JOURNAL OF MATERIALS SCIENCE **36** (2001) 715–722

Thermal behaviour of poly(ε-caprolactone)-poly(ethylene glycol)-poly(ε-caprolactone) tri-block copolymers

J. H. AN*, H. S. KIM, D. J. CHUNG, D. S. LEE
Department of Polymer Science and Engineering, SungKyunKwan University, Chunchun-dong 300, Jangan-gu, Kyunggi-do, 440-146 Korea
E-mail: jhahn@yurim.skku.ac.kr

SANGHYO KIM
Department of Chemistry, University of Sheffield, S3 7HF, U K

Thermal behavior of poly(ε-caprolactone)-poly(ethylene glycol)-poly(ε-caprolactone) tri-block copolymers with different block lengths is examined. Thermal behavior of specimens crystallized under the isothermal and dynamic condition are characterized by DSC. Also WAXD and SAXS are employed to investigate the structure. Depending on the relative length of each block, tri-block copolymers can be classified into three groups: PCL dominant crystallization; PEG dominant crystallization; and the competing case. When the crystallization of PEG and PCL are competing, the crystallization of each block shows strong dependency on the thermal hystory of crystallization, leading to multiple melting and crystallization peaks. Also, the typical micro-phase separation of block copolymers seems to play an important role, competing with crystallization, especially under the dynamic crystallization condition. *© 2001 Kluwer Academic Publishers*

1. Introduction

Recently block copolymers based on poly(ethylene glycol) (PEG) has attracted much attention as biomedical materials, since PEG is nontoxic and cleared by the U.S. food and Drug Administration for internal use in the human body [1]. It is well established by now that the block copolymers consisting of hydrophobic poly(propylene glycol) blocks and hydrophilic poly(ethylene glycol) blocks can form micelles in aqueous solution and show a well-defined thermosensitive sol-gel transition which suggests considerable potential as a new class of drug delivery media [2–5]. However, poly(propylene glycol) moiety does not satisfy one of the requirements as an ideal polymeric carrier, which is the degradibility in vivo during or after drug delivery. Therefore, there exist several attempts to replace nondegradable hydrophobic poly(propylene glycol) with other biodegradable blocks such as polylactide, polyglycolide, polyester, and poly(caprolactone) [6–8].

As a part of on-going efforts to develop PEG-based biodegradable block copolymers, we have prepared and characterized block copolymers of poly(e-caprolactone)/poly(ethylene glycol) (PCL/PEG) with different block lengths. PCL has various useful characteristics such as good biocompatibility, biodegradibility, and permeability to drugs [9, 10]. In addition to a potential application in the biomedical field, PCL/PEG block copolymers are of interest since both constituent polymers are crystalline. Even though extensive studies have been performed on the morphology or crystallization of block copolymers with amorphous and crystallizable blocks [11–17], there are limited numbers of studies on block copolymers with all crystallizable blocks. Recently, there exist a few studies about PCL/PEG block copolymers. Perret and Skoulios investigated the crystallization behaviour of PCL/PEG/PCL triblock copolymers and found that the crystallization behavior is strongly dependent on the crystallization conditions, especially temperature [18, 19]. Martini *et al.* prepared PCL/PEG/PCL triblock copolymer with very short PCL blocks and examined the gelation characteristics in water [5]. Gan *et al.* investigated the crystallization and melting behaviour of PCL/PEG diblock copolymers [20, 21]. Recently, Bogdanov *et al.* compared the melting and crystallization behaviour of PCL and PEG based copolymer with different structures including diblock, triblock and star block copolymers [22].

In our investigation of gelation characteristics of the PCL/PEG/PCL system, it was found that it shows quite different behaviour compared with well known PPG/PEG/PPG block copolymers. It does not show lower gel → sol transition at any composition and the sol → gel transition on cooling, commonly known as hot gelation, is very much dependent on the thermal history of solution preparation. We believe that

---

* Author to whom all correspondence should be addressed.

this is related with the fact that the hydrophobic block, polycaprolactone is crystalline while the PPG in PPG/PEG/PPG block copolymer is completely amorphous. In this report, we have investigated the melting and crystallization behaviors of PCL/PEG/PCL copolymers possessing different block lengths with differential scanning calorimetery (DSC), wide-angle X-ray diffraction (WAXD), small-angle x-ray scattering (SAXS), and polarized optical microscopy (POM).

2. Experimental

2.1. Materials

ε-Caprolactone (CL) (Aldrich) was purified by vacuum distillation over CaH_2. The fraction collected at 96–98 °C (5 mmHg) was used in all the polymerization experiments. PEGs (Aldrich) were dried by an azeotropic distillation in toluene and then evacuated under reduced pressure to remove residual traces of water. The number average molecular weight (M_n) of PEGs was 200, 1000, 2000, 3400, and 4600, respectively. Stannous (II) octoate (SnOct) (Sigma) as catalyst was used as received. Toluene was dried by refluxing over CaH_2 and distilled under nitrogen atmosphere. PCL diol ($M_n = 1250$) was used as received from Aldrich Chemical Co. This polymer contains the ethylene glycol repeating units in the central block the same as PEG, because the polymerization was initiated by di(ethylene glycol), namely PCL_{572}-PEG-$_{106}$-PCL_{572}.

2.2. Polymerization procedure

The block copolymers were prepared by using PEG to initiate the polymerization of ε-caprolactone in toluene with added SnOct. Polymerization was carried out at 130 °C for 24 h under a nitrogen atmosphere. The product was obtained by precipitation from toluene solution into ethyl ether and hexane, and then dried completely in vacuum oven.

PCL homopolymer ($Mn = 1500$) was prepared by coordination polymerization of CL with aluminum isopropoxide in toluene.

2.3. Characterization

The molecular weight and molecular weight distribution of the PCL/PEG/PCL block copolymer were characterized by ^{1}H nuclear magnetic resonance (^{1}H-NMR, Varian Unity Inova 500) and gel permeation chromatography (GPC, Waters 410). The results are summarized in Table I.

