

Sharif University of Technology Scientia Iranica Transactions C: Chemistry and Chemical Engineering www.scientiairanica.com



Synthesis and characterization of biodegradable multiblock copolymers of L-lactide, ε -caprolactone and poly(ethylene glycol)

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Received 5 May 2012; received in revised form 8 December 2012; accepted 4 March 2013

KEYWORDS

Tailor-made polymers; ε -caprolactone; L-lactide; PEG; Multiblock copolymers. Abstract. Two multiblock copolymers of polyethylene glycol (PEG), L-lactide (LLA) and ε -caprolactone (CL) were synthesized and characterized. Triblock prepolymers were first synthesized using PEG with molecular weight (M_n) of 15,000 Daltons, ε -caprolactone or L-lactide in the presence of Sn(Oct)₂ as catalyst. The triblock PCL-b-PEG-b-PCL prepolymer with two hydroxyl functional groups was subjected to further block copolymerization with L-lactide in the presence of Sn(Oct)₂ as catalyst. Similarly, the triblock PLLA-b-PEG-b-PLLA prepolymer was subjected to further block copolymerization with ε -caprolactone in the presence of the same catalyst. The molecular structures of the copolymers were characterized by ¹H NMR and ¹³C NMR analyses. The thermal behavior and thermal stability of these copolymers were evaluated by DSC and TGA thermograms, respectively. Finally, the effect of each discrete block on thermal behavior and stability was studied in the typical pentablock copolymers.

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1. Introduction

Biodegradable thermoplastic elastomer (BTPE) polymers has been known, since the 1970s, by the trade name KRATON[®], but intensive research into BTPE has started recently. It is also remarkable that nowadays there are not many commercial biodegradable thermoplastic elastomeric materials on the market. These polymers could be degraded into CO_2 and H_2O in vivo, since their ester bond can easily be broken by hydrolysis with a wide range of degradation rates.

*. Corresponding author. Tel.: +98 182 4652062; Fax: +98 182 4652600 E-mail address: roshandeh@ut.ac.ir (J. Mohammadi-Rovshandeh) These polymers are mainly based on lactide, glycolide, ε -caprolactone and polyethylene glycol (PEG). Some properties of polylactide (PLA) and Poly(ε caprolactone) (PCL), such as non toxicity, degradability, remoldability, permeability and cytocompatibility, make them more suitable for biomedical applications, especially as cardiovascular assist devices, controlled drug release, biodegradable sutures, artificial skin, absorbable prostheses and tissue engineering scaffolds [1-4].

In the last decade, biodegradable copolymers of ε caprolactone and L, D,-lactide [3,5-8] have been synthesized and characterized. These synthetic materials offer good elasticity and unique properties, making them ideal for the development of new biomaterials. Block copolymers of ε -caprolactone and L-lactide have been prepared by ring-opening polymerization in the melt state using stannous octoate/ethanol as an initiator, and the mechanism of polymerization had been investigated [9]. Entezami [10] synthesized a block, graft and hyperbranched co-polymer using NMP(nitroxide mediated polymerization) and ATRP (atom transfer radical polymerization). In the meantime, ABA triblock copolymers have been synthesized from ε caprolactone, glycolide and lactide. In these copolymers, B block was homopolymer of ε -caprolactone, and two end blocks were random copolymers of glycolide and lactide. These copolymers presented a two-phase structure, i.e. PCL crystalline and PLA amorphous domains [11,12]. The random terpolymer of L-lactide, ε caprolactone and glycolide has been synthesized in bulk using stannous octoate as the coordination-insertion initiator, and the results showed that the desired copolymers with specific properties were difficult to achieve by random copolymerization [13]. Mallakpour and Rafiemanzelat [14] synthesized new kinds of optically active thermoplastic elastomers and concluded that an increase in the soft segment length can cause an increase in phase separation, as well as an increase in the initial thermo-oxidative stability of polymers.

The aim of this study is to synthesize random and block copolymers of PLA and PCL to improve the properties of the constituent monomers by varying the monomer sequencing, molecular weight and composition of the copolymer to meet the specific requirements of particular applications.

