

# A New Macroinitiator for the Synthesis of Triblock Copolymers PA12-*b*-PDMS-*b*-PA12

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**ABSTRACT:** A new PDMS macroinitiator is proposed for the anionic ring-opening polymerization of lactams. This  $\alpha,\omega$ -dicarbamoyloxy caprolactam PDMS macroinitiator was readily obtained in quantitative yield, by an original synthesis scheme in two steps, which involved the scarcely reported reaction of isocyanates with silanol groups. It was then shown that this bifunctional macroinitiator enabled to synthesize triblock copolymers PA12-*b*-PDMS-*b*-PA12 by polymerization of lauryl lactam (LL) at high temperature (200°C) in inert atmosphere under conditions compatible with reactive extrusion processes. Another related high molar weight  $\alpha,\omega$ -diacyllactam PDMS macroinitiator was also successfully used in the polymerization of LL under the same conditions, therefore overcoming the limitations formerly reported for this type of macroinitiators during

the polymerization  $\epsilon$ -caprolactam ( $\epsilon$ -CL) at a much lower temperature (80°C). Triblock copolymers with a wide range of PA12 /molar weights ( $M_n$ ;  $\sim$  10,800–250,000 Da) were eventually obtained by using both types of macroinitiators. DMTA and DSC analyses showed that their thermal properties were strongly dependent upon their respective contents in soft and hard blocks. Such triblock copolymers already appear very promising for the highly effective *in situ* compatibilization of PA12/PDMS blends as shown by recent complementary results obtained in our laboratory. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 2818–2831, 2006

**Key words:** ring-opening polymerization; lactam; macroinitiator

## INTRODUCTION

Thermoplastic elastomers represent an important class of materials that are widely used for different technical applications. Their excellent properties due to their two-phase morphology (i.e., soft and hard phases) can be varied over a wide range by the control of the amount and the nature of these two phases. Block copolymers with hard segments based on polyurethanes, polyamides, polycarbonate, or polystyrene and a soft phase made of polybutadiene, polyisobutylene, or polydimethylsiloxane<sup>1–5</sup> allow achieving improved properties generally not available with either of both homopolymers. They often play the role of compatibilizing agent at the interface of immiscible polymers.<sup>6–8</sup>

The increasing interest in multiphase copolymers based on polydimethylsiloxane (PDMS) is mainly due to their unique combination of properties, which is related to their chemical structure and macromolecular architecture. Several works<sup>9–13</sup> have already reported

the synthesis of block copolymers composed of PDMS and various polyamides (PA). A key finding towards success<sup>11,14</sup> was the design of new activating systems capable of polymerizing  $\epsilon$ -caprolactam ( $\epsilon$ -CL) without the concurrent nucleophilic degradation of the PDMS block, which had been observed in the early work of Lefebvre et al.<sup>15</sup> However, little information is available about the successful synthesis of PDMS/PA block copolymers with fairly long PDMS blocks, which would be highly interesting to improve particular properties of polyamides (e.g., toughness, prevention of moisture absorption) or silicones (e.g., weak mechanical properties).

This work is part of a general project aimed at developing new PA12/PDMS blends by anionic polymerization of lauryl lactam (LL: monomer of PA12) by reactive extrusion. One key factor for good compatibilization is the *in situ* synthesis of block copolymers PDMS-PA12 during melt processing. It has been shown that *in situ* block copolymer formation during melt processing is a very fast, easy, and cost-effective alternative to classical compatibilization methods. Moreover, anionic polymerization has proven to be a valuable method for preparing block copolymers from a functional polymer containing active species at its ends (a macroinitiator), which can allow the polymerization of another monomer.

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The successful synthesis of a well-defined block copolymer via anionic polymerization of lactams on the growth centers of  $\alpha,\omega$ -functionalized PDMS macroinitiators requires a high chain end reactivity and efficient polymerization of the second monomer. To the best of our knowledge, there have been only few scientific papers dealing with the synthesis of such macroinitiators. Veith et al.<sup>14</sup> described the synthesis of a  $\omega$ -acyllactam PDMS by anionic polymerization of hexamethylcyclotrisiloxane, which was then terminated by a chlorosilylacyllactam. Another related macroinitiator was also obtained by Mougin et al.<sup>11</sup> from the reaction of a  $\alpha,\omega$ -dihydro PDMS and undecylenoylcaprolactam by hydrosilylation. Owing to the different methods of synthesis, the functionality of these two macroinitiators differed (i.e., functionality of one or two for the former and the latter, respectively).

In this work, we propose a new telechelic PDMS macroinitiator for the anionic polymerization of lactams useful for the *in situ* generation of compatibilizing triblock copolymers in reactive extrusion processes.

The first part describes the original synthesis of a  $\alpha,\omega$ -dicarbamoyloxy caprolactam PDMS macroinitiator in two steps. To allow a comparison with results formerly reported in the literature, a  $\alpha,\omega$ -diacyllactam PDMS macroinitiator was also synthesized by adapting the procedure of Mougin et al.<sup>11</sup>

In the second part, both  $\alpha,\omega$ -functionalized PDMS macroinitiators are comparatively assessed for the anionic ring-opening polymerization of lauryl lactam in bulk using a newly developed catalyst.<sup>14,16–18</sup>

The last part describes the thermomechanical properties of the triblocks PA12-*b*-PDMS-*b*-PA12 obtained from both macroinitiators and points out the different behaviors of the block copolymers mainly depending upon their PDMS and PA12 respective contents.

## EXPERIMENTAL

### Materials

The  $\alpha,\omega$ -dihydro PDMS ( $M_n = 24,000$  g/mol, kinematic viscosity = 1000 cSt at ambient temperature) was of commercial grade from Aldrich and was used without further purification. Both  $\alpha,\omega$ -dihydroxy PDMS were purchased from ABCR and were dehydrated under vacuum at 70°C during 6 h prior to use. Their number-average molar weights were determined by <sup>1</sup>H-NMR ( $M_n = 600$  and 3100 g/mol, respectively). Their kinematic viscosities were equal to 35 and 120 cSt, respectively.

Lauryl lactam (LL) was kindly supplied by EMS Chemie (Reichenauerstrasse, Switzerland). Sodium caprolactamate (Na  $\epsilon$ -CL) was kindly supplied by Brüggemann Chemical (Heibronn, Germany). 10-Undecenoyl chloride, hydrogen hexachloroplatinate (IV) hydrate (99.9%), sodium bis (2-methoxyethoxy)

aluminum hydride ( $[(\text{CH}_3\text{OCH}_2\text{CH}_2\text{O})_2\text{AlH}_2]\text{Na}$ ),  $\epsilon$ -caprolactam ( $\epsilon$ -CL), 4,4'-diphenylmethane diisocyanate (MDI), toluene, cyclohexane, acetonitrile, and tetrahydrofuran were purchased from Aldrich (Buchs, Switzerland). The dibutyltin diacetate (> 98%) was purchased from Fluka (Buchs, Switzerland).  $\epsilon$ -CL and LL were dried under vacuum at 70°C for 24 h prior to use, the other reagents were used without further purification.

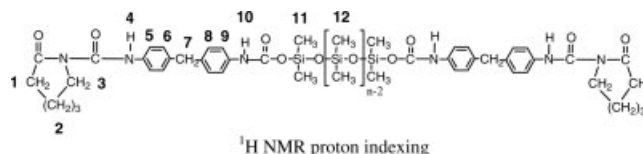
### Synthesis of catalyst<sup>11</sup>

$\epsilon$ -CL ( $5 \times 10^{-4}$  mol) was first dissolved in tetrahydrofuran (2 mL) at ambient temperature, then  $[(\text{CH}_3\text{OCH}_2\text{CH}_2\text{O})_2\text{AlH}_2]\text{Na}$  ( $5 \times 10^{-4}$  mol) was added dropwise until the hydrogen release ceased. The preparation of catalyst was repeated before each polymerization.

