

Poly(bisphenol A carbonate)–poly(dimethylsiloxane) multiblock copolymers

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Abstract

A versatile technique for the synthesis of multiblock copolymers of polydimethylsiloxane (PDMS) and poly(bisphenol A carbonate) (PC) is described. Specific reaction of the phenol end groups of α,ω -bis(bisphenol A)-terminated PDMS with the activated end groups of α,ω -bis(*ortho*-nitrophenylcarbonate)-endcapped PC yields PC–PDMS multiblock copolymers and *ortho*-nitrophenol. The morphology and influence of crystallization of the polycarbonate blocks is studied using solution-cast films. When THF is used as casting solvent instead of chloroform, the crystallinity of the PC blocks increases resulting in smaller domain spacings as measured by Small Angle X-ray Scattering (SAXS) and the solution-cast film has a lower strain to failure as measured by tensile testing. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Polycarbonate; Poly(dimethylsiloxane); Block copolymers

1. Introduction

Block copolymers based on poly(bisphenol A carbonate) (PC) and polydimethylsiloxane (PDMS) provide elastomeric products with excellent toughness at low temperatures. Due to the microphase separation of the soft siloxane blocks and the hard polycarbonate blocks, these materials can be regarded as thermoplastic elastomers (TPEs). The most common synthetic procedure for obtaining these block copolymers involves the reaction between phosgene and bisphenol acetone (BPA) in the presence of BPA-terminated polysiloxanes, as introduced by Vaugh [1–5]. The latter polymers are synthesized via a Lewis-acid-catalyzed equilibration of dimethyldichlorosilane with octamethylcyclotetrasiloxane, yielding a chloro-terminated siloxane, which is phenol-terminated upon reaction with excess BPA in the presence of an acid scavenger, e.g. pyridine [6]. Based on the initial work of Vaugh, new synthetic procedures were developed for such PC–PDMS block copolymers and their properties are studied to a large extent [7–26]. The majority of the previously reported routes for the synthesis of PC–PDMS copolymers

involve a reaction of a modified PDMS reacting as nucleophile, with phosgene and BPA [7], cyclic carbonates [22] or PC. However, due to side-reactions occurring in most of these synthetic procedures, which result in chain extension of the siloxane blocks or chain cleavage of the polycarbonate blocks, the block lengths are rather polydisperse. The extent of microphase separation between the hard and the flexible segments is significantly influenced by the sequential distribution of the various species [6].

The transesterification reaction of a phenol with a carbonate unit is well-known in the synthesis of PC using the melt reaction of diphenylcarbonate and BPA at high temperature in the presence of a base as catalyst [28–30]. Phenol is produced as a condensation by-product and must be removed to facilitate the chain growth reaction. Generally, the preparation of high molecular weight polycarbonate with activated chain ends [31], or with phenolic chain ends is rather difficult, and requires a specific synthetic procedure. As confirmed by experiments in our laboratories, depolymerization (chain cleavage) readily occurs, e.g. the transesterification reaction of BPA with PC under the action of a base, like 4-dimethylaminopyridine (DMAP), yields low molecular weight oligomers.

To prevent the reacting phenol-terminated polymer from reaction with the internal carbonate units, we activated the carbonate group at the end groups of the polycarbonate

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by using *ortho*-nitrophenylcarbonate-terminated PC, as prepared by Brunelle. Previously, Brunelle [31] showed that *ortho*-nitrophenylcarbonates can give a fast transesterification upon reaction with BPA under the action of a basic catalyst. This transesterification reaction affords an efficient formation of polycarbonates at or below ambient temperatures. Polycarbonates with the same *ortho*-nitrophenylcarbonate incorporated as end group can be used as well to favour the reaction of a nucleophile preferentially at those activated end groups. In particular, we studied the reaction of BPA-terminated polysiloxanes with *ortho*-nitrophenylcarbonate end group activated PC, yielding pure PC–PDMS multiblock copolymers. The occurrence of less side-reactions, which affect the block lengths in the obtained copolymer, results in a more distinct microphase separation of the soft PDMS and hard PC blocks. This is the basis for a more facile characterization of the morphology obtained. The influence of crystallization of the PC blocks on the morphology and stress–strain behaviour was investigated. In other reports about PC–PDMS copolymers [11,23], crystallization of the polycarbonate blocks could be detected as well.

