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Synthesis and Characterization of Triblock Terpolymers with three Potentially Crystallisable Blocks: Polyethylene-*b*-poly(ethylene oxide)-*b*-poly(ε-caprolactone)

M. Vivas,[1] J. Contreras,[1] F. López-Carrasquero,[1] A.T. Lorenzo,[2] M.L. Arnal,[2] V. Balsamo,*[2] A.J. Müller,[2] E. Laredo,[3] H. Schmalz,[4] V. Abetz[5]*

Summary: A first attempt was made to produce novel ABC triblock terpolymers with three potentially crystallisable blocks: polyethylene (PE), poly(ethylene oxide) (PEO), and poly(ε-caprolactone) (PCL). Polybutadiene-*b*-poly(ethylene oxide) diblock copolymers were synthesized by living anionic polymerization. Then, a non-catalyzed thermal polymerization of ε-caprolactone from the hydroxyl end group of the PB-*b*-PEO diblock precursors was performed. Finally, hydrogenation by Wilkinson catalyst produced PE-*b*-PEO-*b*-PCL triblock terpolymers. Side reactions were detected that lead to the formation of undesired PCL-*b*-PEO diblock copolymers, however, these impurities were successfully removed by purification. A range of triblock terpolymers with PCL and PEO minor components were prepared. Topological restrictions on the PEO middle block prevented this block from crystallizing while the complex crystallization behavior of the PE and PCL blocks was documented by DSC and WAXS measurements.

Keywords: crystallization; living anionic polymerization; triblock terpolymers

Introduction

Block copolymers with semicrystalline components are very interesting materials that exhibit a complex behavior due to the interplay between microphase separation and self-organizing processes that take place as a consequence of the thermodynamic immiscibility of the covalently linked blocks and their crystallization. To our knowledge, only ABC triblock terpolymers with one or two semicrystalline blocks have been reported. Balsamo et al. reported the synthesis and characterization of polystyrene-*b*-polybutadiene-*b*-poly(ε-caprolactone) triblock terpolymers[1–6] and their hydrogenated counterparts[7–9]; where the first ones possess one crystallizable block (poly(ε-caprolactone)) and the latter ones two semicrystalline components (poly(ε-caprolactone) and polyethylene). Lambert *et al.* synthesized an amphiphilic triarm star terpolymer based on polystyrene, poly(ethylene oxide) and poly(ε-caprolactone); i.e with two crystallizable blocks[10–12]. More recently, Arnal *et al.*[13,14] investigated the thermal properties of polystyrene-*b*-poly(ethylene oxide)-*b*-polycaprolactone (PS-*b*-PEO-*b*-PCL) triblock copolymers, in which the coincident and fractionated crystallization of PEO and PCL makes the behavior highly complex. Other

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[1] Grupo de Polímeros ULA, Departamento de Química, Facultad de Ciencias, Universidad de los Andes, Mérida 5101A, Venezuela
E-mail: jeco@ula.ve

[2] Grupo de Polímeros USB, Departamento de Ciencia de los Materiales and

[3] Departamento de Física, Universidad Simón Bolívar, Apartado 89000, Caracas 1080-A, Venezuela

[4] Makromolekulare Chemie II, Universität Bayreuth, 95440 Bayreuth, Germany

[5] Institut für Polymerforschung, GKSS-Forschungszentrum Geesthacht GmbH, 21502 Geesthacht, Germany

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studies in triblock terpolymers with two crystallizable blocks have been performed by Schmalz *et al*. in polyethylene-*b*-poly(ethylene-*alt*-propylene)-*b*-poly(ethylene oxide)[15–18].

So far, no reports are found on the synthesis and characterization of triblock terpolymers with three potentially crystallizable components. The study of these new potential materials is then a challenging task for the understanding of the interrelationship ‘‘phase separation-crystallization’’. It is therefore the aim of this work to report a first attempt to obtain new ABC triblock terpolymers based on polyethylene, poly(ethylene oxide) and poly(ε-caprolactone). The synthetic strategy used was based on the ‘‘thermal method’’ reported before by Arnal *et al*.[13]. In this method, the synthesis is based on the non-catalyzed thermal polymerization of ε-caprolactone from the hydroxyl end group of different polybutadiene-*b*-poly(ethylene oxide) diblock copolymers as precursors. Some preliminary results of the solid state properties are given in order to point out the complexity of this new ABC system.