### Synthesis of macroinitiators

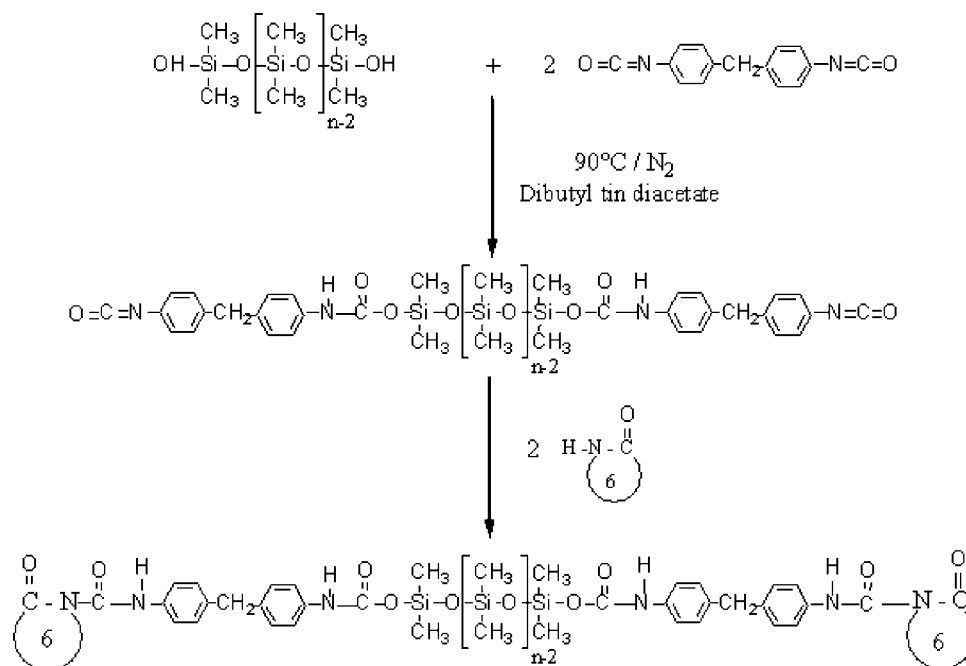
Preparation of  $\alpha,\omega$ -dicarbamoyloxy caprolactam PDMS (Macroinitiator 1)

In a glass reactor, 1.75 g (2.1 equiv.) of MDI and 10 g (1 equiv.) of  $\alpha,\omega$ -dihydroxy PDMS were dissolved in 10 mL of toluene under dry nitrogen and allowed to react at 90°C for 2 h in the presence of 0.05 g (0.5 wt %) of the dibutyltin diacetate catalyst. 0.83 g (2.2 equiv.) of  $\epsilon$ -CL was then added and the reaction was carried out at 90°C during 5 h (Fig. 1). At the end, the mixture was cooled at ambient temperature. The solvent was then evaporated under reduced pressure at 60°C. The  $\alpha,\omega$ -dicarbamoyloxy caprolactam PDMS was characterized by IR and <sup>1</sup>H-NMR with the help of spectra obtained for related models (e.g., di- $\epsilon$ CL MDI) and by elementary analysis.



<sup>1</sup>H NMR ( $\text{CDCl}_3$ , 300 MHz,  $\delta$  ppm): 11.45 (4, NHCONCO singlet), 7.43 (5, CH MDI, doublet poorly resolved), 7.25 (9, CH MDI, doublet poorly resolved), 7.12 (6 and 8, CH MDI doublets poorly resolved), 6.59 (10, NH—CO—PDMS broad peak), 4.05 (7, CH<sub>2</sub> MDI singlet), 3.89 (3, CH<sub>2</sub>—CO CL multiplet), 2.76 (1, CH<sub>2</sub>—N CL multiplet), 1.78 (2, (CH<sub>2</sub>)<sub>3</sub> CL broad peak), 0.34 (11, NHCOOSi(CH<sub>3</sub>)<sub>2</sub>O PDMS singlet), 0 (12, [Si(CH<sub>3</sub>)<sub>2</sub>O] PDMS broad peak).

IR (Film on KBr disk,  $\text{cm}^{-1}$ ): PDMS: 2963 ( $\nu$   $\text{CH}_3$ ), 1261 (symmetric deformation  $\text{SiCH}_3$ ), 1093–1025 (double band,  $\nu$   $\text{SiOSi}$ ), 804 ( $\nu$   $\text{SiC}$ ); imide: 1713 (amide I), 1537 (amide II); urethane: 3333 ( $\nu$   $\text{NH}$ ), 1713 (amide I), 1537 (amide II).



**Figure 1** Synthesis scheme for  $\alpha,\omega$ -dicarbamoyloxy caprolactam PDMS (Macroinitiator 1).

Elementary analysis: Found Si, 30.05; C, 39.95; H, 7.95; N, 2.15; Calculated Si, 30.23; C, 39.52; H, 7.66; N, 2.26.

#### Preparation of $\alpha,\omega$ -diacyllactam PDMS (Macroinitiator 2)

The synthetic procedure for  $\alpha,\omega$ -diacyllactam PDMS was a two-step method adapted from Mougin et al.<sup>11,18</sup> (Fig. 6). In the first step, undecylenoyl-caprolactam was synthesized by reacting 1 equiv. of 10-undecylenoyl chloride first dissolved in 200 mL of toluene at 0°C with 1.2 equiv. of sodium caprolactamate (Na  $\epsilon$ -CL) added dropwise. After standing overnight at 0°C, the reaction mixture was filtered and the solvent evaporated under reduced pressure. The crude product was thoroughly washed with cyclohexane (rather than water to prevent the hydrolysis of potential traces of acid chloride). After evaporating the residual cyclohexane, the product was eventually isolated by distillation under vacuum (Yield  $\sim$  75%). FTIR and <sup>1</sup>H-NMR characterization of undecylenoyl-caprolactam was in good agreement with that formerly reported by Mougin et al.<sup>18</sup> and fully confirmed its chemical structure.

In the second step, 1 equiv. of  $\alpha,\omega$ -dihydro PDMS and 2.6 equiv. of undecenoyl caprolactam (acyllactam) were stirred at 60°C in the presence of 1 mol % of hexachloroplatinic acid in toluene solution ( $1 \times 10^{-4}$  mol/mL) for durations varying from 24 to 30 h. The reaction was followed by IR. After complete conversion of the SiH groups as confirmed by FTIR, the modified polymer was thoroughly washed with acetonitrile to remove the residual acyllactam. The

macroinitiator was then filtered and dried under vacuum at 70°C for 24 h. As expected, the very low amount of terminal groups of this "high" molecular weight macroinitiator ( $M_{\text{PDMS}} = 24,000$  g/mol) could not be characterized by FTIR or <sup>1</sup>H-NMR.<sup>11</sup>

#### Synthesis of PA12-*b*-PDMS-*b*-PA12 copolymers

PA12-*b*-PDMS-*b*-PA12 triblock copolymers were synthesized by anionic polymerization of LL in the presence of either of the  $\alpha,\omega$ -functionalized macroinitiators. 10 g of lauryl lactam and various percentages in weight of macroinitiator were introduced along with a magnetic bar in a glass reactor under nitrogen and heated using a high temperature oil bath. The catalyst was injected when a temperature of 200°C was reached. The stirring speed was held constant during all the polymerization. The gel point was observed when the magnetic bar became motionless due to the very sharp increase in viscosity caused by anionic polymerization. The time between the catalyst injection and the gel point was determined and this simple test was used to compare the reactivity of the two macroinitiators.

The molar concentration of catalyst was fixed to 1 mol % of LL and the total polymerization time was 15 min in all cases. The resulting copolymers were purified by successive extractions of the crude product as follows: (a) methanol extraction, to remove the nonreacted LL monomer; (b) hot hexane was used for the removal of unreacted PDMS macroinitiator. The conversion degrees were determined from the sample weights after this double extraction. Following the method formerly reported by P. Petit et al.,<sup>19</sup> systematic elementary analyzes

enabled to calculate the number average molar weights of the PA12 blocks for the whole series of copolymers.

### Analysis

The infrared spectra were recorded on a Bruker IFS 25 FTIR spectrometer. NMR experiments were performed using a Bruker Avance 300 spectrometer with TMS as internal reference. Elementary analyses were done by the Central Analysis Service of CNRS at Vernaison, France.

