# Synthesis and Characterization of Polystyrene-*b*-poly(ethylene oxide)-*b*-poly(ϵ-caprolactone) Block Copolymers

**M. L. Arnal,*,† V. Balsamo,† F. López-Carrasquero,‡ J. Contreras,‡ M. Carrillo,‡ H. Schmalz,§ V. Abetz,§ E. Laredo,⊥ and A. J. Müller†**

*Grupo de Polímeros USB, Departamento de Ciencia de los Materiales, Universidad Simón Bolívar, Apartado 89000, Caracas 1080A, Venezuela; Grupo de Polímeros ULA, Departamento de Química, Facultad de Ciencias, Universidad de los Andes, Mérida 5101A, Venezuela; Makromolekulare Chemie II, Universität Bayreuth, 95440 Bayreuth, Germany; and Grupo de Física de Sólidos USB, Departamento de Física, Universidad Simón Bolívar, Apartado 89000, Caracas 1080A, Venezuela*

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ABSTRACT: The preparation of polystyrene-*b*-poly(ethylene oxide)-*b*-poly(ϵ-caprolactone) triblock copolymers using three different strategies is described. Experimentally, a method we have called “thermal” is the simplest one of the three employed. However, it presents serious limitations for the preparation of high molecular weight triblock copolymers with low polydispersity. The titration method is a more elegant alternative to prepare the PS-*b*-PEO-*b*-PCL triblock copolymers. Nevertheless, the stoichiometric titration of the precursor terminal hydroxyl groups requires much expertise, and it becomes more difficult as the concentration of such terminal groups decreases when the precursor molecular weight increases. Finally, the sequential method may be regarded as the most convenient one. However, the experimental steps involved a solvent exchange during polymerization that must be performed under conditions of strict purity and high vacuum. Several triblock and pentablock copolymers of varying compositions and molecular weights were successfully prepared. The fact that these copolymers contain two crystallizable blocks, i.e., PEO and PCL, makes them very interesting from a structural point of view. The copolymers were found to be phase segregated according to evidence provided by DSC and WAXS. The crystallization and melting behavior of both PEO and PCL blocks is greatly affected by composition. Fractionated crystallization phenomena were detected when either one or both blocks constituted the minor components within the block copolymers.

## Introduction

The synthesis of ternary ABC triblock copolymers has been one of the challenges in anionic polymerization in the past few years, not only for their rich morphological textures[1−6] but also for their potential applications as compatibilizers in polymer blends[7,8] and in nanotechnology.[9−11] Copolymers containing poly(ϵ-caprolactone) are especially interesting because they are miscible with a wide range of polymers,[12] and they have features like crystallizability,[13−15] lack of toxicity, ability to disperse pigments, low-temperature adhesiveness, and printability.[16,17] On the other hand, the also crystallizable poly(ethylene oxide) has superior properties for being nontoxic, flexible, hydrophilic, and biocompatible.[18] In fact, the synthesis of polyester−polyether type block copolymers has attracted much attention. Different types of polyester−polyether copolymers that include AB and ABA block copolymers and $(A)_2B$ star copolymers have been prepared using either uncatalyzed or catalyzed reactions.[19−24]

The synthesis of an amphiphilic triarm star copolymer based on polystyrene, poly(ethylene oxide), and poly(ϵ-caprolactone) has been reported.[23,24] This material has been achieved by preparing a polystyrene-*b*-poly(ethylene oxide) diblock copolymer, having a protected anionic initiator group at the junction between the two blocks. After deprotection, the anionic polymerization of ϵ-caprolactone is initiated by activation of the deprotected function with diphenylmethylsodium. Nevertheless, no reports have been published on analogous synthesis of linear ABC triblock copolymers using identical blocks. As a matter of fact, there have been only few publications on linear ABC triblock copolymers with crystallizable blocks. Among them are reports on block copolymers based on polystyrene, polybutadiene, and polycaprolactone and their hydrogenated versions,[13,14] in which a complex interrelationship between crystallizability and microphase separation has been found.[25−29]

We report in this paper the synthesis of new crystallizable ABC triblock copolymers based on polystyrene, poly(ethylene oxide), and poly(ϵ-caprolactone). Three strategies have been developed. The first one, which we have named “thermal method”, is based on the previous work of Cerrai et al.[19] for the noncatalyzed thermal polymerization of ϵ-caprolactone with chemically unmodified poly(ethylene glycol) as prepolymer. However, they only reported the synthesis of poly(ethylene oxide)-*b*-polycaprolactone diblock copolymers of relatively low molar mass (up to 10 kg/mol). The second strategy, which we have named “titration method”, uses some elements of the synthesis developed by Lambert et al.[23,24] to obtain amphiphilic triarm star copolymers. In this case, the terminal hydroxyl function of polystyrene-*b*-poly(ethylene oxide) precursors is activated with diphenylmethylsodium to initiate the ϵ-caprolactone polymerization in an apolar media like benzene. It is well-known that the polymerization of this monomer in a polar medium or in the presence of polar blocks like PEO is difficult to control due to the competing polym-

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† Departamento de Ciencia de los Materiales, Universidad Simón Bolívar.

‡ Universidad de los Andes.

§ Universität Bayreuth.

⊥ Departamento de Física, Universidad Simón Bolívar.

* To whom correspondence should be addressed.

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erization and depolymerization reactions in a short time period.[30,31] Another route of synthesis ("sequential") was developed, by which there is no need of stopping the reaction for a subsequent reinitiation. To carry out this synthesis, a change of the reaction media was performed switching from a polar to a nonpolar solvent.

Since the crystallization and stability behavior of block copolymers is a matter of great interest, some preliminary results on thermal and structural characterization are given in order to describe how composition affects their properties.

## Experimental Section

**Reagents.** Styrene and $\epsilon$-caprolactone were first stirred over finely ground $CaH_2$ for 1 day and then distilled twice under reduced pressure over $CaH_2$. Then styrene was distilled from $CaH_2$ under nitrogen, stirred over $Bu_2Mg$, and condensed into storage ampules. Just before polymerization, styrene was degassed by freeze−thaw cycles under high vacuum, and $\epsilon$-caprolactone was distilled into a glass flask and degassed under a high vacuum. Purified ethylene oxide was accomplished by stirring over $CaH_2$ or calcium oxide at 0 °C for 3 h, followed by transfer into glass ampules.

Analytical grade benzene and HPLC grade tetrahydrofuran (THF) were dried by refluxing 2 days over $CaH_2$. Then, they were distilled into a flask containing a potassium/sodium alloy and refluxed again for at least 2 days. Benzophenone was used as indicator for the purity of the THF.

**Synthesis Procedure.** *Preparation of AB Precursors.* Styrene was polymerized at −78 °C in tetrahydrofuran using cumylpotassium as initiator.[30,31] After 1 h, an aliquot was taken to recover the polystyrene (PS) precursor for monitoring purposes. Ethylene oxide (EO) was then cryodistilled into the reactor. At this stage, the orange color of the solution disappeared and a pale yellowish color appeared. After raising the temperature to 40 °C, the reaction was continued for 2 days to complete the polymerization of the second monomer. The polymerization was terminated by methanol addition. The block copolymer was isolated by precipitation in hexane, and then it was carefully dried by dissolution in purified benzene and removal of the solvent through three freeze−thaw cycles in a high-vacuum line.

*Preparation of ABA Precursors.* Styrene and ethylene oxide were polymerized under the same conditions described above but using naphthalene potassium as initiator.[32−34]

All precursors were prepared in Bueche polymerization reactors of 1 L capacity. The yielding of all reactions in the case of the ABA precursors were nearly 100%.

