

Crystallization of Poly (ethylene glycol) in Poly (methyl methacrylate) Networks

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crossref <http://dx.doi.org/10.5755/j01.ms.19.2.4430>

Received 30 December 2011; accepted 28 May 2012

The crystallization of poly(ethylene glycol) (PEG) in poly(methyl methacrylate) (PMMA) networks were studied, which was compared with that of PEG homopolymer. Melting point (T_m) of PEG in PMMA networks is lower than that of pure PEG; the crystallinity and T_m s of PEG in PMMA networks somewhat increase with increasing of PEG content; the cross-linker content of PMMA networks plays an important role for the crystallization of PEG. When the cross-linker content is between 3.5 wt% and 5.8 wt%, the distinct endothermic peak of PEG crystal fusion can be observed. Optical microscopic observation of the crystallized PEG in PMMA networks showed spherulite formation, indicating there was the co-continuous crystalline PEG in PMMA networks.

Keywords: poly(ethylene glycol), poly(methyl methacrylate), spherulitic, crystallization, melting point.

1. INTRODUCTION

Over the last two decades, the blending of polymers to achieve properties suitable for particular applications is of importance. One of the key factors is control of the morphology [1]. Most polymer pairs are immiscible and form multiphase systems with a variety of morphologies. It is well known that the morphology of polymer blends plays a crucial role in their final properties [2–4]. Therefore control over the size, shape, and distribution of the dispersed phase or the degree of co-continuity within polymer blends results in control of their final properties.

Linear poly(methyl methacrylate) (PMMA) can form stable blends with linear poly(ethylene oxide) (PEO) due to van der Waals type bonding between the PMMA chains and the planar PEO segments [5–7]. They are among the most studied polymer systems, and it is reported that the miscible domain formed at the content of 10 % and 30 % of PEO by weight; It was indicated that this blend is probably immiscible with PEO > 30 wt% and crystalline aggregates of PEO can be observed [8–13].

To our knowledge, recently only few attempts have been made to determine the miscibility and thermal behavior of PMMA/PEO blends in which the PMMA was in crosslinked and the PEO in linear form [14, 15]. No studies are reported in the literature concerning the crystallization and the overall morphology of linear poly(ethylene glycol) (PEG) in the PMMA networks. In this report we show the crystallization of PEG in PMMA networks and the effects on PEO crystallization imposed by PMMA. On the other hand, investigation of the specific features of the PEG in the PMMA networks is of substantial practical interest because of their potential applications as shape memory materials.

2. EXPERIMENTAL

Methyl methacrylate (MMA) and azobisisobutyronitrile (AIBN) were of analytical grade obtained from the Chengdu Reagent Factory. Ethylene glycol dimethacrylate (EGDMA) was purchased from Aldrich Chemical Co. MMA was distilled under reduced pressure before use. AIBN, used as a radical initiator, was recrystallized from methanol solution. EGDMA was used as a cross-linker without further purification. PEG (Aldrich) with catalogue number-average molecular weights of 1000, 2000, 4000, 6000, 10000 and 20000 was dried by heating at 70 °C for 7 hr under vacuum.

The PMMA networks were prepared by radical polymerization and crosslinking of (50.5–60.5) wt% MMA in the presence of 0.5 wt% AIBN as an initiator, (0.6–5.8) wt% EGDMA as a crosslinker, and (35–45) wt% linear PEG. The reaction mixture was bubbled with nitrogen for 15 min. to remove the oxygen from the mixture. Polymerization was carried out at 55 °C for 24 hours. The characteristics of the prepared polymer are summarized in Table 1. All specimens were quenched and then dried under vacuum at room temperature for 10 days to remove unreacted monomers. According to the formulations of PEG content and blends' compositions, these polymers were represented as A (molecular weight of PEG) series, B (content of PEG) series and C (cross-linker content of network) series, respectively.

Various molecular weight PEG homopolymer and PEG in PMMA networks can form spherulites. The spherulitic morphology was observed and photographed through a polarized optical microscope (a Jiangnan XPR-2, China) equipped with a digital camera and a heating stage.

TEM measurements were carried out on a JEM-100CX Microscopy (Japan Electronic Company). Samples were prepared by dropping a suspension onto Formvar-coated copper grids.

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The X-ray measurement of the melt-crystallized polymer films was performed at room temperature on a Philips X'pert Pro MPD, using Ni-filtered $\text{CuK}\alpha$ radiation. The wide-angle X-ray diffraction (WAXD) profiles were recorded in the 2θ range of 10° – 40° at a scan rate of $0.02^\circ/\text{min}$.