The effect of the PDMS block on the glass transition temperature and other transitions of the PA12 blocks were studied by dynamic mechanical thermal analysis (DMTA). Measurements were made using a Rheometric Scientific DMTA V. The testing was carried out in dual cantilever bending mode at a vibration frequency of 1 Hz. The temperature ranged from  $-140$  to  $130^{\circ}\text{C}$  with a heating rate of  $3^{\circ}\text{C}/\text{min}$ .

To investigate the influence of the elastomeric phase on the melting and crystallization behavior of the PA12 blocks, samples of neat PA12 and of copolymers PDMS-PA12 were studied by differential scanning calorimetry using a Perkin-Elmer DSC (Model 1. The temperature was scanned from  $-100$  to  $200^{\circ}\text{C}$ . The heating and cooling rates were  $10^{\circ}\text{C}/\text{min}$ . In all cases, the samples were held at  $200^{\circ}\text{C}$  for 2 min prior to cooling to cancel previous thermal history. Heating scans allowed to determine the crystalline melting temperature,  $T_m$ , and the heat of fusion,  $\Delta H_f$ , while cooling scans were used to obtain the crystallization temperature  $T_c$  and heat of crystallization,  $\Delta H_c$ .

## RESULTS AND DISCUSSION

### Synthesis and characterization of macroinitiators

$\alpha,\omega$ -Dicarbamoyloxy caprolactam PDMS (Macroinitiator 1)

The  $\alpha,\omega$ -dicarbamoyloxy caprolactam PDMS (Macroinitiator 1) was synthesized in two steps (Fig. 1):

- In the first step, a macrodiisocyanate was obtained by reacting 1 equiv of a dihydroxy end-terminated PDMS with 2.1 equiv of an aromatic diisocyanate (MDI), following a procedure that is very close to that of the first step of the common step-by-step synthesis of polyurethane materials.<sup>20</sup>
- The second step consisted of end-capping the former macrodiisocyanate with  $\epsilon$ -CL.

One of the originality of the synthesis scheme described in Figure 1 is to make use of a PDMS end-terminated with simple silanol groups SiOH rather than hydroxyalkyl groups (such as  $\text{Si}(\text{CH}_2)_n\text{OH}$ ), which are usually preferred in the polyurethanesi-

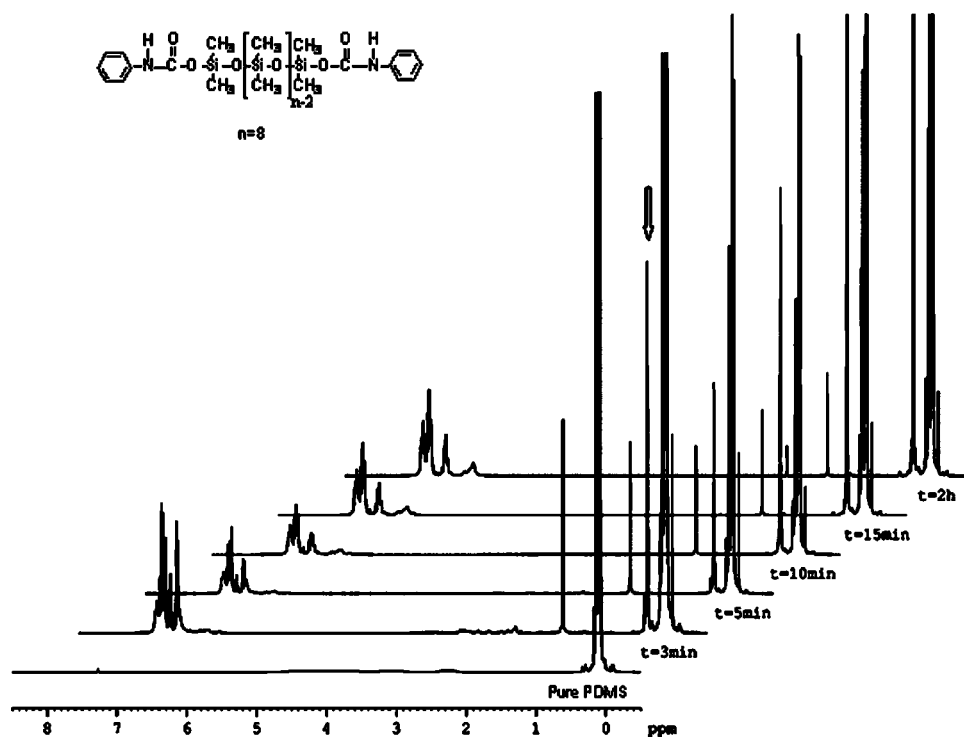
loxane literature. The reasons for this preference are generally the high reactivity of hydroxyalkyl end-groups (whose reactivity is known to be very close to that of simple alkanols<sup>2,21-25</sup>) and the better stability of the corresponding urethane groups, compared with the carbamoyloxy group SiOCONHR (obtained from simple silanols) which are known to be sensitive toward hydrolysis.<sup>26,27</sup>

In the context of this work, the macroinitiator was intended to be used in reactive extrusion processes under inert atmosphere for the *in situ* generation of triblock copolymers capable of controlling the morphology of PA12/PDMS blends.

Given the anticipated reactive extrusion conditions, the sensitivity of the carbamoyloxy groups SiOCONHR toward hydrolysis was a minor factor compared with the price of  $\alpha,\omega$ -dihydroxy PDMS precursors which is 10 times lower than that of the corresponding  $\alpha,\omega$ -dihydroxyalkyl PDMS precursors. Therefore, using a disilanol PDMS precursor was much more cost-effective and this advantage really prevailed for this project which targeted reactive extrusion processes on a pilot or industrial scale.

Nevertheless, if the reaction of simple alkanols or, to a much less extent, related  $\text{Si}(\text{CH}_2)_n\text{OH}$  groups with isocyanates is fairly well documented,<sup>20-25,28,29</sup> the references about the corresponding reaction involving simple silanols are still really scarce in the literature and little is known about the reactivity of this particular hydroxyl group. The first related references described this reaction for simple low molecular weight molecules.<sup>26,27</sup> Later on, a few other works focused on the functionalization of glass- or silica-surfaces based on the reaction of the surface SiOH groups with isocyanate species.<sup>30-33</sup> In one case, Yosomiya et al.<sup>31</sup> reported that the reactivity of the surface SiOH groups was very close to that of the hydroxyl groups of simple alkanols. The reaction of SiOH groups with isocyanates was also described by several industrial companies in a few patents on rather complex PDMS/PU formulations.<sup>34-36</sup> Stanciu et al. also eventually reported the synthesis of polyurethanesiloxanes from PDMS end-functionalized with either dihydroxy or dihydroxyalkyl groups but no comparison was made between the reactivity of both PDMS telechelic oligomers.<sup>2</sup>

To characterize the reactivity of the silanol groups involved in the synthesis scheme of macroinitiator 1, we first analyzed the carbamate formation during the model reaction of a short  $\alpha,\omega$ -dihydroxy PDMS ( $M_n = 600$  g/mol) with phenyl isocyanate.  $^1\text{H-NMR}$  was particularly helpful to follow the carbamate formation, which was responsible for a new peak appearing at 0.35–0.36 ppm (white arrow—Fig. 2). This new peak was assigned to the protons of the  $\text{Si}(\text{CH}_3)_2$  groups in alpha position to the carbamate function and enabled to calculate easily the corre-

