

Polymer Communication

Microphase separation in polyoxymethylene end-capped with a long-chain alkyl

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Abstract

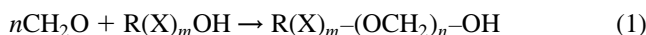
A new type polyoxymethylene (POM) having a long chain alkyl group as an end group was synthesized. This is a block copolymer comprising polar POM and non-polar polyethylene (PE) blocks. Since both the block chains have crystallizability, this copolymer has another aspect of being a crystalline block copolymer. To discuss the effects of the PE block chain length on the crystallizability, differential scanning calorimetric (DSC) measurements were conducted on the POM–PE blocks having different alkyl chain lengths. Small-angle X-ray scattering (SAXS) measurements were also conducted to confirm the microphase separation in the molten state (at 190°C). It was found that the microphase separation even took place at 190°C in a diblock sample having considerably low composition as the fraction of PE moieties is ~0.05. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Polyoxymethylene; Microphase separation; Polar–nonpolar block copolymer

1. Introduction

Polyoxymethylene, which has a recurring unit of oxymethylene, is called polyacetal resin, and is a useful engineering plastic to replace metal. The annual demand of polyacetal resin in the world is about 400,000 t. There are two types of polyacetal resins. One is the acetal homopolymer [1–6], which is produced by the polymerization of formaldehyde, and the other is the acetal copolymer [7–13], which is produced by the copolymerization of trioxane and ethylene oxide.

For the third type of polyacetal resin, the acetal block copolymer, which was obtained by the polymerization of formaldehyde in the presence of a proper chain transfer agent, has been reported [6,14] by one of the current authors. As for the chain transfer agent, a functional polymer with an active hydrogen was reported [6,14] (Eq. (1)).



In the case of the commercially available acetal block copolymer, which is obtained by the polymerization of

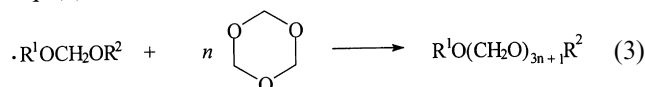
formaldehyde, the end-group of the as-polymerized polymer consists of the thermally stable group of $\text{R}(\text{X})_m$ and thermally unstable hydroxy group, as shown in Eq. (1). Thus, the hydroxy end-group must be stabilized by the acetylation using acetic anhydride. The synthesis of the polymer with both end-groups thermally stable is desired.

From this viewpoint, the authors devised new types of chain transfer agents which supply the both-end-group-capped polyoxymethylene during the trioxane polymerization. The chain transfer agents are shown in the following equation:



Here R^1 is a long chain alkyl such as the stearyl or $\text{C}_{38}\text{H}_{77}$ group and R^2 is a methyl or long chain alkyl like the stearyl group. For example, methyl stearyl formal, distearyl formal and $\text{C}_{38}\text{H}_{77}\text{OCH}_2\text{OCH}_3$ are the new types of chain transfer agent.

By using the chain transfer agent in the trioxane polymerization as shown in Eq. (2), it might be expected to produce a polymer with one end-group-capped with an $\text{R}^1\text{O}-$ group and another end-group-capped with an $\text{R}^2\text{O}-$ as shown in Eq. (3)



This paper concerns the microphase separation between

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the long-chain alkyl of the end-group and oxymethylene main chain of the polymer obtained by the polymerization of trioxane using new types of chain transfer agents.

Microphase separation and its morphology have been intensively studied in block copolymers with both chains of the amorphous type [15–17]. The studies using block copolymers having one component of the crystalline type have also been performed to reveal an interesting correlation between the microphase separation and crystallization [18–33]. There are two extreme cases in the crystallization of crystallizable block chains in these block copolymers. One is crystallization within the microphase-separated domains [18–26] and the other is that from a one-phase melt without microphase separation [27–29]. In the former case, the effects of confined space on the crystallization are discussed, for instance, the kinetics of the crystallization [18] when the driving force of the crystallization is not strong enough to destroy the microphase-separated domain structures [18–24]. On the other hand, when the crystallization driving force overcomes, the microdomains are destroyed by the crystallization [18,25,26]. Thus, utilizing the competition of crystallization with microphase separation enables us to design and control the higher order structures in materials.