Table 1. Characteristics of PMMA/PEG blends prepared.

Notation	Cross-linker content (wt%)	PEG	
		\overline{M}_n	C (wt%)
A (Molecular weight of PEG) series			
A1	3.5	1000	38
A2	3.5	2000	38
A3	3.5	4000	38
A4	3.5	6000	38
A5	3.5	10000	38
A6	3.5	20000	38
B (content of PEG) series			
B1	3.5	4000	35
B2 (A3)	3.5	4000	38
B3	3.5	4000	40
B4	3.5	4000	45
C (Cross-linker content of network) series			
C1	0.6	2000	38
C2	1.2	2000	38
C3 (A2)	3.5	2000	38
C4	5.8	2000	38

The thermal analyses were carried out with a differential scanning calorimeter (Du Pont 9900) over a temperature range from -70°C to 170°C at a heating rate of $10^\circ\text{C}/\text{min}$, purged with nitrogen gas, and quenched with liquid nitrogen. The cell was calibrated using an indium standard; the weight of the sample was (5–10) mg.

3. RESULTS AND DISCUSSION

The effect of the presence of PMMA networks on the spherulitic morphology of PEG was studied by POM. The optical micrographs of neat PEG are shown in Figure 1.

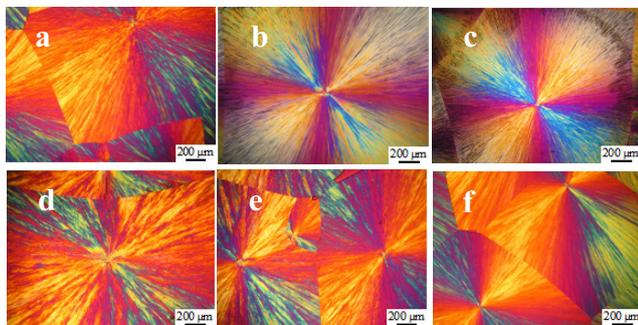


Fig. 1. Optical micrographs of PEG spherulites with various molecular weight of PEG (a – 1000; b – 2000; c – 4000; d – 6000; e – 10000; f – 20000)

Well-developed spherulite grows to a size of about $2000\ \mu\text{m}$ in diameter in the case of neat PEG, as shown in Figure 1, b. Spherulites are the basic morphology for polymers crystallized from melting or concentrated solutions, which are high-order crystal structures with spherical textures composed of lamellar crystallites shaped like ribbons that radiate from the center, separated by amorphous material [16]. In pure PEG spherulites, the Maltese cross along the vibrational directions of the polarizer is clearly discovered (Figure 1, a, d, e, f) without extinction rings when crystallized at 0°C . The polygonal shape of the spherulites with almost equal size indicates that nucleation occurred at the same time.

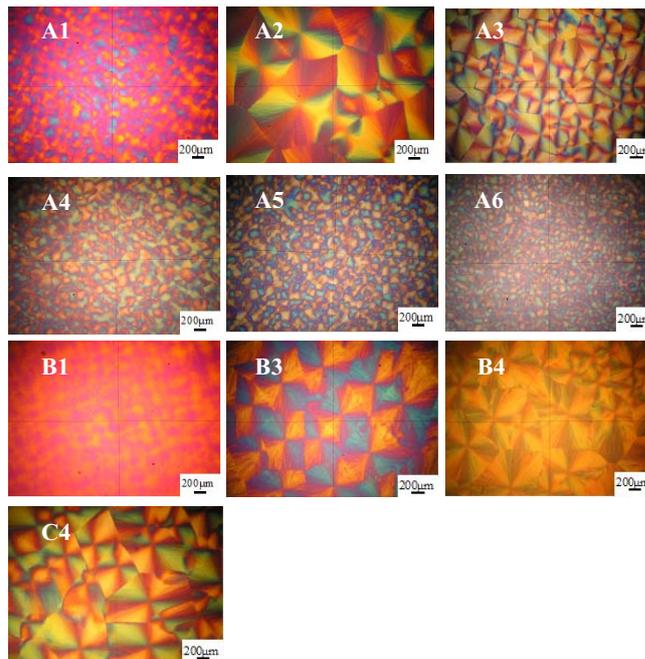


Fig. 2. Optical micrographs of PMMA/PEG blends

Figure 2 shows the optical micrographs of the spherulites in the PEG/PMMA blends. For the blends (Figure 2, A1, A4, A5, A6, and B1), it is clear that the size of PEG spherulites becomes smaller in the presence of PMMA networks, indicative of the increase of nucleation density. In particular, some smaller and imperfect spherulites with a diameter less than $200\ \mu\text{m}$ are observed to grow rapidly, impinge quickly with surrounding spherulites, and restrict further growth, which are characterized by very anisotropic, nonspherulitic shapes with jagged edges; they have no extinction rings or the Maltese cross pattern under the crossed polarized optical microscopy. Extinction rings are clearly shown in Figure 2, C4. These extinction rings, which appear at regular intervals along the radial direction, are commonly observed either due to radially oriented assembly of continuous, helicoidally twisted lamellae [17, 18] or due to structural discontinuities that originate from rhythmic crystal growth [19].