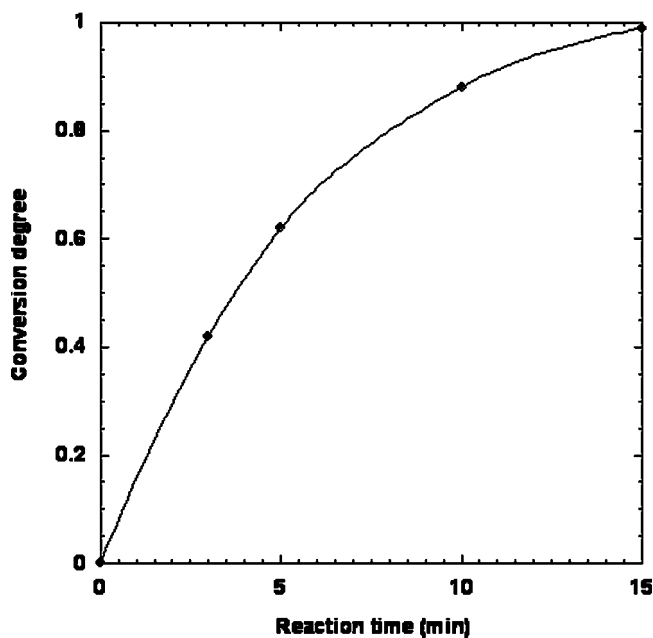


**Figure 2**  $^1\text{H-NMR}$  investigation of the model end-capping of a short  $\alpha,\omega$ -dihydroxy PDMS ( $M_n = 600$  g/mol) with phenyl isocyanate catalyzed by dibutyltin diacetate in toluene at  $90^\circ\text{C}$  (see text for the detailed experimental conditions).

sponding conversion. In the experimental conditions used in this work, the model reaction was fairly fast with a quantitative conversion in  $\sim 15$  min at  $90^\circ\text{C}$  (Fig. 3). These reaction conditions were then easily transposed to the first synthesis step of macroinitiator 1 from a longer  $\alpha,\omega$ -dihydroxy PDMS ( $M_n = 3100$  g/mol) and MDI to lead to the corresponding macrodiisocyanate in 2 h at  $90^\circ\text{C}$ . The end-capping of this macrodiisocyanate with  $\epsilon$ -CL gave the corresponding  $\alpha,\omega$ -dicarbamoyloxy caprolactam PDMS (macroinitiator 1) in quantitative yield. This reaction was carried out with a fairly low molecular weight  $\alpha,\omega$ -dihydroxy PDMS to enable the quantitative characterization of the macroinitiator by  $^1\text{H-NMR}$ . Nevertheless, this methodology could be easily extended to  $\alpha,\omega$ -dihydroxy PDMS with much higher molecular weights if required.

Macroinitiator 1 was then characterized by FTIR and  $^1\text{H-NMR}$ . The FTIR spectrum (Fig. 4) showed a very broad peak at  $3333\text{ cm}^{-1}$  corresponding to the NH stretching vibration and the very characteristic amide I and amide II bands at  $1713\text{ cm}^{-1}$  and  $1537\text{ cm}^{-1}$ , respectively, which were clear signatures for the urethane groups. Figure 4 shows that the amide I and amide II bands characteristic of the terminal imide groups were superposed on the former related urethane bands. Moreover, as expected for this telechelic oligomer of relatively high molecular weight ( $M_n \cong 3800$  g/mol), the other bands of weaker intensity which are usually considered as characteristic

of imide groups ( $\nu\text{ CO} \cong 1770\text{ cm}^{-1}$ ;  $\nu\text{ CN} \cong 1380\text{ cm}^{-1}$  and  $\gamma\text{ CO} \cong 725\text{ cm}^{-1}$ )<sup>37</sup> were of very low intensity and could not be easily identified on the FTIR spectrum. With this respect,  $^1\text{H-NMR}$  was



**Figure 3** Variation of the conversion degree with time for the model end-capping of a short  $\alpha,\omega$ -dihydroxy PDMS ( $M_n = 600$  g/mol) with phenyl isocyanate catalyzed by dibutyltin diacetate in toluene at  $90^\circ\text{C}$  (see text for the detailed experimental conditions).

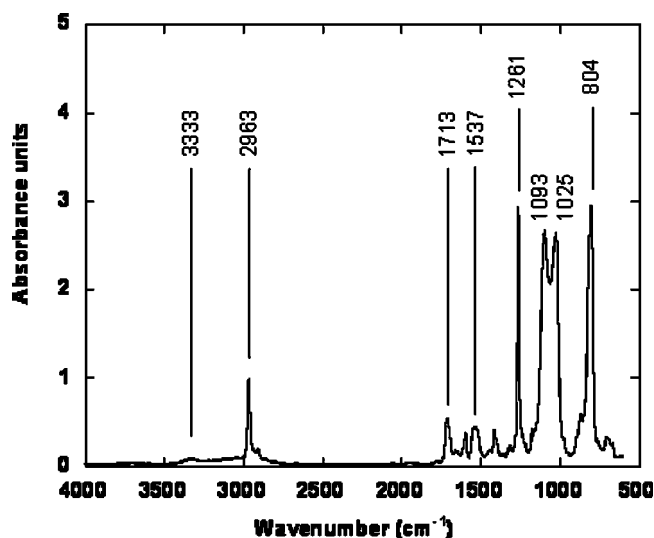


Figure 4 FTIR analysis of  $\alpha,\omega$ -dicarbamoyloxy caprolactam PDMS (Macroinitiator 1).

much more powerful to characterize the terminal imide groups, for instance from the corresponding NH group in alpha position which were responsible for a highly shifted peak at 11.45 ppm. The methylene protons of the terminal  $\epsilon$ -CL were also easily identified (Fig. 5) at 1.78, 2.76, and 3.89 ppm whereas the urethane groups were characterized by a fairly broad singlet at 6.59 ppm. The complete assignment of the  $^1\text{H-NMR}$  spectrum of macroinitiator 1 (detailed in the experimental part) confirmed its chemical structure, while the corresponding integrations were in good agreement with the expected stoichiometry.

#### $\alpha,\omega$ -Diacyllactam PDMS (Macroinitiator 2)

To provide a first comparison with polymerization data formerly reported in the literature with another successful activating system,<sup>11</sup> the corresponding  $\alpha,\omega$ -diacyllactam PDMS macroinitiator (macroinitiator 2) was also synthesized by adapting the synthetic procedure of Mougou et al.<sup>11,18</sup> (Fig. 6) with results in good agreement with the former work.

#### Synthesis of the triblock copolymers PA12-*b*-PDMS-*b*-PA12

Anionic polymerization of lauryl lactam (LL) was carried out in a batch reactor at high temperature (200°C) to enable a first assessment of the reactivity of both macroinitiators in conditions which are typical for reactive extrusion for this kind of systems.

Table I describes the composition and characteristics of the triblock copolymers PA12-*b*-PDMS-*b*-PA12 obtained by varying the ratio of lauryl lactam to macroinitiator from 95/5 to 80/20 w/w %.

For macroinitiator 1, the gel point was reached within 15 s for the polymerization system containing 5 wt % of macroinitiator (Table I—Entry 1). In these conditions, the polymerization yield was fairly high ( $\cong 80\%$ ) and the amount of unreacted PDMS remained very low ( $\cong 10\%$ ). As expected, increasing the amount of macroinitiator, and thus the amount of terminal active sites, led to a quicker gelification which occurred in 5 s only, for the system containing 20 wt % of macroinitiator 1 (Table I—Entry 3). Nevertheless, the strong increase in polymerization



Figure 5  $^1\text{H-NMR}$  analysis of  $\alpha,\omega$ -dicarbamoyloxy caprolactam PDMS (Macroinitiator 1).