2. Experimental

2.1. Materials

α,ω -Bis(*ortho*-nitrophenylcarbonate)-terminated PC was prepared by P. Phelps and D. Brunelle, General Electric Corporate Research and Development in Schenectady, NY, USA. α,ω -Bis(bisphenol acetone)-terminated PDMS was prepared by the reaction of α,ω -bis(chloro)-terminated polysiloxane with an excess of BPA according to a literature procedure [5,6]. All other chemicals were obtained commercially and used without further purification.

2.2. Techniques

The ^1H NMR spectra were recorded using a Bruker AM 400 spectrometer (^1H : 400.13 MHz). δ values are given in ppm relative to TMS, but were referenced to residual CHCl_3 at 7.27 ppm when siloxanes were present in the sample. X-ray diffraction patterns of copolymers were taken using CuK_α radiation and a multi-wire area detector X-1000 coupled with a graphite monochromator. Small Angle X-ray Scattering (SAXS) studies were performed using a Rigaku Denki small angle goniometer. Transmission Electron Microscopy (JEOL 2000-FX) was operated at 80 kV. The TEM-coups (approximately 80 nm) were cut in a direction perpendicular to the plain of the solvent-cast film with a diamond knife at -122°C . No additional staining was applied. Tensile testing of solution-cast films was performed at room temperature using a Zwick 1445 tensile tester. Testing specimen with a length of 20 mm, width of 5 mm and thickness of ca. 1 mm were tested using a DIN 53455 tensile test and a testing speed of 5 mm/min.

2.3. Synthesis of α,ω -bis(*ortho*-nitrophenylcarbonate)-terminated poly(bisphenol A carbonate)

A 5 neck 1 l morton flask equipped with mechanical stirrer, pH electrode, phosgene dip tube, caustic addition port and a chilled brine condenser vented to a phosgene scrubber was charged with BPA (68.4 g, 0.30 mol), dichloromethane (400 ml), water (100 ml) and 1 ml of a aqueous 75% methyltributylammonium chloride solution (0.003 mol). Phosgene was added at 2.00 g/min while pH maintained at ~ 8 by addition of a 50 wt% aqueous NaOH solution. After phosgenation was complete, the pH was trimmed to 11.0 and 0.012 mol of *ortho*-nitrophenol was added, producing a dark orange colour that quickly disappeared as the carbonates are formed. Next 1.0 ml of trimethylamine was added and the pH was kept > 11 , until all chloroformates were gone. At this time the reaction mixture was slightly yellow again so another 2.0 g of phosgene was added to consume any phenolics in solution. In total 63 g of a 50 wt% NaOH solution was required. The polycarbonate was isolated by washing the organic phase, twice with 1 M HCl solution and three times with water. The washed organic layer (~ 0.5 l) was added to 1 l methanol in a blender, then another 1 l of methanol was added. The solid was collected on a filter and returned to the blender, where it was mixed with 2 l water. The polymer was collected and dried in vacuum at 110°C . ^1H NMR (400 MHz, CDCl_3): δ 8.17 (d, 2H, $J = 8.2$ Hz, arom. C–H end group *meta* towards carbonyl, *ortho* towards nitro) 7.70 (t, 2H, $J = 7.8$ Hz, arom. C–H end group *meta* towards carbonyl, *para* towards nitro) $\bar{M}_n = 14.2$ kg mol $^{-1}$ (according to ^1H NMR). SEC (eluent = THF 40°C , RI detection): uncorrected molecular weights using polystyrene standards $\bar{M}_n = 19.1$ kg mol $^{-1}$, $D = 2.75$.

2.4. Synthesis of the α,ω -bis(BPA)-terminated PDMS

The α,ω -bis(BPA)-terminated PDMS was prepared according to a literature procedure [5,6]. ^1H NMR (400 MHz, CDCl_3): δ 1.63 (s, 12H, CH_3 of BPA end groups), 6.72 (d, 4H, $J = 8.7$ Hz, arom. C–H of BPA end groups, *ortho* towards hydroxyl), 6.79 (d, 4H, $J = 8.7$ Hz, arom. C–H of BPA end groups, *orthotowards* carbonate), 7.08 (m, 8H, arom. C–H of BPA end groups, *ortho* towards isopropylidene unit). $\bar{M}_n = 7.81$ kg mol $^{-1}$ (according to ^1H NMR).