*Preparation of ABC and CBABC Block Copolymers.* Three different strategies were evaluated:

(i) Thermal method: A preweighed amount of the dried block copolymer was placed into a glass ampule and connected to a high-vacuum line. Then, a predetermined volume of $\epsilon$-caprolactone ($\epsilon$-CL) was introduced into the ampule with a precision syringe, under argon atmosphere. After cooling to liquid nitrogen temperature, it was evacuated, sealed off, and placed in an oil bath at 180 °C for 30 h.[19] After cooling to room temperature, the ampule was opened and the polymerization product extracted.

(ii) Titration method: A preweighed amount of the dried block copolymer was dissolved in dried and degassed benzene at room temperature. To deprotonate the precursor, diphenylmethylsodium[23,24] in THF was added with a syringe. Then, a predetermined amount of $\epsilon$-CL was injected under vigorous stirring to give a yellow solution. The reaction was stopped after 30 s−1 min with a mixture of 10/1 acetic acid/methanol.

(iii) Sequential method: For this method the termination step of the precursor was not carried out. After having completed the polymerization of ethylene oxide, removal of THF was performed in the vacuum line. Then, dried and degassed benzene was condensed into the reactor. Once the living polymer was completely dissolved, $\epsilon$-CL was added to the solution, which turned immediately yellow. The reaction was terminated after 1 min with a mixture of 10/1 acetic acid/methanol.[13]

**Table 1. Molecular Characteristics of the Block Copolymers Synthesized Using Different Methods**

| polymer[a] | method | $M_n \times 10^{-3}$ (kg/mol)[b] | $M_w/M_n$ | $T_d$ (°C)[c] |
|---|---|---|---|---|
| S | | 15.0 | 1.02 | |
| $S_{81}EO_{19}$ | | 18.5 | 1.07 | 361 |
| $S_{63}EO_{16}C_{21}$ | thermal | 24.0 | 1.12 | 340 |
| $S_{46}EO_{12}C_{54}$ | thermal | 33.0 | 1.16 | 352 |
| $S_{10}EO_4C_{86}$ | thermal | 150.0 | 1.39 | 368 |
| $S_{38}EO_{10}C_{52}$ | titration | 39.0 | 1.29 | 375 |
| S | | 18.0 | 1.01 | 362 |
| PEO | | 100.0 | | 303 |
| PCL | | 37.0 | 1.65 | 384 |
| $S_{39}EO_{61}$ | | 46.0 | 1.20 | 365 |
| $S_{15}EO_{37}$ $C_{48}$ | sequential | 64.0 | 1.24 | 368 |
| S | | 56.0 | 1.01 | |
| $EO_{11}S_{78}EO_{11}$ | | 71.0 | 1.03 | 364 |
| $C_{30}EO_4S_{32}EO_4C_{30}$ | thermal | 175.0 | 1.20 | 358 |
| $C_{28}EO_5S_{34}EO_5C_{28}$ | thermal | 165.0 | 1.28 | 369 |
| $C_{17}EO_{26}S_{14}EO_{26}C_{17}$ | sequential | 25.2 | 2.28 | 357 |
| $C_{10}EO_{37}S_6EO_{37}C_{10}$ | sequential | 126.8 | 1.42 | |

[a] The subscripts represent the amount of each component in weight percent. [b] Determined from $^1H$ NMR using $M_n$ (−PS) obtained from SEC measurements, calibrated with PS standards. [c] Temperature at which 10% of mass loss has occurred.

**Molecular Characterization.** To determine the molecular weight of the polystyrene (S) precursors and the molecular weight distribution of all polymers, size exclusion chromatography (SEC) was performed in THF at 40 °C at a flow rate of 1 mL/min with refractive index and UV detection at 254 nm with Waters equipment. The SEC was calibrated with polystyrene standards. For the block copolymers more reliable molecular weights were calculated on the basis of the $M_n$ molecular weight of the precursor and chemical composition determined from $^1H$ NMR spectra, which were recorded on a 200 MHz Bruker 2000 spectrometer with $CDCl_3$ as solvent.

**Physical Characterization.** Thermogravimetric curves were obtained from a heating scan at 10 °C/min in a Perkin-Elmer TGA 7 under a nitrogen atmosphere.

*Differential Scanning Calorimetry (DSC).* Precursors and final block copolymers were analyzed with a Perkin-Elmer DSC Pyris-1 instrument calibrated with cyclohexane and indium under a helium atmosphere. The DSC scans were obtained at 10 °C/min. All DSC cooling curves were recorded after the samples were held in the melt at 120 °C for 3 min. Melting ($T_m$) and crystallization ($T_c$) temperatures were taken from the peak maxima. Sample weight was kept constant at 10 mg; therefore, all the DSC curves shown can be considered to be normalized with respect to the total weight of the samples.

*Wide-Angle X-ray Scattering (WAXS).* The WAXS spectra were performed on powdered samples of the homopolymers and block copolymers by using Cu Kα−Ni filtered radiation in a conventional horizontal axis Philips diffractometer. The spectra were taken at 20 °C with 2$\theta$ varying from 10° to 51°. The structure of the PCL unit cell is orthorhombic while the PEO which can crystallize in the monoclinic or triclinic system has in this case a triclinic unit cell. The precise value of the WAXS crystallinity degree was determined for the two semicrystalline homopolymers, and the values are 53% for PCL and 75% for PEO, which are in good agreement with the values found by DSC (see Table 2). For the copolymers, the determination of the crystallinity is much less precise as the relevant crystalline reflections are overlapped with the contribution of the amorphous pattern of polystyrene.

## Results and Discussion

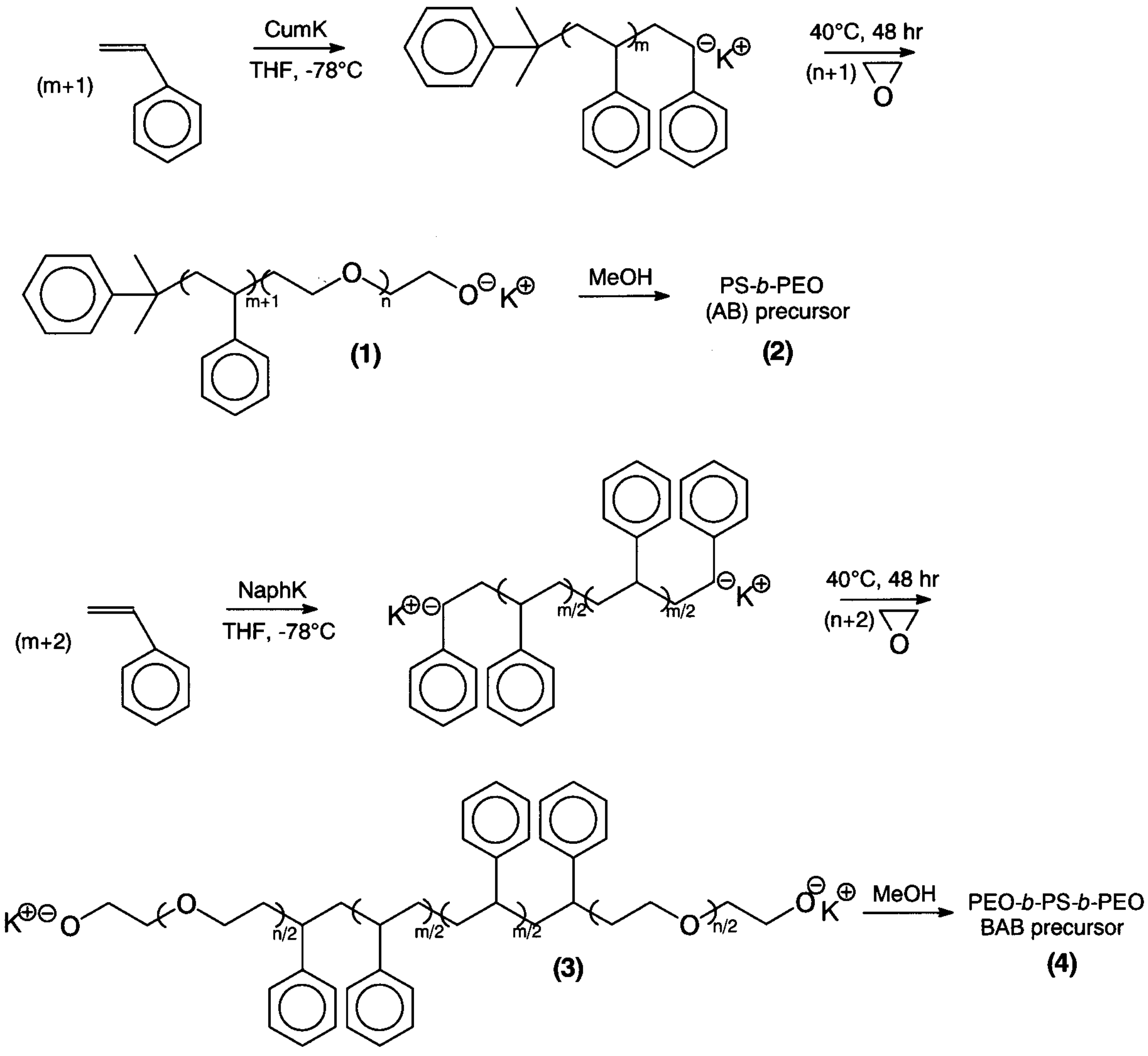
In this work we evaluated three different strategies to obtain polystyrene-*b*-poly(ethylene oxide)-*b*-poly($\epsilon$-caprolactone) ($S_xEO_yC_z^M$) block copolymers. The notation used in the figures to denote the materials includes the composition in weight percent as subindices and the