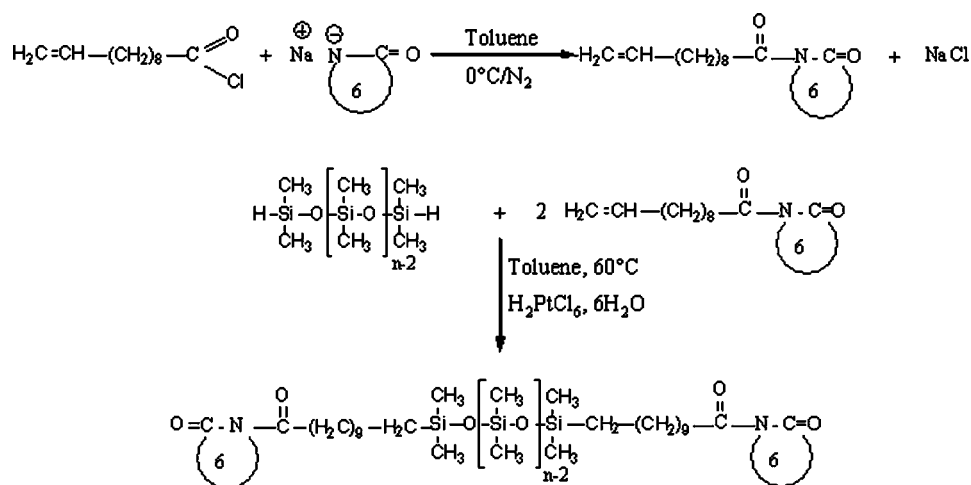


Figure 6 Synthesis scheme of  $\alpha,\omega$ -diacyllactam PDMS (Macroinitiator 2) adapted from Mougin et al.<sup>11</sup>

rate observed for the latter system was in detriment to the polymerization yield ( $\cong 60\%$ ) and the unreacted PDMS increased up to 40%. This behavior is due to the fact that the polymerization was carried out in the melt in a very short time (about 15 min) with a very high increase in viscosity. In these conditions, it is most likely that the chain mobility was so decreased that the remaining active sites could no more be accessible for polymerization. This explains why residual unreacted PDMS macroinitiator and monomer were systematically found at the end of the reaction. Moreover, by increasing the ratio LL/macroinitiator, it was possible to control the average degree of polymerization of the PA12 blocks from 55 to 165 for a constant polymerization time of 15 min at 200°C. The copolymers synthesized were not totally soluble in the classical solvents of PA12 (Formic acid, *m*-cresol, Hexafluoroisopropanol, etc.).

The GPC analysis required first to solubilize the copolymer. To this end, we can use the trifluoroacetylation of the NH groups of polyamide 12. The excess of  $(\text{CF}_3\text{CO})_2\text{O}$  and the  $\text{CF}_3\text{COOH}$  formed during the trifluoroacetylation reaction can deteriorate the PDMS block. So, to prevent this acidic cleavage of the PDMS chains, only elementary analysis is used to calculate the number of molecular weight.

Complementary experiments were also carried out with a related macroinitiator (macroinitiator 2), which had been initially reported for the anionic polymerization of caprolactam at a much lower temperature (80°C).<sup>11</sup> In the former work, the polymerization yield had been shown to be strongly dependent upon the PDMS molar weight. For a PDMS molar weight of 10,000 g/mol, the conversion was limited to 30% for a polymerization time of 2 h. For higher PDMS molar weights, the polymerization yield was extremely low

TABLE I  
Composition and Characteristics of the Triblock Copolymers PA12-*b*-PDMS-*b*-PA12 Obtained by Anionic Polymerization of Lauryl Lactam Using Two Types of Macroinitiators

Sample	LL/macroinitiator (w/w %)	Yield (wt %)	Unreacted PDMS (wt %)	Gel point (sec)	DP <sub>n</sub> of the PA12 blocks		PDMS (wt %) (Exper.) <sup>c</sup>
					(Theor.) <sup>a</sup>	(Exper.) <sup>b</sup>	
Using macroinitiator 1 <sup>d</sup>							
A5	95/5	79	10	15	155	165	5.5
A10	90/10	81	10	8	75	80	10.8
A20	80/20	57	40	5	40	55	14.9
Using macroinitiator 2 <sup>e</sup>							
B5	95/5	67	15	120	1000	1265	4.6
B10	90/10	61	23	60	425	395	13.4
B20	80/20	64	25	45	240	260	19.0

<sup>a</sup> Theoretical DP<sub>n</sub> of the PA12 blocks calculated by taking into account the conversion of lauryl lactam and unreacted PDMS.

<sup>b</sup> Experimental DP<sub>n</sub> of the PA12 blocks calculated from elementary analysis.

<sup>c</sup> Copolymer PDMS content calculated from the experimental DP<sub>n</sub> of the PA12 blocks.

<sup>d</sup>  $\alpha,\omega$ -dicarbamoyloxy caprolactam PDMS ( $M_n = 3800$  g/mol).

<sup>e</sup>  $\alpha,\omega$ -diacyllactam PDMS ( $M_n = 24,000$  g/mol).

( $\leq 5\%$ ), which was ascribed to the poor accessibility of the terminal active sites rather than to a loss in active sites during polymerization. In the present work, the polymerization temperature was much higher, corresponding to conditions much closer to those of extrusion processes. In these new conditions, macroinitiator 2—which had a PDMS molar weight as high as 24,000 g/mol—led to a polymerization yield of 64% after 15 min at 200°C. However, the time for gelation with macroinitiator 2 was increased by a factor 8 comparatively to macroinitiator 1. Nevertheless, the decrease in polymerization rate observed for macroinitiator 2 has to be ascribed mainly to the difference in the PDMS molar weights of both macroinitiators and not to very different intrinsic reactivities. Even if it can be subject to debate, a simple comparison of their estimated gel point times for the same concentration of terminal active sites indeed shows that their intrinsic reactivities are very close (+25% for macroinitiator 1). Moreover, for the same weight ratios LL/macroinitiator, the higher molar weight of macroinitiator 2 enabled to obtain much higher degrees of polymerization of the PA12 blocks which varied from 260 to 1265 for a constant polymerization time of 15 min at 200°C.

Eventually, using both types of macroinitiators allowed to obtain triblock copolymers PA12-*b*-PDMS-*b*-PA12 with a broad range of degrees of polymerization for the PA12 blocks ( $DP_n$ : 55  $\rightarrow$  1265) corresponding to average molar weights  $M_n$  in the range of  $\sim 10,800$ – $250,000$  g/mol.

## Thermomechanical properties

### DMTA properties

Dynamical mechanical analyses were performed for pure PA12 and the triblock copolymers PA12-*b*-PDMS-*b*-PA12, which were obtained with increasing amounts of PDMS macroinitiators 1 or 2.

Figures 7 and 8 show the dependence of the storage modulus,  $E'$  (where the curves have been shifted for clarity), and the loss factor,  $\tan \delta$ , on temperature for the two types of copolymers.

In Figures 7(a) and 8(a), the  $E'$  curves for pure PA12 and those obtained for both series of triblock copolymers displayed the same types of trends with  $E'$  decreasing, which followed the PDMS content in the block copolymers. The data indicate a three-domain morphology. The drop in modulus at temperatures of ca.  $-35^\circ\text{C}$  [Fig. 7(a)—Copolymers A] and ca.  $-28^\circ\text{C}$  [Fig. 8(a)—Copolymers B] can be ascribed to the melting of the PDMS blocks. The magnitude of this transition increased with the PDMS content of the triblock copolymers for the two series of samples. Therefore, the strongest transitions were observed for the copolymers A20 and B20 which were both obtained with a LL/macroinitiator ratio of