Experimental part

Synthesis

The polybutadiene-*b*-poly(ethylene oxide) (B_xEO_y) diblock copolymers (precursors) were synthesized by sequential anionic polymerization following standard procedures[17]. For subsequent reactions, the diblock copolymers were purified by three freeze-drying cycles. A pre-weighted amount of ε-caprolactone (CL) (Aldrich Chemical Co.), purified as reported elsewhere[1], was added under argon atmosphere to the diblock copolymer precursor in a glass ampoule, connected to a high vacuum line. The ampoule (reactor) was cooled down at liquid-nitrogen temperature, evacuated, sealed off and placed in an oil bath at 180 °C for 30 or 36 hours. After cooling to room temperature, the reactor was opened and the reaction product was extracted and purified through dissolution in benzene and precipitation with cold methanol. The purified polybutadiene-*b*-poly(ethylene oxide)-*b*-poly(ε-caprolactone) triblock copolymers were submitted to an hydrogenation procedure for 24h, which was realized using a Wilkinson catalyst[19] at 500 psi and 60 °C.

Molecular Characterization

The copolymers were characterized by Size Exclusion Chromatography (SEC) (Waters model 150CV chromatograph), calibrated with PS-standards using THF as eluent. FTIR measurements (Perkin-Elmer System 2000 FTIR) were carried out on dried thin films of the samples obtained from $CHCl_3$ or benzene solutions onto NaCl or KBr windows. ^{1}H-NMR spectra (Bruker DLX 400 MHz spectrometer) were recorded from deuterated benzene solutions at room temperature for PB-*b*-PEO-*b*-PCL and 60 °C for PE-*b*-PEO-*b*-PCL respectively.

Physical Characterization

The thermal behavior was analyzed using a Perkin-Elmer DSC-7 instrument calibrated with cyclohexane and indium under nitrogen atmosphere. Samples (10 ± 1 mg) were encapsulated in aluminum pans. DSC cooling and heating scans (10 °C/min) were carried out after annealing at 120 °C for three minutes. Melting (T_m) and crystallization (T_c) temperatures were taken from peak maxima.

Wide-Angle X-ray scattering (WAXS) spectra were recorded on powdered samples by using Cu Kα-Ni filtered radiation in an automatic horizontal axis Philips diffractometer. The angular range in 2θ , from 10° to 40°, was swept at a speed of 0.0133 °/s. A variable temperature chamber was adapted with a temperature control better than 0.1 °C.

Results and discussion

Synthesis

The polybutadiene-*b*-poly(ethylene oxide)-*b*-poly(ε-caprolactone) ($B_xEO_yC_z$) triblock terpolymers were synthesized starting from

Table 1.
Molecular characteristics of the precursors and triblock copolymers obtained.

Run	Precursor[a)]	$M_n \times 10^{-3}$ (Kg/mol)[b)]	PDI[b)]
A1	$B_{78}EO_{22}$	59	1.05
A2	$B_{60}EO_{14}C_{26}$[d)]	69	1.08
A3	$E_{46}EO_{14}C_{40}$[c)]	-	-
B1	$B_{78}EO_{22}$	44	1.08
B2	$B_{37}EO_{9}C_{53}$[e)]	65	1.18
B3	$E_{83}EO_{9}C_{8}$[c)]	-	-

[a)] $B_xEO_yC_z$: x, y and z represent the weight percent of each component determined from ^{1}H-NMR.

[b)] Determined from ^{1}H-NMR using $M_{n(PB)}$, obtained from GPC measurements.

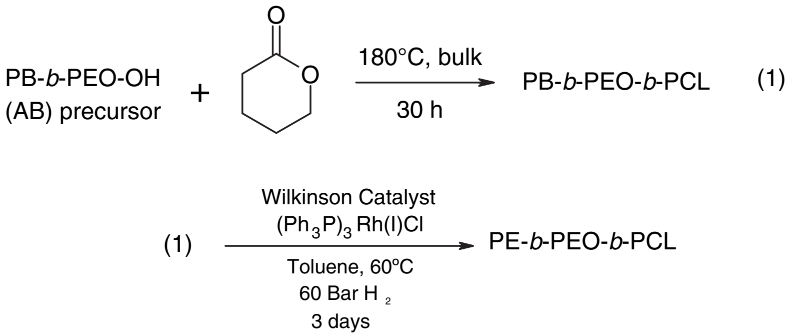
[c)] The polyethylene block contains 4wt.-% insaturations due to incomplete hydrogenation.