**Table 2. Thermal Transitions, Melting Enthalpies and Degree of Crystallinity Obtained by DSC**

| material | $T_g$ (°C) |  | $T_c$ (°C) |  |  | $T_m$ (°C)[a] |  | $\Delta H_m$ (J/g)[a] |  | $X_c$ (%)[a] |  |
|---|---|---|---|---|---|---|---|---|---|---|---|
|  | A | B | I | II | III | I | II | I | II | I | II |
| PEO 1000 |  |  |  | 21 |  | 40 |  | 143 |  | 73 |  |
| PEO 100000 | −55 |  |  | 43 |  | 65 |  | 144 |  | 73 |  |
| PCL 37000 | −62[b] |  |  | 35 |  |  | 58 | 67 |  |  | 47 |
| $S_{81}EO_{19}$ | −58 | 81 | −40 |  |  | 35 |  | 15 |  | 39 |  |
| $S_{63}EO_{16}C_{21}$ | −62 | 85 | −42 |  |  | 30 | 51 | 5 | 14 | 16 | 48 |
| $S_{46}EO_{12}C_{42}$ | −64 | 82 | −39 | 27 |  | 29 | 57 | 4 | 30 | 16 | 51 |
| $S_{10}EO_4CL_{86}$ | −65 | 89 | −38 | 33 |  |  | 56 |  | 53 | 0 | 44 |
| $S_{38}EO_{10}C_{52}$ | −64 | 87 |  | 26 |  | 35 | 57 | 4 | 27 | 20 | 36 |
| $S_{39}EO_{61}$ | −60 | 98 |  | 40 |  | 65 |  | 104 |  | 87 |  |
| $S_{15}EO_{37}C_{48}$ | −65 | 96 | −7 | 31 |  |  | 57 |  | 66 |  |  |
| $EO_{11}S_{78}EO_{11}$ | −50 | 76 | −38 |  |  | 44 |  | 20 |  | 46 |  |
| $C_{30}EO_4S_{32}EO_4C_{30}$ | −65 | 96 | −44 | −14 | 32 | 37 | 57 | 7 | 45 | 47 | 53 |
| $C_{28}EO_5S_{34}EO_5C_{28}$ | −65 | 99 | −41 | −16 | 30 |  | 57 |  | 66 | 6 | 47 |

[a] I and II correspond to the PEO and PCL blocks, respectively. [b] Measured by TSDC.

**Scheme 1. Synthesis of the AB and ABA Precursors**



molecular weight in kg/mol as superindices. The use of anionic polymerization to prepare polystyrene-*b*-poly(ethylene oxide) (SEO) and poly(ethylene oxide)-*b*-polystyrene-*b*-poly(ethylene oxide) (EOSEO) block copolymers (precursors) using cumyl potassium and naphthalene potassium, respectively, has been previously reported in the literature (Scheme 1).[32−34] Nevertheless, their polymerization methods are reported here because they will be used as reference materials in order to compare with the triblock and pentablock copolymers prepared in this work.

**Thermal Method.** Figure 1 shows the results of the SEC analysis of a triblock and a pentablock copolymer, which were synthesized using the "thermal method" previously reported by Cerrai et al.[19] for the synthesis of PEO-*b*-PCL diblock copolymers. The curves for the corresponding precursors are also plotted. In this case noncatalyzed thermal initiation of the ϵ-CL polymerization takes place through the hydroxyl end group of the PS-*b*-PEO or PEO-*b*-PS-*b*-PEO precursors (Scheme 2).

Table 1 presents the molecular weights and molecular weight distributions obtained for the precursors and the

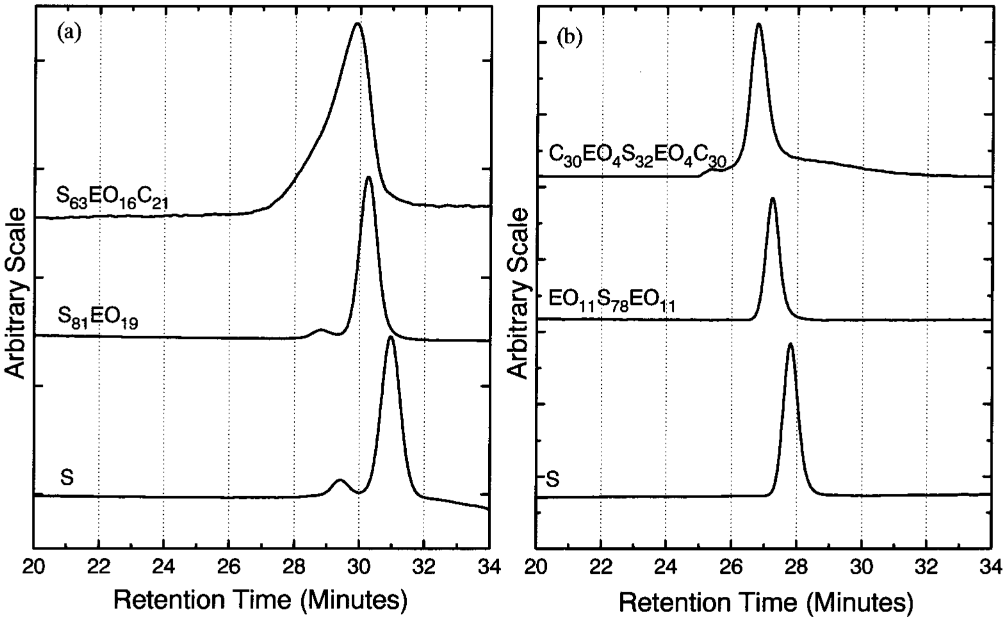


**Figure 1.** SEC traces of (a) $S_{63}EO_{16}C_{21}$ and (b) $C_{30}EO_4S_{32}EO_4C_{30}$ block copolymers and their corresponding precursors. These block copolymers were synthesized using the thermal method.