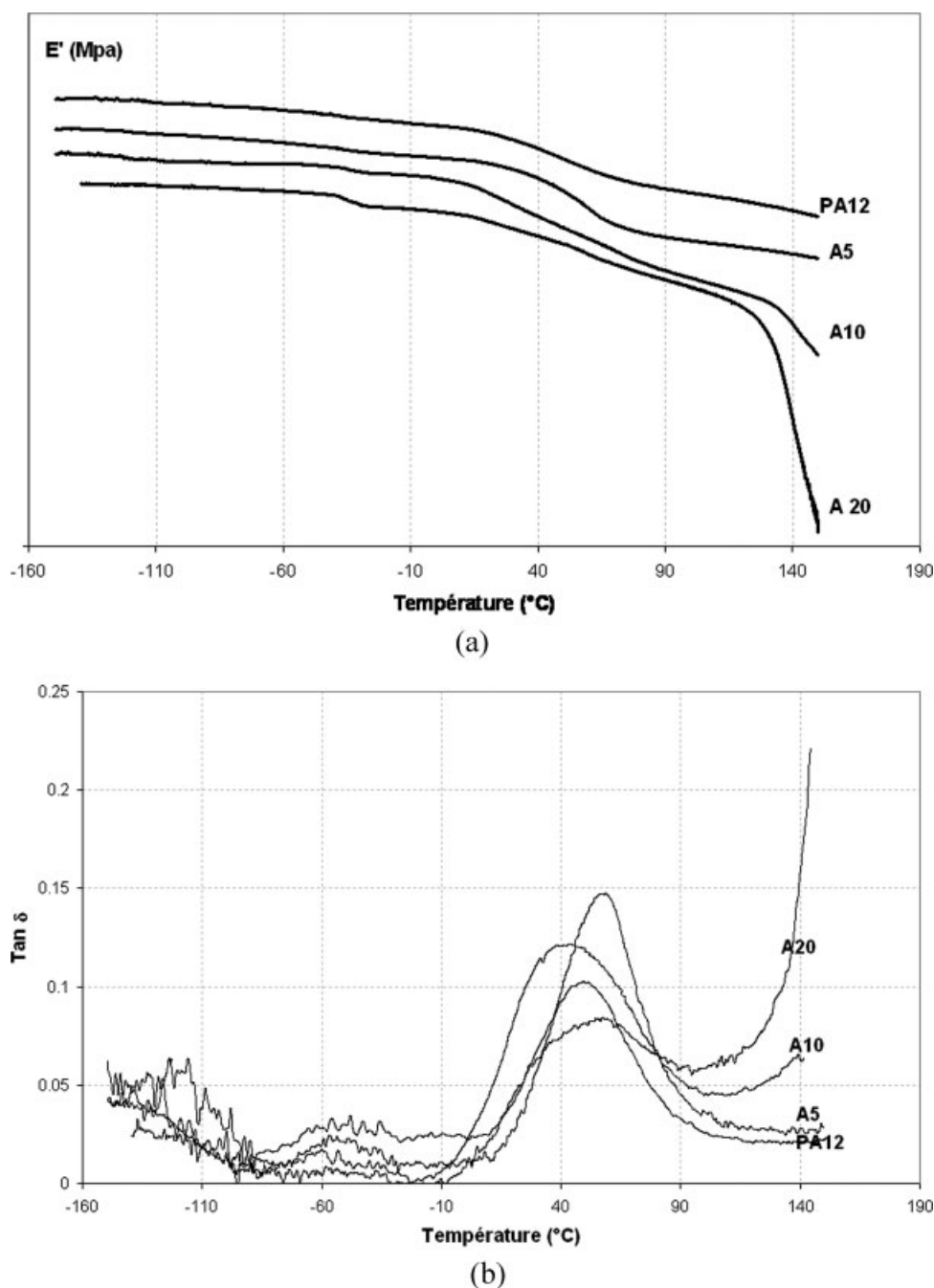
80/20. The melting temperature of the PDMS block was very close to that obtained for pure PDMS and indicated the good microphase separation<sup>38,39</sup> of PDMS in the triblock copolymers. The transition between 20 and 60°C can be ascribed to the glass transition of the PA12 hard blocks.<sup>38,40,41</sup> At a higher temperature typically between 120 and 150°C, the hard segment domains began to melt.

The  $\tan \delta$  curves [Figs. 7(b) and 8(b)] provided further information about the thermal behavior of the triblock copolymers by revealing new transitions in five particular regions. The first transition at low temperature (between  $-150$  and  $-100^\circ\text{C}$ ) was related to the glass transition temperature of PDMS and to the  $\gamma$  relaxation arising from kink and crankshaft motions of sequences higher than four methylene groups of the PA12 hard blocks.<sup>40</sup> The  $\beta$  relaxation of PA12 observed between  $-100$  and  $-50^\circ\text{C}$ , which corresponded to hydrogen-bonded carbonyl groups in the amorphous regions, was influenced by the magnitude of the melting transition of the PDMS phase in the copolymer samples of Series A, which occurred between  $-50$  and  $0^\circ\text{C}$ . As expected, the magnitude of the  $\beta$  transition increased with the copolymer content in PA12. The glass transition of the PA12 hard blocks was found as expected between 0 and 60°C. Here again, the magnitude of this transition clearly increased with the copolymer content in PA12. Nevertheless, for the same weight fraction of hard blocks, the molar weight of the PDMS soft blocks had an influence on the magnitude of the  $\beta$  relaxation of the PA12 hard blocks. In particular, the corresponding peaks of the  $\tan \delta$  curves were of relatively weak intensity for the copolymers B10 and B20 [Fig. 8(b)], comparatively to what was observed for the copolymers A10 and A20 [Fig. 8(a)]. Following this transition, there was a rubbery plateau that extended from 60 to  $\sim 120^\circ\text{C}$ . The extent of this rubbery plateau depended upon the copolymer content in the PA12 hard blocks. Figure 7(b) shows that, as expected, it increased with an increase in the copolymer hard block content. The final transition ( $120$ – $150^\circ\text{C}$ ) was due to the melting of the PA12 crystalline phase. One can notice that the melting point moved to lower temperatures as the silicone content increased. This behavior can be explained by the decrease in the length of the PA12 blocks from samples A5 to A20 and B5 to B20 due to the increase in the macroinitiator concentration, which controls the number of growing PA12 chains and therefore their final length.

### DSC analysis

The melting and crystallization behavior of the copolymers was then investigated by DSC. Samples of copolymers were first heated from  $-150$  to  $200^\circ\text{C}$



