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ORIGINAL PAPER

Effect of temperature and water on microphase separation of PCL–PEO–PCL triblock copolymers

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Abstract Microphase separation of poly(ε-caprolactone-ethylene oxide-ε-caprolactone) (PCL–PEO–PCL), with block number-average molecular weights of 9,100–30,400–9,100 g/mol, was studied. Cylindrical morphology was observed in a solvent-cast sample. When the as-cast sample was heated above the melting points of both PEO and PCL blocks, a change in morphology was observed by Small Angle X-ray Scattering (SAXS). When this sample was cooled to room temperature in the ambient atmosphere, another morphology (lamellae) was observed with SAXS and Atomic Force Microscopy (AFM). This asymmetric change in morphology suggests a role of kinetics (microphase separation and crystallization) in determining the observed microstructures. Addition of water at room temperature also affected microphase separation of the block copolymer due to hydrophilicity of PEO. As the polymer concentration decreases from 100 to 60%, the morphology changes from cylinders to lamellae. Differential Scanning Calorimetry (DSC) data show that water addition decreases PEO crystallinity but PCL crystallinity remains.

Keywords Block copolymers · Microstructure · PCL · PEO · Semi-crystalline

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Introduction

Amphiphilic block copolymers, especially those containing polyethylene oxide (PEO) as a hydrophilic component, have been studied extensively due to their biomedical applications. For example, PEO/poly(ε-caprolactone) (PEO/PCL) block copolymers have been used in drug delivery systems due to the biocompatibility of PEO and PCL and the biodegradability of PCL. Drug loading and release behaviors have been reported [1–3] in addition to the kinetics of enzymatic degradation [4–6]. PEO and PCL are semi-crystalline, and the thermal properties of the PEO/PCL block copolymers in bulk have been studied [7–12]. Micellar self-assembly of PEO/PCL block copolymers in dilute aqueous solutions has been also reported [13]. The phase behavior of low molecular weight PEO/PCL block copolymers was studied at low polymer concentrations up to 35% [14, 15], however, most studies of phase behavior have been limited to either dilute solutions or to bulk systems, yet recently concentrated solutions have been used to form nanostructured and porous hydrogels [16].

In our study, various polymer concentrations (20–100 wt%) in water and high molecular weights of PCL–PEO–PCL were used to study phase behavior using Small Angle X-ray Scattering (SAXS), Atomic Force Microscopy (AFM), and Differential Scanning Calorimetry (DSC). High concentration studies are useful because the block copolymers exhibit multiple morphologies at high concentrations including lamellae and cylinders [17]. The influence of the crystallinity of both PEO and PCL upon microphase separation was examined both by varying the temperature and by adding water, the latter of which should affect PEO crystallinity more strongly than PCL crystallinity due to its hydrophilic nature.

Materials and methods

Materials

Two PEO homopolymers (nominal viscosity-average molecular weight $M_v =$ 100,000 g/mol while number-average molecular weight determined by GPC $M_\mathrm{n} = 30{,}400$ g/mol; nominal $M_\mathrm{n} = 10{,}000$ g/mol while M_n by GPC = 15,000 g/mol), ε-caprolactone, and stannous octoate were purchased from Sigma-Aldrich and used without further purification. Sodium azide and methanol were purchased from Mallinckrodt (Phillipsburg, NJ), and the solvents (dichloromethane, n-hexane) were obtained from EMD Chemicals (Gibbstown, NJ).

Synthesis of PCL–PEO–PCL triblock copolymers

Ten grams of PEO (M_n determined by GPC = 30,400 g/mol) was reacted with 17 mL of ε-caprolactone in the presence of three drops of stannous octoate (~0.03 g; 0.1 wt%) as a catalyst at 130 °C for 21 h under a nitrogen atmosphere. A synthesized block copolymer was dissolved in dichloromethane and precipitated into cold n-hexane three times to remove unreacted monomers and PEO

Table 1 PCL–PEO–PCL triblock copolymer synthesized

	M_n (PEO)[a] (g/mol)	M_n (NMR)[b] (g/mol)	M_n^c (g/mol)	M_w/M_n^c
E30CL36	30,400	9,100–30,400–9,100	43,100	1.17