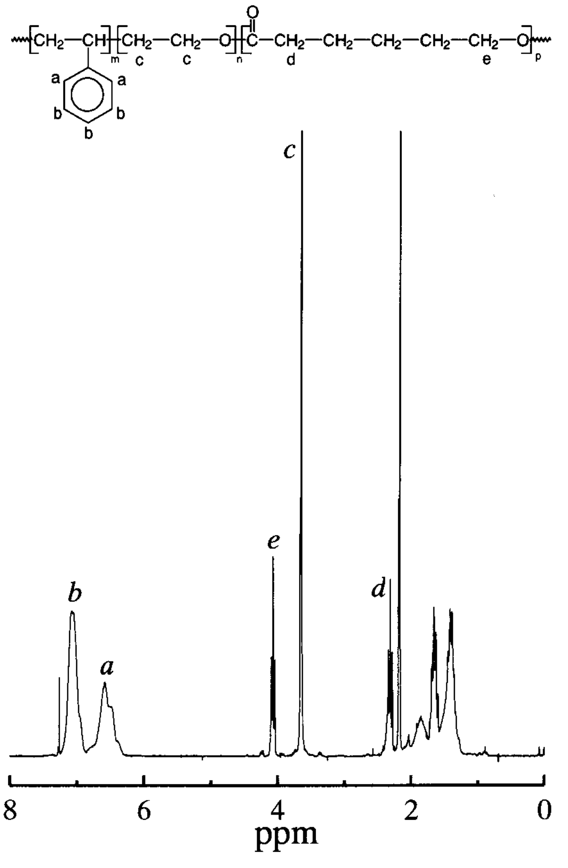


**Figure 2.** $^1H$ NMR spectrum of $S_{63}EO_{16}C_{21}$.

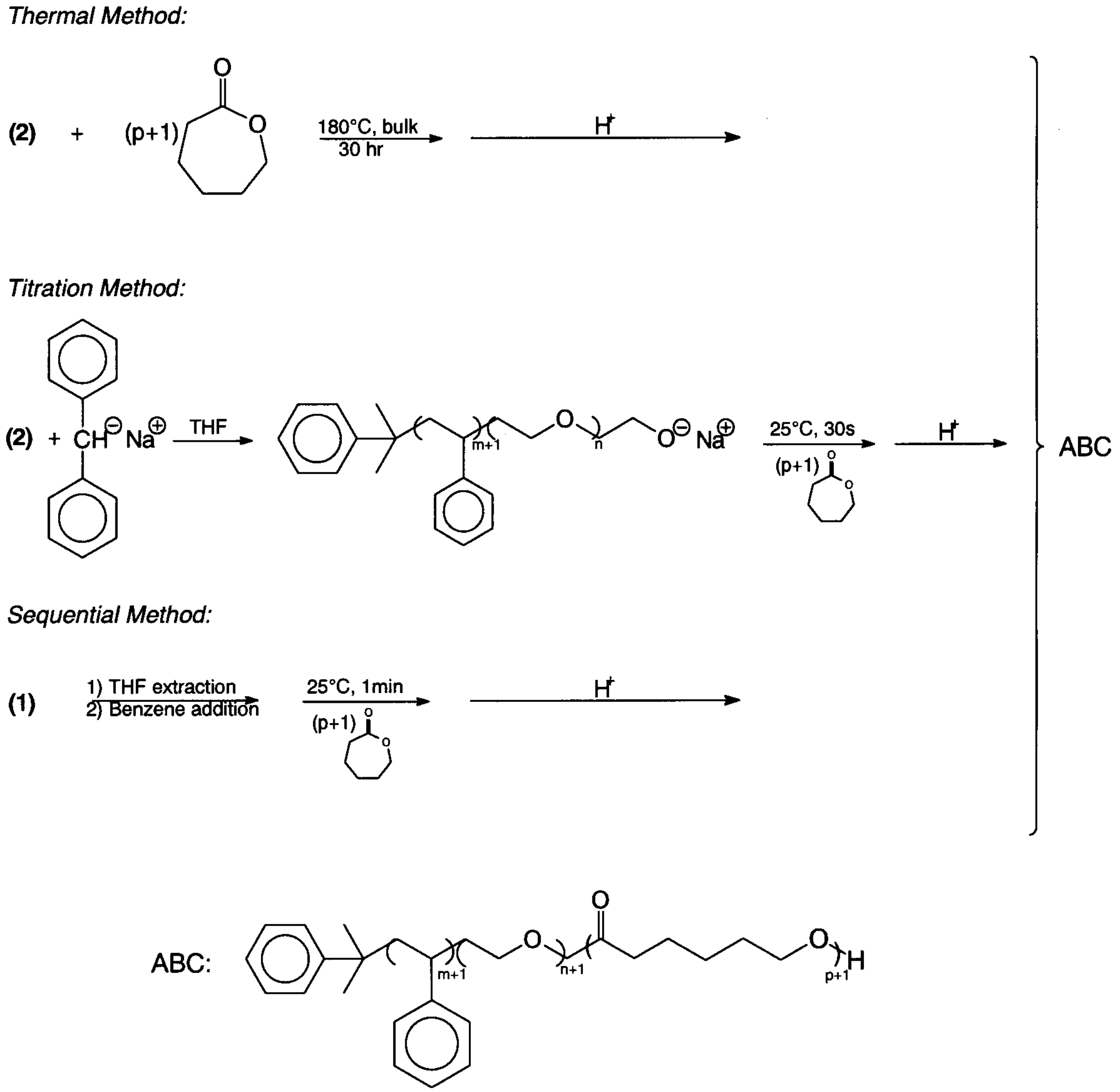
final products, and Figure 2 shows a typical $^1H$ NMR spectrum of a triblock copolymer. The resonance bands of the three blocks are clearly visible. The signals at about 6.7 and 7.2 ppm are due to the "a" and "b" aromatic protons of the polystyrene block, the sharp singlet at 3.7 ppm corresponds to the "c" methylene protons of the oxyethylene units of PEO, and the triplets at 4.1 and 2.4 ppm are attributed to the "e" and "d" methylene protons of the poly($\epsilon$-caprolactone) block.

It is important to mention that the presence in Figure 1a of a small peak at low elution volume (high molecular weight region), even in the $S^{15}$ precursor, can be attributed to the presence of impurities in the cumylpotassium that led to the formation of dianions that are also able to initiate chain growth.[32] (The peak molecular weights of the two signals correspond to $M_{p1} = 15$ kg/mol and $M_{p2} = 29$ kg/mol.) In fact, it is observed that such peak is shifted to lower elution volume with the addition of the next monomer. Although the final product ($S_{63}EO_{16}C_{21}{}^{24}$) exhibits a slight broadening of the molecular weight distribution, its distribution remains monomodal and narrow ($M_w/M_n = 1.12$), with an apparent asymmetry due to the overlapping with the small peak previously mentioned. The lack of broadening of the SEC curve in the low molecular weight region indicates the absence of detectable side reactions like depolymerization of the EO block or homopolymerization of $\epsilon$-CL.

On the other hand, the final product in Figure 1b ($C_{30}EO_4S_{32}EO_4C_{30}{}^{175}$) exhibits a low molecular weight tail due to $\epsilon$-CL homopolymerization. This PCL homopolymer could be the product of protic impurities present in the precursor from the previous termination step. The PCL homopolymer can be removed by fractionated precipitation by dissolving the sample in THF and slowly adding methanol to the solution. Methanol is a good precipitant for PCL. When the solution becomes cloudy, it is centrifuged and the two phases are separated. The preparation of the triblock and pentablock copolymers by the thermal method was performed in glass ampules. The addition of $\epsilon$-caprolactone was done in a high-vacuum line, once the addition of $\epsilon$-CL was over; the ampules were sealed and transferred to an oil bath where the polymerization took place. We used between 3 and 5 g of precursor in each reaction, and the rates of conversion were variable as indicated below.

