ORIGINAL ARTICLE

Crystallization of graft copolymers 1. Graft chains miscible with main chains

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Crystallization of graft chains was investigated using poly(methyl methacrylate)-*graft*-poly(ethylene glycol), in which poly(ethylene glycol) (PEG) is miscible with poly(methyl methacrylate) (PMMA). Various compositions of PEG (98, 83, 76 wt%) were used in poly(methyl methacrylate)-*graft*-poly(ethylene glycol) (GR98, GR83, GR76, respectively). More spherulites, that is, nucleations, were generated for GR98 than for the corresponding PEG/PMMA homopolymer blend having a corresponding blend composition. However, the growth rate G of spherulites was remarkably low for all graft copolymers. In the relationship between the value of G and the PEG composition, the extrapolation to pure PEG did not yield the G value for pure PEG. The apparent activation energy of crystallization was high for graft copolymers, which was attributed to a high large surface free energy due to the restriction of PEG chains by grafting. The rate of overall crystallization for GR98 was not very different from that for PEG/PMMA blends. The Avrami index for graft copolymers was similar to that for blends and for the PEG homopolymer. Both melting temperatures and degrees of crystallinity in the graft copolymers were depressed. In the blends of the graft copolymer with the PEG homopolymer, the G value of spherulites was governed by the G value of the PEG homopolymer.

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INTRODUCTION

The crystallization behavior of multicomponent polymer systems such as polymer blends and block copolymers has been investigated extensively.^{1–12} In immiscible polymer blends and block copolymers, competition or combination between crystallization and phase separation affects both crystallization and the resulting structure.^{5–7} Especially in the crystallization of block copolymers from microphase-separated melts, the restriction of crystallization by microdomains is also important.^{7–10} By contrast, for miscible polymer blends, the kinetics of crystallization is affected by diluent effects and by the composition-dependent glass transition temperature (see Mandelkern,² Chapter 11).^{2,4,11,12}

On the other hand, crystallization in graft copolymers has not been investigated as systematically (see Mandelkern,¹ Chapter 5).¹³ Crystallization of graft chains may depend on graft densities.¹³ If the main chains and graft chains are immiscible with each other, the effect of microphase separation may also have an important role, similar to block copolymers. Therefore, the effects of both grafting and microphase separation on the crystallization behavior of graft copolymers should be investigated more thoroughly.

In this series of reports, we present the crystallization behavior of graft copolymers. First, we reveal the crystallization of the graft chain itself before describing the results of our investigation on the effect of microphase separation. In this paper, we focus on the crystallization of graft chains, using poly(methyl methacrylate)-*graft*-poly(ethylene

glycol). Because poly(methyl methacrylate) (PMMA) and poly(ethylene glycol) (PEG) are miscible with each other for PMMA/PEG homopolymer blends,^{14,15} crystallization of graft PEG chains is not affected by microphase separation (For graft copolymers, our unpublished data suggest that PMMA main chains and PEG graft chains are miscible with each other. PMMA-*graft*-PEG with 50 wt% or 2.0 mol% of PEG ($M_n=5000$) was quenched rapidly to -30°C from the melt and crystallized isothermally at that temperature. No peak was observed in the differential scanning calorimetry thermogram during isothermal crystallization; in the subsequent heating process at $10^\circ\text{C min}^{-1}$, a broad exothermal peak appeared in the range of -14 to 38°C . This onset temperature of crystallization (-14°C) is close to the T_g value of -16°C obtained from the Fox equation, with $T_g=-80^\circ\text{C}$ for PEG and 110°C for PMMA. These results suggest that the graft copolymer is in a glassy state at -30°C . Therefore, we conclude that PMMA and PEG in the graft copolymer are miscible with each other in the melt.). Therefore, features of the crystallization of graft chains are elucidated by comparing with those in the corresponding polymer blends of PMMA/PEG.

EXPERIMENTAL PROCEDURE

Material

A series of poly(methyl methacrylate)-*graft*-poly(ethylene glycols) were prepared by free-radical polymerization of methacrylate-type PEG-macromono-

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mer (PEG-MA) and copolymerization of PEG-MA and methyl methacrylate (MMA).