[d)] Reaction time 30 h.

[e)] Reaction time 36 h.

two B_xEO_y precursors of different molecular weight (Table 1) by means of the "thermal method"[13]. In this method the non-catalyzed thermal ring opening polymerization of ε-caprolactone (C) takes place from the hydroxyl end group of the precursor. The synthetic procedure is shown in Scheme 1.

The molecular weight characteristics of the synthesized $B_xEO_yC_z$ triblock terpolymers are also shown in Table 1, and Figure 1 depicts the SEC chromatograms of series A and B. From Figure 1 the expected increase of the molecular weight (shift to lower elution volume) after the addition of ε-caprolactone (CL) can be detected, indicating that this monomer has been incorporated into the chain. The shape of the chromatogram for $B_{60}EO_{14}C_{26}$ is similar to that of the precursor, and a relative narrow molar mass distribution is obtained. This evidences that the polymerization has taken place without significant side reactions such as ε-caprolactone homopolymerization or degradation of the PEO block. On the other hand, in series B, $B_{37}EO_9C_{53}$ shows a bimodal distribution, indicating that besides ε-caprolactone addition, other reactions have occurred. Nevertheless, although the high molecular weight peak exhibits a slight broadening, it remains monomodal and narrow (PDI = 1.18). The low molecular weight peak (not taken into account when calculating the molecular weight) was attributed to the formation of PCL-*b*-PEO diblock copolymer. This side product could arise from the thermal degradation of the PEO block in the precursor through random chain scission, that probably occurred in the C-O bond as indicated in Scheme 2, a fact that was corroborated by ^{1}H-NMR analysis of the product present in the low molecular weight peak. This low molecular weight AB diblock copolymer was extracted from the hydrogenated sample by first refluxing in chloroform for 1h to extract the soluble fraction which is later recovered by precipitation into methanol. The successful separation is evident upon comparison of SEC chromatograms of samples $EO_{10}C_{90}$ and $B_{37}EO_9C_{53}$ in Figure 1 (right); the



Scheme 1.
Synthesis of PE-*b*-PEO-*b*-PCL ABC Triblock Copolymers.

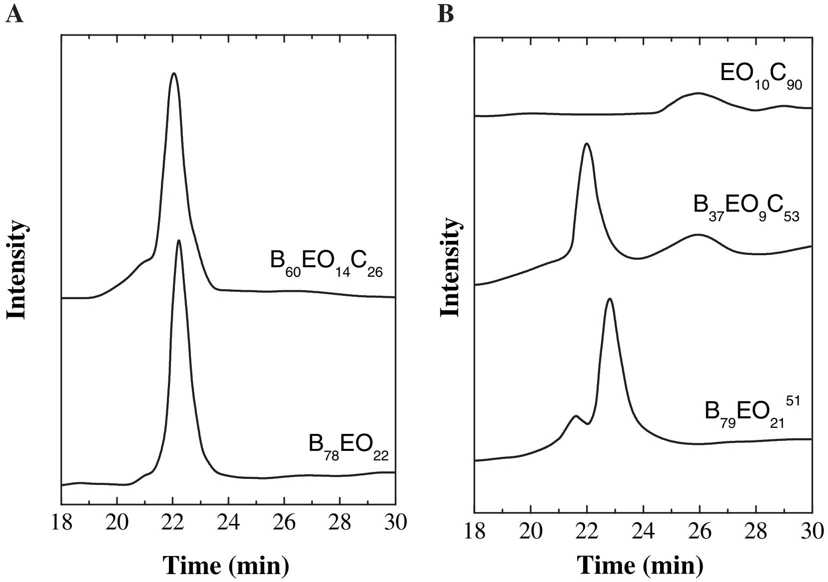


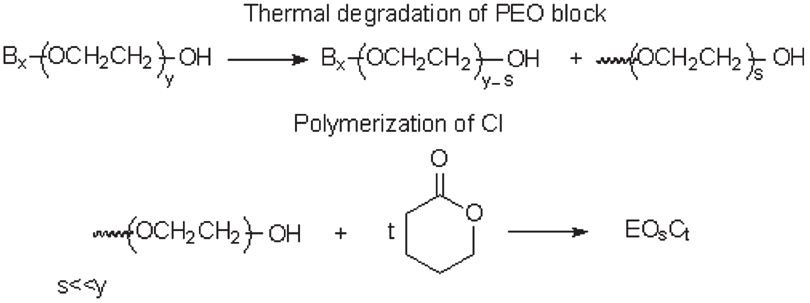
Figure 1.
SEC traces of series A (left) and B (right).

composition of the side product as determined by ^{1}H-NMR was $EO_{10}C_{90}$.

