

Poly(ϵ -caprolactone)/Poly(ethylene oxide) Diblock Copolymer. I. Isothermal Crystallization and Melting Behavior

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SYNOPSIS

The isothermal crystallization and melting behavior of the poly(ϵ -caprolactone)(PCL)/poly(ethylene oxide)(PEO) diblock copolymer has been studied by WAXD, SAXS, and DSC methods. Only the PCL block is crystallizable; the PEO block of weight fraction 20% cannot crystallize, although its corresponding homopolymer has strong crystallizability. The long period, amorphous layer, and crystalline lamella of the PCL/PEO block copolymer all increase with the rise in the crystallization temperature, and the thickness of the amorphous layer is much larger than that of crystalline lamella due to the existence of the PEO block in the amorphous region. The isothermal crystallization of the PCL/PEO block copolymer is investigated by using the theory of Turnbull and Fischer. It is found that the amorphous PEO block has a great influence on the nucleation of PCL block crystallization, and the extent of this influence depends on crystallization conditions, especially temperature. The outstanding characteristics are the phenomenon of the double melting peaks in the melting process of the PCL/PEO block copolymer after isothermal crystallization at different temperatures and the transformation of melting peaks from double peaks to a single peak with variations in the crystallization condition. They are related mainly to the existence of the PEO block bonding chemically with the PCL block. In summing up results of investigations into the crystallization and melting behavior of the PCL/PEO block copolymer, it is interesting to notice that when the PCL/PEO block copolymer crystallizes at three different crystallization temperatures, i.e., below 0°C, between 0 and 35°C, and above 35°C, the variation of peak melting temperature is similar to that of overall crystallization rates in the process of isothermal crystallization. The results can be elucidated by the effect of the PEO block on the crystallization of the PCL block, especially its nucleation. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Extensive studies have been done on the morphology and crystallization of block copolymers with amorphous and crystallizable blocks,¹⁻⁷ however, there are few studies on block copolymers with all crystallizable blocks. One typical example was the study on the crystallization and morphology of the poly(ϵ -caprolactone)(PCL)/poly(ethylene oxide)(PEO)/

poly(ϵ -caprolactone)(PCL) triblock copolymer in which all blocks were crystallizable.^{8,9} Perret and Skoulios indicated that the overall morphology of this PCL/PEO/PCL triblock copolymer and the crystallization behavior of three blocks depended heavily on crystallization conditions, particularly temperature. Misra and Garg investigated the crystallization behavior of the poly(ethylene terephthalate)(PET)/poly(butylene terephthalate)(PBT) diblock copolymer with PET as the major component and the amount of PBT varying from 1.0 to 20.0 wt %.^{10,11} The results had shown that the PBT block crystallized at a much faster rate and

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provided nucleating sites and thus increased the crystallization rate considerably over that of PET. However, much work needs to be done on block copolymers with all crystallizable blocks to elucidate their crystallization behavior and crystalline structure.

In this present paper, we investigate the isothermal crystallization and melting behavior of the poly(ϵ -caprolactone) (PCL)/poly(ethylene oxide) (PEO) diblock copolymer, and, furthermore, we interpret the nature of double melting peaks and the mutual influence of PEO and PCL blocks.

EXPERIMENTAL

Materials

5,10,15,20-Tetraphenylporphine (TPPH₂) was synthesized from pyrrole and benzaldehyde in propionic acid.¹² Ethylene oxide (EO) was dried over calcium hydride, CaH₂, distilled over the mixture of CaH₂ and potassium hydroxide K(OH) in a nitrogen atmosphere, and then collected in an ampoule cooled with liquid nitrogen. ϵ -Caprolactone (CL) (Aldrich) was dried with CaH₂ over 2 days and then distilled under reduced pressure in a nitrogen atmosphere. Dichloromethane, CH₂Cl₂, was washed with concentrated sulfuric acid, neutralized with an aqueous solution of sodium bicarbonate, dried over calcium chloride, and then distilled over CaH₂ in a nitrogen atmosphere. Diethylaluminum chloride Et₂AlCl (Fluka) was used without treatment.