Two kinds of ABCBA pentablock copolymers of PEG, L-lactide and ε -caprolactone were synthesized and characterized to investigate the effects of each block on copolymer structure and thermal stability. In the first type, A and B blocks were polylactide and poly(ε -caprolactone), respectively. In the second type, A and B blocks were poly(ε -caprolactone) and polylactide, respectively. PEG constitutes the central block (C) in both types of block copolymer. The structures of the block copolymers were characterized by ¹H NMR and ¹³C NMR spectroscopy. Thermal properties of the copolymers were investigated by Differential Scanning Calorimetry (DSC) and thermogravimetric analysis (TGA).

2. Materials and methods

2.1. Materials

L-lactide was prepared from 90% L-lactic acid solution (Merck Inc. Darmstadt Germany) according to a previous report [15]. The monomer was purified by multiple recrystallizations with ethyl acetate. The catalyst, tin-2-ethyl hexanoate, $Sn(Oct)_2$ (Sigma, St. Louis, USA). was purified by vacuum distillation. ε -caprolactone was purchased from Merck (Germany) and used without any further purification. Poly(ethylene glycol) (M_n = 15,000) was obtained from Merck (Germany) and used as received. All other chemicals or solvents were reagent grade (Merck, Darmstadt, Germany) and, if necessary, were purified according to the established procedures [16].

2.2. Polymerization

2.2.1. Preparation of prepolymers:

PCL-b-PEG-b-PCL and PLLA-b-PEG-b-PLLA Appropriate amounts of PEG (for example 7.5 g, 0.125 mol) and $\text{Sn}(\text{Oct})_2$ [0.5-mL catalyst solution (3%) stannous $octoate(Sn(Oct)_2)$ in toluene] were poured into a 100 mL polymerization tube and kept under vacuum at 70°C for 1 h. Then, the calculated amount of ε -caprolactone (28.5 g, 0.25 mol) or L-lactide was added and kept under vacuum at 40°C for 2 h, until all the volatiles were removed. The tube was then sealed under vacuum and placed in the silicon oil bath at 110°C for 48 h. Subsequently, the tube was broken and the contents cut into small pieces and dissolved in ethyl acetate, and precipitated in hexane. The resulting triblock copolymers were purified under vacuum at ambient temperature for 24 h and used as the central block in the synthesis of pentablock copolymers.

2.2.2. Preparation of pentablock copolymers: PLLA-PCL-b-PEG-b-PCL-PLLA and PCL-PLLA-b-PEG-b-PLLA-PCL

For the preparation of pentablock copolymer, predetermined amounts of PCL-b-PEG-b-PCL prepolymer and $Sn(Oct)_2$ were placed in a polymerization tube and kept under vacuum at 70°C for 1 h. Then, the calculated amount of lactide was added under the nitrogen atmosphere, and the mixture was kept under vacuum at 50°C for 2 h. The tube was sealed under vacuum and then immersed in the silicon oil bath at 120°C for 48 h. Subsequently, the glass tube was broken, the contents dissolved in ethyl acetate and precipitated in hexane, and then subjected to high vacuum at ambient temperature for 24 h.

2.3. Characterizations

 $^1\mathrm{H}$ NMR and $^{13}\mathrm{C}$ NMR spectra of the copolymers were recorded on a Brucker-DRX-500 spectrometer at 500 and 125 MHz, respectively. The analyses were performed at ambient temperature with 5% (w/v)polymer solution in CDCl₃, and tetramethylsilane was used as the internal reference. Thermal analysis was performed with DSC (TA DSC-60) under an ultra high purity nitrogen atmosphere. Samples were heated to 140°C for 5 min to erase previous thermal history and then cooled to -80° C at a nominal rate of 10°C/min. Thermogravimetric measurements were conducted with a TGA Q50 V6.3 system in platinum pans at a prescribed heating rate of 10°C/min under a steady flow of nitrogen of 80 mL/min. The glass transition temperature (T_q) , the melting temperature (T_m) and melting enthalpies were obtained from the thermograms.

3. Results and discussion

Triblock copolymers (A–B–A type) were synthesized via ring opening polymerization of ε -caprolactone (CL) or L-lactide (LLA) monomers initiated by PEG as macro-initiator and Sn(Oct)₂ as catalyst. The A block is PCL or PLLA, and the B block is poly(ethylene glycol), (PEG) (Figure 1). These triblock copolymers act as macro-initiators, and are used for the preparation of pentablock copolymers.

