Crystalinity Behaviour in Poly(ε-caprolactone)-b-Poly(dimethylsiloxane) Diblock and Triblock Copolymers through FTIR and DSC

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Well-defined block poly(ε-caprolactone)-b-poly(dimethylsiloxane) (PCL-b-PDMS) copolymers with one or two PCL blocks were obtained via coordinated anionic polymerization of ε-caprolactone by using hydroxy terminated PDMS oligomers both as initiators and comonomers. Molecular weights of these copolymers were varied over a wide range between 7200 and 30400 g/mol and the formation of copolymers with desired backbone composition were monitored by ^1H NMR spectroscopy and SEC. DSC studies illustrated the formation of two phase morphologies, with PDMS and PCL transitions respectively and the influence of the copolymers structure on their thermal properties has been examined.

Keywords: coordinated anionic ring-opening polymerization; block copolymer; crystallization

Poly(dimethylsiloxanes) (PDMS) are extremely interesting materials since they possess unique combination of properties which are not shown by any other polymeric materials. These properties include extremely low glass transition temperatures (-120°C), very high chain flexibility, good oxidative, thermal and UV stability, hydrophobicity, biocompatibility, high gas permeability, low surface energy, high lubricity and excellent atomic oxygen plasma resistance[1,2]. Despite their many unique properties, pure PDMS are mechanically too weak to be used as a polymer and they show cold flow even at very high molecular weights (M_n = 500.000). Due to their very large volumes, low cohesive energy densities and high chain flexibility, PDMS have extremely low surface tension, surface energies and low solubility parameters and are immiscible with most organic polymers. In practice, PDMS has little use for surface modification by blending, since it tends to be rejected from the matrix. An effective way to increase the compatibility of such blends is to form copolymers of siloxanes with other polymers [3,4].

Various PDMS based block copolymers were synthesized through the reaction of hydroxy-functional PDMS oligomers with various organic monomers. Different block copolymers based on PDMS were synthesized using various methods for obtaining the second block: PDMS-b-PCL [1,5] or PDMS-b-poly(lactic acid)/poly(glycolic acid) [6] by anionic coordinated ring-opening polymerization, PDMS-b-polystyrene (PS) by anionic polymerization [7], cationic polymerization [8] or Atom Transfer Radical Polymerization (ATRP) [9], PDMS-b-poly(methyl methacrylate) by living radical polymerization [10] or ATRP [9], poly(ethylene oxide)-b-PDMS or poly(ethylene glycol)-b-PDMS through coupling reaction between end-capped PDMS and PEO or PEG[11,12], PDMS-b-poly(decyl methacrylate) by Reversible Addition Fragmentation Chain Transfer [13] or poly(butylene tereftalate)-b-PEO-b-PDMS by polycondensation [14].

Poly(ε-caprolactone) (PCL), a semicrystalline linear aliphatic polyester is a biocompatible and biodegradable polymer and is well known to be miscible with a large variety of polymers[15- 17]. Block copolymers based on PDMS and PCL combine the excellent properties of PDMS with the compatibilization effect of PCL. It makes them excellent candidates for surface modifying additives, drug encapsulation and biomaterials applications [1].

The purpose of the present work was the synthesis of a wide range of well-defined PDMS-b-PCL diblocks copolymers and their characterization using various techniques such as Nuclear Magnetic Resonance (^{1}H- NMR), Size Exclusion Chromatography (SEC), Infrared Spectroscopy (FTIR) and Differential Scanning Calorimetry (DSC).

Experimental part
Materials
ε-caprolactone (CL, 99%, Aldrich) was dried over CaH_2 and distilled under vacuum just before use. Hydroxyl terminated poly(dimethylsiloxane) (PDMS-OH, M_n = 4900, X-22-170-DX, ShinEtsu-Japan) was dried over molecular sieves (3Å). Triethyl aluminum (TEA, 0.9 M in hexane, purum, Fluka) was used without further purification. Toluene (99.5%, Fluka) was distilled over CuCl/NaOH and over sodium, and dried over molecular sieves (3Å). Nitrogen (99,998%, water ≤ 3ppm, oxygend ≤ 5ppm, packaged in lecture bottles, Merck) was used without further purification.

Syntheses
PCL-b-PDMS diblock copolymers
The polymerizations were carried out in a previously dried Schlenk tube equipped with a magnetic stirring bar under nitrogen. The tube was degassed three times by repeated vacuum/nitrogen cycles.