Crystallization and melting behaviors were measured by a TA 2910 differential scanning calorimeter (DSC). The polymer samples were melted at 90 °C for 5 min, in the DSC, then cooled at various rates, and rapidly to an isothermal crystallization temperature. After crystallization, the polymer samples were heated at various rates to a molten state. Crystallinity was calculated from the enthalpy of melting.

The spherulite growth and morphology were analyzed with polarized optical microscope (POM, Nikon-OPTIPHOT2-POL). The sample was first melted on a manually operated hot stage at 90 °C for 5 min and then quickly transferred to another hot stage equilibrated at the crystallization temperature.

TABLE I Characteristics of the polymers used in this study

Samples	M_n of PCL & PEG blocks (^{1}H-NMR)	Total M_n[a] (^{1}H-NMR)	M_w[b]/M_n (GPC)
T-1	PCL_{1150}-PEG_{200}-PCL_{1150}	2500	1.05
T-2	PCL_{1250}-PEG_{1000}-PCL_{1250}	3500	1.07
T-3	PCL_{1250}-PEG_{2000}-PCL_{1250}	4500	1.07
T-4	PCL_{1100}-PEG_{3400}-PCL_{1100}	5600	1.08
T-5	PCL_{1030}-PEG_{4600}-PCL_{1030}	6660	1.03
T-6	PCL_{400}-PEG_{4600}-PCL_{400}	5400	1.03
T-7	PCL_{572}-PEG_{106}-PCL_{572}	1250	1.02

[a] Number average molecular weight.
[b] Weight average molecular weight.

The wide-angle X-ray diffraction (WAXD) spectra were obtained using a Rigaku X-ray diffraction with Ni filtered Cu K_α radiation at room temperature. The 2θ scan rate was 2°/min. The X-ray tube worked at 40 kV and 50 mA.

The small-angle X-ray scattering (SAXS) experiments were performed on the beam line (4C2) at Pohang Light Source, Korea. The incident beam was monochromatized with double crystals at a wavelength of 0.1608 nm. A one-dimensional position-sensitive detector (Si diode-array detector) was used.

3. Results and discussion

3.1. Homopolymers

The melting behaviors of PEG and PCL homopolymers are investigated by DSC measurement as shown in Fig. 1. All samples are first heated above the melting temperature (T_m), and then allowed to crystallize at a cooling rate of 10°C/min and reheated at a rate of 10°C/min. PEG is known to show multiple melting

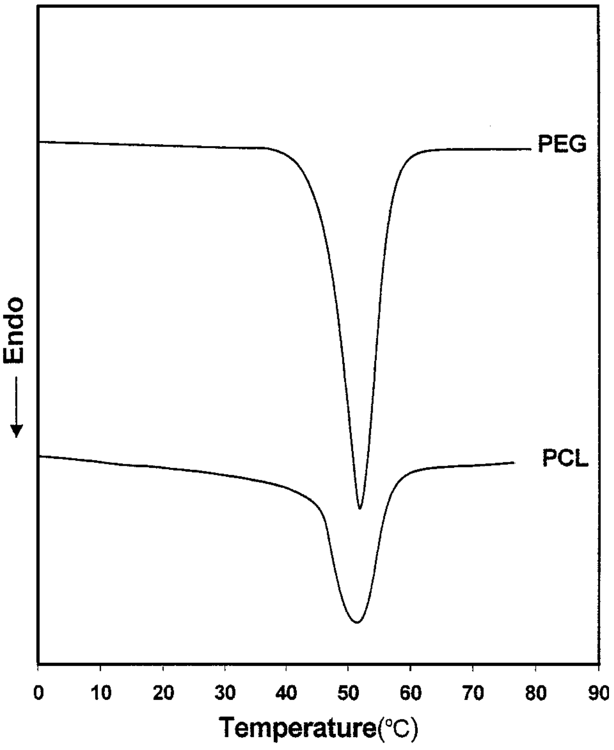

Figure 1 DSC melting curves of PEG ($M_n = 2000$) and PCL ($M_n = 1500$) homopolymers crystallized at 10°C/min from the molten state.

peaks when its molecular weight is higher than a certain value. This may be attributed to the production of several crystal forms with the various chain folding numbers [23, 24]. PEG with molecular weight of 2,000 shows a single melting peak due to forming an extended chain crystal in this condition, while PEG above molecular weight of 3,000 shows double melting peaks [22–25]. The crystallinities of the PEG and PCL homopolymers are 84.3 and 61.2%, respectively, based on the heat of fusion with the perfect crystals of each homopolymer [26, 27]. It should be noted that these two homopolymers have similar melting temperature around 50°C. The crystallinity of the PEG homopolymer is higher than that of PCL homopolymer and the crystallization rate of this homopolymer monitored with POM is faster than that of PCL [21]. Therefore, the PEG homopoymer has stronger driving force of crystallization compared to PCL.

3.2. Triblock copolymers

Figs 2 and 3 show the block length effects of PCL/PEG/PCL triblock copolymers on the crystallization and melting behavior, respectively. All samples were melted at 90°C for 5 min in the DSC in order to remove the residual thermal history, and then cooled at a rate of 10°C/min and reheated at a rate of 10°C/min. All of these triblock copolymers appeared semicrystalline with melting peaks and the melting peaks of each corresponding polymer in the triblock copolymer are lower than those of the homopolymers indicating melting point depression due to the hindered crystallization. Fig. 4 shows the WAXD patterns of the

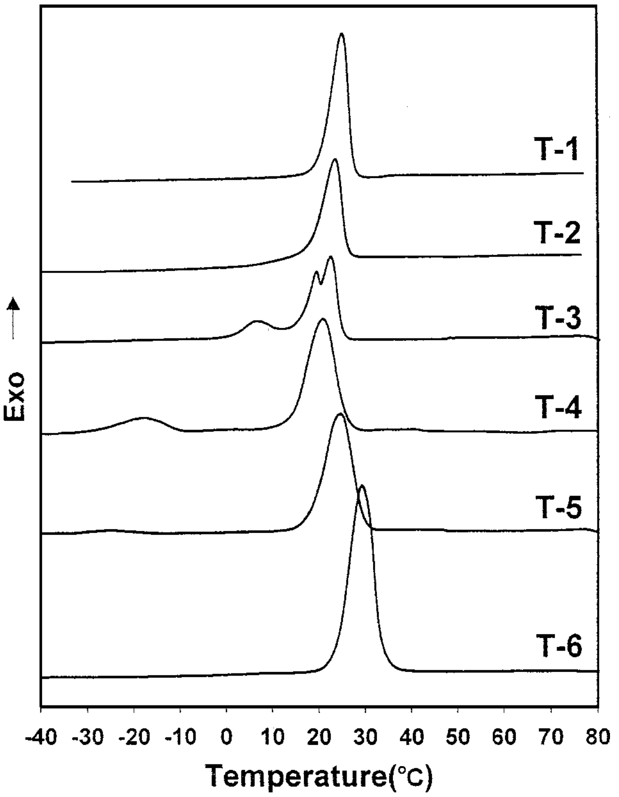

Figure 2 DSC crystallization curves of triblock copolymers melted at 90°C for 5 min.