Preparation of Catalyst

The catalyst of (5,10,15,20-tetraphenylporphinato)aluminum chloride (TPP) AlCl was prepared by the reaction of Et₂AlCl with TPPH₂ in a solution of CH₂Cl₂ according to the method of Aida and Inoue.¹³

Polymerization

The PCL/PEO diblock copolymer was prepared by sequential addition polymerization as described elsewhere.¹⁴ The prepolymer of EO was prepared first. After a definite time, unreacted EO was removed under reduced pressure, and the second monomer CL was added into the prepolymer formed. After purification to remove residual catalyst and homopolymers, the pure PCL/PEO diblock copolymer was a white or light yellow powder.

Characterization

The structure and molecular weight of the PCL/PEO block copolymer were characterized by NMR spectra and gel permeation chromatograph (GPC). PEO block: the number average molar mass, $\bar{M}_n = 7,900$, $\bar{M}_w/\bar{M}_n = 1.36$; PCL/PEO block copolymer: $\bar{M}_n = 17,100$, $\bar{M}_w/\bar{M}_n = 1.65$. The weight fraction of the PEO block in the PCL/PEO block copolymer was 20%.

DSC Measurement

Investigations of the isothermal crystallization and melting behavior of the PCL/PEO block copolymer were carried out using differential scanning calorimetry (DSC) (Perkin-Elmer DSC-7). The polymer samples were melted at 80°C for 5 min and then cooled rapidly to an isothermal crystallization temperature. After crystallization, the polymer samples were heated at a fixed rate to a molten state.

SAXS and WAXD Studies

Small-angle X-ray scattering (SAXS) measurements were carried out by means of a Philips PW1700 with Krathy compact camera. The x-ray tube worked at 40 kV and 35 mA. The wide-angle x-ray diffraction (WAXD) patterns were obtained using a Philips diffractometer with Ni filtered Cu K α radiation. PCL/PEO block copolymer samples after isothermal crystallization at different temperatures by cooling dramatically from molten state (80°C) were used for the SAXS and WAXD studies.

RESULTS AND DISCUSSION

WAXD Study

Skolios and Perret found that PCL and PEO blocks in the PCL/PEO/PCL triblock copolymer could crystallize and formed an alternating crystalline layer structure.⁸ Our results of WAXD studies of PCL/PEO block copolymer, which crystallized isothermally at different temperatures by cooling dramatically from molten state, are shown in Figure 1. We have known that the crystal systems of poly(ethylene oxide) and poly(ϵ -caprolactone) are different. The PEO is a monoclinic system and PCL is an orthorhombic system. From the above WAXD patterns we find that there are diffraction peaks of the PCL block, which is the major component (80 wt %) in the block copolymer, but no diffraction

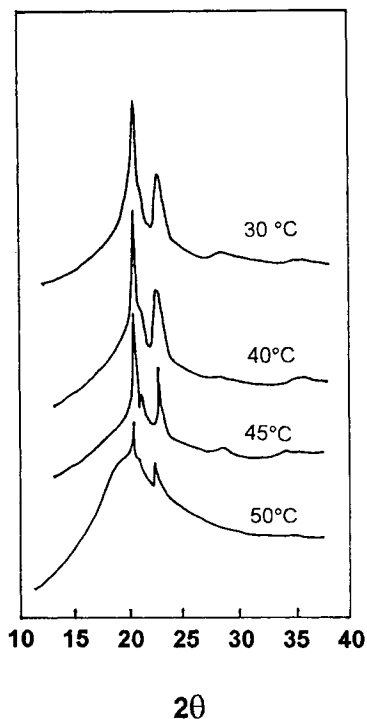


Figure 1 WAXD patterns of the PCL/PEO block copolymer after isothermal crystallization at different temperatures by cooling rapidly from the molten state.

peaks of the PEO block. These results have shown that although PEO and PCL homopolymers are of strong crystallizabilities, only the PCL block in the PCL/PEO block copolymer can crystallize; the PEO block with weight fraction of 20% cannot crystallize.