The PEG monomethyl ether ($M_n=5000$), which was purchased from Sigma-Aldrich (St Louis, MO, USA), was purified through an alumina column (diameter: 2.6 cm, length: 100 cm) to remove any PEG with hydroxy groups on both chain ends. The resultant PEG was reacted with sodium naphthalene to form sodium alcoholates (PEG-Na). The PEG-MA was prepared by reaction of PEG-Na with methacryloyl chloride in tetrahydrofuran for 12 h at 25 °C. After desalting, PEG-MA was purified by reprecipitation with methanol/petroleum ether (2/8), followed by freeze drying from a benzene solution. The product was characterized by ^1H NMR (JNM-GX400, JEOL Ltd., Tokyo, Japan) and size exclusion chromatography, and its functionality was determined to be 90%.

Free-radical polymerization of PEG-MA and copolymerization of PEG-MA with MMA were performed in a degassed 20 wt% benzene solution for 72 h and 60 or 40 h, respectively, at 60 °C using 1 wt% AIBN as an initiator. The resulting polymers were fractionated with an acetone/*n*-hexane system to remove unreacted PEG-MAs and then freeze-dried from a benzene solution. Molecular weights were measured by size exclusion chromatography relative to a polystyrene standard, and PEG compositions were determined by ^1H NMR. Polymer characteristics are shown in Table 1; the methacryloyl group was excluded in the calculation of the PEG composition expressed in wt% for the graft copolymers. The blends of PEG and PMMA homopolymers are also shown in Table 1. The molecular weight of PMMA, which was purchased from Scientific Polymer Products Inc. (Ontario, NY, USA), was 30 000; the PEG was identical to that used for the MA synthesis. Blend samples were prepared by precipitation in petroleum ether from a 5 wt% chloroform solution, followed by freeze-drying from a benzene solution.

Measurements

Differential scanning calorimetry measurements were taken with 10 mg for the PEG homopolymer and blends and with 20 mg for graft copolymers using a SEIKO I&E DSC20 apparatus (SEIKO I&E Ltd., Tokyo, Japan). For isothermal crystallization, the sample was annealed for 15 min at 85 °C and then rapidly cooled to a desired crystallization temperature T_c . Isothermal crystallization was analyzed by time resolution of the exothermal peak. Melting behavior was observed by heating the sample from T_c at 10 °C min $^{-1}$ after isothermal crystallization. Spherulites were observed by polarized optical microscopy under crossed polarizers with a 530 nm retardation plate using an OLYMPUS BH-2 instrument (Olympus Corporation, Tokyo, Japan) equipped with an OLYMPUS PM-10AK camera and a laboratory-made hot stage controlled by a LABOX-115-8-03T regulator (RKC Instrument Inc., Tokyo, Japan).

RESULTS AND DISCUSSION

Crystallization of graft copolymers and homopolymer blends

The degree of crystallinity and the equilibrium melting temperature, T_m^0 , for the samples crystallized isothermally in the indicated range of

T_c are summarized in Table 2. Although the degree of crystallinity of PEG in the blends is not significantly decreased, the degree of crystallinity values of graft copolymers are considerably lower than those of the PEG homopolymer. These differences may have resulted from the connection of the PEG chain end and main chain preventing crystallization.

Equilibrium melting temperatures T_m^0 were evaluated from Hoffmann–Weeks plots shown in Figure 1. The T_m^0 obtained here for the graft chain with $M_n=5000$ may be an apparent value, because the grafting effect may be diminished with an increasing molecular weight of the graft chains. As shown in Table 2, the T_m^0 values in blends are lower than that of the PEG homopolymer because of the melting depression effect. The T_m^0 values for the graft copolymers are even lower, which may have been caused by the grafting effect, as the junctions between the graft and main chains are excluded from crystallization. Such a melting depression has been investigated theoretically and experimentally in randomly crosslinked crystalline networks (see Mandelkern,¹ Chapter 7), revealing the randomness of

Table 2 Equilibrium melting temperature (T_m^0), degree of crystallinity (DC) and Avrami index (n) obtained in the range of the indicated crystallization temperature T_c

Sample	T_c (°C)	T_m^0 (°C)	DC (%) ^a	n
PEG	34.5–46.3	63.3	90–95	2.1–2.3
GR98	30.3–40.5	60.5	60–62	2.3–2.7
GR83	24.0–32.0	55.8	71–73	2.0–2.5
GR76	16.2–24.0	51.7	64–65	2.4–2.6
BL95	32.5–36.3	61.7	89–90	2.1–2.4
BL83	34.0–42.1	61.1	84–87	2.3–2.6
BL76	32.1–40.2	60.1	75–82	2.7–3.0

^aEstimated using $-8.79 \text{ kJ mol}^{-1}$, normalized to PEG.