In contrast to the crystalline–amorphous type block copolymers, there are a small number of studies using block copolymers composed of both block chains of the crystalline type. Although much more interesting phenomena, for instance, the competition of spherulite growth, are available from past studies even as compared to the case using crystalline–amorphous type block copolymers, the interpretation of complicated observations is not always straightforward [30]. This may be one of the main reasons for the limited number of studies. In the present study, a novel type polyoxymethylene (POM) having a long chain alkyl group as the end group was synthesized. This is a block copolymer comprising polar POM and non-polar polyethylene (PE) blocks. Since both the block chains have crystallizability, this copolymer has another aspect of being a crystalline–crystalline block copolymer. To simplify the discussion in this communication we focus our attention on the microphase separation in the molten state (above the melting temperatures of both components), since the segregation between the polar POM and non-polar PE is considerably strong. For competing crystallization against the microphase separation, the sensitive control of both miscibility and crystallizability is required. However, this is not difficult because both of them can be attained by a trivial modification of the chain length of the PE block chains with a relatively low composition of PE as low as ~0.05. Thus, three kinds of copolymers were used, POM(DP319)–PE(C38), POM(DP288)–PE(C18) and PE(C18)–POM(DP280)–PE(C18). Here, DP and C denote the degree of polymerization of the POM chains and the number of carbon atoms in the PE chains, respectively. Note that these samples have a similar number of

DP(POM). To discuss the effects of chain length of the PE block on the crystallizability, the differential scanning calorimetric (DSC) measurements were conducted. Moreover, SAXS measurements were carried out in the molten state to confirm the microphase separation.

2. Experimental

2.1. Materials

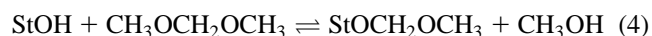
Trioxane, which was produced at Asahi Chemical, was used. It was further purified by recrystallization in dichloromethane. Commercially available stearyl alcohol was used without further purification.

As an alcohol having carbon number 38, Uniline 550 (trade name), which was supplied by Toyo Petrolite and said to be a linear primary alcohol [34], was used without further purification.

Polyoxymethylene powder (grade name: Tenac 7000) supplied by Asahi Chemical was used as the reference sample.

2.2. Synthesis of new type chain transfer agent

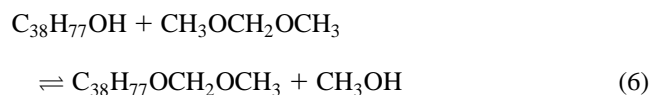
Synthesis of methyl stearyl formal. In the mixtures composed of stearyl alcohol and methylal, using cationic exchange resin as the catalyst by the acetal exchange reaction, by removing methanol from the reaction mixture, methyl stearyl formal was synthesized (for the reaction scheme, see Eq. (4))



Synthesis of distearyl formal. Distearyl formal was synthesized from methyl stearyl formal by the acetal exchange reaction. (For the reaction scheme, see Eq. (5).)



Formalization of the alcohol with carbon number 38. The synthesis similar to methyl stearyl formal operation was done. The alcohol with carbon number 38 was dissolved in cyclohexane, then methylal was intermittently added, then the distillate from the reaction system was removed (For the reaction scheme, see Eq. (6).)