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For example, PCL-b-PDMS diblock copolymer (B) (4900-4900) (table 1) was synthesized as following: into a Schlenk tube were added 10 g (2.04 mmol) of hydroxyl terminated PDMS, 0.23 mL (0.204 mmol) of triethyl aluminum and 200 mL of dry toluene. The reaction mixture was stirred at 55°C, under nitrogen for 2h. Then 8.66 mL (81.6 mmol) of CL were added to the mixture, and the reaction was allowed to proceed for 2h at 55°C. Finally, 4 mL of ethyl alcohol were added for stopping the reaction and the copolymer was precipitated into heptane, filtered and dried under vacuum.

Copolymer PCL-b-PDMS (B) (4900-4900): M_n (SEC) =10100; PDI = 1,17; conversion = 100% for CL (SEC).

PCL-b-PDMS-b-PCL triblock copolymers
All the linear triblock copolymers used in this study were provided by Prof. I. Yilgor Department of Chemistry, College of Arts and Sciences, Koc University, Istanbul, Turkey.

Measurements
Nuclear Magnetic Resonance (^{1}H NMR) spectra were recorded on a 400 MHz spectrometer (Brucker AC 400) in deuterated chloroform as a solvent.

Size exclusion chromatography (SEC) was carried out using a Waters 2690 liquid chromatograph equipped with three columns, Waters Styragel 5 μm, 10^4, 500 and 100 Å columns; injection and refractometer temperature, 35°C; injection volume, 100 μL; solvent, THF at 1mL/min, a refractive index detector (Waters 410). Size exclusion chromatography was calibrated with PS standards.

Differential Scanning Calorimetry (DSC). Thermal analyses were performed with a Mettler TA 4000 differential scanning calorimeter and thermograms were recorded between –150°C and +150°C with a heating rate of 10°C/min.

Transmission Infrared Spectroscopy (FTIR). Diblocks and triblocks copolymers powders in KBr pellets were analyzed by FTIR device. Measurements were performed with an IFS48 Bruker spectrometer and the number of scans was fixed to 100 with a resolution of 4 cm^{-1}.

Results and discussions
Copolymers Syntheses
Block copolymers were prepared by coordinated anionic polymerization of CL initiated with aluminum alkoxides formed in situ by reaction of TEA with hydroxyl terminated PDMS [18] (fig. 1).

A large variety of well-defined PCL-b-PDMS diblock copolymers of different molecular weights has been obtained as given by table 1. PCL-b-PDMS-b-PCL triblock copolymers were provided by Prof. I. Yilgor Department of Chemistry, College of Arts and Sciences, Koc University, Istanbul, Turkey. ^{1}H-NMR analyses
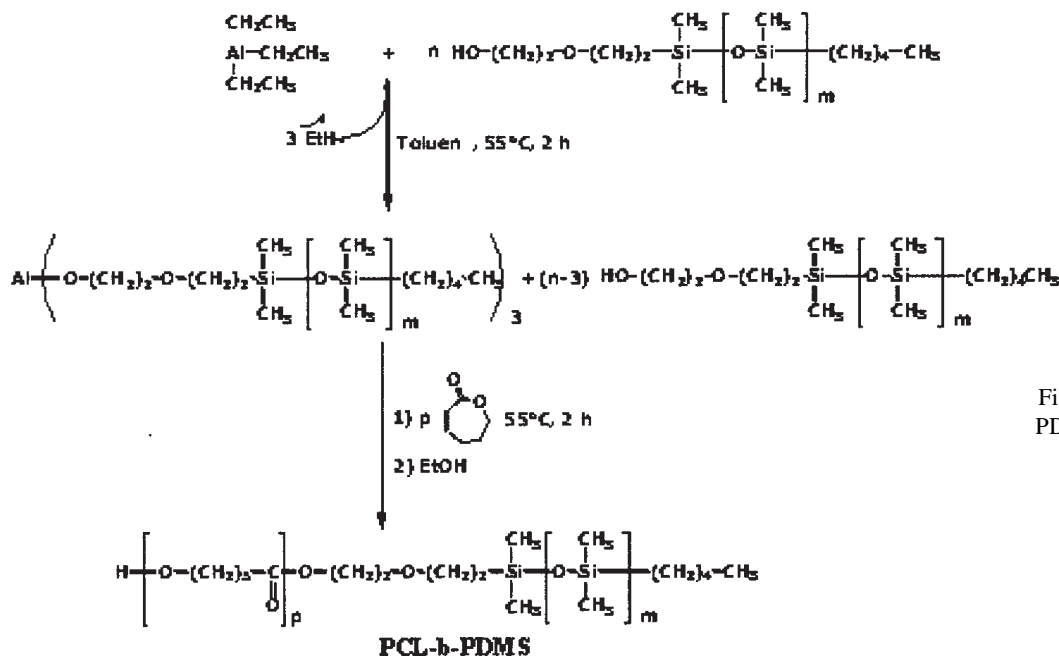