Figure 1 Hoffmann–Weeks plots for graft copolymers, PMMA/PEG blends and the PEG homopolymer.

Table 1 Characteristics of graft copolymers (GR) and blends with PMMA^a (BL)

Sample	$M_n \times 10^{-4}$ PEG	$M_n \times 10^{-4}$ copolymer ^b	Comp. of PEG ^c	
			(mol %) ^d	(wt. %) ^e
PEG	0.50	—	—	100
GR98	0.50	3.3	100.0	98.0
GR83	0.50	3.7	10.6	82.7
GR76	0.50	3.1	6.7	75.8
BL95	0.50	—	—	95.0
BL83	0.50	—	—	82.7
BL76	0.50	—	—	75.8

^aMw of blended poly(methyl methacrylate) (PMMA) homopolymer is 30 000.

^bDetermined by size exclusion chromatography relative to polystyrene.

^cDetermined by ^1H NMR for graft copolymers.

^dComposition of poly(ethylene glycol) (PEG) macromonomer.

^eFraction of PEG part in which the methacryloyl group is excluded for graft copolymers.

crosslinking, as well as the exclusion of junctions as contributing factors to lower T_m^0 values. Risch *et al.*¹³ observed T_m^0 values for three-arm and six-arm nylon-6 polymers that were 5 and 8 °C lower than that for the linear one, respectively. They attributed this depression to greater fold surface energies due to local defects. The melting depression in the graft copolymers studied herein may also be caused by high fold surface free energies due to restriction of the chain end by

its connection to the amorphous main chain in addition to exclusion of junctions. In fact, the T_m^0 values of GR83 and GR76 are considerably lower.

Figure 2 displays the characteristics of the generation and development of spherulites for graft copolymers and blends. The number of generating spherulites, that is, nucleations, is larger for GR98 than BL95, even though their crystallization temperatures, T_c values, are

Figure 2 Development of spherulites for graft copolymers, PMMA/PEG blends and the PEG homopolymer. Numbers indicate the crystallization time and are expressed in seconds.

Figure 3 Growth rates of spherulites for graft copolymers, PMMA/PEG blends and the PEG homopolymer.

Figure 4 Reciprocals of the half-crystallization time for graft copolymers, PMMA/PEG blends and the PEG homopolymer.

Figure 6 Dependence of spherulite growth rate on the total PEG fraction at $1/\Delta T = 3.5 \times 10^{-2} \text{ K}^{-1}$. The symbols for PMMA/PEG homopolymer blends and neat graft copolymers are the same as those indicated in Figure 5, and those for blends with graft copolymers are the same as in Figure 8.

Figure 5 Dependence of the logarithm of the crystallization rate on $1/(T_c \Delta T)$: (a) growth rates of spherulites and (b) overall crystallization rates.

Crystallization rates were analyzed on the basis of the Turnbull–Fischer equation.¹⁶ By extension to dilute systems, the crystallization rate G can be written as

$$G = \phi_2 G_0 \exp(-\Delta E/RT_c) \exp(-\Delta\Phi/RT_c), \quad (1)$$

where ϕ_2 is the volume fraction of the crystallizable component, G_0 is a constant and ΔE is the activation energy of transport. In addition, $\Delta\Phi$ is the free energy for nucleation, which can be expressed as¹⁷

$$\Delta\Phi = k_i b_0 \sigma_e \sigma_s T_m^0 / \Delta H_f \Delta T - 2 \sigma_e R T_c \ln \phi_2 / (b_0 \Delta T), \quad (2)$$

where k_i is the constant depending on Regime, b_0 is the distance between two adjacent fold planes, σ_s and σ_e are the lateral and end surface energies, respectively, ΔH_f is the enthalpy of fusion per unit volume and ΔT is the degree of supercooling.