Crystalline Structure of the PCL/PEO Block Copolymer

Little work has been done on the morphology of block copolymers with all crystallizable blocks. Figure 2 is the long period, amorphous layer, and crystalline lamella of the PCL/PEO block copolymer after isothermal crystallization at different temperatures by cooling from a molten state.

It is found that the long period, amorphous layer, and crystalline lamella of the PCL/PEO block copolymer all increase with the rise in crystallization temperature, and increase dramatically when the temperatures are above 30°C.

The thickness of the crystalline lamella of PCL/PEO block copolymer is less 100 Å, but that of the EO homopolymer is generally 150–200 Å.¹⁵ These indicate that the crystalline lamella of the PCL/PEO block copolymer is composed of the PCL block,

not the PEO block, and these results correspond to the above-mentioned WAXD results.

The amorphous PEO block has a great influence on the variation of thickness of the amorphous layer and crystalline lamella of the PCL/PEO block copolymer, especially with the rise in crystallization temperature. Because the thickness of the crystalline lamella of the EO homopolymer is much longer than that of the CL homopolymer, the PEO block, whose weight fraction is 20% in the PCL/PEO block copolymer, has insufficient chains to arrange regularly to form a crystalline structure; therefore it could form only an amorphous layer of the PCL/PEO block copolymer. With the rise in crystallization temperature, especially above 30°C, the PEO block chains in the amorphous region have a certain ability to move, although they cannot form a regular crystalline structure; the motion of the PEO block chains leads to an increase in the thickness of the amorphous layer of the PCL/PEO block copolymer and makes the thickness of the amorphous layer much larger than that of the crystalline lamella composed of the PCL block. These results are shown in Figure 2.

Isothermal Crystallization of the PCL/PEO Block Copolymer

The isothermal crystallization of the PCL/PEO block copolymer cooling rapidly from a molten state to a fixed temperature is shown in Figure 3.

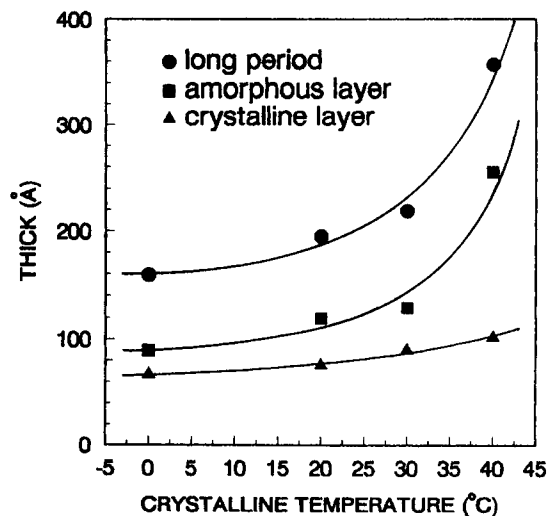


Figure 2 Long period, amorphous layer, and crystalline lamella of the PCL/PEO block copolymer at different crystallization temperatures.

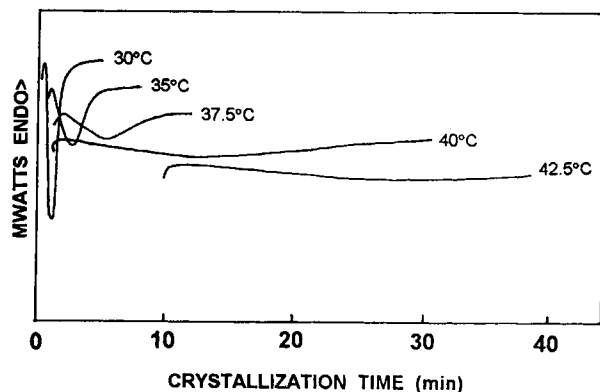


Figure 3 DSC crystallization curves of the PCL/PEO block copolymer crystallizing at different temperatures from the molten state.

Only a single peak is found as the PCL/PEO block copolymer crystallizes at a designated temperature. To describe the effect of the amorphous PEO block on the crystallization of the PCL block, we investigated the isothermal crystallization behavior of the PCL/PEO block copolymer within a wide range of crystallization temperatures.