Fig.1. Synthesis of PCL-b-PDMS diblock copolymers

Table 1
CHARACTERISTICS OF THE DIFFERENT BLOCK COPOLYMERS

Sample	DP_n PCL expected	DP_n PCL obtained	M_n PCL (^{1}H-NMR)	M_n PDMS	M_n copolymers (^{1}H-NMR)	M_n copolymers (SEC)[c]	PDI
PCL-b-PDMS							
A	27,0	27,1	3100	4900 [a]	8000	13000	1,16
B	40,0	45,5	5100	4900 [a]	10100	10100	1,17
C	88,0	91,9	10500	4900 [a]	15400	15600	1,14
PCL-b-PDMS-b-PDMS							
D	52,0	52,6	6000	5000 [b]	10900	6600	1,95
E	36,0	36,7	4200	3000 [b]	7200	7900	1,81
F	178,0	178,7	20400	10000 [b]	30400	16200	1,91
G	157,0	156,8	17800	5000 [b]	22900	14700	1,76

[a] Determined by ^{1}H NMR
[b] According to Yilgor and al. [1]
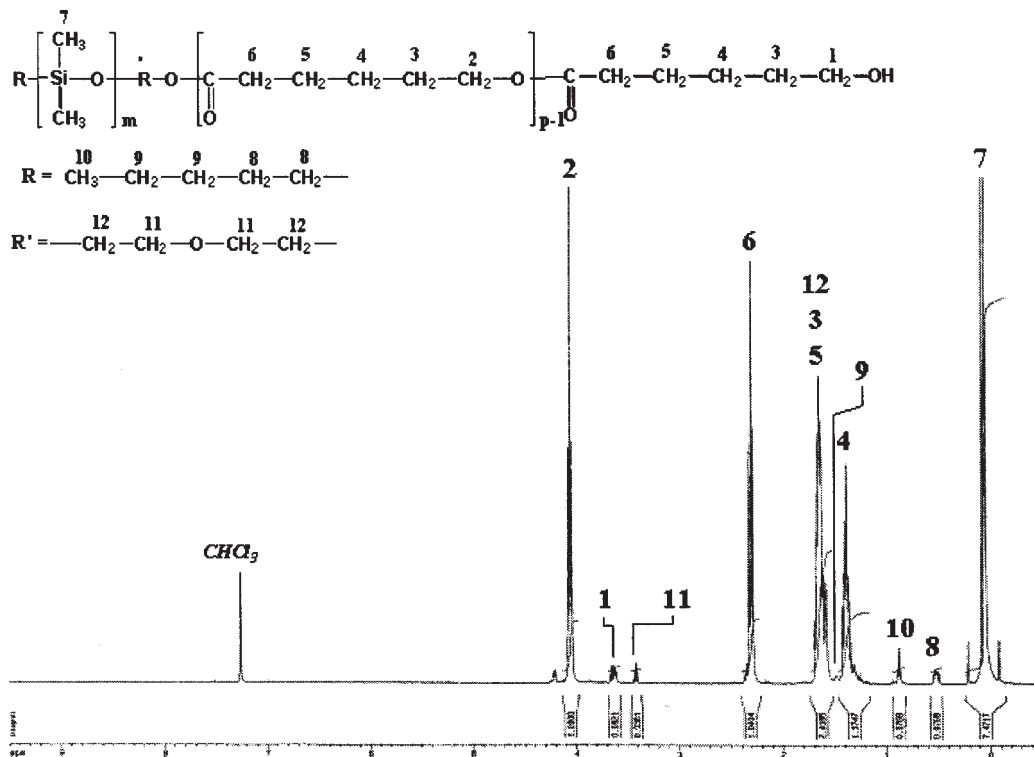[c] Determined by SEC using a PS calibration curve

Fig. 2. ¹H NMR spectrum of a PCL-b-PDMS block copolymer (A) (CDCl₃, 400 MHz)

were used to determine the molecular average number (DP_n) of the PCL block by comparing the PCL and PDMS characteristic resonance signals (I_6 and I_7 respectively) (fig.2). These DP_n are close to those expected showing a total conversion of the CL polymerization.