To study the effect of the $\epsilon$-CL/precursor ratio on the polymerization, two more copolymers were synthesized from the same precursor PS-*b*-PEO ($S_{81}EO_{19}$). The resulting copolymers were $S_{46}EO_{12}C_{42}$ and $S_{10}EO_4C_{86}$. The corresponding SEC curves had the same shape with

**Scheme 2. Synthesis of the Polystyrene-*b*-poly(ethylene oxide)-*b*-poly(ε-caprolactone) ABC Triblock Copolymers**



a broadening of the molecular weight distribution as the ε-CL/precursor ratio was increased. Simultaneously, slightly lower conversions were obtained (93% for $S_{46}EO_{12}C_{42}$ and 81% for $S_{10}EO_4C_{86}$). Table 1 presents the molecular characterization results for these copolymers.

It has been reported that a linear relationship between the feed mole ratio and the ratio of ε-CL structural units to EO units in the copolymer is obtained at 100% conversion. However, this linear relationship was obtained when low molecular weight copolymers were synthesized (up to 10 kg/mol).[19] Our results indicate that, using this thermal method, a quantitative conversion can only be reached with a high molecular weight precursor for short PCL blocks. Nevertheless, high yields and low polydispersity are obtained even when synthesizing block copolymers of about 40 kg/mol. Under the same conditions a yield reduction is also obtained if the same reaction is carried out from a higher molecular weight precursor $EO_{11}S_{78}EO_{11}$ (71 kg/mol). In fact, an important drop in yield was observed for $C_{30}EO_4S_{32}EO_4C_{30}$ (51%) and $C_{28}EO_5S_{4034}EO_5C_{28}$ (65%), together with broader molecular weight distributions as depicted in Table 1. This lower yield is attributed to a reduced reactivity due to a lower concentration of hydroxyl initiating groups in the reaction media.

The previous copolymers were obtained from precursors that contained high amounts of PS. When the initiation was carried out from a precursor with high PEO content, only a small triblock copolymer fraction was obtained, with a high diblock (precursor) content, whose molecular weight distribution was considerably affected. Apparently, those precursors with high PEO content undergo degradation during the reaction. The reduction in yield of the polymerization reactions as well as the increase in polydispersity with the increase of the precursor molecular weight indicates that there seems to be a competence between the polymerization of ε-caprolactone and degradation processes of the PEO block. These degradation processes are more apparent when the size of the PEO block is larger and the molecular weight of the precursor is bigger.

The results obtained by the thermal method indicate that PS-*b*-PEO-*b*-PCL triblock copolymers can be prepared with this procedure. However, the results obtained by the use of different precursors indicate that a better control of the molecular architecture of the triblock copolymers can be achieved by the use of low molecular weight precursors. Under these conditions the concentration of reactive chain ends is higher; nevertheless, it is still possible to prepare PS-*b*-PEO-*b*-PCL triblock copolymers of higher molecular weights (e.g., 150 kg/mol) using the thermal method but with polydispersities that increase to 1.4.

All the results described above indicate that the thermal method is successful with low molecular weight precursors as reported by Cerrai et al.,[19] a fact that makes it an easy alternative to obtain a series of triblock or pentablock copolymers with similar PS and PEO blocks.

More elegant strategies to obtain PS-*b*-PEO-*b*-PCL triblock copolymers were investigated using the "titration" and "sequential" methods. In these cases special attention must be paid to the anionic polymerization of $\epsilon$-CL because of the possibility of the simultaneous occurrence of competing polymerization and depolymerization reactions, which would result in a multimodal distribution of chain lengths and poor molecular weight control. Limiting the polymerization time of this monomer to about 1 min[30,31] in polar media or to 4 min[13] in apolar media, in the absence of polar blocks, is a way to avoid such side reactions.

**Titration Method.** In the titration method the anionic activation, which consists of transforming the hydroxyl function of the PS-*b*-PEO precursor into an alcoholate to initiate the anionic ring-opening polymerization of $\epsilon$-CL,[23,24] is achieved by addition of diphenylmethylsodium dissolved in benzene to the diblock copolymer solution, as shown in Scheme 2. The polymerizations by the titration method were performed in a 250 mL Bueche polymerization reactor using approximately 5 g of precursor dissolved in benzene at a concentration of 8−10% (w/v).

Lambert et al.[23] have shown that diphenylmethylsodium is a good activating agent due to its low basic character that limits potential side reactions on the precursor chains and the use of sodium as counterion. Potassium as counterion would lead immediately to backbiting reactions during $\epsilon$-CL polymerization. An essential requirement that has to be satisfied by this method is a stoichiometric addition of the activating agent. Otherwise, (a) an excess would produce a mixture of PCL homopolymer and SEOC triblock copolymer. (b) An insufficiency would produce a mixture of PS-*b*-PEO diblock and SEOC triblock copolymer.

Nevertheless, the solubility differences between the products would allow fractionation to remove PCL homopolymer or PS-*b*-PEO diblock copolymer. The fractionation strategy was varied according to copolymer composition. AB and ABA precursors that are rich in PS are easy to precipitate in methanol, while those rich in PEO can be precipitated in hexane. The addition of the PCL block induces a solubility reduction; therefore, the triblock copolymers can be separated from the diblock precursors by slowly adding methanol to a THF or benzene solution of the mixture of both. Once the solution is turbid, the precipitated triblock copolymer can be recovered by centrifugation while the diblock copolymer remains in solution. If homopolymerized PCL is present, this can be extracted with butyl acetate at 40 °C.

Size exclusion chromatography (SEC) of a triblock copolymer prepared in this way (see Figure 3 and Table 1) shows a shoulder in the low molecular weight region, which is due to a small fraction of diblock copolymer that was not activated. This might be attributed to a slight addition defect of diphenylmethylsodium in the titration procedure. It should be mentioned that titration is a procedure that depends very much on expertise; addition of diphenylmethylsodium depends on the color developed by the reaction media. The alcoholate has a slight yellow color, but a small excess of the activating agent would also appear yellowish. After fractionation, a monomodal molecular weight distribution can be obtained.

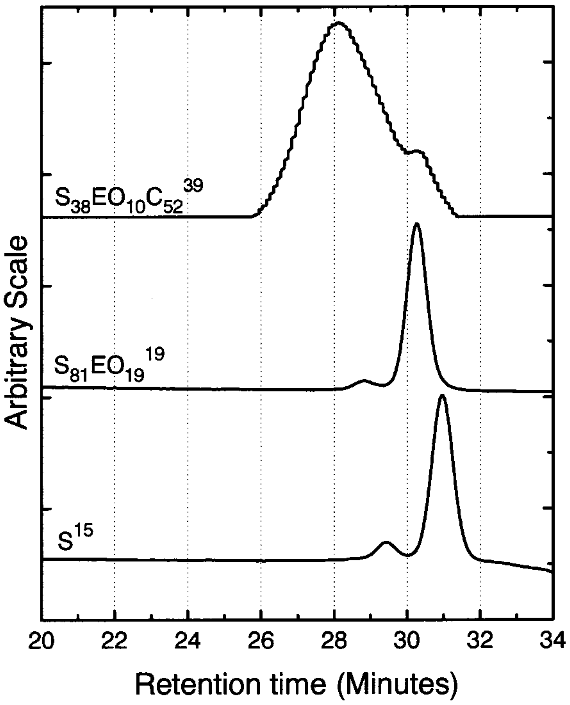


**Figure 3.** SEC traces of $S_{38}EO_{10}C_{52}$ block copolymer and its corresponding precursors. This block copolymer was synthesized using the titration method.