The crystallization kinetics of polymers in bulk is usually described by using the theory of Turnbull and Fisher.^{16,17} According to their theory, the linear growth rate of spherulites, G , can be expressed by

$$G = G^0 \exp\left(-\frac{\Delta E}{RT_c}\right) \exp\left(-\frac{\Delta F_g^*}{kT_c}\right) \quad (1)$$

Where G^0 is a constant, R and k are the gas constant and Boltzmann constant, respectively, T_c is the crystallization temperature, ΔE is the activation energy for the transport of crystallizing units across the crystalliquid interface, and ΔF_g^* is the free enthalpy required to form a nucleus of critical size on a crystal face.

In the above equation, $\exp(-\Delta E/RT_c)$ is generally called the diffusion term, whereas, $\exp(-\Delta F_g^*/kT_c)$ is regarded as the nucleation term.

The overall crystallization rate can also be expressed by the following equation:

$$t_{0.5}^{-1} = (t_{0.5}^0)^{-1} \exp\left(-\frac{\Delta E}{RT_c}\right) \exp\left(-\frac{\Delta F_g^*}{kT_c}\right) \quad (2)$$

where $t_{0.5}$ is the half-time of crystallization, which is defined as the time taken for half of the crystallinity to develop, and $t_{0.5}^0$ is a constant. Since $t_{0.5}^{-1}$ is directly proportional to t_{\max}^{-1} , which is the maximum

crystallization rate in the crystallization process, we replaced the $t_{0.5}^{-1}$ with t_{\max}^{-1} to describe the overall crystallization rate in our crystallization kinetics investigation. Meanwhile we notice that eq. (2) is basically the same as eq. (1).

The theory of Turnbull and Fisher has been applied to all kinds of semicrystalline polymers.^{18,19} However, the nucleation term must be modified for random copolymers.²⁰

We have investigated the overall crystallization rate t_{\max}^{-1} of the PCL/PEO block copolymer after isothermal crystallization at different temperatures.

Figure 4 shows that t_{\max}^{-1} is the fastest at ca. 20°C. A plot of the natural logarithm of t_{\max}^{-1} , $\ln(t_{\max}^{-1})$, as a function of the reciprocal of the crystallization temperature $1/T_c$, shown in Figure 5, gives two straight lines as the crystallization temperature above 35 or below 0°C, and a curve between 0 and 35°C. The results show that it was appreciate to use eq. (2) to describe the crystallization process of the PCL/PEO block copolymer. When the temperature is above 35 or below 0°C, the nucleation term and diffusion term in eq. (2) play different roles on the variation of crystallization rate with temperature.

At a great degree of overcooling, the crystallization process of the PCL/PEO block copolymer is controlled by diffusion. With the rise in temperature, the mobility of the molecular chains increases and results in an increase in the overall crystallization rate of the PEO/PCL block copolymer (line C in Fig. 5), whereas at a lower value of undercooling, i.e., at a high crystallization temperature, the nucleation term plays a decisive role. The higher the

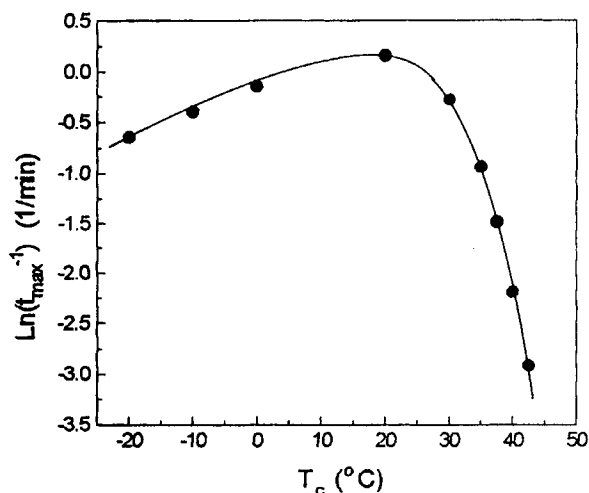


Figure 4 Plots of overall crystallization rate t_{\max}^{-1} of the PCL/PEO block copolymer versus crystallization temperature T_c .