The triblock prepolymers with two hydroxyl functional groups were subjected to further block copolymerization with L-lactide or ε -caprolactone in the presence of Sn(Oct)₂ as catalyst. Two ABCBA pentablock copolymers were obtained. The A block was a L-lactide or ε -caprolactone block, B block was a ε -caprolactone or L-lactide block and C block was the PEG. The polymerization reactions are shown in Figure 2.

The typical ¹H NMR spectrum of the PLLA₆₀-PCL-PEG-PCL-PLLA₆₀ copolymer is shown in Figure 3. The characteristic ¹H NMR methylenic moiety in PEG appears at 3.66 δ ppm. The caprolactyl methylenic protons appear at 4.08 δ ppm (CH₂-O) and 2.27 δ ppm (CH₂-CO) and the inner methylenic protons appear at 1.28–1.41 δ ppm. The CH₃ and CH protons of lactide appear at 1.61 and 5.19 δ ppm, respectively.

The PLA/PEG/PCL ratios in the multiblock copolymer were calculated from the integral signal areas at 5.19 δ ppm (lactide), 2.27 δ ppm (ε -caprolactone)



Figure 1. Ring opening polymerization of ε -caprolactone and L-lactide with PEG in the presence of $Sn(Oct)_2$.



Pentablock Copolymer (PCL-PLLA-PEG-PLLA-PCL)





Figure 3. ¹H–NMR spectrum of PLLA₆₀-PCL-PEG-PCL-PLLA₆₀ multiblock copolymer.

and 3.38 δ ppm (polyethylene glycol). The calculated results are listed in Table 1, and verify the feed ratios. This may be related to the high yield (>95%) in the block copolymerization. For simplicity, the feed ratio was used as the composition ratio in the discussion.

The ¹³CNMR spectrum of this multiblock copolymer is shown in Figure 4. The CH and CH₃ carbons of lactide moiety appear at 70.0 and 17.05 δ ppm, respectively. The inner caprolactyl methylenic carbons appear at 28.7, 25.94 and 24.98 δ ppm. The caprolactyl methylenic carbons appear at 64.55 δ ppm (CH₂-O) and 34.53 δ ppm (CH₂-CO). The carbon peak of PEG is also observed at 70.97 δ ppm. The carbonyl carbons of ε -caprolactone and lactide appear at 170 and 173.9 δ ppm, respectively.

The ¹H NMR and ¹³C NMR spectra confirm the structure of PLLA₆₀-PCL-PEG-PCL-PLLA₆₀ multiblock copolymer.

The typical ¹H NMR spectrum of a PCL₈₀-PLLA-PEG-PLLA-PCL₈₀ copolymer is shown in Figure 5.

Polymer	$egin{array}{llllllllllllllllllllllllllllllllllll$	Mole ratio calculated from 1 H-NMR LLA/ ε -CL/PEG (%)
PLLA	100/0/0	100/0/0
$\operatorname{PEG}15000$	0/0/100	0/0/100
PCL	0/100/0	0/100/0
PCL-PEG-PCL	0/33/67	0/35/65
$\mathrm{PLLA}_{60}\text{-}\mathrm{PCL}\text{-}\mathrm{PEG}\text{-}\mathrm{PCL}\text{-}\mathrm{PLLA}_{60}$	60/27/13	59/29/12
$PLLA_{80}$ - PCL - PEG - PCL - $PLLA_{80}$	80/13/7	80/15/5
PLLA-PEG-PLLA	46/0/54	44/0/56
PCL_{60} -PLLA-PEG-PLLA-PCL $_{60}$	18/60/22	17/62/21
PCL_{80} -PLLA-PEG-PLLA-PCL $_{80}$	9/80/11	6/85/9

Table 1. Characteristics of homo and block copolymers.



Figure 4. ¹³C–NMR spectrum of PLLA₆₀-PCL-PEG-PCL-PLLA₆₀ multiblock copolymer.



Figure 5. ¹H–NMR spectrum of PCL₈₀-PLLA-PEG-PLLA-PCL₈₀ multiblock copolymer.

The CH₃ and CH protons of lactide appear at 1.59 and 5.14 δ ppm, respectively. The proton peak of PEG is also observed at 3.67 δ ppm. The caprolactyl methylenic protons appear at 4.07-4.16 δ ppm (CH₂-O) and 2.20-2.43 δ ppm (CH₂-CO), and inner methylenic protons appear at 1.41–1.59 δ ppm.