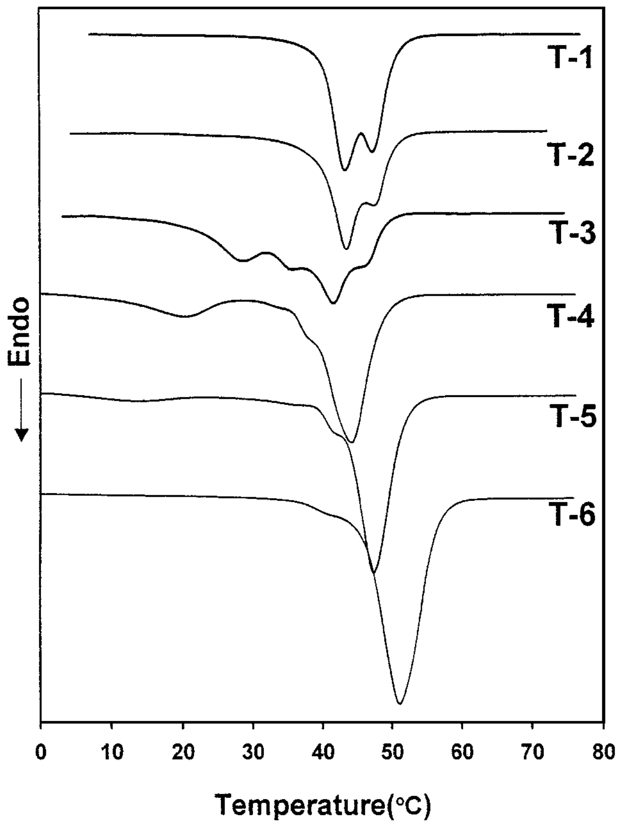

Figure 3 DSC melting curves of triblock copolymers crystallized from the molten state at a rate of 10°C/min (90°C).

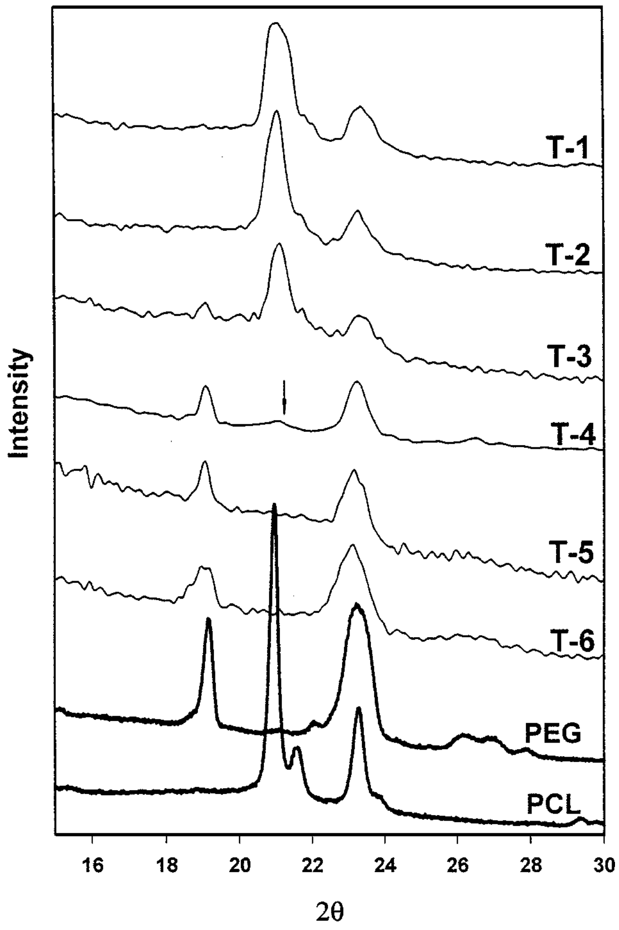

Figure 4 WAXD patterns for T-1, T-2, T-3, T-4, T-5, T-6, PEG ($M_n = 2000$) and PCL ($M_n = 1500$); All samples were crystallized from the molten state at a rate of 10°C/min. The arrow indicates PCL trace.

triblock copolymers in Figs 2 and 3. Since the melting temperatures of PCL and PEG are rather similar, the identification of melting peaks are difficult in the DSC thermogram. On the other hand, the WAXD patterns of PCL and PEG are clearly distinguishable. The crystalline behaviour of triblocks can be classified into three groups. The first one is that the center block, PEG, is shorter than the side PCL blocks such as T-1 and T-2, in which the crystallization of PCL blocks is dominant. The second group (T-3 and T-4), which has two or three times larger center block compared with PCL blocks, shows that both PEG and PCL blocks crystallize. In the last group, the crystallization of PEG blocks becomes predominant due to the relatively short length of PCL blocks. The relative length of each block rather than the absolute length seems to be the controlling factor of crystallization suggesting the two crystallization processes are competing. For example, in T-1 and T-6, the length of PCL blocks are almost the same but the PCL crystal cannot be found in T-6 while the PCL crystallization is dominant in T-1.

3.3. Thermal behaviors of T-1 and T-2 samples

The triblock copolymers of T-1 and T-2 in Fig. 2 have similar PCL block lengths of 1150 and 1250 respectively while the molecular weight of the center PEG block are 200 and 1,000, respectively. In these samples, the molecular weight of the center block is either much less than that of the side block or is comparable to the side block. Both samples show that only PCL phase can crystallize on this condition. That is supported by WAXD graphs as given in Fig. 4. In the melting thermogram shown in Fig. 3, both T-1 and T-2 have double melting peaks.