The attribution of peaks for the diblockcopolymer B as can be seen in figure 2 are: 1. -C$\underline{H}_2$-OH (3.63 ppm), 2. -CH₂-C$\underline{H}_2$-O- (4.06 ppm), 3. -CH₂-C$\underline{H}_2$-CH₂-O- (1.62 ppm), 4. -CO-CH₂-CH₂-C$\underline{H}_2$- (1.42 ppm), 5. -CO-CH₂-C$\underline{H}_2$- (1.62 ppm), 6. -CO-C$\underline{H}_2$- (2.30 ppm), 7. -Si (C$\underline{H}_3$)₂- (0.07 ppm), 8. -CH₂-C$\underline{H}_2$-CH₂- (0.53 ppm), 9. CH₃-C$\underline{H}_2$- (1.48 ppm), 10. C$\underline{H}_3$-CH₂- (0.88 ppm), 11. -C$\underline{H}_2$-O- (3.42 ppm), 12. -Si-C$\underline{H}_2$-(1.62 ppm).

The synthesis of well-defined copolymers was confirmed by the SEC monomodal chromatogram and by the weak values of polydispersity index (PDI). For all copolymers we did not notice the presence of residual PDMS homopolymer, showing the total initiation from the PDMS precursor (fig.3).
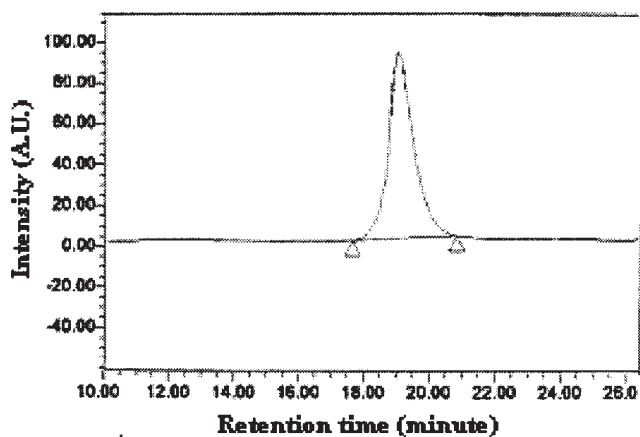

Fig. 3. SEC chromatogram of a PCL-b-PDMS block copolymer (B) [Ret. Time (min) 19.554, Mn (Daltons) 10112, Mw (Daltons) 11871, Polydispersity 1.173960]

Triblock copolymers were obtained from dihydroxyl terminated PDMS using tin octoate as catalyst instead of TEA [1]. Larger molecular weight distributions were obtained for these copolymers. These results are far from being surprising concerning the presence of tin octoate which is known to act both as ring-opening polymerization initiator and ester interchange catalyst [19].

Infrared analyses

Blockcopolymers (diblock and triblock) in KBr pellets were analyzed as well as pure PCL and PDMS homopolymers in order to correlate the resulting signals with the composition of the corresponding sample. In figure 4 we compare the infrared spectra obtained in the transmission mode for PCL and PDMS homopolymers as well as for one of the PCL-b-PDMS diblock copolymer (B).

On the basis of figure 4, we can describe the infrared response of each polymer. For the PCL homopolymer we can identify its characteristic bands such as the carbonyl stretching mode around 1727 cm⁻¹, the asymmetric and symmetric CH₂ stretching mode at 2949 and 2865 cm⁻¹, as well as the C-O and C-C stretching mode in the crystalline and amorphous phases respectively at 1293 and 1157 cm⁻¹[15, 20-24]. We should highlight the fact that the important intensity of the crystalline band at 1293 cm⁻¹ is in good agreement with the high crystallinity degree (77%) of the PCL homopolymer calculated from DSC.