The PLA/PEG/PCL ratios in the multiblock copolymer were calculated from the integral signal areas at 5.14 δ ppm (lactide), 2.3 δ ppm (ε -caprolactone) and 3.67 δ ppm (polyethylene glycol). The calculated results are also listed in Table 1. Clearly, the calculated results for lactide and polyethylene glycol are lower than the feed ratios. The difference is mainly due to the elution of short polymeric linkages during the purification stage. Therefore, the efficiency of copolymerization decreases because the small amounts of lactide and polyethylene glycol were washed by the used solvents.

The ¹³C NMR spectrum of this multiblock copolymer is shown in Figure 6. The inner caprolactyl methylenic carbons appear at 28.76, 25.94 and 24.99 δ ppm. The caprolactyl methylenic carbons appear at 64.55 δ ppm (CH₂-O) and 34.53 δ ppm (CH₂-CO). The carbon peak of PEG is also observed at 70.97 δ ppm. The peak at 173.94 δ ppm is attributed to the carbonyl carbon of ε -caprolactone. No peaks are attributed to the lactide block. The ¹³C NMR peaks of lactide carbons have weak intensities and cannot be identified. This is due to the very low amounts of lactide content present in the resulting copolymer.

The thermal behavior of the homo and copolymers was investigated by DSC thermograms. DSC thermograms of PLLA homopolymer, PLLA-PEG-PLLA triblock copolymer and PLC-PLLA-PEG-



Figure 6. ¹³C-NMR spectrum of PCL₈₀-PLLA-PEG-PLLA-PCL₈₀ multiblock copolymer.



Figure 7. DSC thermograms of PLLA, PLLA-PEG-PLLA and multiblock copolymers.

PLLA-PCL multiblock copolymers are shown in Figure 7. The PLLA homopolymer shows an endotherm at 156°C with $\Delta H_m = 35.3$ J/g. The PLLA-PEG-PLLA triblock copolymer shows two endotherms at 53.29° C with $\Delta H_m = 25.4$ J/g and 198.5° C with ΔH_m = 17.7 J/g. These endotherms are attributed to PEG and PLLA blocks, respectively. The obtained results are listed in Table 2.

Table 2 indicates that T_m and ΔH_m of the lactide block have decreased compared to the lactide homopolymer. The difference is related to a decrease in the length of the lactide block and its crystallinity in the PLLA-PEG-PLLA triblock copolymer. The appearance of two discrete blocks in the DSC thermogram (Figure 7) confirms that the synthetic copolymer consists of three blocks. PEG is the central block and the terminal blocks are PLLA.

It could also be observed in Figure 7 that pentablock copolymers with 60 and 80 mol% of PCL block show the endotherms at 50.5°C with $\Delta H_m =$ 63.9 J/g, and 48.6°C with $\Delta H_m =$ 57.5 J/g, respectively (Table 2). These endotherms are attributed to



Figure 8. DSC thermograms of PEG and PCL homopolymers.

terminal PCL blocks in each pentablock copolymer. Nevertheless, these thermograms do not show any endotherm for PEG and PLLA blocks. This is due to the very low amounts of polyethylene glycol and lactide present in the resulting pentablock copolymers.

DSC thermograms of PEG and PCL homopolymers are depicted in Figure 8. PEG and PCL homopolymers show the endotherms at 65.0°C with $\Delta H_m = 191.8 \text{ J/g}$, and 59.0°C with $\Delta H_m = 56.1 \text{ J/g}$, respectively (Table 2). With increasing mol% of PCL from 60% to 80%, the thermal behavior of the resulting copolymer is nearly the same as the PCL homopolymer, but with lower melting characteristics. These results can be confirmed by comparing the melting points and enthalpies shown in Table 2.

It also could be observed in Figure 8 that the peak area of PEG is more than PCL. Therefore, the melting enthalpy and crystallinity of PEG are greater than PCL.