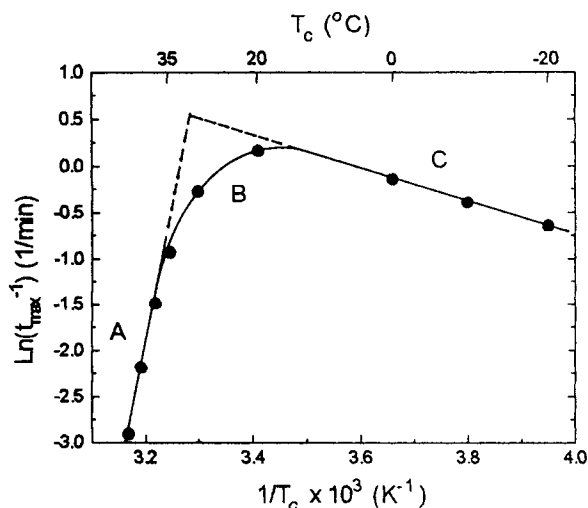


Figure 5 Plots of the natural logarithm of overall crystallization rate t_{\max}^{-1} of the PCL/PEO block copolymer, $\ln(t_{\max}^{-1})$, versus the reciprocal of crystallization temperature $1/T_c$.

temperature, the more difficult it is to form a stable nucleus. Although the mobility of macromolecular chains of the PCL/PEO block copolymer increases with the rise in temperature, the overall crystallization rate goes down (line A in Fig. 5). The curve between straight line A and B (part B in Fig. 5) can be considered as the transformation from diffusion control into nucleation control with the rise in temperature in the crystallization process of the PCL/PEO block copolymer. Meanwhile, it is worth noticing that the slope of straight line A is much larger than that of straight line C. These results show that the effect of the nucleation term is stronger than that of the diffusion term on the crystallization process of the PCL/PEO block copolymer, i.e., the amorphous PEO block has a great influence on the nucleation of the crystallization of the PCL block.

Melting Behavior of the PCL/PEO Block Copolymer

There are two outstanding characteristics during the melting process of the PCL/PEO block copolymer after isothermal crystallization. One is the phenomenon of melting peaks and the other is the transformation of melting peaks from double peaks into a single peak with the variation of crystallization conditions (Fig. 6).

It is found in Figure 6 that there are two melting peaks when the crystallization temperatures are below 30°C; however, only a single melting peak is

found when the crystallization temperatures are above 30°C. The result shows that the melting peaks of the PCL/PEO block copolymer transform from double peaks into single peak with the rise in crystallization temperature. Conclusive evidence is that there is only one melting peak with a shoulder for the PCL/PEO block copolymer after isothermal crystallization at 30°C (Fig. 7).

The multiple peak endotherms arise usually from recrystallization during DSC measurement, i.e., imperfect crystals melt and recrystallize into crystals with higher order. To elucidate the nature of the double melting peaks of the PCL/PEO block copolymer, the copolymer crystallized at 10°C and