**Sequential Method.** We present here results for an SEOC triblock copolymer prepared by the sequential method, whose SEC curve is shown in Figure 4. Two pentablock copolymers were also produced by this method as reported in Table 1, where the corresponding molecular characteristics can be found. This method has the advantage that the polymerization does not need to be stopped and then reinitiated again after the purification procedure of the precursor. The sequential polymerizations were performed in a vacuum line; approximately 5 g was used per experiment.

A tail in the low molecular weight region is observed in Figure 4 for the $S_{15}EO_{37}C_{48}$ triblock copolymer. This has been attributed to some PCL oligomer formation by backbiting reactions. Although a change of solvent was carried out from THF to benzene, it is possible that some THF traces accelerated the reaction and promoted such side reactions. The shoulder observed in the low retention time region of the SEC trace corresponds to a molecular weight that is almost twice that of the peak in the SEC curve. Therefore, such behavior is caused by the presence of some dianions in the initiator, as was previously discussed. Although an advantage of this sequential method is the continuity of living chain ends, it has also a shortcoming: prior to the addition of the third monomer, an evacuation step is needed, and this makes the incorporation of impurities into the system possible if the connections to the vacuum line are not perfectly fitted.

The sequential method can be employed to prepare triblock and pentablock copolymers of varied composi-

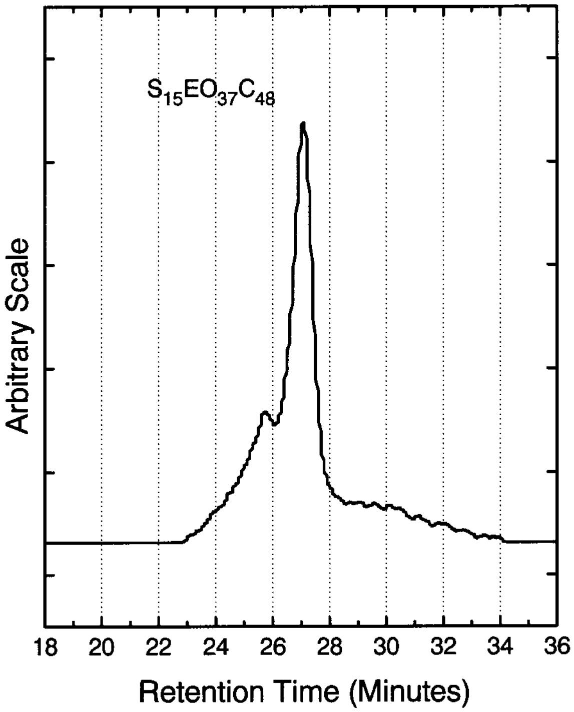


**Figure 4.** SEC trace of $S_{15}EO_{37}C_{48}$ block copolymer synthesized using the sequential method.

tions and molecular weights of controlled structure (see Table 1). Another important advantage of the sequential method is the possibility of introducing high PEO contents in the copolymers, something that cannot be done with the thermal method.

We have presented three different strategies for the preparation of PS−PEO−PCL triblock copolymers. Experimentally, the thermal method is the simplest one. However, it implies serious limitations for the preparation of narrowly distributed triblock copolymers of high molecular weight, since it works better with low molecular weight precursors. The titration method is a more elegant alternative; nevertheless, the stoichiometric titration of the hydroxyl groups requires much expertise, and it gets more difficult as the concentration of such terminal groups decreases when the precursor molecular weight increases. Finally, the sequential method may be regarded as the most convenient one. However, the experimental steps involved in THF evaporation and its substitution by benzene must be performed under conditions of strict purity and high vacuum because otherwise termination reactions caused by impurities can dominate the reaction.

**Thermal Stability.** A preliminary evaluation of the thermal stability of the copolymers was performed by thermogravimetric analysis (TGA), the results are shown in the weight loss curves of Figure 5, and characteristic degradation temperatures are reported in Table 1. An improved stability of the synthesized copolymers as compared to the PEO homopolymer, which is the most sensitive component, can be observed. Table 1 presents the temperature at which 10% of mass loss has occurred. PEO usually undergoes thermal degradation via a random chain scission mechanism. The thermal stability of the copolymers is improved so much that it is very similar to that of the PS precursor, despite the low PS content in some of them. The detailed differences among the copolymers do not follow a specific trend. It seems that some of the variables involved may produced either higher or lower stability. These variables are the composition of the copolymer, its molecular weight, and also the synthesis method. For instance, the two triblock copolymers with the lowest $T_d$ (S63EO16C21 and S46EO12C54) were obtained by the thermal method. A more detailed study is needed to understand the subtle variation is thermal stability among the prepared copolymers, but the general fact that they have an improved thermal stability with respect should be highlighted. The improved thermal stability would be advantageous for potential applications of the prepared copolymers.

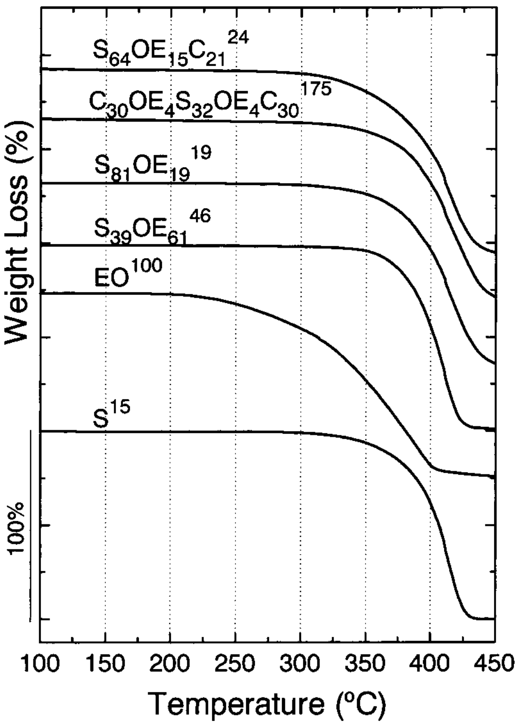


**Figure 5.** TGA curves obtained at a heating rate of 10 °C/min under nitrogen atmosphere.

**Solid-State Behavior.** To get information on the microphase separation of the components and on the crystallization of the PEO and PCL blocks, the precursors and final block copolymers were investigated by means of differential scanning calorimetry (DSC). Figures 6 and 7 present the crystallization and melting behavior of selected triblock and pentablock copolymers, respectively. Table 2 summarizes the observed transitions together with the values for PCL and PEO homopolymers, which will be used as reference materials.

Because of the overlap of the PCL and PEO glass transitions, it was possible only to detect one vitreous transition ($T_{gA}$) at about −60 °C and a high glass transition temperature ($T_{gB}$) at about 90 °C corresponding to the PS block, indicating that the block copolymers are microphase separated, as expected (other evidences are presented below).

The characteristics of the cooling DSC scans in Figure 6a can be attributed to the effect of increasing PCL content. $S_{63}EO_{16}C_{21}$ has minor PCL and PEO contents. For this reason their crystallization takes place in a fractionated and coincident fashion at −42 °C.