A very interesting phenomenon is observed that the spherulite of B3 shows positive birefringences, but that of C4 shows negative. By comparing the micrograph of B2, B3, B4 with that of B1 in Figure 2, more PEG content in PMMA networks seems to lead to more complete

crystallization of the PEG; below 3.5 wt% of cross-linker content the crystal can not be observed by optical microscopy, indicating PMMA/PEG blends are fully amorphous; the cross-linker content dramatically influences the crystallization behavior of PEG, as shown in Figure 2 (C3 and C4); the more the cross-linker content, the smaller the crystal of PEG. The crystal morphology is strongly altered by the PMMA networks presence, resulting in more, smaller, and nonisotropic crystallites.

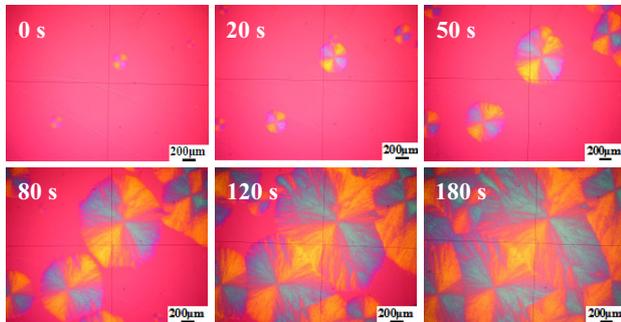


Fig. 3. Time dependence of spherulitic growth pattern of B3

PMMA/PEG blends are slightly opaque at room temperature but they become transparent as soon as the temperature increased to above the melting point of PEG crystal. To see directly how the crystallization occurs, a progression of a growing crystallite is shown for B3 in Figure 3. Sample B3 is heated to 74 °C and then quenched to 15 °C. In the melt, no birefringence is observed and sample B3 becomes completely amorphous. Consequently, the microscopy results indicate that the blend is phase mixed at these temperatures. Near 53 °C, the nucleation and growth of PEG spherulites are seen; spherulites are similar in size, and prior to impinging upon one another, they appear circular, suggesting an isotropic (spherical) three-dimensional shape. After initial appearance of spherulitic nucleus, the melt-crystallized PEG spherulite grows rapidly within few minutes until it impinges with adjacent spherulites, indicating that there is the co-continuous crystalline PEG4000 in PMMA/PEG blend. These phenomena indicate that the primary crystallization, characterized by radial growth of spherulites, is very quick. It has been known that the crystallization rate is lower just below the melting point. We also find that the growth rate is somewhat slower if the crystallization temperature is higher, though not shown here.

It is of great interest to study the effect of the presence of PMMA networks on the crystal structure of PEG in the blends. Figure 4 illustrates the WAXD patterns of neat PEG4000 and B series blends, which were crystallized at 0 °C for 12 h. It is obvious that both pure PEG4000 and B series blends are crystalline at room temperature.

It should be noted that PEG4000 and B series blends have similar diffraction patterns, and so are their diffraction angles and crystal plane distances. Neat PEG4000 shows two main diffraction peaks at about 18.9° and 23.1°, whose positions don't change in PMMA networks, which demonstrates that neat PEG4000 and PMMA/PEG blends have similar crystal structure and crystal cell type, and there are no significant distortions of the crystal structures of PEG in PMMA/PEG blends. In

other words, the crystal structure of PEG has not been changed by the procedure of blending, and therefore, there are no chemical changes at all. The main difference between neat PEG4000 and PMMA/PEG blends is that the diffraction peak height and half-width of the former are lower and narrower than those of the latter, which means that the dimension of spherulites becomes smaller and the degree of crystallization decreases; the result is in good agreement with POM results.