2.2. Polymer synthesis

Polymerization of trioxane using methyl stearyl formal as the chain transfer agent. Trioxane and methyl stearyl formal (6×10^{-3} mol/mol-trioxane) were mixed, then melted at 64°C under a nitrogen atmosphere, and $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ was injected. The obtained solid reactants in the bulk state were crushed with a hammer into a powder, poured into

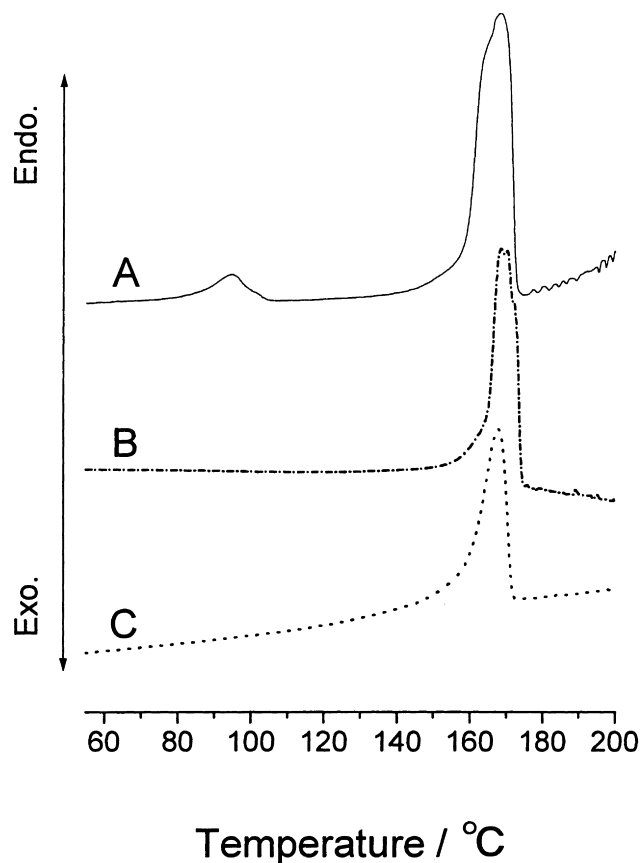


Fig. 1. DSC chart of the polymers: (A) POM-PE(C38); (B) POM-PE(C18); (C) PE(C18)-POM-PE(C18).

an ethanolic solution of KOH, and reaction was stopped. The powdery products were washed with toluene (90°C), methanol, and then acetone to remove any unreacted trioxane and chain transfer agent. The powdery polymer was obtained after drying under vacuum at 80°C.

The estimated molecular weight from the end-group analysis by the ^1H NMR spectroscopy is as follows: $M_n = 8900$. We now denote this polymer as "POM-PE(C18)".

Polymerization of trioxane using distearyl formal as the chain transfer agent. A procedure similar to the case of methyl stearyl formal was done. The estimated molecular weight is as follows: $M_n = 8900$. We now denote this polymer as "PE(C18)-POM-PE(C18)".

Polymerization of trioxane using $\text{C}_{38}\text{H}_{77}\text{OCH}_2\text{OCH}_3$ as the chain transfer agent. A similar procedure was done as in the case of methyl stearyl formal except that the polymerization temperature was 90°C. The estimated molecular weight is as follows: $M_n = 10,100$. We now denote this polymer as "POM-PE(C38)".

2.3. Measurement

Differential scanning calorimetry (DSC) measurement. DSC measurements were performed using a Perkin-Elmer DSC 7, elevating the temperature at 25°C/min under a nitro-

gen atmosphere from -100 to 220°C , for a sample weight of 4 mg.

Small-angle X-ray scattering (SAXS) measurements. SAXS measurements were conducted using synchrotron X-rays at the beamline BL-10C of the Photon Factory, Tsukuba, Japan. The incident X-ray beam was monochromatized by a couple of Si(111) single crystals and was focused on a detector plane (1d-PSPC (position-sensitive proportional counter)) by a bent-cylindrical mirror which is Pt-coated. The wavelength, λ , of the X-ray is 0.1488 nm. Details of the facility are described elsewhere [16,17,35]. The sample-to-detector distance was 1.9 m. To confirm the microphase separation in the molten state, powder samples were subjected to the SAXS measurements at 190°C which is above the melting temperature of the POM chains. The sample was soaked at 190°C for at least 10 min prior to the measurement. Contribution of the air scattering was subtracted from the sample scattering by taking into account the absorption due to the sample.