DSC thermograms of PLLA and PLLA-PCL-PEG-PCL-PLLA multiblock copolymers with 60 or 80 mol% of PLLA are shown in Figure 9. The obtained

Polymer	$T_m \ (^\circ \mathrm{C})$	$\Delta H_m ~({ m J/g})$	Weight in crude feed LLA/ ε -CL /PEG (%)
PLLA	156.0	35.3	100/0/0
$\operatorname{PEG}15000$	65.0	191.8	0/0/100
PCL	59.0	56.1	0/100/0
PCL-PEG-PCL	58.7	59.9	0/33/67
$\mathrm{PLLA}_{60}\text{-}\mathrm{PCL}\text{-}\mathrm{PEG}\text{-}\mathrm{PCL}\text{-}\mathrm{PLLA}_{60}$	50.8, 157.6	4.9, 28.5	60/27/13
$\mathrm{PLLA}_{80}\text{-}\mathrm{PCL}\text{-}\mathrm{PEG}\text{-}\mathrm{PCL}\text{-}\mathrm{PLLA}_{80}$	154.9	49.9	80/13/7
PLLA-PEG-PLLA	$53.29,\ 108.5$	25.4, 17.7	46/0/54
PCL_{60} -PLLA-PEG-PLLA-PCL ₆₀	50.5	63.9	18/60/22
PCL_{80} -PLLA-PEG-PLLA-PCL ₈₀	48.6	57.5	9/80/11

Table 2. Thermal properties of homo and block copolymers (DSC data).



Figure 9. DSC thermograms of PLLA and PLLA-PLC-PEG-PCL-PLLA multiblock copolymers with different PLLA mol%.

results are listed in Table 2. The DSC thermogram of a pentablock copolymer with 60 mol% of PLLA block shows two endotherms at 50.8°C with $\Delta H_m =$ 4.9 J/g, and 157.6°C with $\Delta H_m =$ 28.5 J/g. These endotherms are attributed to PCL and PLLA blocks, respectively. Figure 9 illustrates that the peak of the PCL block is weak and the PEG central block does not show any endotherm. This is because of the fact that the mole ratio of PCL and PEG blocks is very low in this multiblock copolymer (Table 1).

In contrast, the DSC thermogram of the pentablock copolymer with 80 mol% of PLLA block shows only one endotherm at 154.9°C with $\Delta H_m = 49.9$ J/g. This thermogram does not show any endotherms for PEG and PCL blocks. This is because of their low amounts in the pentablock copolymer (Table 1).

Table 2 indicates that the endotherm of PLLA appears at 156.0°C with $\Delta H_m = 35.3$ J/g. Therefore, with the increasing of mol% of PLLA from 60% to 80%, the thermal behavior of the resulting copolymer is nearly the same as the PLLA homopolymer, but with higher crystallinity. These results can be confirmed by comparing the melting points and enthalpies shown in Table 2.

The thermal stability of the triblock and pentablock copolymers was studied by TGA and DTG thermograms. Typical TGA and DTG thermograms of the PLLA-PEG-PLLA triblock copolymer are shown in Figures 10 and 11, respectively.

TGA and DTG thermograms exhibit two degradation peaks for this triblock copolymer. The degradation peaks of the central block (PEG) and terminal blocks (PLLA) appear at 397.3°C and 270.8°C, respectively. These results are listed in Table 3.

The appearance of two degradation peaks in the PLLA-PEG-PLLA triblock copolymer confirms the block structure of the copolymer.



Figure 10. TGA thermograms of homopolymers, triblock copolymer and multiblock copolymers with different PCL mol%.



Figure 11. DTGA thermograms of homopolymers, triblock copolymer and multiblock copolymers with different PCL mol%.

The degradation peaks of PLLA, PCL and PEG in the DTG thermogram of the pentablock copolymer with 60% PCL appear at 290°C, 381°C and 404.5°C, respectively (Table 3).

These peaks confirm that the copolymer has three various blocks. It also could be observed in Figure 10 that the degradation peak of PCL overlaps with PLLA and PEG. Therefore, the PCL degradation peak is broader.

The amounts of PEG and PLLA are very low in the PCL_{80} -PLLA-PEG-PLLA-PCL₈₀ multiblock copolymer (Table 2). Hence, the degradation peak of PLLA is weakened and the PEG degradation peak disappeared in the related TGA and DTG thermograms (Figures 10 and 11). These thermograms only show one degradation peak at 399.7°C (Table 3).