The efficiency of the purification method was corroborated by thin layer chromatography (TLC), performed both on the precursors and the triblock copolymers. In this technique a solvent, called mobile phase, travels through a stationary phase, carrying the sample with it.

The different components in the sample move up the plate at different rates due to differences in their partition coefficient between the mobile liquid phase and the stationary phase. TLC can be very useful because it is an inexpensive and relatively quick technique, and it requires small quantities of material. This technique has been proved to be useful in the characterization of block copolymers[20]. Chloroform, tetrahydrofuran and acetone were tested as mobile phases. As can be gathered from Figure 2, when acetone is used as mobile phase, PCL homopolymer moved up the plate, while PB-*b*-PEO and PB-*b*-PEO-*b*-PCL did not (Figure 2a).

Figure 2a shows that the PB-*b*-PEO-*b*-PCL triblock copolymer obtained in series A is free from PCL-*b*-PEO in agreement



Scheme 2.
Formation of PEO-*b*-PCL diblock copolymer.

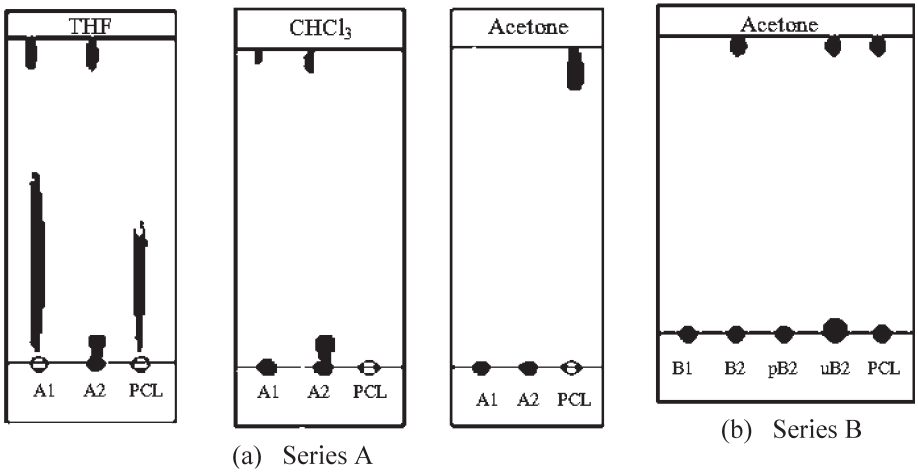


Figure 2.
Thin-layer chromatography of the series A and B (see nomenclature in Table 1). PCL: policaprolactone homopolymer, B1: $B_{78}EO_{22}$, B2: $B_{37}EO_9C_{53}$, pB2: purified hydrogenated $B_{37}EO_9C_{53}$ and uB2: unpurified hydrogenated $B_{37}EO_9C_{53}$ fraction.

with SEC results. On the other hand, the triblock copolymer obtained in series B exhibits a more complex behavior (Figure 2b). The soluble fraction present in the unpurified hydrogenated triblock copolymer (uB2) moves up the plate in acetone, indicating the presence of a product which is composed mainly by PCL, and that corresponds to a PEO-*b*-PCL (AB) diblock copolymer as demonstrated by ^{1}H-NMR. The absent of a mobile fraction in the purified hydrogenated triblock (pB2) confirm the purity of the final triblock copolymer, in agreement with SEC.