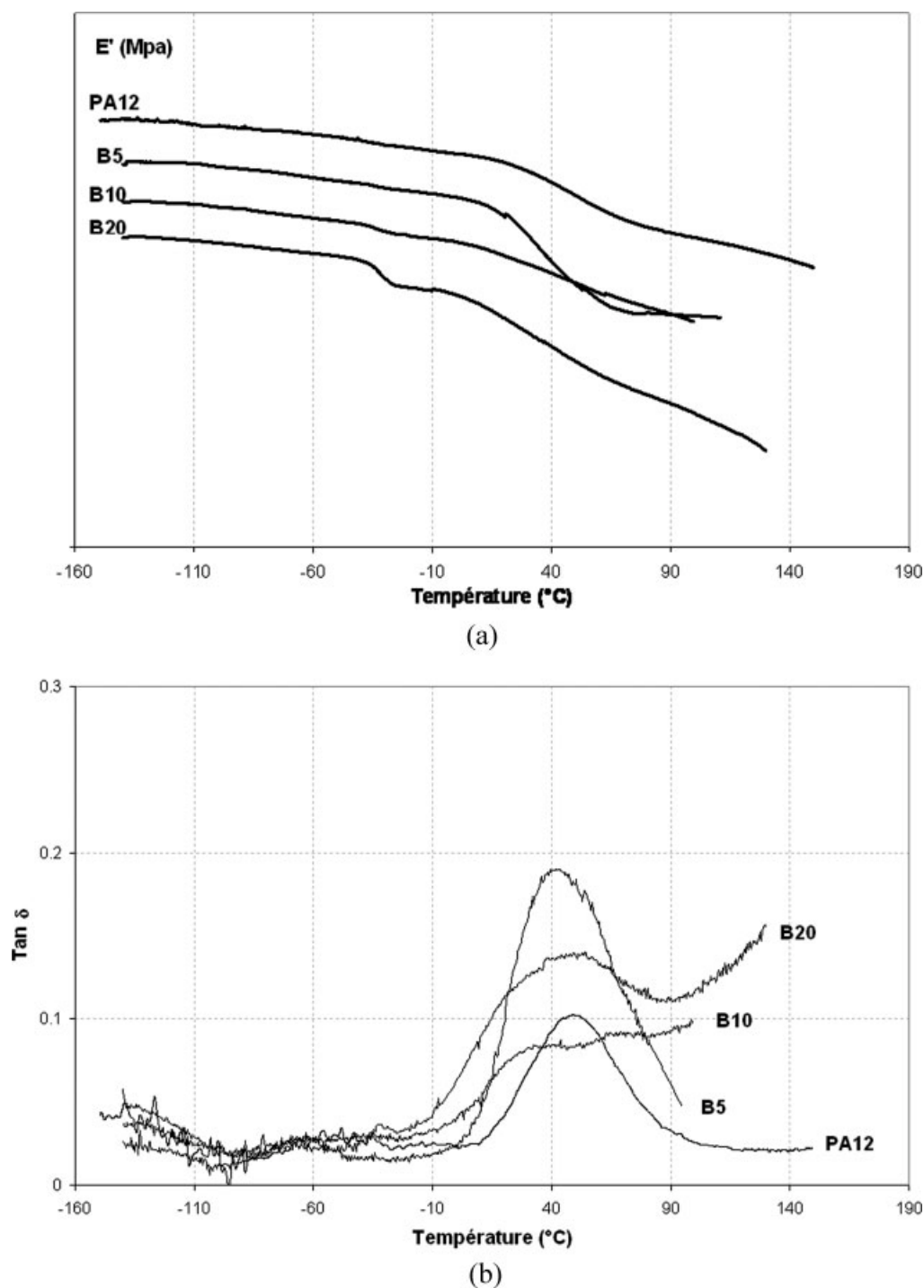


**Figure 7** Dynamic mechanical properties of pure polyamide 12 and triblock copolymers PA12-*b*-PDMS-*b*-PA12 obtained with macroinitiator 1. (a) Storage modulus. Note:  $E'$  traces have been displaced vertically for clarity, (b)  $\tan \delta$ .

(heating scan), then cooled to  $-150^{\circ}\text{C}$  (cooling scan) at a rate of  $10^{\circ}\text{C}/\text{min}$ . Figures 9 and 10 show the DSC thermograms for pure PA12, the PDMS precursors and the triblock copolymers PA12-*b*-PDMS-*b*-PA12, which were obtained with increasing amounts of PDMS macroinitiators 1 or 2, respectively. The thermal parameters corresponding to both heating and cooling scans are listed in Table II.

Only the DSC trace of the relatively high molar weight PDMS (i.e.,  $\alpha,\omega$ -dihydro PDMS,  $M_n = 24,000$  g/

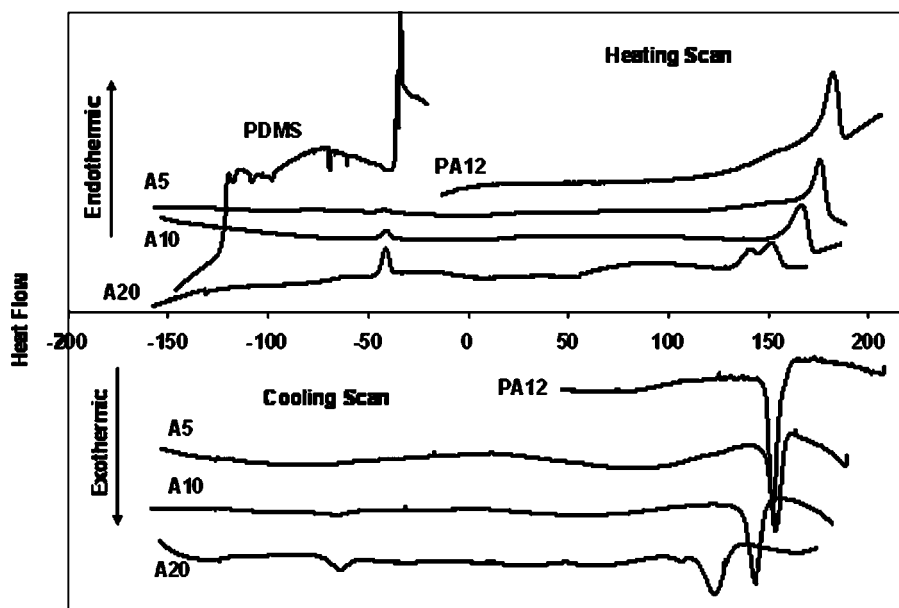
mol) showed all the characteristic transitions of PDMS (Fig. 10). The corresponding thermogram showed a glass transition temperature of ca.  $-120^{\circ}\text{C}$ , then a single exothermic peak for crystallization and a double melting peak. The double melting peak has been interpreted in various ways in the literature, as the reorganization of small and imperfect crystallites during heating process,<sup>42</sup> or as the melting of two different crystal forms of PDMS.<sup>43–45</sup> For the low molecular weight PDMS ( $M_n = 3100$  g/mol), Figure 9



**Figure 8** Dynamic mechanical properties of pure polyamide 12 and triblock copolymers PA12-*b*-PDMS-*b*-PA12 obtained with macroinitiator 2. (a) Storage modulus. Note:  $E'$  traces have been displaced vertically for clarity, (b)  $\tan \delta$ .

shows that only one type of crystal structure was detected by DSC, in good agreement with observations reported formerly.<sup>46</sup> The multiple small melting peaks in PDMS and its copolymers are usually ascribed to the premelting and reorganization of crystals although no cold crystallization peak can be observed in cooling scan for the PDMS precursor.<sup>47</sup>

For the triblock copolymers, a single melting peak was observed for the PDMS, as shown in Table II and comparatively to their related PDMS precursors, the melting temperature of the PDMS soft block was slightly lower (typically 4°C—Column 4) for all the triblock copolymers. Nevertheless, this melting temperature did not vary with the copoly-

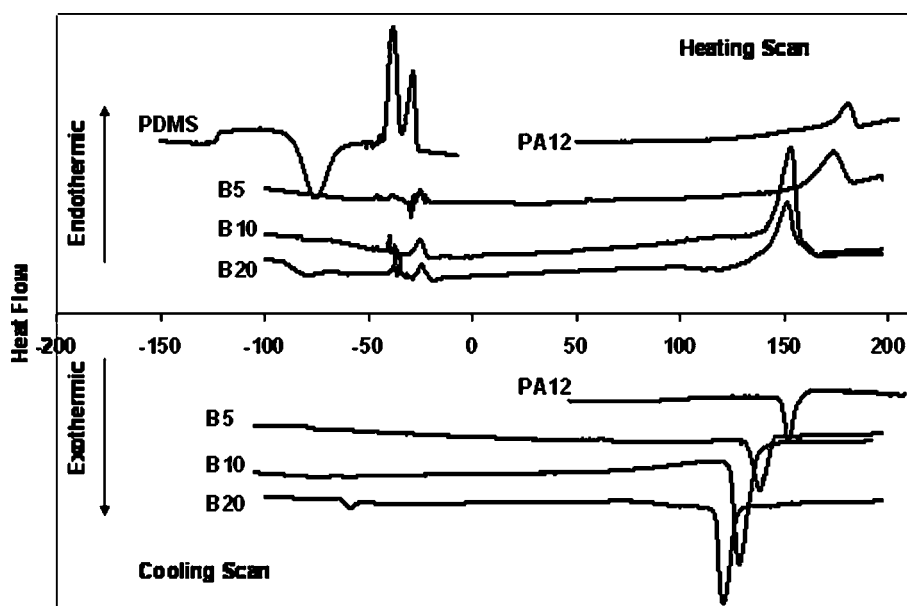


**Figure 9** DSC of pure polyamide 12, pure PDMS and triblock copolymers PA12-*b*-PDMS-*b*-PA12 obtained with macroinitiator 1. Note: DSC traces have been displaced vertically for clarity.

mer PDMS content within a given series of triblock copolymers.

The very low heat of fusion  $\Delta H_m$  of the PDMS soft blocks (low molar weight PDMS,  $M_n = 3100$  g/mol) for the copolymers of series A was subject to great experimental uncertainty. The single possible related conclusion is that the crystallinity of the PDMS soft blocks is very low, same observation has already been reported by Boulares et al.<sup>41</sup> for low molar weight soft blocks of polyoxypropylene and poly-

oxyethylene in PA12 copolymers. For the copolymers of Series B with a much longer PDMS soft block ( $M_n = 24,000$  g/mol), the melting heat of the PDMS soft block was much higher and close to that of high molar weight PDMS.<sup>48</sup> Moreover, it should be noted that only the triblock copolymers B10 and B20 showed single exothermic peaks for crystallization of PDMS in both heating and cooling scans, while the triblock copolymers A10 and A20 showed a crystallization peak only in the cooling scan. Therefore, if



**Figure 10** DSC of pure polyamide 12, pure PDMS and triblock copolymers PA12-*b*-PDMS-*b*-PA12 obtained with macroinitiator 2. Note: DSC traces have been displaced vertically for clarity.