Figure 5 shows the plots of $\ln G$ and $\ln(1/t_{1/2})$ against $1/(T_c \Delta T)$. Here, ΔT for graft copolymers was taken on the basis of the T_m^0 values

of blends with the corresponding composition. The slopes of the plots of $\ln G$ for the blends (Figure 5a) are almost the same for BL95, BL83 and BL76 and are close to that for the PEG homopolymer. On the other hand, the slopes for graft copolymers are also identical for the three graft copolymers, but their slope is steeper than that for the blends and the homopolymer. The slope of the plots corresponds to the apparent activation energy of crystallization, which is the surface free energy. Therefore, the surface free energy in the spherulite growth is higher for the graft copolymer than for the blend and homopolymer, whereas that for the blend is similar to that of the homopolymer. These results coincide with the above discussion on melting temperatures. Transport energy may have affected the plots as well, especially for the graft copolymer, because of the restricted movement of the graft chains.

As shown in Figure 5b, although the slope of $\ln(1/t_{1/2})$ is considerably steeper for GR83 and GR76, the slope of GR98 is not significantly different from that of the blends and homopolymer. Accounting for the nucleation behavior described above for GR98, the total apparent

Figure 7 Avrami plots for graft copolymers and PMMA/PEG homopolymer blends.

activation energy of nucleation and growth for GR98 is not so high, compared with that for the blends and homopolymer.

At a constant ΔT , Equation (1) with (2) can be expressed as a function of $\ln\phi_2$:

$$\ln G = A + B \ln \phi_2 \quad (3)$$

when T_c is assumed to be the same at a constant ΔT . Figure 6 shows the plots of $\ln G$ vs $\ln\phi_2$ for a series of graft copolymers and blends at $1/\Delta T = 3.5 \times 10^{-2} \text{ K}^{-1}$. Both the graft copolymers and blends have a linear relationship to $\ln\phi_2$ as expressed by Equation (3). In blends, extrapolation to $\ln\phi_2 = 0$ gives the value of $\ln G$ for the PEG homopolymer; the results for blends reproduce Equation (3) for the diluted system. By contrast, in graft copolymers, extrapolation to $\ln\phi_2 = 0$ does not yield the value of $\ln G$ for the PEG homopolymer. Therefore, the crystallization kinetics in the diluted system cannot be simply applied to graft copolymers.

Figure 7 shows Avrami plots based on the following equation:

$$\log[-\ln(1-X_t)] = \log K + n \log t, \quad (4)$$

which is derived from the Avrami equation

$$X_t = 1 - \exp(-Kt^n), \quad (5)$$

where X_t is the fraction of crystallinity at crystallization time t , K is the overall crystallization rate constant and n is the Avrami index, which depends on the type of nucleation and the dimension of the crystal growth. Index n can be estimated from the initial slope of the Avrami plots. The values of n obtained from the plots shown in Figure 7 are listed in Table 2. The values of n are almost the same (2–3) for all of the samples, suggesting that the type of nucleation in the graft copolymer is the same as that in the homopolymer.

CRYSTALLIZATION OF BLENDS OF GRAFT COPOLYMER WITH PEG HOMOPOLYMER

Figure 8 shows the growth rate of spherulites for blends of the graft copolymer with the PEG homopolymer at various crystallization

Figure 8 Growth rates of spherulites for graft copolymers and their blends with PEG. The ratio in parenthesis indicates the blend ratio of (graft copolymer):(PEG homopolymer) by wt.

temperatures. Graft copolymers GR83 and GR76 were used in blend ratios of GR/PEG of 7:3 and 3:7 (wt). The plots of $\ln G$ against $\ln\phi_2$ at $1/\Delta T = 3.5 \times 10^{-2} \text{ K}^{-1}$ are shown in Figure 6. A linear relationship was obtained including the point for the PEG homopolymer, in contrast to the results for the neat graft copolymers, suggesting that spherulite growth is governed by the homopolymer. As shown in Figure 9, extinction rings appear and the inside structure becomes less regular in spherulites as T_c increases; in addition, the homopolymer content is large. During the development of spherulites, crystalline lamellae are distorted by some interaction between the graft copolymer and homopolymer. It is not clear whether graft copolymers and homopolymers cocrystallize at the level of the crystalline lamellae, although both polymers cooperate to form a single spherulite. Further investigations, such as observations of long periods by small-angle X-ray scattering techniques, are needed to reveal cocrystallization.

Figure 9 Morphology of spherulites for blends of graft copolymer with PEG homopolymer at the respective blend ratios and crystallization temperatures.

CONFLICT OF INTEREST

The authors declare no conflict of interest

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