2.5. Synthesis of PC–PDMS multiblock copolymer

α,ω -Bis(*ortho*-nitrophenylcarbonate)-terminated PC (28.89 g, 2.04 mmol) was dissolved in 800 ml chloroform at room temperature. Subsequently were added, α,ω -bis(BPA)-terminated PDMS (15.93 g, 2.04 mmol) and DMAP (0.32 g, 2.62 mmol). Upon reaction the colourless solution turns yellow upon reaction. After stirring for 1 day at room temperature, the reaction mixture was precipitated in methanol (10 l) The obtained polymer was dried in

vacuum oven at 70°C. Yield: >95%. SEC (eluent = THF 40°C, RI detection): uncorrected molecular weights using polystyrene standards $\bar{M}_n = 39.5 \text{ kg mol}^{-1}$, $D = 2.16$. Solution-cast films were prepared from 10 wt% solutions in THF or chloroform. Films were dried in a vacuum oven during 1 day at 160°C to eliminate all residual solvent.

3. Results and discussion

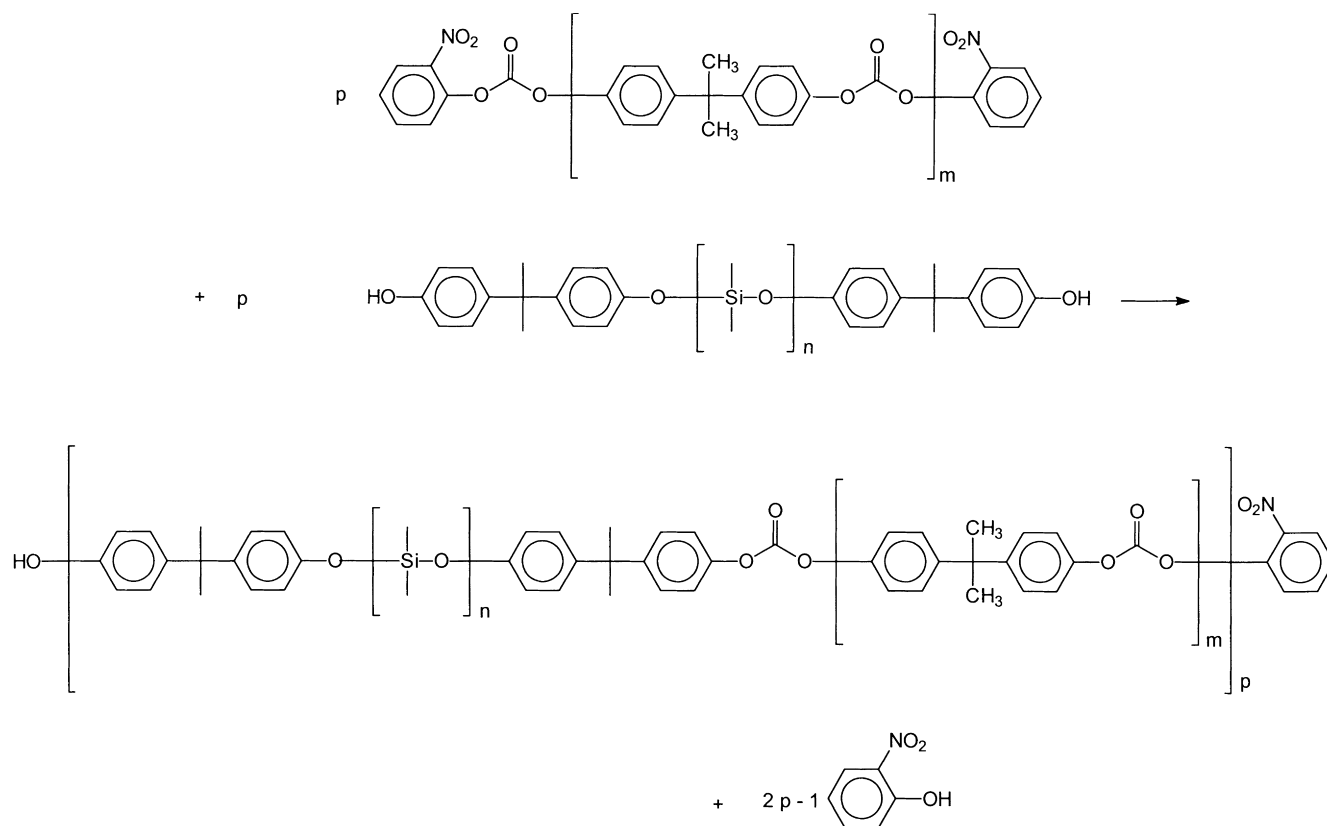
A new method is described for the preparation of PC–PDMS copolymers using a polycarbonate telechelics possessing activated end groups. Due to the presence of the activated end groups a selective reaction can be obtained only at the end groups. In similar methods described to produce PC–PDMS block copolymers usually no selectivity is obtained and depolymerization of the PC block might occur when internal carbonate groups are attacked by a nucleophile. An example of such a blockcopolymer synthesis is described by Mie [32]. In this work an amino-propyl terminated PDMS was reacted with phosgene and BPA. The amino group is able to react with every in-situ formed carbonate group. Therefore reaction of the amino terminated PDMS with the in-situ formed PC leads to poly-disperse blocks.