One possible explanation for the origin of the double melting peaks is the fold length variation which was reported by Cheng *et al.* [24] in a series of low molecular weight poly(ethylene oxide)s. In Cheng's report, depending on the molecular weight and the crystallization condition, the PEO crystals become a mixture of crystals with different chain fold numbers, resulting in multiple melting peaks (up to quadruple) in the DSC thermogram.

If a similar process is also possible in poly(caprolactone), the variation of the molecular weight of PCL block may affect the melting behavirour. In order to verify, a T-7 sample with the half lengths of the T-1 was prepared and characterized as shown in Fig. 5. The T-7 sample shows also double melting peaks, suggesting that the double melting peaks are not caused by the difference in the chain fold number. In fact, the molecular weight of PCL blocks in sample T-1, T-2, and T-7 are too short to have a multiple fold number and the PCL chains in the crystal presumably have the form of full chain extention.

Another possible explanation would be a successive melting, recrystallization, and remelting process [28, 29]. If this process is followed, when the heating rate is increased, the lower melting peak will be magnified and the peak with higher melting temperature will finally disappear. However, the higher melting peak was not decreased with increasing heating rate (not shown here). Therefore the double melting behavior is not originated from the recrystallization during the heating process.

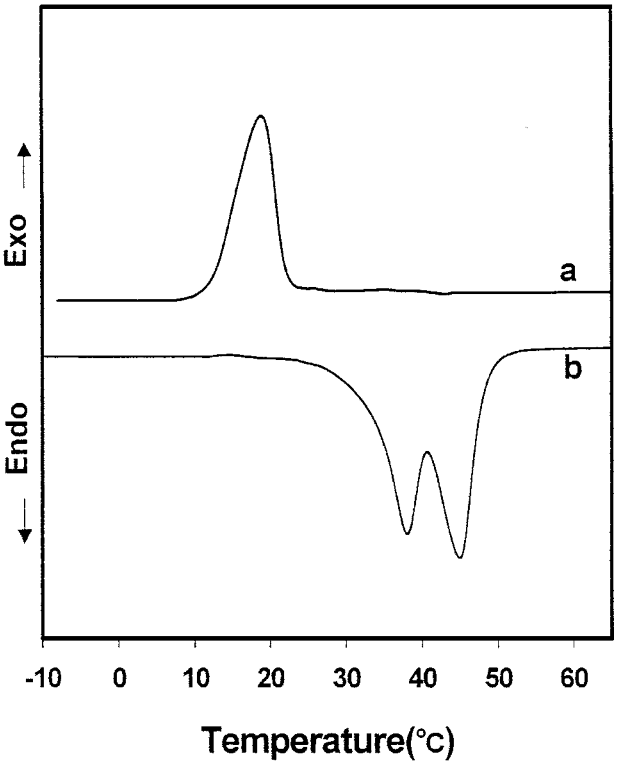

Figure 5 DSC thermograms of T-7 sample at scan rate of 10°C/min; a) Crystallization curve of the sample melted at 90°C for 5 min, b) Melting curve of the sample crystallized at a rate of 10°C/min.

Multiple melting peaks could be caused by completely different origin such as the competing process of crystallization and phase separation [13, 20, 21, 30]. A different cooling history is applied to the T-1 sample and characterized as shown in Fig. 6. During the cooling process, the crystallization of PCL and the phase separation are competing with each other. If a fast cooling rate, such as quenching, is applied, the thermodynamic driving force for the crystallization process is large enough while the time for the kinetic development of phase separation is not enough. Therefore, the crystallization of PCL blocks dominates resulting in more perfect crystals with higher melting temperature. On the other hand, if a slower cooling process is applied, the phase separation becomes more complete. In the very slow cooling condition, such as 3°C/min, the phase separation is dominant, then the crystallization occurs in the presence of the phase separated structures. In the block copolymers, the phase separated domains are very small due to its typical micro-phase separation resulting in imperfect crystal structure with lower melting temperature. The melting behaviour in Fig. 6 follows the above mentioned pattern. It is worthwhile to note that there is a slight shift to higher temperature of the low melting peak in the 3°C/min cooled sample. This may be attributed to the perfection of the crystal structure by the destruction of the micro-phase separated morphology [11, 13].

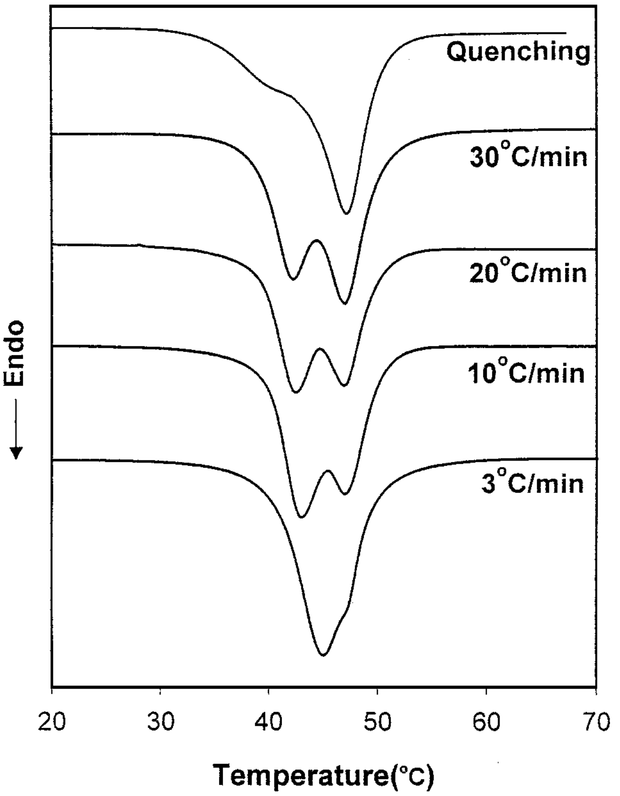

Figure 6 DSC heating curves at 10°C/min of T-1 after cooling at various cooling rates indicated.