Figure 3 shows the FTIR spectra of series A. The appearance in spectrum (b) of bands at 1730 cm^{-1} due to the stretching mode of C=O group is another evidence of the incorporation of caproyl units. After hydrogenation, spectrum (c) shows, as

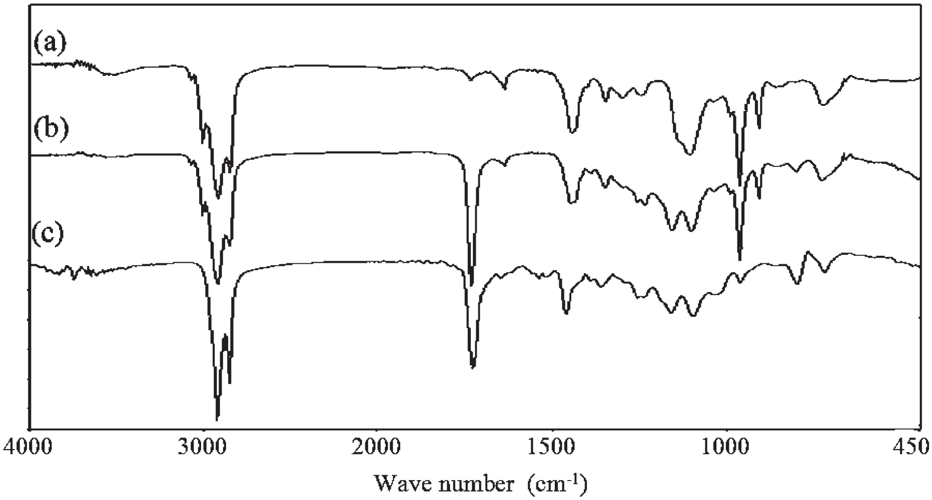


Figure 3.
FTIR spectra of (a) $B_{78}EO_{22}$ precursor, (b) $B_{60}EO_{14}C_{26}$ and (c) $E_{46}EO_{14}C_{40}$.

expected, the disappearance of bands located at 3050 cm^{-1} and 1636 cm^{-1}, due to the stretching mode of =C–H and C=C bonds, which evidences the hydrogenation of the double bonds.

In order to gain insight into the evolution of chemical structure during the synthesis and hydrogenation of the triblock terpolymers, they were evaluated by ^{1}H-NMR spectroscopy. Figure 4 displays typical ^{1}H-NMR spectra of series A. Spectra (B) and (C) exhibit a triplet at 4.1 ppm attributed to protons (j) and signals of the internal protons (i), (g) and (h) in 1–1.5 ppm of the PCL block. The decrease of the olefinic signals at 5.50 and 5 ppm (signals (b) and (d)), and the new signal (k) which appear at 1.3 ppm in spectrum (C), corresponding to the new PE methylene protons, confirms the hydrogenation of the PB block. Nevertheless, under the hydrogenation conditions used in this study, a remaining content of 4 wt.-% double bonds could be calculated from the spectra.

Solid state behavior

As an example of the crystallization and melting behavior of the new polyethylene-