In our case we have predominantly reaction at the chain ends, and will therefore hardly affect the polydispersity of

the starting telechelic PC. To obtain the optimal selectivity we also reacted the polymer reactants in equimolar amounts. In conclusion, the objective of this work was to evaluate a novel efficient synthetic method for the preparation of PC–PDMS block copolymers. The elegance of the employed reaction strategy is the easiness of the block copolymer formation, which is performed using a one-pot synthesis at room temperature.

The transesterification reaction of a phenol with the nitrophenyl carbonate end group can be used for the preparation of PC-block copolymers. We now require a phenol-terminated polymer, instead of a low molecular weight phenol, which preferentially has free *ortho*-positions. We studied the formation of block copolymers using BPA-terminated polysiloxanes in a reaction with *ortho*-nitrophenylcarbonate-encapped PC, as presented in Scheme 1 (Synthesis PC–PDMS multiblock copolymers). *Ortho*-nitrophenyl carbonate encapped PC can be prepared by copolymerization of BPA and phosgene with *ortho*-nitrophenol. We reacted the modified PDMS and activated PC, both dissolved in chloroform, under the action of DMAP. The occurring reaction is visualized by the formation of *ortho*-nitrophenol, which coloured the reaction mixture orange.

We studied the microphase segregation of the hard PC and soft PDMS block using Transmission Electron Microscopy (TEM) of cryosections of solution-cast films. The PC–PDMS copolymer dissolves easily in chloroform at



Scheme 1. Synthesis PC–PDMS multiblock copolymers.

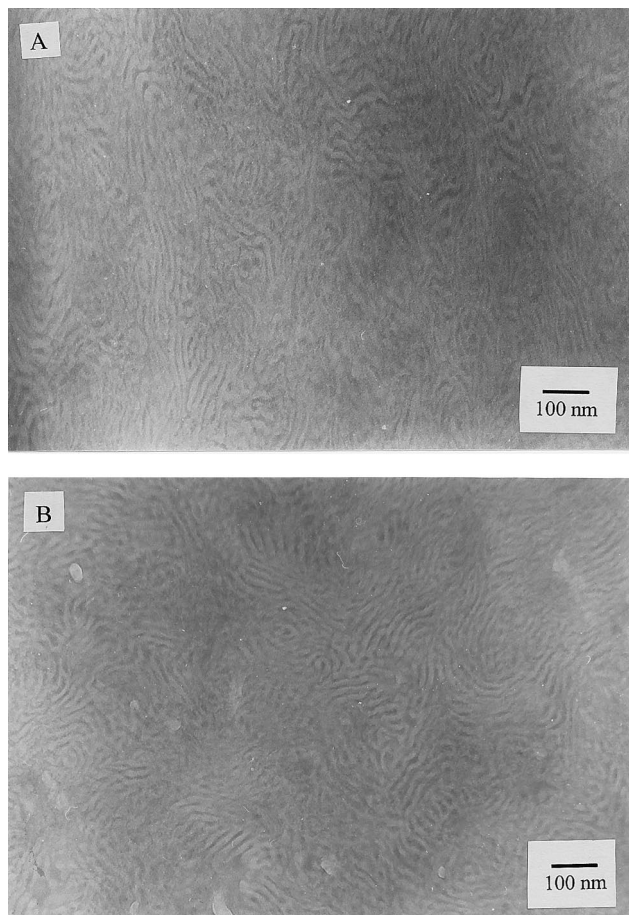


Fig. 1. TEM-pictures of solution-cast film of PC-PDMS copolymers: (A) cast from THF; and (B) cast from CHCl_3 .