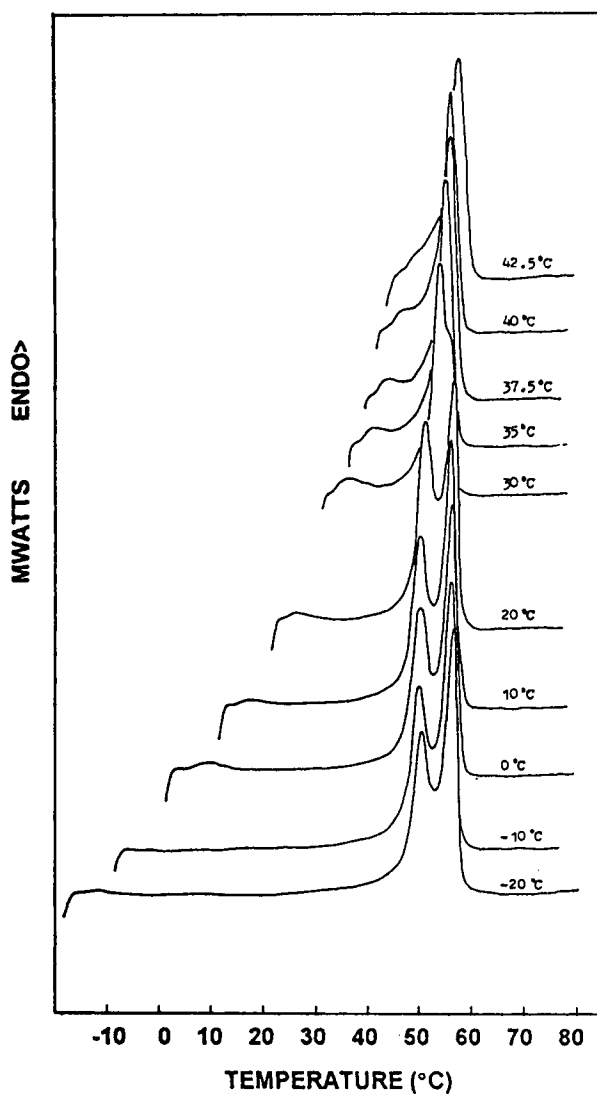


Figure 6 DSC melting curves of the PCL/PEO block copolymer after isothermal crystallization at different temperatures. Heating rate = 10°C/min.

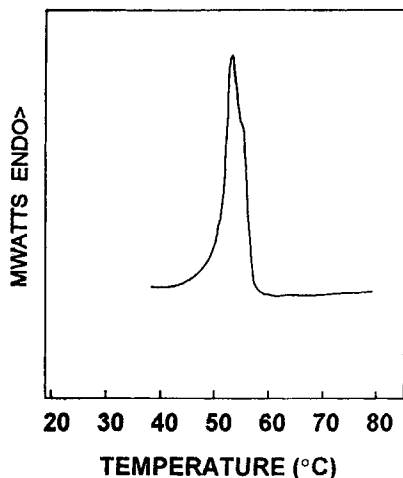


Figure 7 DSC melting curves of the PCL/PEO block copolymer after isothermal crystallization at 30°C. Heating rate = 10°C/min.

then melted at different heating rates. The DSC thermograms are shown in Figure 8. The two melting peaks all widen when the heating rates increase from 5 to 80°C/min, and from the width of the melting peak of the PCL/PEO block copolymer heating at 80°C/min, we can infer that the origin of the wide peak is from the partial overlap of the two melting peaks. Therefore, different heating rates result only in variances of the shape and overlapping degree of the two melting peaks, they do not lead to the disappearance of the melting peak with lower temperature or higher temperature. Thus it has been shown that the occurrence of the double melting peaks of the PCL/PEO block copolymer does not result from recrystallization when heating in the course of the DSC run. Therefore the phenomena of the double melting peaks reflects the complicated crystallization mechanism of the PCL/PEO block copolymer.

From WAXD patterns we have known that only the PCL block is crystallizable. The PEO block, of which the weight fraction is 20% in the PCL/PEO block copolymer, is partially compatible with the PCL block. Thus when the PCL/PEO block copolymer crystallizes isothermally, the amorphous and microphase separating PEO block reduces the entropy of PCL block chains due to the chemical bond between the PEO and PCL blocks, and provides nucleating sites for the crystallization of the PCL block. The peak with lower melting temperature is the reflection of the PCL block crystallizing with PEO as nucleating sites. With the rise in crystallization temperature, the control over crystallization of the PCL block will be transformed gradually from dif-

fusion to nucleation as discussed above. The microphase separating the PEO block will provide nucleating sites and is advantageous for the crystallization of the PCL block. Thus the area of melting peak with lower melting temperature increases gradually, and finally the peak with higher melting temperature disappears and only one peak remains.

On the other hand, it is found in Figure 9 that the melting temperature of the peak with lower melting temperature is invariant in the range of crystallization temperatures below 0°C, rises gradually with temperatures from 0 to 35°C, and finally increases linearly when the crystallization temperatures are above 35°C. It is interesting that similar variations of overall crystallization rate and melting temperature of the peak with lower melting temperature occurred in these three different sections of crystallization temperatures (Figs. 5 and 9).