The fractionated crystallization phenomenon is typical of dispersed microphases (i.e., like in immiscible blends or in block copolymers[13,14,26,35−38]) and manifests itself by the appearance of several crystallization exotherms or only one for the dispersed polymer at tem-

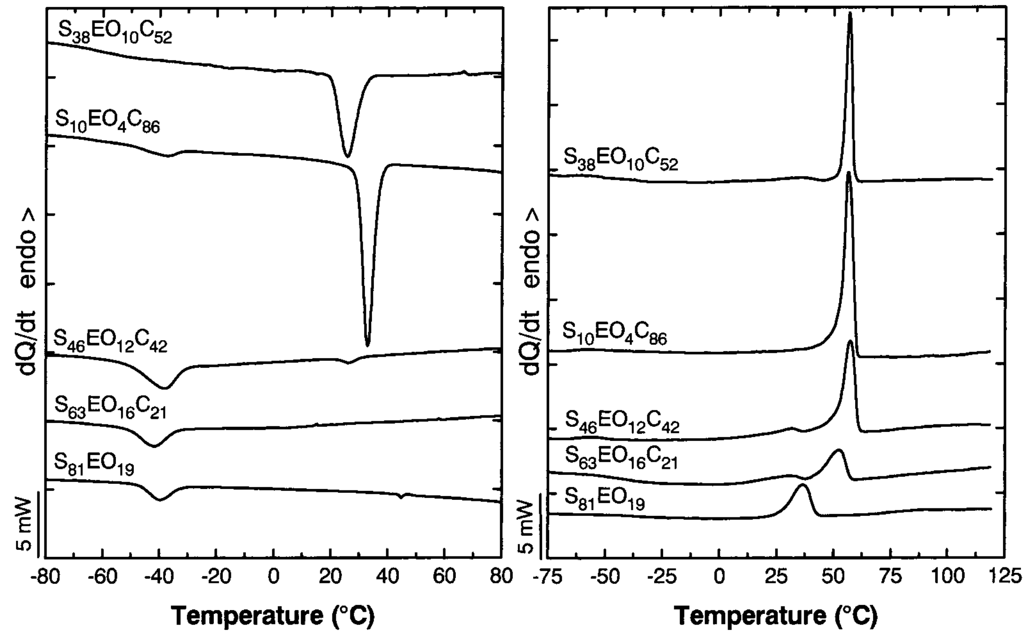


**Figure 6.** DSC (a) cooling and (b) heating curves (10 °C/min) of the triblock copolymers and an AB diblock copolymer precursor.

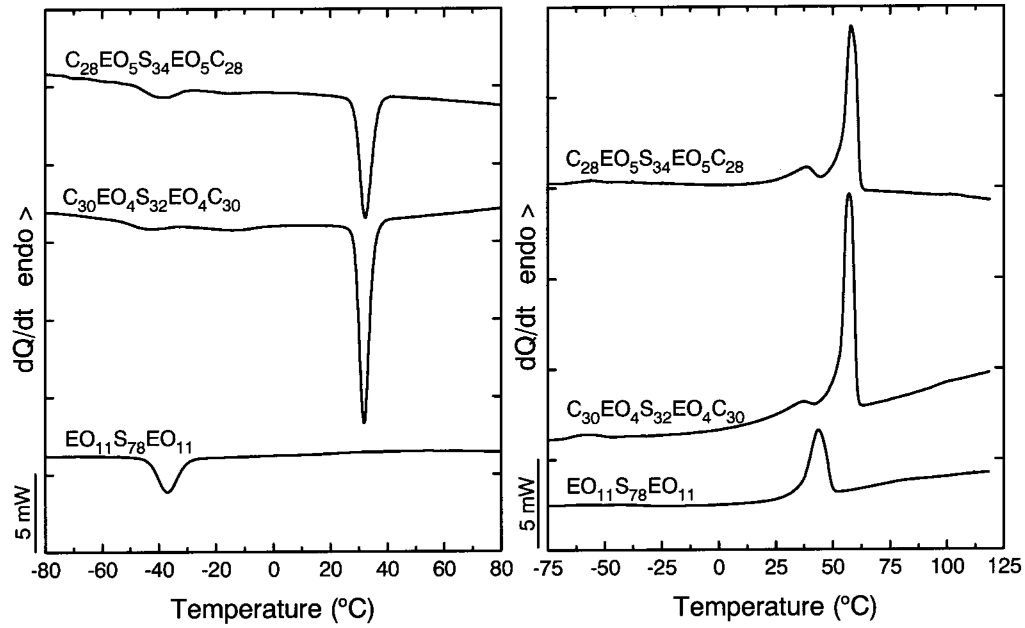


**Figure 7.** DSC (a) cooling and (b) heating curves (10 °C/min) of the pentablock copolymers and an ABA triblock copolymer precursor.

peratures that are much lower than the characteristic crystallization temperature of the corresponding homopolymer in the bulk state. The reason for this phenomenon is likely the dispersion of the crystallizable blocks into a much larger number of spatially isolated microphases (i.e., droplets, spheres, cylinders, etc.) rather than impurities present in the system. Most polymers can be nucleated heterogeneously by existing impurities of undetermined origin. This is the reason for a specific undercooling necessary for crystallization. When a bulk polymer is dispersed into droplets and the number of droplets is much greater than the number of heterogeneities originally present in the bulk polymer, then fractionated crystallization arises since less active heterogeneities can also nucleate the polymer.[14,35] In the limit where heterogeneities are completely absent or greatly outnumbered by the amount of pure droplets, homogeneous nucleation takes place at its characteristic extreme undercoolings.[14]

Either in the triblock or in the diblock precursor of Figure 6a, the fractionated crystallization of the PEO block proceeds via homogeneous nucleation as indicated by the undercooling obtained ($T_c$: −42 and −40 °C, respectively).[13,14,37] Such crystallization temperatures are so low and close to $T_g$ that they can only be due to crystal growth from homogeneous nuclei. Through a magnification of the scale, it was possible to detect a second small exotherm at about −8 °C, but no exotherms were observed at the usual crystallization temperatures for PCL and PEO homopolymers (Table 2). This indicates that the PCL and PEO blocks are dispersed as small microphases in a PS matrix, as expected on the basis of the composition of these block copolymers.

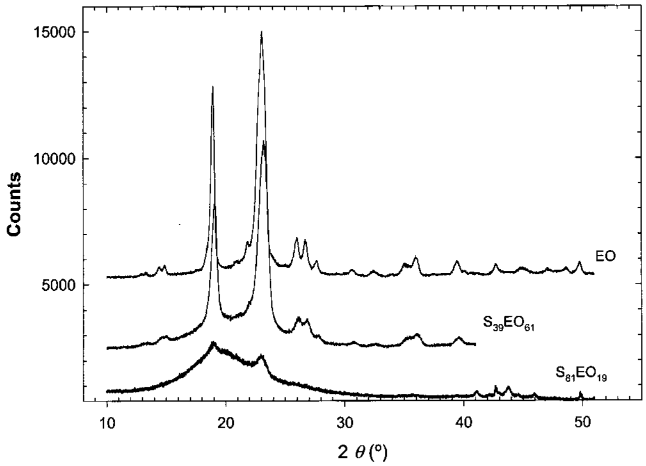


**Figure 8.** WAXS curves for poly(ethylene oxide) and the indicated SEO diblock copolymers.

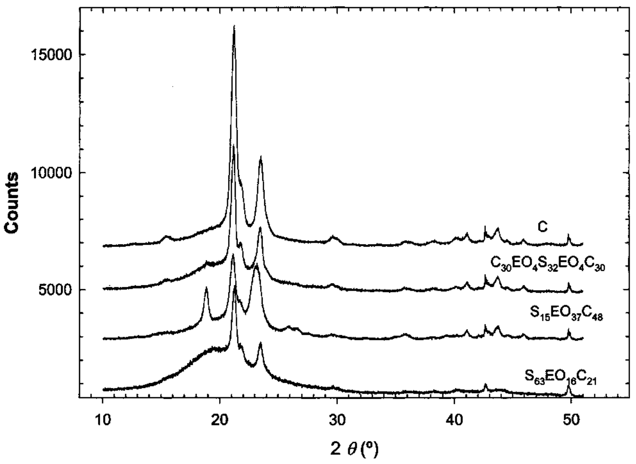


**Figure 9.** WAXS curves for poly($\epsilon$-caprolactone) and the indicated tri- and pentablock copolymers.

The WAXS trace of the precursor diblock copolymer $S_{81}EO_{19}$ (Figure 8) exhibits very low crystallinity at room temperature after being stored for several months in a freezer at −15 °C, thus confirming the existence of fractionated crystallization.