room temperature, while dissolving in THF requires elevated temperatures (50°C). TEM-micrographs of copolymer films, cast either from THF or CHCl_3 , showed similar morphologies as presented in Fig. 1. The dark regions represent the PDMS phase, which has a higher electron density [38] caused by the presence of Si-atoms with high atomic number. The light areas represent the PC phase. From the volume ratios of PC towards PDMS we could expect a mixed morphology with predominantly lamellar structures and some cylindrical regions. The blockcopolymer has the following polymer volume ratios: 59.4% (v/v) PC and 40.6% (v/v) PDMS. The ratio between lamellar and cylindrical structures are different in films obtained from casting either from THF or chloroform. This is a result of the crystallization of the PC blocks as observed in case of the THF casted films. Due to the crystallization of the PC block the volume ratio PC/PDMS shifts to a more lamellar structure with a 50/50 polymer volume ratio for the THF casted film. However, from the TEM-micrographs it appears that even in the case of films obtained from chloroform lamellar morphology is predominant. Furthermore a relatively wider spread in lamellar thickness can also be observed. The wider spread in lamellar thickness can be associated

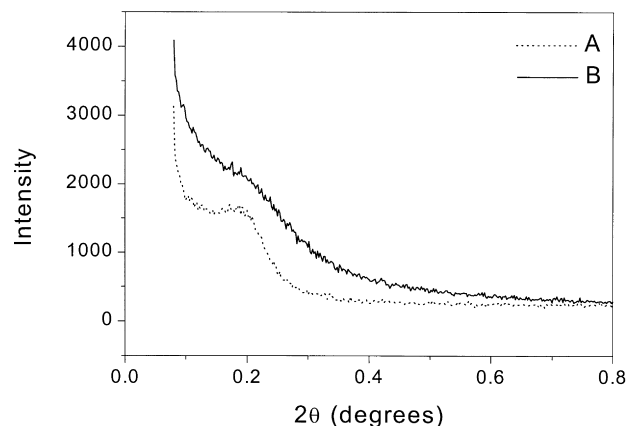


Fig. 2. SAXS-results of PC-PDMS copolymer film, intensity as a function of scattering angle (2θ): (A) cast from CHCl_3 ; and (B) cast from THF.

to polydispersity as well as partial crystallization in THF casted films.

Due to the microphase separation in the block copolymer, the SAXS-analysis shows a single reflection. The absence of higher orders of reflections is a consequence of a wider spread in lamellar thickness and the absence of regular stacking of lamella. In this respect the SAXS-pattern is in agreement with the TEM-micrographs. The position of the SAXS-reflection corresponds to an average distance of PC and PDMS phases. A clearer reflection is shown in a Lorentz-corrected plot, in which the $I s^2$ is plotted as a function of s , where s represents the scattering vector (s) and I the scattering intensity (I). The scattering vector is defined as the reciprocal value of the distance (d). Fig. 2 shows the intensity profile of the solution-cast films of the prepared block copolymer, whereas Fig. 3 shows the corresponding Lorentz-corrected plots. The PC-PDMS film cast from THF shows a reflection at larger scattering angle (2θ) in the intensity profile and at larger scattering vector (s) in the Lorentz-corrected plot, corresponding to a smaller domain spacing (d). From the Lorentz-corrected plots a domain spacing of $424 \pm 10 \text{ \AA}$ could be determined for a copolymer cast film from chloroform, while a copolymer film cast from THF shows a domain spacing of $371 \pm 20 \text{ \AA}$. This difference in domain spacings can be explained by a difference in density [33] due to a difference in crystallinity, which will be shown by Wide Angle X-ray Scattering (WAXS) studies in this paper. Furthermore, the reflection peak from the cast film from THF is broader due to a decrease in electron density difference between the PC phase and PDMS phase. This decrease in electron density is caused by a higher density of crystalline PC ($\rho_c = 1.31 \times 10^3 \text{ kg/m}^3$) [33,36] in comparison with amorphous PC ($\rho_a = 1.20 \times 10^3 \text{ kg/m}^3$).