Therefore, the occurrence of the double melting peaks of the PCL/PEO block copolymer is related mainly to the existence of amorphous the PEO block

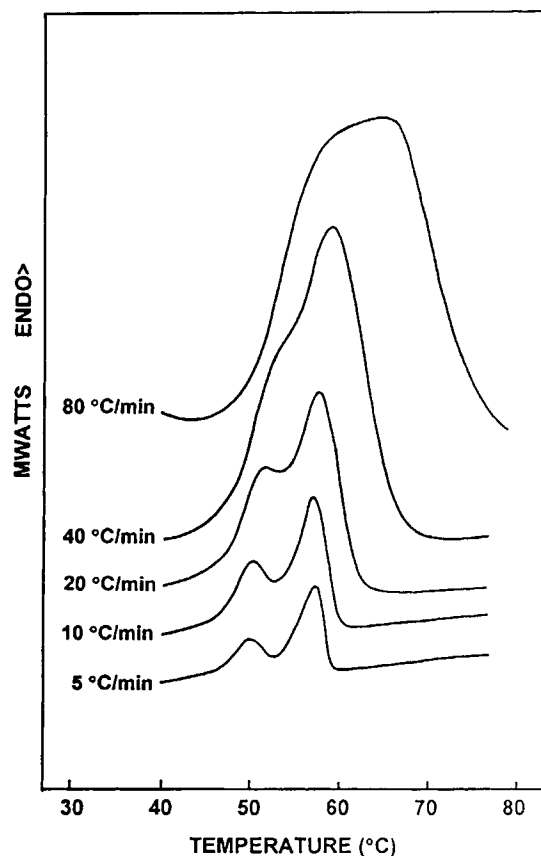


Figure 8 DSC thermograms of the PCL/PEO block copolymer after isothermal crystallization at 10°C. The heating rate is indicated above the curve.

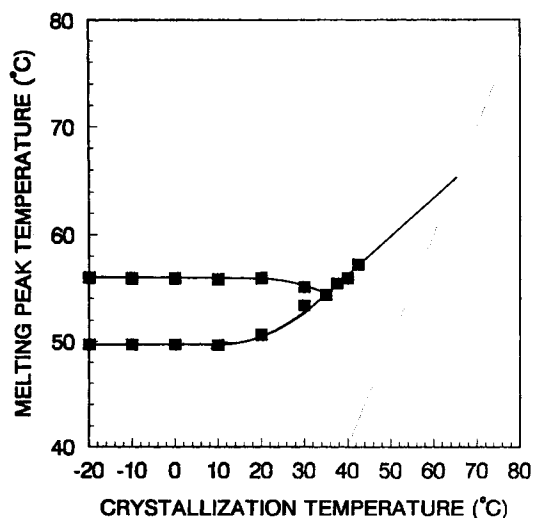


Figure 9 Temperatures of the melting peaks of the PCL/PEO block copolymer after isothermal crystallization at different temperatures. Heating rate = 10°C/min.

bonding chemically with the PCL block. Meanwhile it has also been proved that the effect of the PEO block on crystallization of the PCL block lies mainly in the nucleation.

CONCLUSION

Only the PCL block is crystallizable; the PEO block of which the weight fraction is 20% in the PCL/PEO block copolymer cannot crystallize, although its corresponding homopolymer PEO has strong crystallizability. With the rise in crystallization temperature, PEO block has insufficient chains to arrange regularly to form a crystalline structure; however, its motion leads to an increase in the thickness of the amorphous layer of the PCL/PEO block copolymer and makes the thickness of the amorphous layer much larger than that of the crystalline lamella composed of the PCL block. The PEO block bonding chemically with the PCL block has a great influence on the crystallization of the PCL block, particularly the nucleation of the PCL block, and the extent of influence depends heavily on the crystallization temperature. The variation of overall crystallization rate of the PCL/PEO block copolymer and the transformation of melting peaks from double peaks to a single peak at three different crystallization temperatures, i.e., below 0°C, between 0

and 35°C, and above 35°C, are similar and therefore have proved that the effect of the PEO block on the crystallization of the PCL block lies mainly in the nucleation.

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