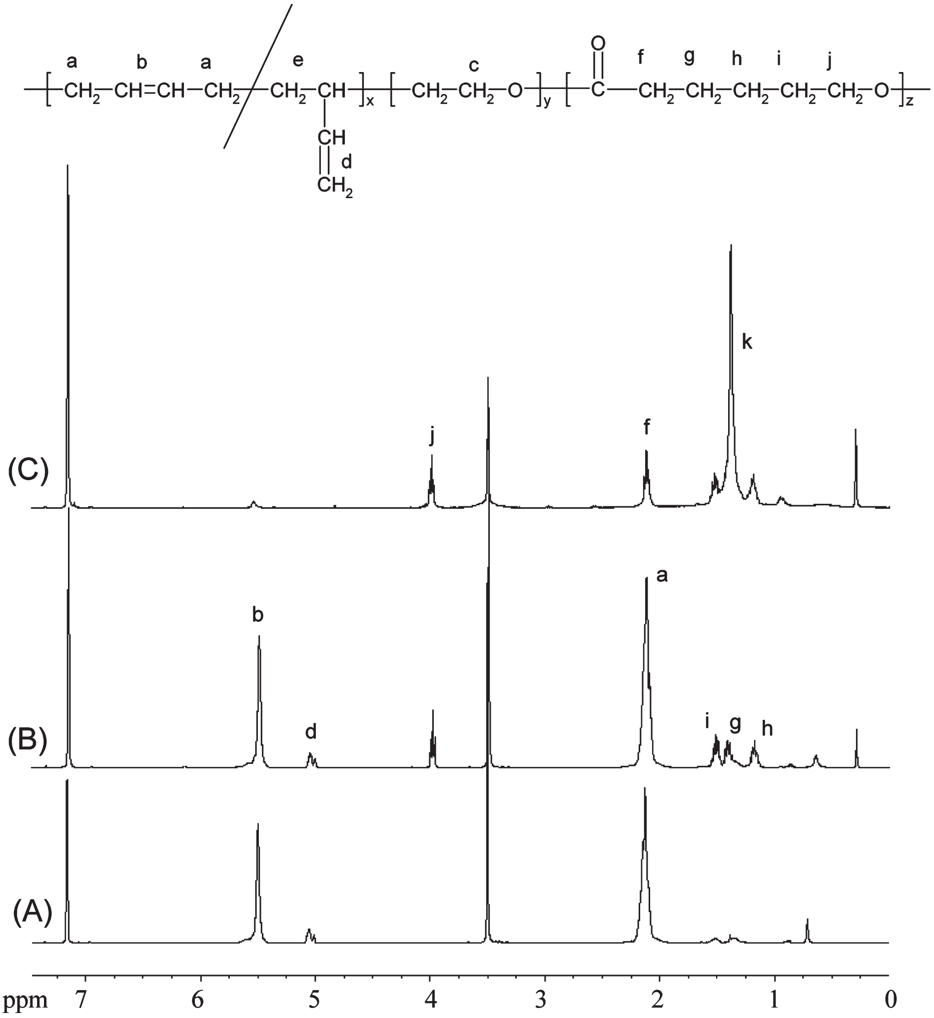


Figure 4.
^{1}H-NMR spectra of (A) $B_{78}EO_{22}$ precursor, (B) $B_{60}EO_{14}C_{26}$ and (C) $E_{46}EO_{14}C_{40}$.

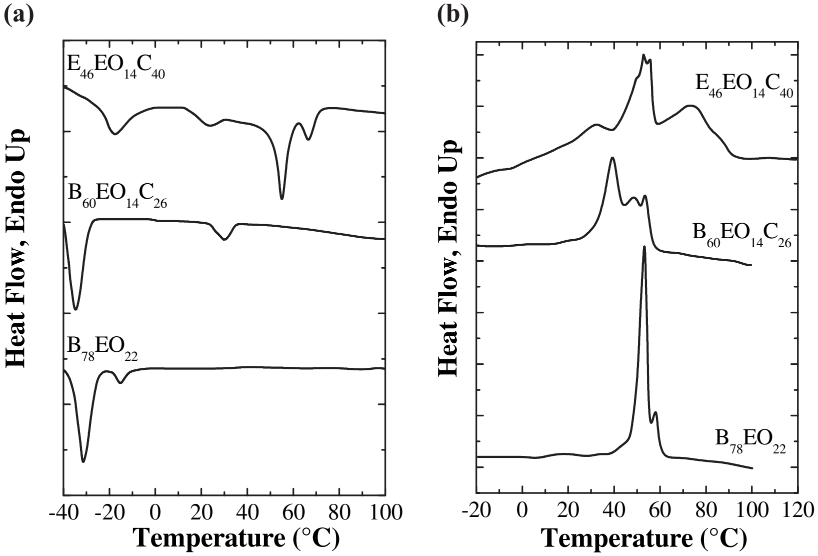


Figure 5.
DSC (a) cooling and (b) heating scans (10 °C/min) for series A.

b-poly(ethylene oxide)-*b*-poly(ε-caprolactone) triblock terpolymers DSC cooling and heating scans of series A are depicted in Figure 5. The starting $B_{78}EO_{22}$ diblock copolymer presents two crystallization exotherms at −15.1 °C and −31.2 °C (Figure 5a); which correspond to supercoolings that are much higher than those usually obtained for PEO homopolymer[21], independently of the molecular weight. This phenomenom is denominated fractionated crystallization, and it has been reported in polymer blends and copolymers where the crystallizable component is dispersed in a matrix, such that the number of spatially isolated domains is much larger than the nucleating heterogeneities present in the system[22]. Upon heating $B_{78}EO_{22}$ shows a bimodal endotherm, with a main melting peak temperature at 53.2 °C (Figure 5b). The bimodality of the melting process may be attributed to a lower long-range order of the microdomains that has been reported to be present in semicrystalline block copolymers when they have not been thermally annealed at high temperatures.[5]