For the PDMS homopolymer the FTIR spectrum shows that all bands typically related to siloxanes are present. The bands at 2906 and 2962 cm⁻¹ are assigned to symmetric and asymmetric CH₃ stretching modes, respectively. The strong band around 786 cm⁻¹ is assigned to the CH₃ rocking mode. Strong absorption at 1257cm⁻¹ is due to the Si(CH₃) symmetric bending mode. Two adjacent bands located around 1009 and 1079 cm⁻¹ are assigned to the backbone Si-O-Si stretching absorption [25].
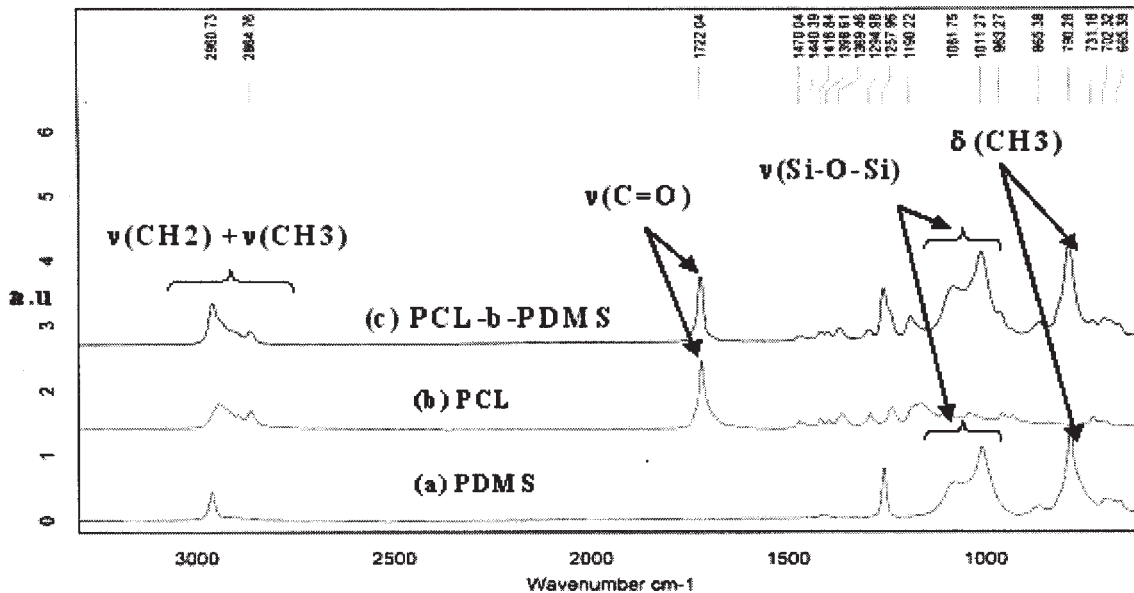
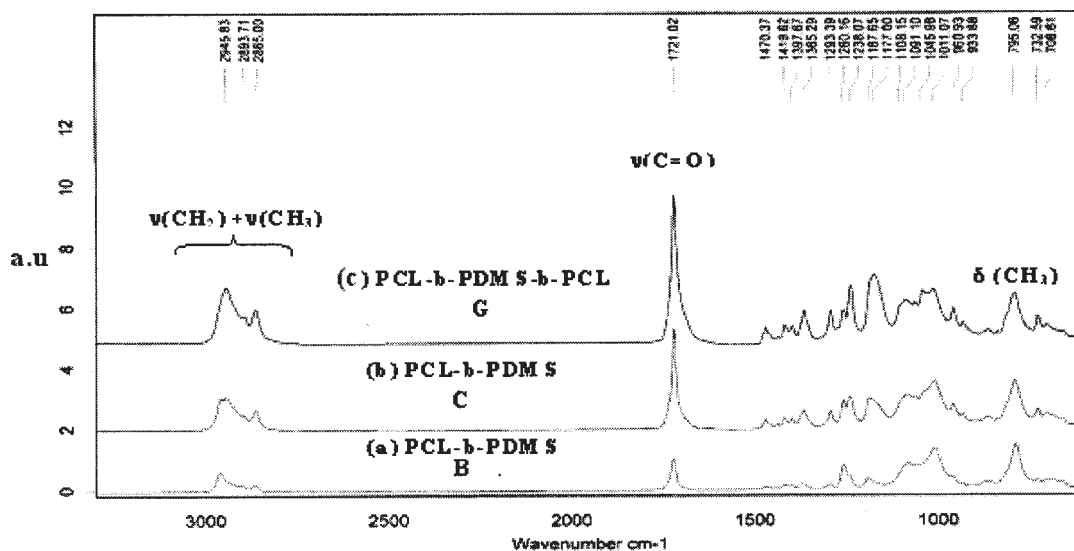Fig. 4. FTIR spectra for PDMS (a), PCL (b), and PCL-b-PDMS (B) (c)