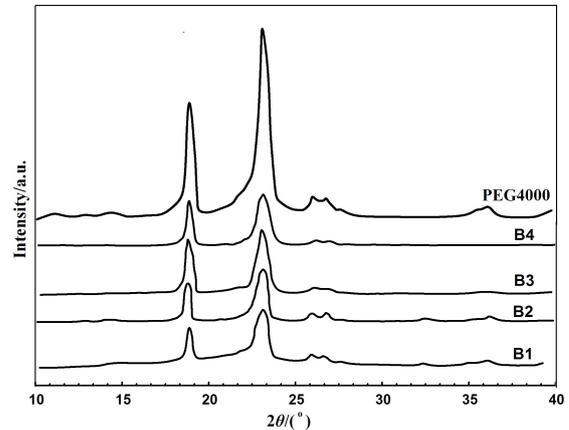


Fig. 4. WAXD patterns of neat PEG4000 and B series blends

TEM provides additional evidence that the crystalline structure exists in the PMMA/PEG blend. It is known that PMMA network prepared by radical polymerization is amorphous, which shows an amorphous halo in Figure 5, a. PEG is a semicrystalline polymer with higher crystallinity and can show typical crystal diffraction pattern, corresponding to regular lattice structure, as shown in Figure 5, b. Figure 5, c, is the PMMA/PEG blends diffraction pattern, testifying the amorphous phase is richer than the crystal phase in the blend at the room temperature; it is believed that the crystalline PEG is separated from amorphous phase.

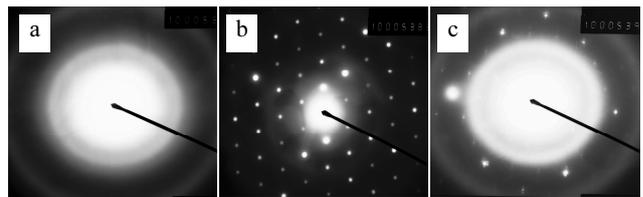


Fig. 5. TEM diffraction photographs of PMMA networks (a), PEG1000 homopolymer (b) and PMMA/PEG1000 blends (c)

PEG, a semicrystalline polymer and PMMA network, an amorphous crosslinked polymer, produce a semicrystalline mixture when the proportion of PEG exceeds 35 wt% in our experiments. For the concentration used in this study (≥ 35 wt% PEG), the two-component system is expected to be composed of amorphous blended regions with some crystalline regions made up entirely of PEG.

All the thermal properties and characteristic temperatures such as the glass transition temperature (T_g) and melting temperature (T_m) were measured using DSC. The apparent enthalpies of fusion and the melting temperature are derived respectively from the area and the maximum of the DSC endotherm peaks. The weight

crystallinity indexes of the PEG phase, X_c , and of the overall PMMA/PEG blends, Y_c are calculated from:

$$X_c(\text{PEG}) = \Delta H^*_{\text{PEG}} / \Delta H^{\circ}_{\text{PEG}}; Y_c(\text{blends}) = \Delta H^*_{\text{blends}} / \Delta H^{\circ}_{\text{PEG}} \quad (1)$$

Where $\Delta H^{\circ}_{\text{PEG}}$ is the heat of fusion per gram of 100 % crystalline PEG (from literature data [20], $\Delta H^{\circ}_{\text{PEG}} = 45 \text{ cal g}^{-1}$), ΔH^*_{PEG} and $\Delta H^*_{\text{blends}}$ are the apparent enthalpies of melting per gram PEG in the PMMA networks and for a gram of blends respectively.

The melting temperatures (T_m) and crystallinity indices of the PEG homopolymer are reported in Table 2. T_m s increase with increasing of PEG molecular weight and the PEG homopolymer with higher molecular weight has relatively high crystallinity.

Table 2. Melting temperature, T_m (°C) and crystallinity of PEG homopolymer

Sample	Molecular weight of PEG	T_m (°C)	Crystallinity (%)
PEG1000	1000	40.7	92.7
PEG2000	2000	56.8	94.0
PEG4000	4000	62.9	96.5
PEG6000	6000	64.8	97.8
PEG10000	10000	66.8	98.4
PEG20000	20000	68.5	99.2

The melting temperatures (T_m), the glass transition temperature (T_g) and crystallinity indices of these blends are summarized in Table 3.