3.4. Thermal behaviors of T-4, 5, and 6 samples

The WAXD pattern in Fig. 4, suggests that the PEG crystallization is dominant in T-4, 5, and 6, which have relatively higher PEG molecular weight. In the WAXD pattern of T-4, which has the smallest PEG molecular weight among the three, a small but identifiable peak of PCL crystal could be observed. Therefore, in the melting peaks in Fig. 3, the ones at the higher temperature correspond to the PEG phase, while those at the lower temperature are related to the PCL phase. It suggests that, if the PEG block is long enough, its crystallization is dominant and effectively hinders the crystallization of the PCL phase even though the mobility of the PEG block is limited, since it constitutes the center block. With increased PEG molecular weight, the crystallization and melting peaks of PEG shift gradually to higher temperature, while those of PCL go down. It should be noted that, in the T-6 sample, the crystallization of the PCL phase is negligible and the PCL moiety behaves as a nucleating site rather than forming a separate crystal phase.

3.5. Thermal behavior of T-3 sample

The behavior of the T-3 sample is the most complex among the samples tested. In Figs 2 and 3, it shows three crystallization and four melting peaks. Fig. 7 shows a schematic disintegrated crystallization peak corresponding to the T-3 peaks shown in Fig. 2. During the dynamic crystallization process, PCL crystallizes first (Peak c) and then PEG chain crystallizes (Peak b) prior to finishing the complete crystallization of PCL. The pre-formed PCL crystal phase disturbs the PEG crystallization to leave imperfect crystals with the relatively lower melting temperature. The residual crystallizable PCL phase can crystallize upon super-cooling (Peak a). These crystallization behaviors can be explained by the fractionated crystallization, which have been reported by several researchers in the case of PCL containing copolymer or blends [14, 17, 31, 32].

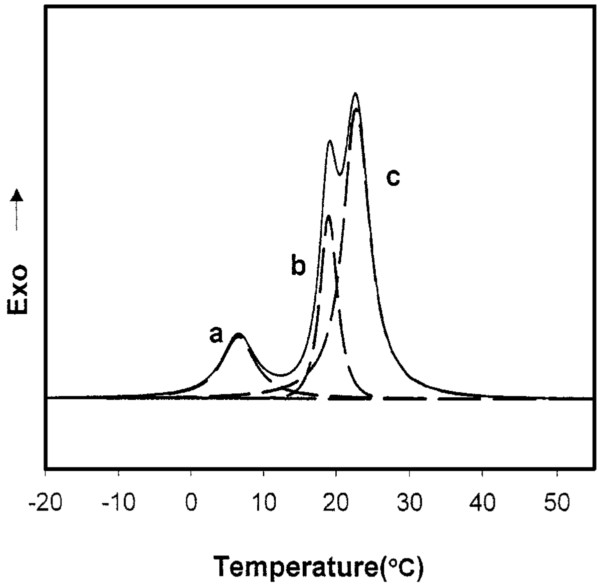

Figure 7 The disintegrated crystallization curve of T-3 sample in Fig. 2.

The melting behaviors of the T-3 sample with different cooling history are summarized in Fig. 8. The

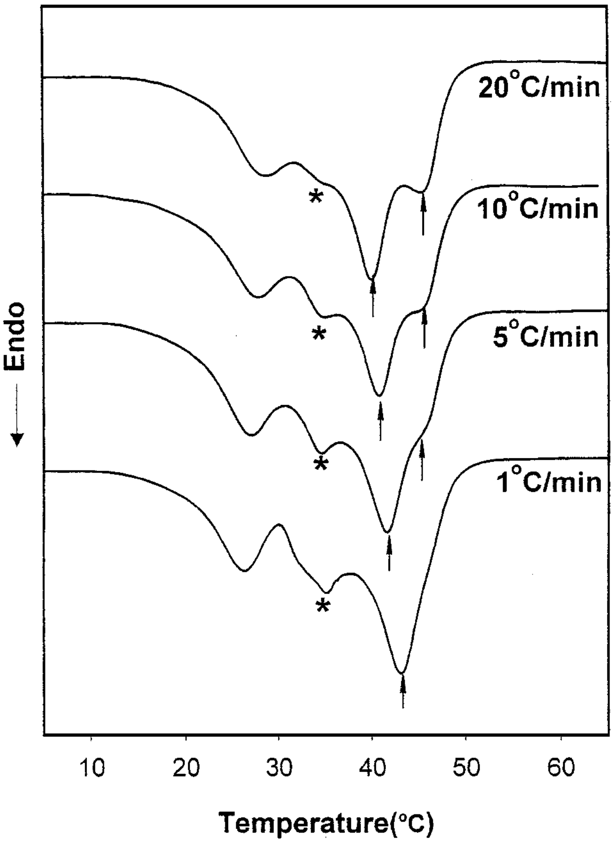

Figure 8 DSC melting curves at 10°C/min of T-3 sample cooled at various cooling rates indicated. The arrows and stars indicate PCL and PEG peaks, respectively.

melting peaks marked by the arrows in Fig. 8 behave very similar to the PCL peaks of the T-1 sample shown in Fig. 6, implying that these peaks are related with the PCL crystal phase. Regarding the other two peaks, including the star-marked one and the unmarked one, the melting of PEG crystals with different folding number is one possibility. It has been reported that PCL/PEG/PCL triblock copolymer (Molecular weight: 4300/4000/4300) shows three melting peaks and the two peaks in the low temperature region are explained as the result of PEG crystals with different folding numbers [22]. However, the molecular weight of the PEG block of T-3 in this study is 2,000 and the PEG homopolymer with molecular weight of 2,000 has only one sharp melting peak as shown in Fig. 1. The molecular weight of 2000 is less than the limit molecular weight which can have multiple folding numbers according to Chen *et al.* [25] and is in the region which forms crystals with full chain extention. Therefore, it is reasonable that the melting peak marked by the star comes from PEG crystal that was formed during the cooling process such as the peak b in Fig. 7. The lowest melting peak comes from the crystallization of residual PCL shown in Fig. 7 as peak a.