Fig. 5. FTIR spectra for PCL-b-PDMS diblocks (B) (a) and (C) (b) and PCL-b-PDMS-b-PCL triblock (G) (c)

Table 2
MELTING TEMPERATURES (Tm), ENTHALPIES (ΔHm) AND CRISTALLINITY CONTENT (Xc)
OF PCL AND PDMS HOMOPOLYMERS AND SYNTHESIZED COPOLYMERS

Sample	Tm PDMS (°C)	Tm PCL (°C)	ΔHm PDMS	ΔHm PCL	% PCL (w/w)	% PDMS (w/w)	Xc PDMS (%)	Xc PCL (%)
PDMS	-124.5	-	15,2	-			24.0	-
PCL	-	60	-	109.8			-	77.3
PCL-b-PDMS								
A	- 48.5	58.3	33.3	116.5	38.7	61.3	52.5	82.0
B	- 42.9	61.9	35.4	111.2	51.0	49.0	55.8	78.3
C	- 48.8	62.8	7.3	113.0	68.2	31.8	11.5	79.6
PCL-b-PDMS-b-PCL								
D	- 43.5	64.6	14.9	130.8	54.5	45.5	23.5	92.1
E	- 46.6	63.7	5.8	121.1	58.3	41.7	9.1	85.3
F	- 40.7	64.3	30.0	118.6	67.1	32.9	47.3	83.6
G	- 40.1	59.0	24.3	113.9	78.1	21.9	38.4	80.2

Before analyzing the PCL-b-PDMS (B) copolymer spectrum we should mention that for all the other compositions the same global shape is observed but with different bands intensities due to the composition as well as to the crystallinity degree in the various samples. As it can be seen in figure 4, the diblock FTIR spectrum is somehow the summation of the PCL and PDMS spectra since the characteristic bands of each polymer are present. That was already predicted since the formation of the diblock structure is already confirmed. The correspondence between the composition and the bands

A

PDMS block   PCL block

(thermogram A with illegible annotation values)

B

PDMS block   PCL block
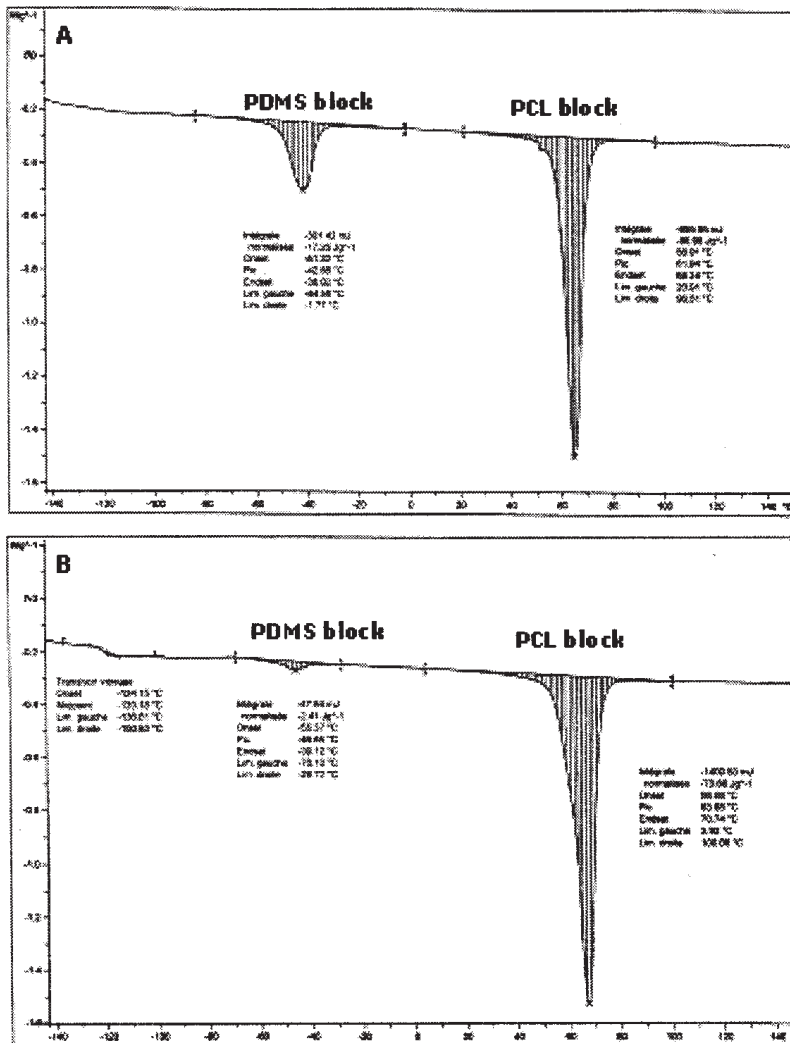
(thermogram B with illegible annotation values)