Table 3. T_m (°C), T_g (°C) and crystallinity of PEG in blends

Sample	T_m (°C)	T_g (°C)	Y_c (%)	X_c (%)
A1	32.3	66	4.6	12.2
A2	46.8	80	5.3	13.9
A3	52.8	83	12.2	32.0
A4	55.4	86	14.8	38.9
A5	57.4	88	15.9	41.8
A6	60.2	93	16.8	44.4
B1	51.2	95	5.8	16.6
B2 (A3)	52.8	83	12.2	32.0
B3	52.9	78	13.1	32.7
B4	53.6	72	15.0	33.4
C1	–	77	–	–
C2	–	78	–	–
C3 (A2)	46.8	80	5.3	13.9
C4	43.9	84	7.9	20.7

As Table 3 indicates, in comparison to the PEG homopolymer, T_m of PEG crystallized in blends is always lower than that of pure PEG. It may be attributed to the crystal size reduction [21], the changes in the surface free energy in the PEG crystals, an increase in the concentration of crystalline defects, or a change in the structure of the PEG crystals [22], as evidenced by the former POM observation. Meanwhile, the weight crystallinity of PEG in blends also rapidly decreases; the smaller the molecular weight, the more decreased crystallinity, as shown in Table 3. The main reason is that

most of PEG is miscible with PMMA network, which makes the crystallinity depress in blends. Moreover, PEG with low molecular weight is more miscible than that with high molecular weight. It turned out that the Flory-Huggins interaction ($\chi_{1,2}$) decreases with the increasing of the PEG molecular weight [23], which contributes to phase separation.

In further experiments, we have studied the influence of the PEG content on PMMA/PEG blends. The crystallinity and T_m s of PEG in blends somewhat increase with increasing of PEG content (see Table 3). In the case of T_g of blends, it decreases with increasing of PEG content (see Table 3). It is believed that more addition of PEG to PMMA networks not only produces an increase in crystal content and but also introduce more amorphous PEG into blends, because of PEG being a semicrystalline polymer; the former effect can increase the crystallinity of blends, and, according to a qualitative analysis of the Fox equation, the latter decreases T_g of polymer. More crystal content can not mean distinct increases of T_m , because T_m is mainly related to crystal size, the surface free energy in the PEG crystals, and so on.

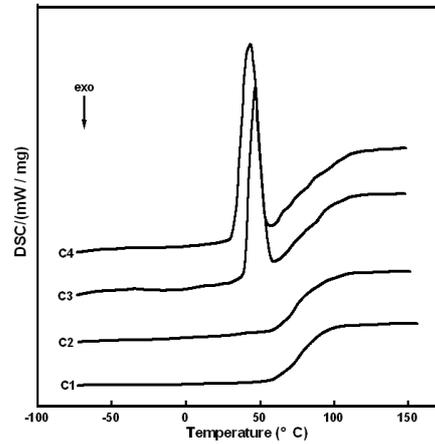


Fig. 6. DSC scans of series C blends with various cross-linking degrees

The influence of cross-linker content on the thermal behavior of PMMA/PEG blends is presented in Figure 6. It is worth noting that cross-linker content plays an important role for phase separation of blends. When the weight fraction of the cross-linker is less than 3.5 wt%, the PMMA/PEG blends show only one single glass transition temperature and the endothermic peaks due to the melting of PEG crystallites wasn't observed, suggesting that blends are fully miscible with a homogeneous amorphous phase. When the cross-linker content is between 3.5 wt% and 7 wt%, the distinct endothermic peak of PEG crystal fusion can be observed, indicating that the phase separations occur in blends. Furthermore, with increasing of cross-linker content in blends, the crystallinity of PEG increases, but T_m of PEG decreases. These results may be interpreted as follows: on the one hand, the Flory-Huggins interaction ($\chi_{1,2}$) decreases with the increasing of the cross-linker content, which results from decreases of free volume and gives an unfavourable contribution to the miscibility [23]; on the other hand, higher cross-linker content (corresponding to more network nodes) of PMMA network would reduce crystal perfectness and crystal size of PEG

by the restricted chain mobility, as evidenced by the former optical microscopy (OM) observation, which causes a T_m depression.

4. CONCLUSION

The results indicate that the content of PEG and the cross-linker content of PMMA networks have an important influence on the crystallization of PEG in PMMA networks. When the content of PEG and cross-linker content is more than 35 wt% and 3.5 wt%, respectively, PEG crystal exists in the PMMA/PEG blends. Melting point (T_m) of PEG in PMMA networks is lower than that of pure PEG; the crystallinity and T_m s of PEG in PMMA networks somewhat increase with increasing of PEG content; The melting behaviour of PEG/PMMA networks blends crystallized at low temperature may probably be accounted for by assuming that the non-crystallizable component is able to act as a diluent for PEG. The crystalline regions of the PEG crystallized from blends are smaller and less perfect than in the pure PEG. The crystallized PEG in PMMA networks shows spherulite formation, indicating there is the co-continuous crystalline PEG in PMMA networks.

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