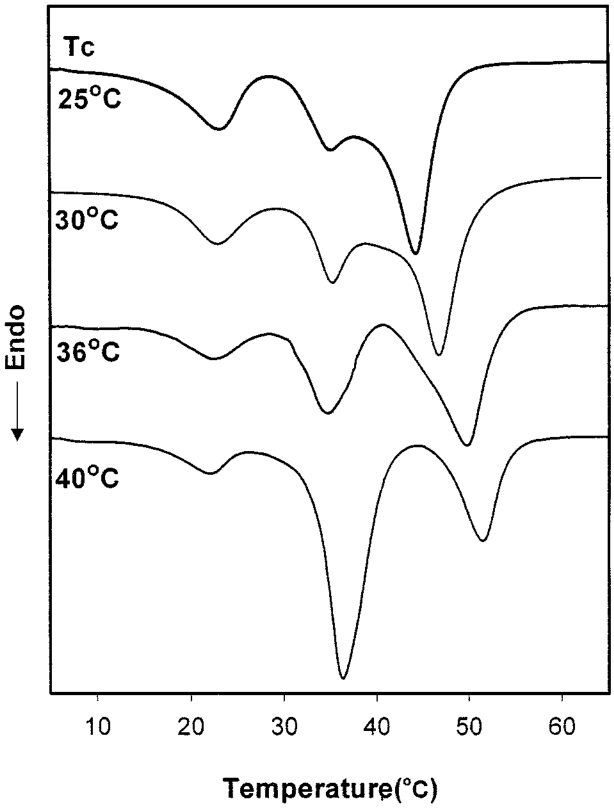

Figure 9 DSC melting curves at 10°C/min of T-3 sample crystallized at different crystallization. Temperatures (T_C) indicated for 2 days.

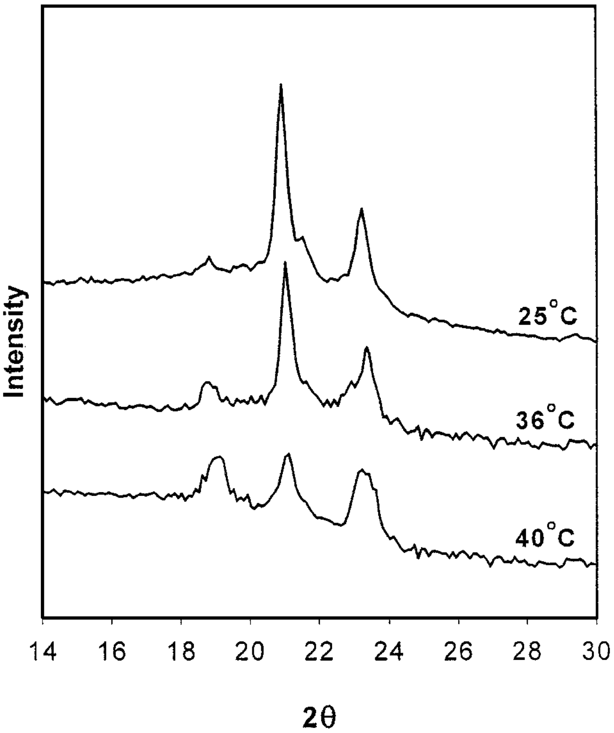

Figure 10 WAXD patterns of T-3 sample crystallized at various crystallization temperatures indicated for 2 days.

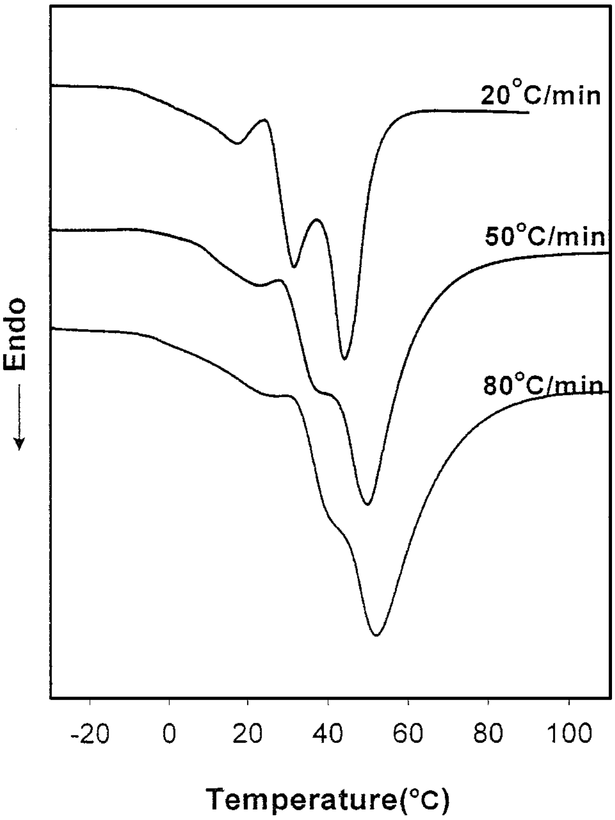

Figure 11 DSC melting curves of T-3 sample which had been heated at various rates indicated after crystallization at 27°C.

Fig. 9 shows the melting behaviors of T-3 which have different isothermal crystallization temperatures (T_C). With increasing the T_C, the middle melting peak becomes enlarged and the peak height of the melting at the highest temperature is reduced and shifts to the higher temperature. If both melting peaks were from the same block constituent, the middle melting peak would be reduced or disappear and the higher melting peak would become enlarged under the isothermal crystallization process at a temperature between the middle and higher melting peaks [29]. This implies that the above two peaks come from the different block constituents and the highest melting peak comes from PCL crystals. It is intereting that the PCL crystal exhibits the single peak on the isothermal condition, while