The determined domain distances can be compared with distances theoretically predicted from the polymer molecular weights. If we assume that Gaussian chain statistics can be utilized and that the average block length only depends on block molecular weight, then we can estimate the domain

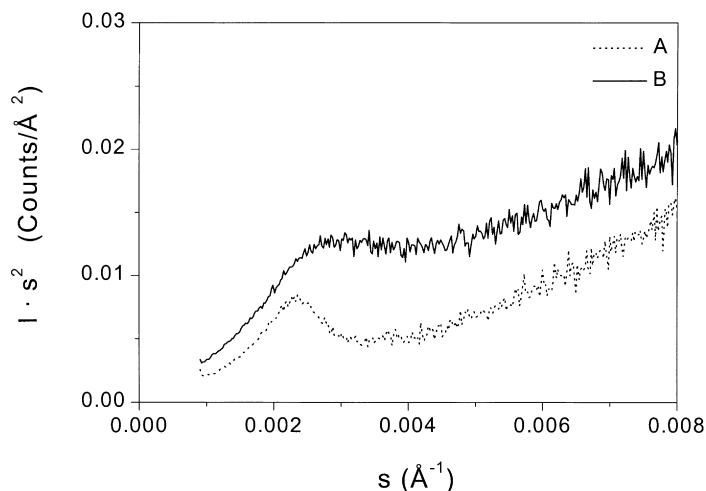


Fig. 3. SAXS-results of a PC–PDMS copolymer film, Lorentz corrected plot: (A) cast from CHCl_3 ; and (B) cast from THF.

spacings by calculation of the unperturbed chain dimensions of the PC and PDMS blocks [34]. The root mean square unperturbed end-to-end distance for PDMS chains can be expressed as: $(\langle R_0^2 \rangle)^{1/2} = (6.3nl^2)^{1/2}$, where $l = 1.64 \text{ \AA}$ and n is the number of Si–O bonds [35]. For PC chains, the unperturbed chain dimensions can be calculated using the equation: $(\langle R_0^2 \rangle)^{1/2} = (3.55nl^2)^{1/2}$. In our calculations, we used $l = 7.01 \text{ \AA}$, corresponding with the distance from the carbonyl to the isopropylidene unit [36,37]. We calculated the unperturbed end-to-end distance for the PDMS block ($\bar{M}_n = 7.8 \text{ kg/mol}$, $n = 210.6$) as 59.7 \AA and for the PC block ($\bar{M}_n = 14.2 \text{ kg/mol}$, $n = 104.9$) as 135.3 \AA . For the less crystalline block copolymer cast from chloroform, we determined a domain spacing of 424 \AA using SAXS. Calculation of the domain spacings via the unperturbed chain dimensions results in smaller distances. Similar discrepancies were found for PDMS–PS multiblock copolymers [38]. The higher value obtained by SAXS can be caused by

deviation of the characteristic ratio (i.e. 6.3 for PDMS and 3.55 for PC) for lower molecular weights. The larger chain dimensions as measured by SAXS can be caused as well by a chain extension near the junction points in the block copolymer and mobility restriction due to linkage of the different blocks. Consequently these chains cannot be considered as unperturbed chains following the Gaussian approximation. It is obvious that in strongly segregating polymers the domain size is greater than the radius of gyration. Determination of an exact scaling factor to see whether the expected $2/3$ scaling factor is also valid in this system requires a study using various blockcopolymers possessing different blocklengths.

This difference in domain spacings between the two samples cast from different solvents obtained by SAXS can be due to a difference in crystallinity. Therefore, we extended our investigation with Differential Scanning Calorimetry (DSC) and WAXS. Poly(bisphenol A carbonate) is known