[a] Determined by GPC using starting PEO homopolymer; [b] determined by ^{1}H-NMR based on the M_n of PEO measured by GPC; [c] from GPC

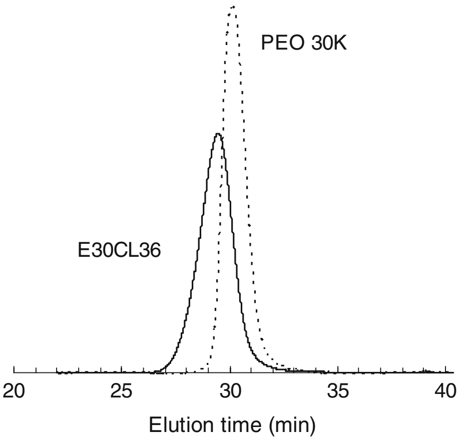


Fig. 1 GPC chromatograms of the starting PEO homopolymer (*dotted line*) and PCL–PEO–PCL triblock copolymer synthesized (E30CL36; *solid line*)

homopolymer. The final product was dried in a hood at room temperature for 1 day and in a vacuum oven at 40 °C for another 2 days. Table 1 shows the PCL–PEO–PCL block copolymer synthesized, whose molecular weights were determined by ^{1}H-NMR and GPC. The polymerization yield was 33%, which was determined by comparing the amount of added ε-caprolactone monomer and the M_n (NMR) of the PCL block. The low yield is probably due to impurities in starting materials. When the starting chemicals are purified, quantitative yields are obtained [18, 19]. The block copolymer is denoted as E30CL36, signifying that 30,400 g/mol of PEO was used, and that the volume percent of PCL is 36%. Figure 1 shows GPC chromatograms of the starting PEO homopolymer and E30CL36.

Morphology of PCL–PEO–PCL triblock copolymers

The morphologies of the dried powder samples of the block copolymer were studied after drying the purified polymer solutions (mainly in dichloromethane as a solvent) in a hood at room temperature for 1 day and in a vacuum oven at 40 °C for another 2 days. The synthesis and purification of the polymer in addition to solvent evaporation were repeated twice, and those separately prepared powder samples yielded reproducible morphology results obtained using Small Angle X-ray Scattering (SAXS) (described in more detail in the Characterization section). Aqueous polymer samples were prepared by adding Milli-Q water with 0.01% NaN_3 to make 20, 40, 60, and 80% polymer concentrations, and after equilibration at room temperature for a week, morphologies of those samples were studied using SAXS.

Crosslinking of PCL–PEO–PCL by electron beam irradiation

The morphology formed at an 80% polymer concentration was fixed by electron beam crosslinking so it can be observed by AFM in a dry state. In order to form a solution of 80% polymer concentration, Milli-Q water with 0.01% NaN_3 was added to PCL–PEO–PCL in a 5-cm diameter Petri dish. After equilibration at room temperature for a week, the aqueous solution underwent electron beam irradiation to crosslink primarily the PEO block in the block copolymer. Under an electron beam, water is degraded to produce $^{\bullet}OH$ and $O^{\bullet -}$ radicals that abstract hydrogen from the PEO block, and crosslinks are formed by the combination of these $-^{\bullet}CH-$ radicals [16, 20]. The hydrophobic PCL is not expected to be crosslinked significantly as water plays such an important role [16]. A 50 Mrad dose was applied, and the temperature during irradiation was not controlled. An average molecular weight between crosslinks (M_c) of the PEO block of the crosslinked sample was ~7,700 g/mol, determined by aqueous swelling experiments of PEO homopolymer ($M_n = 30{,}400$ g/mol) crosslinked at 80% polymer concentration and 50 Mrads. The crosslinked block copolymer was not used to determine the M_c because the presence of hydrophobic PCL blocks affects equilibrium swelling. The M_c of the PEO hydrogel was calculated by using the following equation,

$$\frac{1}{M_c} = \frac{2}{M_n} - \frac{\ln(1 - v_{2s}) + v_{2s} + \chi_{FH} v_{2s}^2}{V_1 \rho_2 v_{2s}^{1/3} - v_{2s}/2} \tag{1}$$

where M_n is number-average primary polymer molecular weight, v_{2s} is polymer volume fraction at aqueous equilibrium swelling, V_1 is molar volume of water, ρ_2 is polymer density, and χ_{FH} is Flory–Huggins interaction parameter (0.426 between water and PEO at room temperature as determined by osmometry [20]). The crosslinked block copolymer was extracted with 0.01% NaN_3 Milli-Q water, and dried in a vacuum oven at 40 °C for 2 days for AFM measurement.