In Figure 5 it can be appreciated that $B_{60}EO_{14}C_{26}$ also has two crystallization exotherms at 30.1 °C and −34.7 °C respectively, and a multimodal endotherm (Figure 5). The exotherm at −34.7 °C indicates that the crystallization of the PEO block is again fractionated, and that the previous crystallization of a PCL fraction at 30.1 °C does not have a nucleating effect on the PEO that crystallizes at about the same temperature as in the precursor. In addition, it should be mentioned that, as has been previously reported[23], it is possible that a fraction of the PCL crystallizes in a coincident fashion with the PEO at low temperature. The low degree of crystallinity (17%) obtained for PCL, taking into account only the exotherm at 30.1 °C, supports this interpretation. With respect to the melting behavior, a comparison of $B_{78}EO_{22}$ and $B_{60}EO_{14}C_{26}$ shows a significant depression (~13 °C) of the PEO melting point with the incorporation of the PCL block. This is due to the topological restrictions encountered by the PEO block when it is double tethered with an amorphous block (PB) at one end and a semicrystalline block (PCL) at the other one. The effect of double tethering has been previously investigated by Müller et al. in PS-*b*-PE-*b*-PCL triblock terpolymers[8,9,24].

After hydrogenation the DSC scans are more complex. New signals, attributed to the polyethylene crystallization, appear at about 66.6 °C and 55.0 °C. At this point it should be noted that the PE block is structurally similar to a random copolymer of ethylene and 1-butene due to the 1,4- and 1,2- units in the polybutadiene block prepared via anionic polymerization. In fact, certain overlapping of the PE low melting temperature tail with the PCL endotherm is observed in the DSC heating scan.

In addition to the exothermic signals due to the PE block, other exotherms at −23.2 °C and −17.6 °C can be detected in the corresponding cooling scans (Figure 5a). These exotherms are attributed only to the fractionated crystallization of the PCL block as will be shown below from the X-ray diffraction experiments; in fact, no evidences of PEO crystallization could be found. This indicates that the hydrogenation of the PB block in the triblock copolymers modifies the confinement of the PEO middle block, and prevents its crystallization, so that the PEO remains amorphous in this case. Crystallization of the PEO block would be expected for higher PEO contents within the triblock terpolymers.

As can be seen from the above discussion on the preliminary thermal characterization of the new PE-*b*-PEO-*b*-PCL triblock copolymers, comprising three potentially crystallizable components covalently linked in the same chain, the behavior is very complex, and a variety of phenomena can take place. For series B similar behavior was obtained since the PEO and PCL blocks are minority components. Copolymers with different compositions will be prepared in the future.

The homopolymers, the starting precursors and the synthesized copolymers were studied by WAXS to check their respective crystallinities. Figure 6 presents the spectra obtained for the homopolymers and the copolymers at 22 °C for 2θ varying from 10 to 40°. The unit cells for PCL and PE are orthorhombic, space group $P2_12_12_1$ and Pnam, respectively[25], while the PEO crystallizes in the monoclinic system (space group $P2_1/a$)[26]. It is easily seen that the three homopolymers exhibit well-defined Bragg reflections characterizing their semicrystalline state at room temperature. PCL and PE exhibit main reflections in the same angular range, but PEO shows the (120) reflection at 19.0° well separated from the PCL and PE Bragg peaks. The WAXS trace for the precursor diblock copolymer $E_{82}EO_{18}$ shows the presence of a significant degree of crystallization in the PEO block. This crystalline order disappears once the PCL block is attached in the triblock

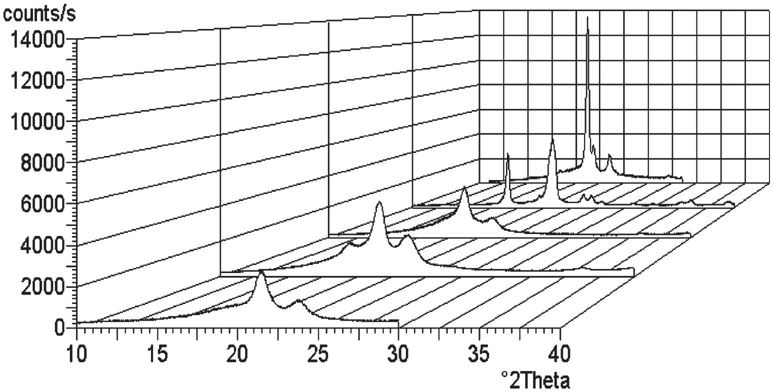


Figure 6.
WAXS spectra for homopolymers and block copolymers at 22 °C, Ni-Filtered Cu Kα radiation. From back to front PCL, PEO, PE, $E_{82}EO_{18}$ and $E_{46}EO_{14}C_{40}$.