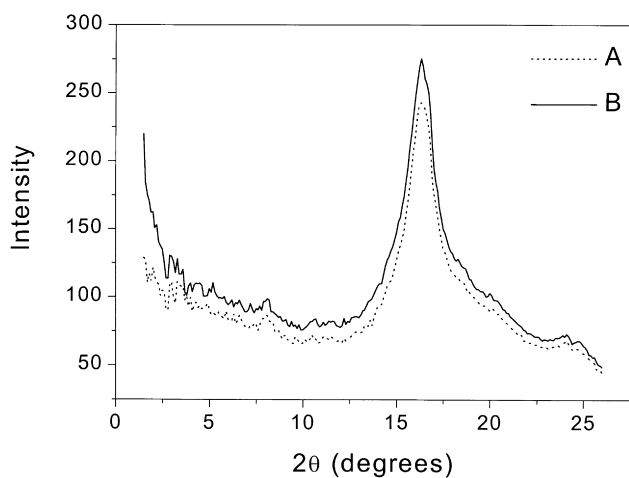


Fig. 4. WAXS-patterns of solution-cast PC films: (A) cast from CHCl_3 ; and (B) cast from THF.

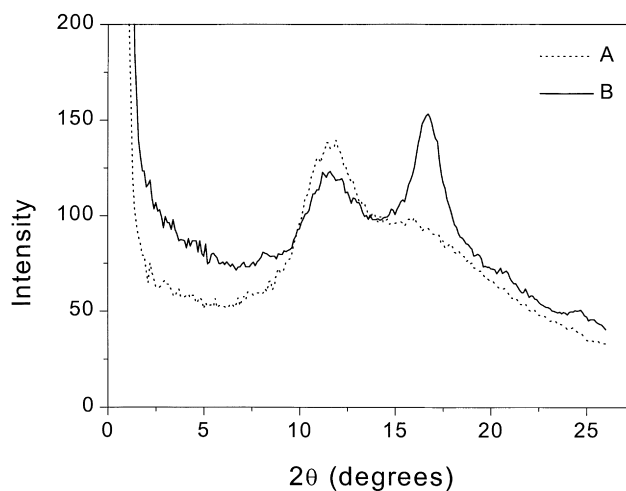


Fig. 5. WAXS patterns of solution-cast PC–PDMS copolymer films: (A) cast from CHCl_3 ; and (B) cast from THF.

Table 1
DSC results of solution-cast films

	Parameters phase transitions	PC cast from THF		PC cast from CHCl ₃		PC-PDMS cast from THF		PC-PDMS cast from CHCl ₃		
		<i>T_g</i> (°C)	ΔC_p (J/g K)	<i>T_m</i> (°C)	ΔH (J/g)	% Cryst.	<i>T_g</i> (°C)	ΔC_p (J/g K)	<i>T_g</i> (°C)	ΔC_p (J/g K)
1st Heating run 20 K/min		148.9	0.076	224.0	21.68	19.8	154.7	0.036	211.7	4.43
					22.54	20.6	155.2	0.027	216.7	10.9
										6.3
2nd Heating run 20 K/min		144.3	0.169	146.2	150.0	0.099	151.8	0.041		

Table 2

Stress-strain behaviour PC homopolymer and PC-PDMS copolymer cast films

Material films	Casting solvent	<i>E</i> (N/mm ²)	ϵ (%)
PC	CHCl ₃	1930 ± 20	0.7 ± 0.2
PC	THF	1150 ± 10	0.3 ± 0.1
PC-PDMS	CHCl ₃	570 ± 10	96 ± 5
PC-PDMS	THF	580 ± 10	19 ± 5

to crystallize slowly from the melt [39]. Much faster rates of crystallization may be obtained by solvent-induced crystallization [40–42], vapor-induced crystallization [43,44] or nucleation using organic salts [45,46]. PC crystallization using a non-solvent like acetone is well-known [47]. However, PC crystallization using solution casting from a good solvent, like chloroform, or from poor solvents, like THF [40], has only been studied to a limited extent. Therefore, we studied also crystallization of the PC homopolymer, as a comparison to the crystallization in the PC-PDMS block copolymers.