Characterization

Number and weight average molecular weights (M_n and M_w, respectively) and polydispersities (M_w/M_n) were obtained using a Waters Gel Permeation Chromatograph (GPC) equipped with a series of six Waters Styragel columns (HR 0.5, HR 1, HR 3, HR 4, HR 5, and HR 6) and a refractive-index detector (Optilab, Wyatt Technology) at the University of Akron using tetrahydrofuran (THF) as the solvent at a 1 mL/min elution rate with calibration through use of polystyrene standards.

Small Angle X-ray Scattering (SAXS) experiments were performed at the Institute for Soldier Nanotechnologies (ISN) at MIT. Wet samples of triblock copolymers (emulsions in water) were enclosed in Kapton^{TM} tape. SAXS data were collected for 1,000 s. Background calibration was performed by subtracting the signals from the corresponding empty Kapton^{TM} tape holders. Scattering data were analyzed using Datasqueeze^{TM} and integrated using the "average" function. The "sum" integration method was used for Figs. 2 and 8 to make the peaks more pronounced in the graphs; however, the peak positions were same as the integration results obtained using "average."

An Atomic Force Microscopy (AFM) image was taken with a Veeco Metrology Group Nanoscope IV Scanning Probe Microscope (Digital Instruments) at the MIT Center for Material Science and Engineering (CMSE). A dry sample was microtomed to produce a smooth surface for AFM measurement.

Melting peaks (T_m) and crystallization peaks (T_c) of the block copolymer were obtained with a Perkin Elmer Pyris 1 Differential Scanning Calorimeter (DSC) at CMSE. Powder samples of 5–10 mg were enclosed in aluminum pans and were heated at the rate of 10 °C/min from 20 to 100 °C, held at 100 °C for 3 min, and cooled at the rate of 10 °C/min to 20 °C. These samples were heated again to 100 °C at the same rate to collect the DSC results for the heating cycle, so as to erase previous thermal history. Aqueous samples are prepared using high pressure stainless steel pans with O-rings to prevent the evaporation of water.

Results and discussion

Microphase separation of the block copolymer by solvent evaporation

Microphase separation of the block copolymer, E30CL36 (Table 1), was induced by solvent (dichloromethane) evaporation at room temperature for 1 day and by further drying at 40 °C for 2 days. Crystallization of PEO of the block copolymer competes with the microphase separation process [10] because the morphology induced by microphase separation raises the free energy of the crystalline phase, most likely through domain size-associated surface free energy. E30CL36 has a 36% volume fraction of PCL, and its microphase separation was studied using SAXS (Fig. 2). SAXS shows three peaks whose q ratios are $1:\sqrt{3}:\sqrt{7}$. The expected q ratio for a cylindrical microphase is $1:\sqrt{3}:\sqrt{4}:\sqrt{7}\ldots$[21], but as peak positions for $\sqrt{3}$ and $\sqrt{4}$ lie close together, the sample is identified as having a cylindrical morphology

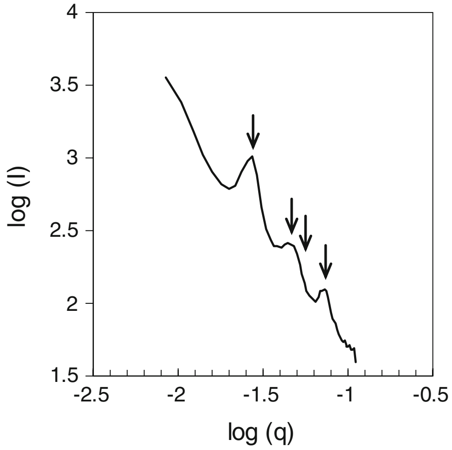


Fig. 2 SAXS of E30CL36 powders prepared by solvent evaporation; *the arrows* are expected peak positions for a cylindrical microphase; the first order peak is 24 nm

(cylinders of PCL in PEO matrix) despite of the absence of a separately identifiable peak at the $\sqrt{4}$ position.