Fig. 6. Characteristic thermograms for PCL-b-PDMS diblock copolymer B (A) and (B) PCL-b-PDMS-b-PCL triblock copolymer E

intensity should be easily revealed when comparing various diblock and triblock spectra as shown in figure 5.

Regarding figure 5, we can clearly observe that the intensity of PCL bands such as the C=O stretching mode one (at 1722 cm^{-1}) normalized to a PDMS one such as the CH$_3$ deformation mode around 786 cm^{-1} on the diblock and triblock spectra reveals the composition evolution between the different samples: the ν(C=O) band intensity increases with the increasing weight percentage of the PCL block in the copolymer (table 2).

DSC analyses

Thermal properties of PCL-b-PDMS copolymers (diblock and triblock) were determined by conventional differential scanning calorimetry (DSC), using a Mettler Toledo DSC 822 apparatus. 10 mg polymer samples are heated from –150°C to 150°C at a scanning rate of 10°C.min^{-1}. A representative thermogram is given in figure 6.

Characteristic endotherms are observed, corresponding to the melting temperature of PDMS blocks (low temperature peak) and PCL blocks (high temperature peak) in the copolymers. The integrated area of the melting peak over the sample mass in PDMS or PCL blocks, gives rise to the melting enthalpy of the respective blocks and to the cristallinity content of PCL and PDMS within the copolymers. Thermodynamic melting enthalpies of perfect (100%) crystals were taken equal to 142 for PCL and 63.4 J.g^{-1} for PDMS [12,15].

In table 2 we have reported the melting temperatures, the melting enthalpy and the cristallinity content of PDMS and PCL blocks in the copolymer. Values for pure PDMS and PCL homopolymers are also indicated, as reference values. Let's first consider melting temperatures of both blocks. It appears that melting temperature of PDMS is lowered in copolymers compared to the pure homopolymer. This could be explained by the fact that PDMS is a very flexible polymer with high chain mobility and thus its ability to crystallize is hindered by the presence of PCL blocks. More surprising is the fact that, especially for triblocks copolymers, the melting temperature of PDMS decreases as the mass weight of PDMS increases in the copolymer (-47,7°C for PCL-b-PDMS-b-PCL **D** to –40°C for PCL-b-PDMS-b-PCL **G**). This means that lamellar thicknesses in PDMS crystals are affected by the presence of PCL blocks.

At this point, three main facts should be considered. First, melting temperature of PDMS chains is lowered due to the presence of PCL blocks. Second, on the contrary, organization of PCL chains is favoured, as their melting temperature increases relative to the homopolymer even if rather constant whatever is PCL content. Third, cristallinity content of PCL is strongly affected and increases in proportion with PDMS amount.

These three main facts suggest unambiguously that PDMS chains play a major role in the cristallization of PCL blocks. More precisely, PDMS acts as a co-crystallizing agent for PCL chains. This hypothesis is supported by the fact that the melting enthalpy of PCL blocks is always greater than the melting enthalpy of

PCL homopolymers. However, a detailed study of the cristallization of our copolymers will be the subject of a separate paper.

Conclusions

Controlled syntheses of block poly(ε-caprolactone)-b-poly(dimethylsiloxane) copolymers were realized. These copolymers were obtained via ring-opening polymerization of cyclic ε-caprolactone by using hydroxyl terminated PDMS oligomers as initiators and comonomers. Formation of desired structures was confirmed by ¹H-NMR spectroscopy and SEC analyses. The copolymers obtained displayed two-enthalpy fusion relative to PDMS and PCL blocks polymers. Important facts were observed concerning the PCL cristallization evolution as a function of the PDMS content in these copolymers.

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