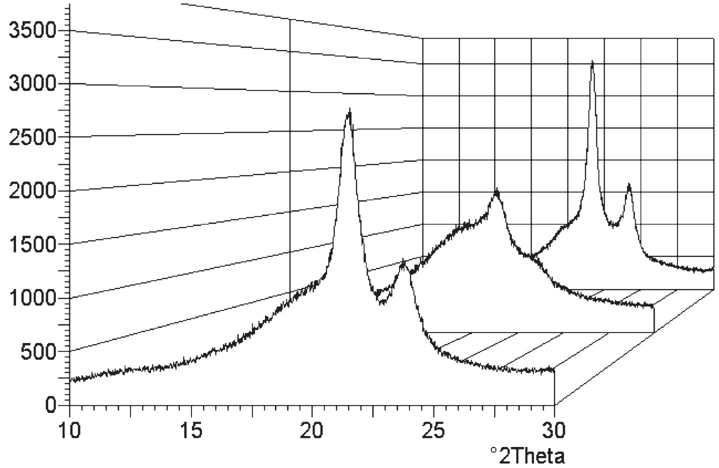


Figure 7.
WAXS spectra at different temperatures for block copolymer, $E_{46}EO_{14}C_{40}$. Ni-Filtered Cu Kα radiation. From back to front 22 °C, 61 °C and −75 °C.

terpolymer, as the hydrogenated triblock terpolymer $E_{46}EO_{14}C_{40}$ exhibits only crystalline reflections corresponding to the PCL and PE blocks. This confirms that the restrictions imposed by the inclusion of the PEO block between two blocks that crystallize first are sufficient to suppress any further molecular chain ordering in the shortest PEO middle block.

As the PEO block crystallizes in a fractionated fashion in the $B_{78}EO_{22}$ diblock copolymer, attempts were made to crystallize the PEO block in the hydrogenated triblock copolymer $E_{46}EO_{14}C_{40}$. The temperatures chosen for the isothermal crystallization were −19 °C and −30 °C. However, Bragg peaks characteristic for the PEO crystal structure did not evolve, even after a 2 hours thermal treatment.

Figure 7 shows a comparison of WAXS spectra corresponding to $E_{46}EO_{14}C_{40}$ after different thermal treatments. In one case the sample was slow cooled (at 2.2 °C/min) to −75 °C in order to give the PEO block an opportunity to crystallize, however, no characteristic PEO reflections were found and the WAXS trace looks very similar to that of an untreated sample measured at 22 °C. These results confirm that the PEO block remained amorphous. The reflections observed in these WAXS traces are the result of the overlap of the reflections corresponding to the PE and the PCL block crystals. If the sample is heated to 61 °C, a temperature at which the PCL crystals are already molten, Figure 7 shows that only PE crystal reflections remain.

Gan et al.[27], have reported the inhibition of PEO crystallization in the diblock copolymer $C_{80}EO_{20}$ using WAXS; however, this could be a consequence of fractionated crystallization since they did not cool the samples to low enough temperatures. Shiomi et al.[28] have studied PCL-*b*-PEO-*b*-PCL block copolymers by WAXS of a wide composition range. They have observed WAXS patterns at room temperature that are superpositions of those for PEO and PCL homopolymers for intermediate compositions (PCL: 60 and 66 wt-%). For PCL contents of 34 and 83 wt-% only the majority component crystallizes in agreement with our findings.

Conclusions

The preparation of polybutadiene)-*b*-poly(ethylene oxide)-*b*-poly(ε-caprolactone) triblock terpolymers by a combination of sequential living anionic polymerization and "thermal" polymerization followed by hydrogenation, results in copolymers with two or three crystallizable blocks. The preliminary evaluation of their properties in the solid state resulted in a complex behavior where the crystallization of the central block is suppressed by substantial restrictions caused by the previous crystallization of the end blocks. Other interesting aspects were observed such as the fractionated crystallization, the overlap of the melting ranges for two of the crystallizable blocks and lack of any nucleating type interaction among the crystalline phases of the poly(ethylene oxide) and the poly(ε-caprolactone) in the non-hydrogenated triblock terpolymers. The preparation and characterization of further PB-*b*-PEO-*b*-PCL triblock terpolymers in a wider composition range will allow a further understanding of the results obtained in this study.

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