Effect of temperature on morphology of E30CL36

The melting behavior of E30CL36 powder samples was studied using DSC. PCL homopolymer, 8,000 g/mol, has a melting peak (T_m) at 59 °C [11], while PEO homopolymer, 30,400 g/mol has a T_m at 67 °C (data not shown). However, the block copolymer, E30CL36, exhibited lower T_ms as shown in Fig. 3. The T_m of PEO was reduced to 61 °C probably due to the imperfect crystallization rendered by microphase separation, while the T_m of PCL was observed at ~54 °C. PCL crystallinity was suppressed significantly due to the shorter block length of PCL than that of PEO (Fig. 3). Comparable results were reported by Gan et al.[7], who suggested that the shorter PEO block length relative to that of PCL (20 wt% PEO) in their PEO–b–PCL sample resulted in complete suppression of PEO crystallinity. The cooling cycle also shows two crystallization peaks, and the peak at 42 °C is that of PEO. Presence of both crystallization peaks of PEO and PCL in addition to melting peaks of PEO and PCL further confirms microphase separation of the block copolymer.

The effect of temperature on microphase separation of the block copolymer was studied using SAXS (Fig. 4). Powder samples of E30CL36 were enclosed in Kapton Tape^{TM}, and mounted on a hot stage to increase the temperature to 70 °C. Before collecting scattering data, samples were equilibrated at each reported temperature for 30 min. At low temperatures, three peaks were observed, and their q ratios are $1:\sqrt{3}:\sqrt{7}$, indicating a cylindrical morphology. This morphology is retained until melting of PEO and PCL occurs. After melting at ~60 °C, the first order peak decreased to a lower q, representing an increase in the domain size, but the changed morphology could not be identified due to the presence of only one peak. The block copolymer is expected to have an equilibrium morphology at temperatures above the melting points of both blocks. The mean-field theory suggests that the block copolymer has a gyroid microphase as the volume fraction of PCL is 36% [22]. Therefore, the change in morphology observed at temperatures above melting points of PEO and PCL suggests that the cylindrical morphology obtained by solvent

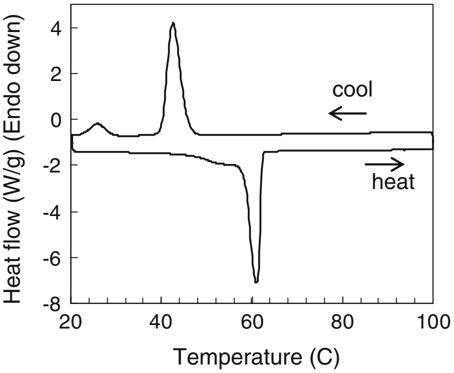


Fig. 3 DSC of E30CL36 powders; the second heat cycle of DSC is shown in addition to the cooling cycle; the first melting peak is the T_m of PCL (54 °C), while the second at 61 °C is the T_m of PEO; in the cooling cycle, $T_{c,PCL} = 25$ °C and $T_{c,PEO} = 42$ °C

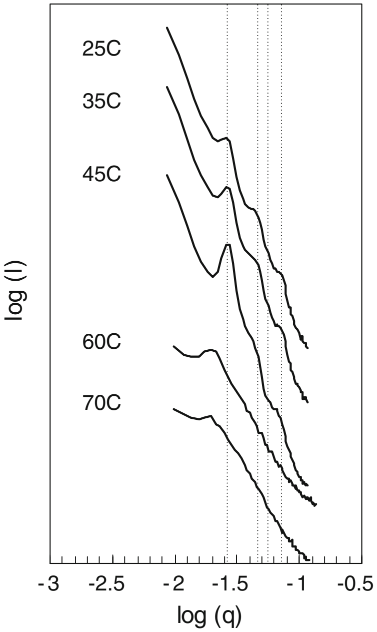


Fig. 4 SAXS of E30CL36 powders; *the dotted lines* are expected peak positions for a cylindrical microphase; the first order peaks are 24 nm for 25, 35, and 45 °C, and 31 nm for 60 and 70 °C

evaporation at below the melting points was determined kinetically through competition between microphase separation and the crystallization of PEO and PCL. The kinetically captured cylindrical morphology was reproducible upon multiple observations.