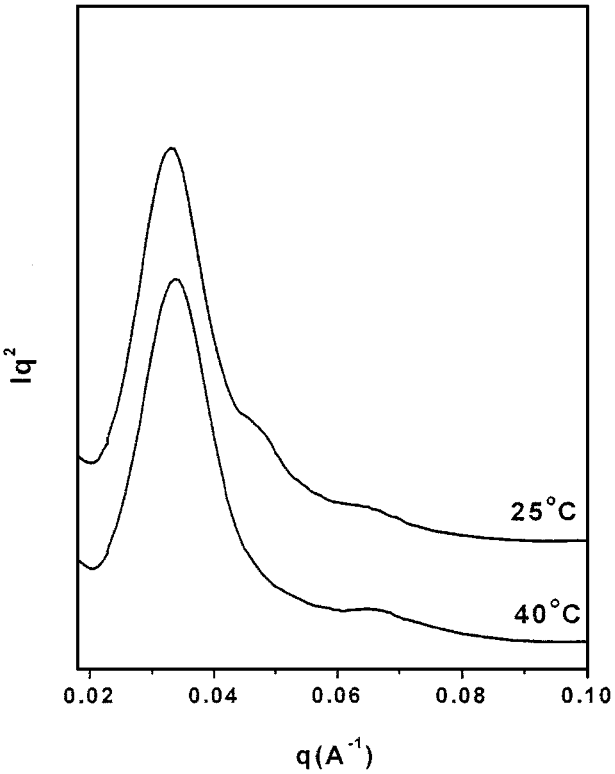

Figure 12 SAXS curves for T-3 sample crystallized at each T_c indicated. $q = (4\pi/\lambda)\sin\theta$, where λ is the X-ray wavelength and 2θ is the scattering angle.

it shows double peaks under the dynamic condition as discussed previously. This is understandable since the isothermal condition can be considered as similar to very slow dynamic crystallization. In order to confirm this peak assignment, WAXD patterns of these samples are examined as shown in Fig. 10. The intensity of the PEG characteristic peak is increasing with increased T_c, supporting the idea that the middle melting peaks come from PEG and the melting peak at the highest temperature is related with the PCL phase.

In Fig. 11, different heating rates are applied to T-3 crystallized at 27°C. The fact that the overall shapes and the relative heights of the two peaks are maintained regardless of heating rate supports the idea that the multiple melting peaks are not the result of recrystallization during the DSC measurement.

It seems that the linkage of covalent bonds between the PCL and the PEG blocks limits the chain mobility of PEG, making PEG blocks difficult to crystallize. When the T_c is increased, PEG chains can be more mobile and easily crystallize due to having a stronger driving force of the crystallization compared to PCL.

It has been reported that SAXS could be an useful tool to examine the morphological features in block copolymers having the combined effect of crystallization and microphase separation [13, 15]. In Fig. 12, the SAXS intensity curves for T-3 samples prepared at two different T_c, values 25°C and 40°C, are compared. Two bumps other than the primary maximum are observed in the 25°C crystallized sample while a very broad secondary peak is observed in the 40°C crystallized one, suggesting some kind of morphological changes. However, the broadness and weak intensity do not allow a conclusive interpretation. This is no wonder considering that two different kinds of crystals are present as discussed for the DSC and WAXD results of Figs 9 and 10. This is well contrasted with the result of crystalline-amorphous

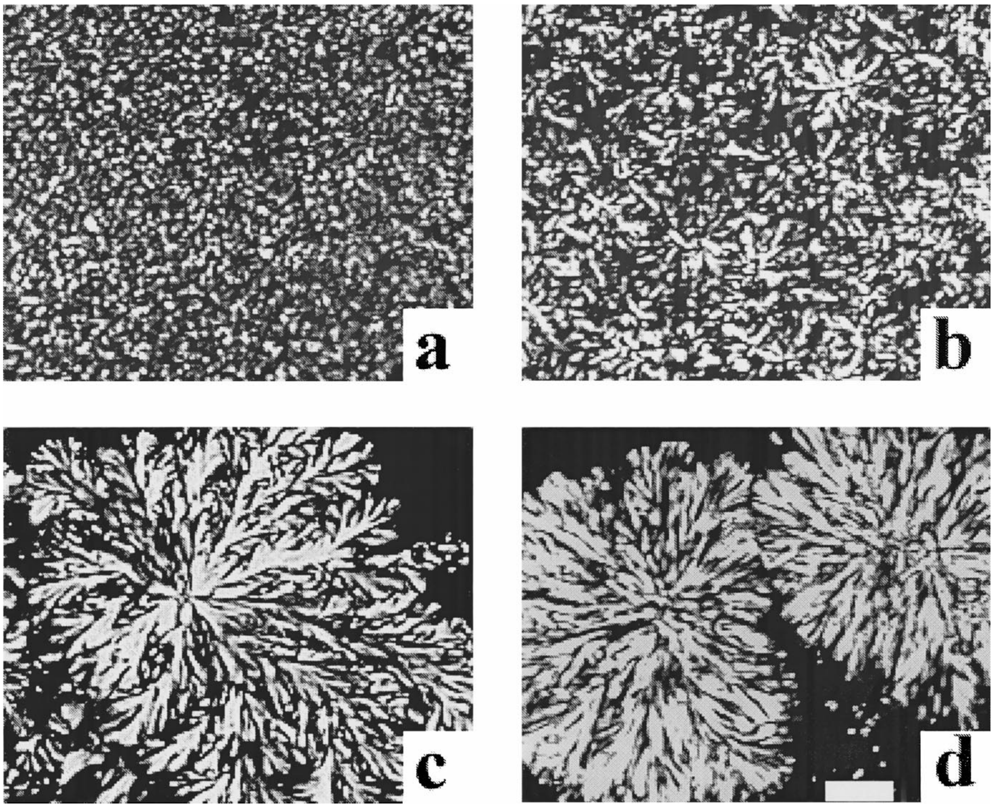

Figure 13 POM photographs of T-3 samples crystallized at different crystallization temperatures; a) 25 °C, b) 30°C, c) 36°C, d) 40°C; (white bar = 30 μm).

diblock, in which well defined signals are obtained [13, 15]. Since the molecular weight of the current sample is very low, there is no possiblity of crystallization within the microdomain structure. On the other hand, due to the crystallinity of the center block, the microdomain structure seems to be not completely destroyed by the crystallization as observed in crystalline-amorphous block copolymer. A direct observation of morphology has been attempted with AFM (Atomic Force Microscopy). However, due to the small size of domain and interference of crystalline structures, no useful image could be obtained. In order to elucidate the relationship in more detail, more elaborated experiments should be conducted.