In the case of the diblock copolymer with a lower PS content, $S_{39}EO_{61}$, the crystallization process of the PEO block is similar to that of the homopolymer (see Table 2), and the WAXS trace shows a higher crystallinity for the PEO block (see Figure 8). Even though the triclinic unit cell of the PEO is maintained, a broadening and shift of the PEO reflections were detected, possibly indicating a compression of the unit cell and the presence of many defects in the crystalline lamellae of the diblock as compared to the homopolymer. These restrictions may be associated with the presence of a rigid PS block in the triblock copolymer.

$S_{46}EO_{12}C_{42}$ and $S_{10}EO_4C_{86}$ exhibit a low-temperature exotherm (Table 2) and a second one at about 27 and 33 °C, respectively, which correspond to PCL crystallization, since this is the component that is being incorporated with respect to the diblock precursor $S_{81}EO_{19}$ in Figure 6. These crystallization temperatures are comparable with the crystallization temperature of a PCL homopolymer (Table 2). In view of the small size of the exotherm corresponding to the PCL component in the $S_{46}EO_{12}C_{42}$ copolymer, it is possible that part of it is crystallizing in a fractionated fashion at coincident temperatures with the PEO component at around −40 °C.

The absence of a clear low-temperature exotherm in $S_{38}EO_{10}C_{52}$, despite its low PEO content, is unexpected. However, it could be possible that a fractionated crystallization occurs and that it is hidden in the baseline. Self-nucleation experiments are in progress to find an explanation for this behavior.[39]

Figure 6b presents the corresponding DSC heating scans after the cooling scans shown in Figure 6a. $S_{63}EO_{16}C_{21}$, $S_{46}EO_{12}C_{42}$, and $S_{38}EO_{10}C_{52}$ show two melting endotherms. From a comparison with the $S_{81}EO_{19}$ precursor it can be deduced that the endotherm located at lower temperatures is due to the melting of PEO crystals. Nevertheless, their melting peak temperatures are slightly shifted to lower temperatures (30, 29, and 20 °C for the copolymers vs 35 °C for the diblock precursor; see Table 2). This can be attributed to increased topological restrictions, a consequence of the chemical link with another crystallizable block (PCL) and the resulting morphology.[14,27] The comparison of the crystallinity degrees between the precursors and triblock copolymers in Table 2 corroborates this explanation, since the PEO blocks in the latter have a lower crystallinity. Similar effects were found previously in the polyethylene block of polystyrene-*b*-polyethylene-*b*-polycaprolactone triblock copolymers due to the absence of free chain ends.[27]

$S_{10}EO_4C_{86}$ has apparently only one melting endotherm in Figure 6b. However, self-nucleation experiments[39] revealed the presence of two melting transitions. Floudas et al.[40] have reported interesting effects on the crystallization behavior of PS-*b*-PEO-*b*-PCL star-block copolymers. In the case of different sizes of the PEO and PCL block, it appears that only the block with the longer length crystallizes. Nojima et al.[41] have studied the isothermal crystallization of PEO−PCL diblock copolymers and reported melting point depressions of the blocks with respect to homopolymers or polymer blends of equivalent compositions.

Figure 7 shows that the pentablock copolymers exhibit a thermal behavior that is similar to that of the triblock copolymers. This result is confirmed by the WAXS patterns reported in Figure 9. The pentablock $C_{30}EO_4S_{32}EO_4C_{30}$ shows a trace of crystallinity for the PEO block whereas in the triblock $S_{63}EO_{16}C_{21}$ this trace is still smaller despite the higher abundance of the PEO in the triblock.

The crystallization in the pentablocks occurs in a fractionated fashion with the presence of multiple exotherms due to the PCL and PEO blocks. Two melting endotherms appear, with a depression of the PEO melting temperature as in the case of the triblock copolymers above. A detailed report of the thermal behavior of the copolymers prepared in this work is under preparation.[39]

The above-mentioned trends in the WAXS measurements are in agreement with the calorimetric determination of the crystallinity degree, which gives 47% for the $C_{30}EO_4S_{32}EO_4C_{30}$ pentablock and 16% for the $S_{63}EO_{16}C_{21}$ triblock (Table 2). The crystallization process in this triblock is interfered by the existence of the rigid PS block which is predominant in the case of the triblock and restricts the crystallization more efficiently than in the case of the pentablock.

The $S_{15}EO_{37}C_{48}$ block copolymer exhibits a peculiar behavior in that it only displayed a single melting endotherm (not shown here), and therefore only one melting point is reported in Table 2. However, it is expected on the basis of the compositions of the PEO and the PCL blocks that both would crystallize, and therefore two endotherms should have been observed unless a total overlap of both melting endotherms is occurring (i.e., coincident melting). The fusion enthalpy reported in Table 2 for this copolymer is too high to be attributed to the melting of only the PEO block or only the PCL block; therefore, this indicates that coincident melting of both blocks is possibly present. The WAXS measurements made at room temperature confirmed that this was the case, since the WAXS diffractogram (Figure 9) displays sharp reflections characteristic of each homopolymer without any structural change. In addition, the intensities of the reflections indicate comparable crystallinities, showing that they were able to crystallize separately but their melting events occur in the same temperature range. Gan et al.[42] have reported the inhibition of PEO crystallization in the diblock copolymer $C_{80}EO_{20}$ using WAXS. This could be a consequence of fractionated crystallization and comparable with our results in the triblock copolymer with a similar PEO weight percent. Shiomi et al.[15] have made WAXS to PCL-*b*-PEO-*b*-PCL block copolymers for several compositions. They have observed WAXS patterns that are superpositions of those for PEO and PCL homopolymers.

## Conclusions

We have investigated three different routes for the preparation of PS-*b*-PEO-*b*-PCL triblock copolymers. The simplest technique is the thermal method, a route that works well if the molecular weight of the precursors is kept low. With this method we were able to produce several triblock copolymers as well as pentablock copolymers.

The use of a titration method employing diphenylmethylsodium to transform the terminal hydroxyl groups into alcoholates was also successful in producing the PS-*b*-PEO-*b*-PCL triblock copolymers. However, the polymerization time of the PCL block must be very short in view of the presence of the polar PEO block. This method was found to require a good experimental expertise since titration becomes difficult as the concentration of terminal hydroxyl groups is reduced upon increasing the molecular weight of the precursor.

A sequential method was also developed with the advantage that interrupting the reaction at the diblock copolymer precursor stage is not necessary to obtain the triblock copolymer. Nevertheless, a high level of purity under vacuum needs to be maintained during a process that involves changing solvents and adding the third monomer sequentially.

The prepared tri- and pentablock copolymers were found to be microphase segregated according to our DSC and WAXS results. The copolymers contain two crystallizable blocks, PEO and PCL, with crystallization and melting behaviors that are greatly affected by composition. When either one or both of these blocks are minor components, they crystallize in a fractionated fashion at temperatures below 0 °C. The thermal stability of the prepared copolymers studied by TGA is better than that of PEO homopolymers and comparable to that of polystyrene.

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