An as-cast sample of the block copolymer was heated at 70 °C for 1 day to melt the crystalline structures, and then re-cooled to room temperature at ambient atmosphere. The resulting sample was investigated by SAXS, and it was found that the sample has a lamellar morphology as shown in Fig. 5. This is perhaps because PCL and PEO blocks crystallize while cooling, producing PCL crystalline lamellae next to amorphous regions of PEO [7, 23, 24]. Slow cooling is expected to produce more complete microphase separation, and PEO will crystallize within microphase-separated structures [10], which will render cylinders as in the as-cast of E30CL36 from dichloromethane. When water is added to decrease the polymer concentration to 80%, the lamellar morphology is retained, and the length scale of the lamellae increases from 27 to 29 nm due to swelling of the PEO.

The lamellar structures of E30CL36 were also observed by AFM. The sample for AFM was prepared by crosslinking the block copolymer at 80% polymer concentration by electron beam irradiation [16] to fix the microstructure. Figure 6 shows an AFM phase image of the sample in a dry state. The domain size of the lamellar structure is 23 nm.

Effect of water on morphology of E30CL36

Good solvent reduces the melting points of crystalline polymers, and is mixed with the polymer chains in the amorphous regions [25]. The effect of water on the

Fig. 5 SAXS of E30CL36 at room temperature; *the arrows* are expected peak positions for an indicated morphology followed by a domain size in parentheses; *80%* indicates 80% polymer concentration in water

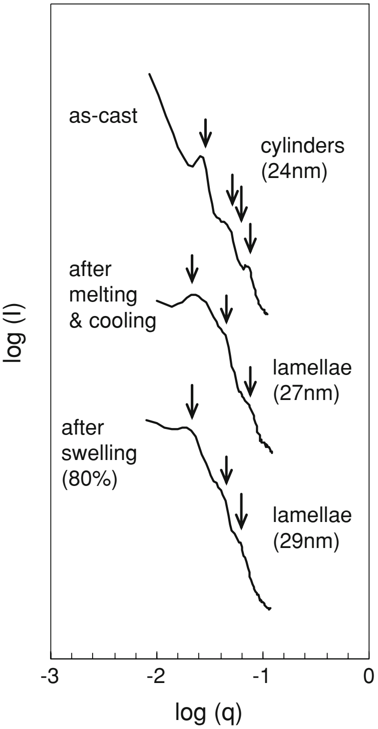
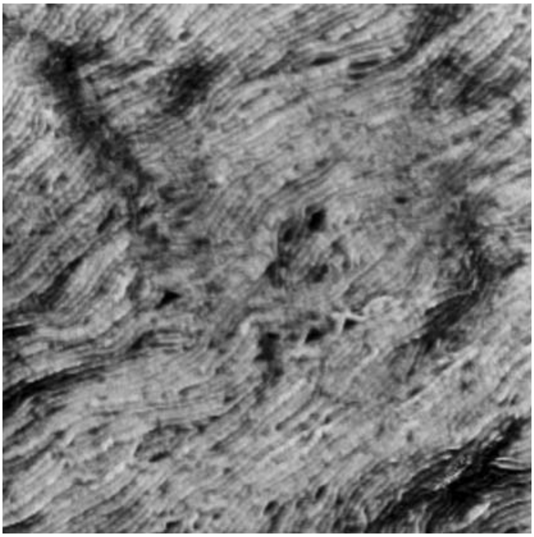