Fig. 13 displays polarized optical micrographs of T-3 samples prepared under the various isothermal crystallization temperatures. When using low T_c (25 and 30°C), numerous nonspherulitic crystals are observed. With increasing the T_c, spherulites begin to form. However, all of the spherulites have coarse and open structure grow to form impinged spherulites with many branches, suggesting much of the uncrystallizable portion resides in the interfibrliear regions. Since the DSC and WAXD patterns suggest the existence of PEG as well as PCL crystals in all of the samples, it is difficult to identify the composition of the spherulites. It seems that in low T_c, the limited mobility and covalent linkages of block copolymer do not allow the formation of complete crystals. On the other hand, under low supercooling such as 40°C, the PEG center block has enough mobility to prevail over PCL in crystallization.

4. Conclusions

PCL-PEG-PCL tri-block copolymer with varying block lengths have been prepared by PET-initiated ring opening polymerization. The crystallization and melting behavior of the prepared samples can be categorized into three groups. The first one occurs when the center block, PEG, is shorter than the side PCL blocks, in which the crystallization of PCL blocks is dominant. The second group, which has a two or three times larger center block compared with the PCL blocks, shows that both PEG and PCL blocks crystallize. In the last group, the crystallization of PEG blocks becomes dominant due to the relatively short length of the PCL blocks. The specimens belonging to the second group show the most complex behaviour among the samples tested, showing multiple crystallization and melting peaks. The origin of these multiple peaks seems to be neither the result of multiple folding number nor recrystallization during heating. WAXD, isothermal, and dynamic crystallization data support the idea that the multiple melting peaks are caused by the balance between phase separation and competitive crystallization of the two types of block (PEG and PCL).

Acknowledgements

This work was supported by Korea Science and Engineering Foundation (Grant No. 96-0300-04-01-3).

References

1. J. M. HARRIS, *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **C25**(3) (1985) 325.
2. Z. K. ZHOU, *Macromolecules* **21** (1988) 2548.
3. G. WANKA, H. HOFFMAN and W. ULBRICHT, *Colloid Polym. Sci.* **268** (1990) 101.
4. P. LINSE and M. MALMSTEN, *Macromolecules* **25** (1992) 5434.
5. L. MARTINI, D. ATTWOOD, J. H. COLLETT, C. V. NICHOLAS, S. TANODEKAEW, N. J. DENG, F. HEATLEY and C. BOOTH, *J. Chem. Soc. Faraday Trans.* **90** (13) (1994) 1961.
6. D. S. HU and H. J. LIU, *J. Appl. Polym. Sci.* **51** (1994) 473.
7. E. PISKIN, X. KITIAN, E. B. DENKBAS and Z. KUCUKYVUZ, *J. Biometer. Sci. Polymer Edn.* **7**(4) (1995) 359.
8. S. M. LI, I. RASHKOV, J. L. ESPARTERO, N. MANOLOVA and M. VERT, *Macromolecules* **29** (1996) 57.
9. C. G. PITT, A. R. JEFFCOAT, R. A. ZWEIDINGER and A. SCHINDLER, *J. Biomed. Mater. Res.* **13** (1979) 497.
10. M. CHASIN and R. LANGER, "Biodegradable Polymers as Drug Delivery Systems" (Marcel Dekker, New York, 1990).
11. S. NOJIMA, S. YAMAMOTO and T. ASHIDA, *Polymer J.* **27** (1995) 673.
12. S. NOJIMA, M. KURODA and S. SASAKI, *ibid.* **29** (1997) 642.
13. S. NOJIMA, K. HASHIZUME, A. ROHADI and S. SASAKI, *Polymer* **38** (1997) 2771.
14. M. C. LUYTEN, E. J. F. BOGELS, G. O. R. ALBERDA, G. TEN BRINKE, W. BRAS, B. E. KOMANSCHEK and A. J. RYAN, *ibid.* **38** (1997) 509.
15. S. NOJIMA, H. TANAKA, A. ROHADI and S. SASAKI, *ibid.* **39** (1998) 1727.
16. H. L. CHEN, L. J. LI and T. L. LIN, *Macromolecules* **31** (1998) 2255.
17. M. VANNESTE and G. GROENINCKX, *Polymer* **36** (1995) 4253.
18. R. PERRET and A. SKOULIOS, *Makromol. Chem.* **162** (1972) 147.
19. *Idem., ibid.* **162** (1972) 163.
20. Z. GAN, B. JIANG and J. ZHANG, *J. Appl. Polym. Sci.* **59** (1996) 961.
21. Z. GAN, J. ZHANG and B. JIANG, *ibid.* **63** (1997) 1793.
22. B. BOGDANOV, A. VIDTS, A. VAN DEN BULCKE, R. VERBEECK and E. SCHACHT, *Polymer* **39** (1998) 1631.
23. C. P. BUCKLEY and A. J. KOVACS, *Colloid and polymer Sci.* **254** (1976) 695.
24. S. Z. D. CHENG, J. CHEN, J. S. BARLEY, A. ZHANG, A. HABENSCHUSS and P. R. ZSCHACK, *Macromolecules* **25** (1992) 1453.
25. B. WUNDERLICH, "Macromolecular Physics, Vol. 2" (Academic Press, New York, 1976) p. 166.
26. *Idem.*, "Macromolecular Physics, Vol. 3" (Academic Press, New York, 1980) p. 67.
27. M. AUBIN and R. E. PRUD'HOMME, *Macromolecules* **21** (1988) 2945.
28. P. J. HOLDSWORTH and A. TUENER-JONES, *Polymer* **12** (1971) 195.
29. P. J. LEMSTRA, T. KOOISTRA and G. CHALLA, *J. Polym. Sci., Polym. Phys. Ed.* **10** (1972) 823.
30. S. ISHIKAWA, K. ISHIZU and T. FUKUTOMI, *Polymer Communications* **32** (1991) 374.
31. V. BALSAMO, A. J. MULLER, F. VON GYLDENFELDT and R. STADLER, *Macromol. Chem. Phys.* **199** (1998) 1063.
32. V. BALSAMO, F. VON GYLDENFELDT and R. STADLER, *ibid.* **197** (1996) 3317.

Received 26 August
and accepted 16 December 1999