Typical TGA and DTG thermograms of $PLLA_{60}$ -PCL-PEG-PCL-PLLA₆₀ multiblock copolymer show three degradation peaks for PLLA, PEG and PCL, at 320.6°C, 389.0°C and 361.1°C, respectively (Fig-

Polymer	T_{d1} (°C)	T_{d2} (°C)	T_{d3} (°C)
PLLA	321.0	-	-
PEG	407.5	-	-
PCL	415.9	-	-
PCL-PEG-PCL	363.2	421.0	-
$\operatorname{PLLA}_{60}\operatorname{-PCL}\operatorname{-PEG}\operatorname{-PCL}\operatorname{-PLLA}_{60}$	320.6	361.1	389.0
$\mathrm{PLLA}_{80}\text{-}\mathrm{PCL}\text{-}\mathrm{PEG}\text{-}\mathrm{PCL}\text{-}\mathrm{PLLA}_{80}$	314.2	349.7	390.0
PLLA-PEG-PLLA	270.8	397.3	-
PCL_{60} -PLLA-PEG-PLLA-PCL ₆₀	290.0	381.0	404.5
PCL_{80} -PLLA-PEG-PLLA-PCL ₈₀	399.7	-	-

Table 3. Thermal properties of homo and block copolymers (TGA data).

ures 12 and 13). In contrast, typical TGA and DTG thermograms of PLLA₈₀-PCL-PEG-PCL-PLLA₈₀ multiblock copolymer show three degradation peaks for PLLA, PEG and PCL at 314.2°C, 390°C and 349.7°C, respectively (Figures 12 and 13).



Figure 12. TGA thermograms of homopolymers, triblock copolymer and multiblock copolymers with different PLLA mol%.



Figure 13. DTGA thermograms of homopolymers, triblock copolymer and multiblock copolymers with different PLLA mol%.

In the TGA and DTG thermograms attributed to the PLLA-PCL-PEG-PCL-PLLA multiblock copolymer with 60 or 80 mol% PLLA, the mol% of PEG and PCL decreases by increasing the mol% of lactide from 60% to 80%. Therefore, the degradation peak of PEG is weakened and the PCL peak appears as the little peak connected to the lactide degradation peak. Moreover, the thermal stability of the multiblock copolymer with 80 mol% lactide increases and its thermal properties are similar to the PLLA homopolymer. On the other hand, the TGA and DTG thermograms of PCL-PLLA-PEG-PLLA-PCL multiblock copolymer with 60 or 80mol% PCL shows that, by increasing the PCL mol%from 60 to 80, the thermal stability of the copolymer decreases, and it is similar to the PCL homopolymer (Figure 13).

4. Conclusion

Two multiblock copolymers of polyethylene glycol (PEG), L-lactide (LLA) and ε -caprolactone (CL) were synthesized in the presence of $Sn(Oct)_2$ as catalyst. The structures of the prepolymers and pentablock copolymers were confirmed by means of ¹H NMR and ¹³C NMR. The thermal analysis results have shown that increasing the lactide mol% in PLLA-PCL-PEG-PCL-PLLA multiblock copolymer increases the thermal stability of the obtained copolymer, and the melting point of the polylactide block is similar to the melting point of the lactide homopolymer. On the other hand, increasing the PCL mol% in the PCL-PLLA-PEG-PLLA-PCL multiblock copolymer decreases the thermal stability of the resulting copolymer, and the melting point of the PCL block is similar to the melting point of the PCL homopolymer.

The thermal analysis has also shown that the thermal stability of the obtained copolymers increases with increase in the lactide mol%, and the melting point of polylactide block is similar to the lactide homopolymer. On the other hand, increasing the PCL mol% in the PCL-PLLA-PEG-PLLA-PCL multiblock copolymer decreases the thermal stability of the resulting copolymer, and the melting point of the PCL block is similar to the melting point of the PCL homopolymer.

The comparison of ΔH_m obtained from DSC thermograms for multi block copolymers and their related homopolymers indicates that the position of each block affects the crystallinity. In fact, the amount of cystallinity of the terminal blocks is lower than their related homopolymers. The existence of a triblock copolymer in the center of the multiblock copolymer decreases crystallinity in the terminal blocks. Moreover, these terminal blocks play an important role in the general properties of pentablock copolymers. Therefore, by varying the position of the blocks in the multiblock copolymers, it is possible to synthesize the biodegradable copolymers with the desired biodegradability and thermal behavior for medical applications.

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Biographies

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1847

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