Fig. 6 AFM phase image of crosslinked E30CL36 at 80% polymer concentration; image size is 1 μm × 1 μm, and a domain size of the lamellae is 23 nm (*dry sample*)



hydrophilic PEO homopolymer ($M_n = 15{,}000$ g/mol) was studied using DSC. In the bulk phase, it has a T_m peak at 66 °C. However, when water is added to decrease the polymer concentration to 80%, the T_m decreases to 51 °C (data not shown). Furthermore, as more water was added to reduce the polymer concentration further to 20%, the melting peak disappeared, suggesting dissolution of the PEO in water. Since PCL–PEO–PCL is amphiphilic, water can produce interesting morphology changes in the block copolymer systems. Previously, it was described that having a PCL block shorter than the PEO block resulted in significant suppression of PCL crystallinity. When water is added to the block copolymer, water will increase the amorphous regions of PEO, and hence improve PEO mobility. This may improve PCL crystallization and PCL crystalline lamellae formation may be enhanced considerably.

In order to study the effect of water on the crystallinity of PCL–PEO–PCL block copolymer, DSC experiments were performed at various polymer concentrations (Fig. 7). As described previously, the bulk (100% concentration) sample has crystallization peaks of both PCL and PEO (25 and 42 °C, respectively). At 80% polymer concentration, the T_c of PEO decreased, and the T_c of PCL increased which made the PCL peak overlap with that of PEO. The crystallization peak height of PEO also decreased relative to that of PCL, suggesting the crystallization portion was reduced and the amorphous region increased. When more water was added to make 60% polymer concentration, two crystallization peaks were completely overlapped.

The effect of water upon the block copolymer morphology was studied using SAXS (Fig. 8). As described above, a bulk (100% concentration) sample of the block copolymer exhibits a cylindrical morphology following solvent evaporation. When water was added to reduce the concentration to 80% followed by a week of equilibration, the cylindrical morphology was retained with a slight increase in length scale due to swelling of PEO by water. However, as more water was added to reduce the polymer concentration to 60%, a dramatic morphology change occurred. The 60% SAXS spectrum shows three peaks, and the q ratios are 1:2:3, indicating lamellar structure. This morphology remains with 20 and 40% samples. The morphology change from cylinders to lamellae is probably related to decreased PEO crystalline portion, hence increased amorphous region.

These SAXS and DSC data suggest that water reduces PEO crystallinity and increases PEO mobility, hence might improve PCL crystallinity that was suppressed by PEO crystallization. This suggested idea was schematically drawn in Fig. 9. In the figure, water increases an amorphous portion of PEO and mixes with the PEO

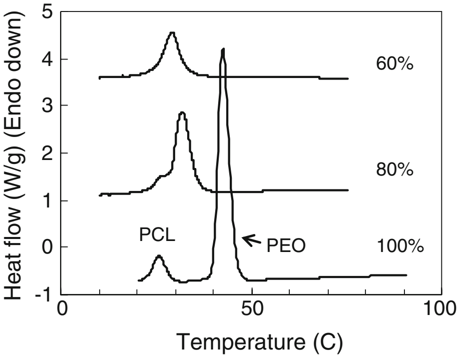


Fig. 7 DSC cooling curves of E30CL36; in a 100% sample, the crystallization peak at 25 °C is T_c of PCL, while the one at 42 °C is that of PEO; for 60 and 80% aqueous samples, 5 °C/min cooling rate was used, while 10 °C/min was used for a 100% sample

Fig. 8 SAXS of E30CL36 in water at various polymer concentrations; *the arrows* for 20, 40, and 60% are expected peak positions for a lamellar microphase, while 80 and 100% a cylindrical microphase; the first order peak for 20, 40, 60, 80, and 100% are 52, 45, 40, 25, and 24 nm, respectively

