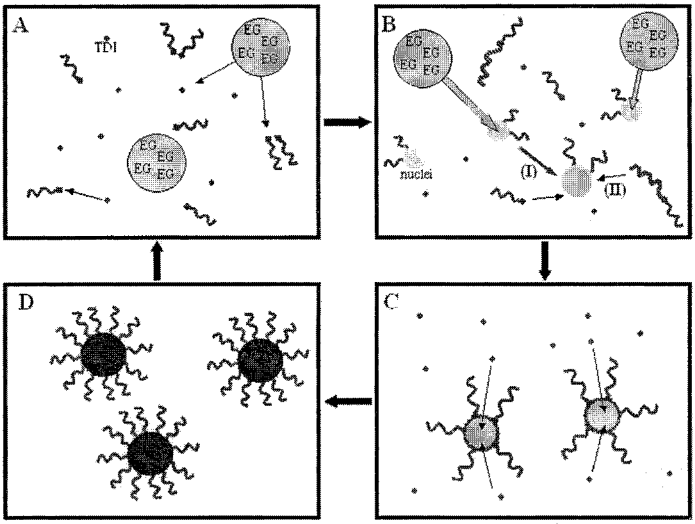
At the very beginning of the reaction, fine droplets of EG are present together with some soluble TDI and PDMS-(NCO or OH) (stage A). The reaction starts leading to the formation of the first nuclei composed of oligourethanes and block copolymers PDMS-PUR (stage B). During this initial period and before TDI addition, the formation of translucent spherical particles, detected by SEM analysis, was observed (see Figure 9a). This phenomenon was attributed to the swelling of the former nuclei by EG molecules which diffuse from the monomer droplets towards these particles (stage C). The polyaddition then occurs through the drop-wise addition of TDI which penetrates the particles to react with alcohol functions. The size of the particles was not found to vary too much after stage C, as already observed by SEM (stage D, Figure 9b).



(a) Stage C

(b) Stage D

Figure 9. Transmission electronic micrographs of PUR-PDMS particles after 30 minutes (a) and 7 hours (b) reaction time (Table 1, entry c3).



Scheme 2. Proposed mechanism for the polyaddition between ethylene glycol and tolylene diisocyanate in cyclohexane as the dispersant medium and using PDMS-(NCO or OH) as steric reactive stabilizers.

Conclusions

Core-shell polyurethane-polydimethylsiloxane particles of calibrated size have been synthesized in an organic dispersant medium. A mechanism of particle formation is proposed. The latter materials exhibit specific surface properties that are currently investigated.

[1] M. F. Cunningham, *Prog. Polym. Sci.* **2002**, 27, 1039.

[2] J. Qiu, B. Charleux, K. Matyjaszewski *Prog. Polym. Sci.* **2001**, 26, 2083.

[3] R. Arshady, *Colloid & Polym. Sci.*, **1992**, 270, 717.

[4] M. Antonietti, K. Landfester, *Prog. Polym. Sci.* **2002**, 27, 689.

[5] Nippon Paint Co, *US Patent* 5,603,986, **1997**.

[6] L.S. Ramanathan, P.G. Shukla, S. Sivaram, *Pure & Appl. Chem.* **1998**, 70,1295.

[7] E. Cloutet, B. Radhakrishnan, H. Cramail, *Polym. Int.* **2002**, 51, 978.

[8] B. Radhakrishnan, E. Cloutet, H. Cramail, *Colloids & Polym. Sci.* **2002**, 280, 1122.

[9] B. Radhakrishnan, P. Chambon, E. Cloutet, H. Cramail, *Colloids & Polym. Sci.* **2003**, 281, 516.

[10] P. Chambon, E. Cloutet, H. Cramail, *Macromolecules* **2004**, 37, 5856.

[11] P. Chambon, E. Cloutet, H. Cramail, T. Tassaing, M. Besnard, *Polymer*, in press.