We used WAXS and DSC to obtain information about respectively the crystal lattice size of the semi-crystalline PC blocks in the PC-PDMS block copolymer and the degree of crystallinity [47]. If the starting PC homopolymer is slowly cast from THF or chloroform, crystallization occurs, which yields a sharp peak in the WAXS pattern as shown in Fig. 4. When the PC-PDMS film is prepared by solution casting, a more pronounced crystallization occurs in film cast from THF. During evaporation of the solvent, chain collapse and aggregation can occur when the polymer solution becomes more concentrated [27]. This chain collapse and aggregation can induce crystallization. In films prepared from THF the crystallization is more pronounced, probably caused by the low solubility of the PC blocks in THF, in comparison with CHCl₃. The crystallization can start already during aggregation in concentrated solutions or is enhanced by the microphase separation of the PC and PDMS blocks in the solid polymer film. Fig. 5 shows the WAXS patterns of the PC-PDMS copolymer, cast either from THF or CHCl₃. A sharp reflection is detected in the wide-angle area for the crystalline PC ($2\theta = 11.7^\circ$), besides the reflection corresponding to the interchain distance of the PDMS ($2\theta = 16.7^\circ$). These WAXS results are consistent with the DSC results as shown in Table 1. The melting peak of crystalline PC is only detected in the first heating run using DSC, which is in agreement with the slow melt crystallization rates. Crystallinities are calculated using $\Delta H_0 = 109.6$ J/g (26.2 cal/g) as reported by Mercier [47]. The presence of more crystallinity in the copolymer films in combination with smaller domain spacings as determined by SAXS in films prepared from THF solutions in comparison with films prepared from CHCl₃ can be explained by a higher density in crystalline PC [33]. However, more research is required to predict whether folded-chain or extended-chain crystallization dominates in these block copolymers.

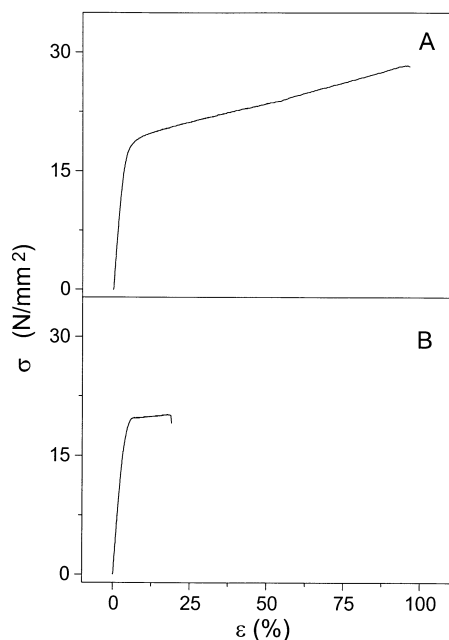


Fig. 6. Stress–strain behaviour of solution-cast PC–PDMS copolymer films: (A) cast from CHCl_3 ; and (B) cast from THF.

The crystallization of the PC is also reflected in the stress–strain behaviour. If crystallization takes place, disentanglement can occur in these relatively low molar mass polymers. This brittle fracture at low strain is especially observed in tensile test of the homopolymer PC films. Introducing elastomeric PDMS blocks yields a higher strain at break, especially for copolymers cast from chloroform with very low crystallinity. The obtained tensile testing results are summarized in Table 2. A typical stress–strain curve of a PC–PDMS copolymer cast-film is shown in Fig. 6. The film cast from THF shows a lower strain, essentially because of its higher crystallinity. Besides the difference in crystallinity, the variation in mechanical properties could be caused by a difference in development of the morphology during the solvent-casting.

4. Conclusions

A new strategy is described for the preparation of PC–PDMS multiblock copolymers with well-defined block length. For this purpose PC with *ortho*-nitrophenylcarbonate activated end groups was reacted with bis(bisphenol A)-terminated PDMS. The resulting copolymer shows a microphase-separated morphology, as is evident from TEM-analysis. The observed morphology is mainly lamellar with some cylindrical structures, as expected from the polymer volume ratios: 59.4% (v/v) PC and 40.6% (v/v) PDMS. In a comparison to previous reports, the results of this research extended our knowledge on the influence of solvent casting on the crystallinity obtained in these materials. The copolymer films cast from THF show a

higher crystallinity than those from CHCl_3 , resulting in shorter domain spacings as measured by SAXS. Films cast from THF have a lower strain to failure, possibly due to disentanglement when the PC crystallizes. The relatively low molar mass PC homopolymer is toughened by the addition of PDMS blocks, like in the PC–PDMS block copolymer. In comparison to the reported studies on crystallized PC–PDMS block copolymers [23], this research extends the understanding in the structure–property relationships of these polymers. This can be of importance when crystallized PC–PDMS copolymers are used as selective membranes for gas separation [23].

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