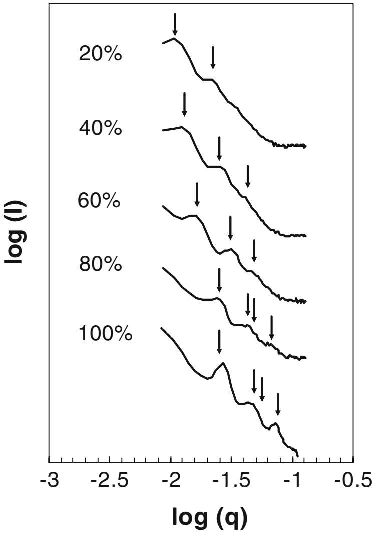
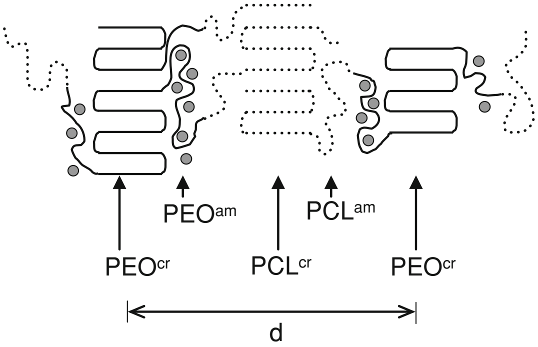


Fig. 9 Brief schematic drawing of the lamellar morphology of E30CL36 at 60% polymer concentration; *gray dots* denote water molecules; *PEO^{cr} and PEO^{am}* denote the crystalline and amorphous regions of PEO; *PCL^{cr} and PCL^{am}* denote the crystalline and amorphous regions of PCL; *d* denotes the domain size



chain in the amorphous regions only [25]. This amorphous region improves PEO mobility, and makes it easier to form PCL crystalline lamellae, resulting in lamellar microphase separation between PEO and PCL in the block copolymer. Unfortunately, few studies have been reported about morphologies of PEO/PCL block copolymers when both blocks are comparably crystalline. An et al. [10] used SAXS to study a morphology change between two different crystallization temperatures, however, they did not succeed in identifying the morphology observed at the ~18 nm length scale due to experimental difficulties. Further studies are required to understand better the morphology effect of water addition.

Conclusions

The microphase separation of PCL–PEO–PCL (M_n = 9,100–30,400–9,100 g/mol, volume fraction of PCL = 0.36) was studied using SAXS, AFM, and DSC. The morphologies of the block copolymer at room temperature were determined by competition between microphase separation and crystallization of PEO and PCL. Two different morphologies (cylinders and lamellae) were observed at room temperature in addition to the unidentified one at temperatures above melting points of both blocks. A cylindrical morphology was formed by solvent evaporation of the block copolymer at room temperature and annealing at 40 °C. Lamellae were observed after the block copolymer was melted and cooled to room temperature. Addition of water at room temperature also changed the morphology from cylinders to lamellae.