TABLE II  
Thermal Characterization of the Triblock Copolymers PA12-*b*-PDMS-*b*-PA12 by Differential Scanning Calorimetry

Sample	Heating scan						Cooling scan			
	Crystallization and melting parameters						Crystallization parameters			
	Soft segment			Hard segment			Soft segment		Hard segment	
$T_c$ (°C)	$-\Delta H_c$ (J/g) <sup>a</sup>	$T_m$ (°C)	$\Delta H_m$ (J/g) <sup>a</sup>	$T_m$ (°C)	$\Delta H_m$ (J/g) <sup>b</sup>	$T_c$ (°C)	$-\Delta H_c$ (J/g) <sup>a</sup>	$T_c$ (°C)	$-\Delta H_c$ (J/g) <sup>b</sup>	
PA12	–	–	–	–	181	25.2	–	–	151	29
PDMS <sup>c</sup>	–	–	–35	4.2	–	–	–	–	–	–
A5	–	–	–39	–	176	15.5	–	–	152	25.7
A10	–	–	–39	15.7	167	18.7	–67	3.8	142	23.9
A20	–	–	–40	3.35	152	10.9	–66	18.8	120	18.6
PDMS <sup>d</sup>	–74	30.7	–38	19.2	–	–	–	–	–	–
			–28	29						
B5	–	–	–24	54.3	175	30.7	–	–	137	33.1
B10	–77	20.9	–24	31.3	154	57.7	–62	5.2	128	57.7
B20	–80	48.4	–24	27.9	152	49.1	–62	20.5	120	61.7

<sup>a</sup> J/g of PDMS soft block in the triblock copolymer.

<sup>b</sup> J/g of PA12 hard block in the triblock copolymer.

<sup>c</sup>  $\alpha,\omega$ -dihydroxy PDMS had a  $\bar{M}_n = 3100 \text{ g mol}^{-1}$  and  $v = 10^2 \text{ CSt}$ .

<sup>d</sup>  $\alpha,\omega$ -dihydro PDMS had a  $\bar{M}_n = 24,000 \text{ g mol}^{-1}$  and  $v = 10^3 \text{ CSt}$ .

the  $T_m$  of the PDMS soft block was independent of the copolymer PDMS content within a given series of triblock copolymers, the soft block was crystallizable only if its molar weight was sufficiently high.<sup>41,49</sup>

In contrast to the constant melting temperature of the PDMS soft block within a given series of copolymers, the melting temperature of the PA12 hard blocks systematically decreased by increasing the PDMS content in the triblock copolymers (Table II—Column 6). The same type of phenomenon has already been observed by Xie and Camberlin<sup>49</sup> and by Sheth et al.<sup>38</sup> for PEBA copolymers containing various fractions of PA12 hard blocks and PTMO soft blocks. These authors showed that the melting peak of the PA12 hard blocks increased with the copolymer content in PA12 hard blocks. Nevertheless, a comparison of the  $T_m$  of the PA12 hard blocks for copolymers with the same PDMS content for both series of copolymers (i.e., A5/B5 etc) clearly shows that it did not depend significantly upon the molar weight of the PA12 hard blocks. It might also be noted that the PA12 melting endotherm of the triblock copolymer A20 exhibited a shoulder at lower temperature (120–150°C). This observation is in good agreement with that formerly reported by Yu et al.<sup>50–52</sup> for poly(ether-*block*-amide)s (PEBA) having short soft blocks as it is also the case for the triblock copolymer A20. In that case, the multiple endotherms were ascribed to the melting of PA12 lamellae of different thickness, to crystallites of different sizes,<sup>50–52</sup> or to the presence of small and imperfect crystallites.<sup>41</sup>

During the cooling scan, all the triblock copolymers exhibited crystallization peaks of PA12 between 110

and 150°C. The DSC traces displayed in Figures 9 and 10 clearly show that the crystallization temperature  $T_c$  of the PA12 hard blocks shifted to lower temperatures as the PDMS content of the triblock copolymers increased. This effect may be ascribed to the enhanced flexibility of the copolymers by the addition of soft segments. For the triblock copolymers with the longest PDMS block (Series B), the melting heat,  $\Delta H_m$ , of the PA12 hard blocks was usually higher than that of pure PA12 in the same conditions of thermal analysis. Due to the greater immiscibility of the two phases favored by the high molecular weight of the PDMS soft block ( $M_n = 240,000 \text{ g/mol}$ ), the interface of the phase-separated domains may provide favorable nucleation sites for the hard block crystallization in good agreement with the observation formerly reported by Del'Ébra et al.<sup>39</sup> for poly(L,L-lactide)/poly( $\epsilon$ -caprolactone) blends (PLA/PCL). On the other hand, the heats of fusion and crystallization of the PA12 hard blocks for the copolymers of series A with the short PDMS soft block ( $M_n = 3100 \text{ g/mol}$ ) were much lower than those of the copolymers of Series B. This behavior can be related to the reduced length of both hard and soft blocks, which seems to hinder crystallization.

## CONCLUSIONS

A new telechelic macroinitiator for the anionic polymerization of lactams was developed in this work. This  $\alpha,\omega$ -dicarbamoyloxy caprolactam PDMS macroinitiator (macroinitiator 1) was obtained by an original synthesis scheme involving the reaction of a diisocyanate with silanol groups. This scarcely reported

reaction readily led to the new macroinitiator in two steps and quantitative yield.

This macroinitiator was then used for the successful anionic polymerization of lauryl lactam at high temperature (200°C). By adjusting the molar ratio of lauryl lactam to macroinitiator, a series of triblock copolymers PA12-*b*-PDMS-*b*-PA12 was obtained with increasing molar weights of the PA12 hard blocks. The gel points were reached within less than 25 s, which indicated high polymerization rates compatible with reactive extrusion processes.

For the sake of comparison, complementary polymerization experiments at the same temperature were also carried out with a related macroinitiator ( $\alpha,\omega$ -diacyllactam PDMS macroinitiator—macroinitiator 2), which had been initially reported for the anionic polymerization of caprolactam at a much lower temperature (80°C).<sup>11</sup> The present work shows that it was also possible to polymerize lauryl lactam in high yield even with a macroinitiator 2 of high molar weight (24,000 g/mol), therefore overcoming the limitations formerly reported for the polymerization of caprolactam at low temperature with this type of macroinitiators.

Using both types of macroinitiators eventually enabled to obtain a family of triblock copolymers with a broad range of molar weights for the PA12 blocks ( $M_n$ : ~10,800–250,000 g/mol).

The thermal properties of the triblock copolymers PA12-*b*-PDMS-*b*-PA12 were then shown to depend strongly upon their respective contents in soft and hard blocks.

A DMTA analysis showed that the triblock copolymers exhibited two distinct  $T_g$ 's, a first one at low temperature corresponding to the  $T_g$  of the PDMS soft block and a second one at high temperature corresponding to the  $T_g$  of the PA12 hard blocks. This observation indicated a high degree of phase separation between the soft and hard blocks.

A complementary DSC analysis showed that, if the  $T_m$  of the PDMS soft block was independent of the copolymer PDMS content, the PDMS crystallization occurred only for the soft block with the highest molar weight. On the other hand, the melting and crystallization properties of the PA12 hard blocks were strongly influenced by the copolymer PDMS content. In particular, the crystallization of the PA12 hard blocks was favored by increasing the size of both hard and soft blocks.

These first promising results obtained with macroinitiator 1 opened the way for the highly efficient compatibilization of PA12/PDMS blends by *in situ* synthesized triblock copolymers PA12-*b*-PDMS-*b*-PA12. The corresponding original reactive extrusion process developed in our laboratory has recently led to PA12/PDMS nanocomposites with particularly good mechanical properties.<sup>53</sup>

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