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References

1. Yoo Y, Kim D-C, Kim T-Y (2009) Preparation and characterization of enalapril maleate-loaded nanoparticles using amphiphilic diblock copolymers. J Appl Polym Sci 74:2856–2867
2. Ge H, Hu Y, Jiang X, Cheng D, Yuan Y, Bi H, Yang CJ (2002) Preparation, characterization, and drug release behaviors of drug nimodipine-loaded poly(ε-caprolactone)-poly(ethylene oxide)-poly (ε-caprolactone) amphiphilic triblock copolymer micelles. Pharm Sci 91:1463–1473
3. Yu Z, Liu L (2005) Microwave-assisted synthesis of poly(ε-caprolactone)-poly(ethylene glycol)-poly(ε-caprolactone) tri-block co-polymers and use as matrices for sustained delivery of ibuprofen taken as model drug. J Biomater Sci Polym edn 16:957–971
4. Gan Z, Jim TF, Li M, Yuer Z, Wang S, Wu C (1999) Enzymic biodegradation of poly(ethylene oxide-b-ε-caprolactone) diblock copolymer and its potential biomedical applications. Macromolecules 32:590–594
5. Zhao Y, Hu T, Lv Z, Wang S, Wu C (1999) Laser light-scattering studies of poly(caprolactone-b-ethylene oxide-b-caprolactone) nanoparticles and their enzymatic biodegradation. J Polym Sci B 37:3288–3293
6. Nie T, Zhao Y, Xie Z, Wu C (2003) Micellar formation of poly(caprolactone-block-ethylene oxide-block- caprolactone) and its enzymatic biodegradation in aqueous dispersion. Macromolecules 36:8825–8829
7. Gan Z, Jiang B, Zhang J (1996) Poly(ε-caprolactone)/poly(ethylene oxide) diblock copolymer. I. Isothermal crystallization and melting behavior. J Appl Polym Sci 59:961–967
8. Gan Z, Zhang J, Jiang B (1997) Poly(ε-caprolactone)/poly(ethylene oxide) diblock copolymers. II. Nonisothermal crystallization and melting behavior. J Appl Polym Sci 63:1793–1804
9. Bogdanov B, Vidts A, Van Den Bulcke A, Verbeeck R, Schacht E (1998) Synthesis and thermal properties of poly(ethylene glycol)-poly(ε-caprolactone) copolymers. Polymer 39:1631–1636
10. An JH, Kim HS, Chung DJ, Lee DS, Kim S (2001) Thermal behavior of poly(ε-caprolactone)-poly(ethylene glycol)-poly(ε-caprolactone) tri-block copolymers. J Mater Sci 36:715–722
11. Piao L, Dai Z, Deng M, Chen X, Jing X (2003) Synthesis and characterization of PCL/PEG/PCL triblock copolymers by using calcium catalyst. Polymer 44:2025–2031
12. Loh XJ, Colin Sng KB, Li J (2008) Synthesis and water-swelling of thermo-responsive poly(ester urethane)s containing poly(ε-caprolactone), poly(ethylene glycol) and poly(propylene glycol). Biomaterials 29(22):3185–3194
13. Zhao Y, Liang H, Wang S, Wu C (2001) Self-assembly of poly(caprolactone-b-ethylene oxide-b-caprolactone) via a microphase inversion in water. J Phys Chem B 105:848–851
14. Hwang MJ, Suh JM, Bae YH, Kim SW, Jeong B (2005) Caprolactonic poloxamer analog: PEG–PCL–PEG. Biomacromolecules 6:885–890
15. Bae SJ, Suh JM, Sohn YS, Bae YH, Kim SW, Jeong B (2005) Thermogelling poly(caprolactone-b-ethylene glycol-b-caprolactone) aqueous solutions. Macromolecules 38:5260–5265

16. Kang J, Beers KJ (2006) Synthesis and characterization of PCL-b-PEO-b-PCL-based nanostructured and porous hydrogels. Biomacromolecules 7:453–458
17. Wanka G, Hoffmann H, Ulbricht W (1994) Phase diagrams and aggregation behavior of poly(oxyethylene)-poly(oxypropylene)-poly(oxyethylene) triblock copolymers in aqueous solutions. Macromolecules 27:4145–4149
18. Yilgor I, Steckle WP Jr, Yilgor E, Freelin GR, Riffle JS (1989) Novel triblock siloxane copolymers: synthesis, characterization, and their use as surface modifying additives. J Polym Sci A Polym Chem 27(11):3673–3690
19. Cerrai P, Tricoli M, Andruzzi F, Paci M, Paci M (1989) Polyether-polyester block copolymers by noncatalyzed polymerization of ε-caprolactone with polyethylene glycol. Polymer 30(2):338–343
20. Dennison KA (1986) Radiation crosslinked poly(ethylene oxide) hydrogel membranes, Chap 3. Ph.D. Thesis, Massachusetts Institue of Technology
21. Chu B, Hsiao BS (2001) Small-angle X-ray scattering of polymers. Chem Rev 101:1727–1761
22. Bates FS, Fredrickson GH (1999) Block copolymers-designer soft materials. Phys Today 52:32–38
23. Nojima S, Hashizume K, Rohadi A, Sasaki S (1997) Crystallization of ε-caprolactone blocks within a crosslinked microdomain structure of poly(ε-caprolactone)-block-polybutadiene. Polymer 38:2711–2718
24. Perret R, Skoulios A (1972) Crystallization of trisequenced poly(ε-caprolactone)/poly(oxyethylene)/poly(ε-caprolactone) copolymers. I. Copolymers with sequences of very different lengths. Makromol Chem 162:147–162
25. Sharples A (1966) Introduction to polymer crystallization, Chap 9. Edward Arnold, London