3. Results and discussion

In Fig. 1, the DSC chart of the polymer, POM-PE(C38), is shown. This polymer shows an endothermic peak at 95°C . Considering the fact that the melting point of $\text{C}_{38}\text{H}_{77}\text{OCH}_2\text{OCH}_3$ is 92°C , this fusing peak at 95°C may result from the melting of the $\text{C}_{38}\text{H}_{77}$ group attached to the polymer chain end.

To study the effect of the carbon number of the chain transfer agent on the fusing peak, we measured the DSC of the polymers, POM-PE(C18) and PE(C18)-POM-PE(C18). However, no fusion peak, which corresponds to the fusion of the stearyl group, was observed from -100 to 200°C except for the melting of the main chain oxymethylene linkage (170 – 174°C).

Thus, at present, the appearance of the melting peak at 95°C may suggest microphase separation. Namely, the long chain alkyl group having the carbon number 38 might be anticipated to undergo microphase separation from the main chain oxymethylene linkage in the molten state and therefore it can crystallize upon cooling, and causes the fusion in the DSC measurement. However, the possibility of the PE chains crystallizing from a homogeneous amorphous phase, in which the PE chains are mixed with POM chains in the amorphous state, cannot be ruled out. Therefore, SAXS measurements are required in the molten state to confirm the microphase separation.

SAXS profiles obtained at 190°C are shown in Fig. 2, where the scattering intensity, $I(q)$, is plotted as a function of q , the magnitude of the scattering vector defined as $q = (4\pi/\lambda) \sin(\theta/2)$ with λ and θ being the wavelength of X-rays (0.1488 nm) and the scattering angle, respectively. Note that the appreciable upturn scattering towards $q \rightarrow 0$ for all samples might be ascribed to an impurity when considering that no scattering should be observed at 190°C (above T_m of

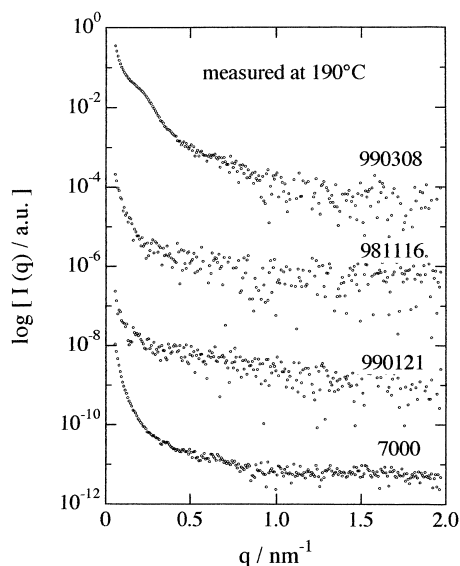


Fig. 2. SAXS profiles obtained at 190°C, where the logarithm of the scattering intensity, $I(q)$, is plotted versus q : (990308) POM–PE(C38); (981116) POM–PE(C18); (990121) PE(C18)–POM–PE(C18).

POM) for sample-7000 which is the POM homopolymer, although the exact reason is unknown at this moment. To eliminate that contribution, we decided to normalize each SAXS profile by that for sample-7000. Namely, each SAXS profile was divided by that for sample-7000.

Fig. 3 shows thus normalized SAXS profiles, where the normalized scattering intensity, $\bar{I}(q)$, is plotted versus q . A single but distinct peak appears in the SAXS profile for 990308 which is a diblock POM–PE with DP (degree of polymerization of the POM block chain) = 319 and n (number of carbon atoms) = 38 in the PE block chain. This is a clear signature of microphase-separation. From the peak position $q^* = 0.238 \text{ nm}^{-1}$, the dominant domain spacing $d (= 2\pi/q^*) = 26.4 \text{ nm}$ was evaluated for the microphase-separated structure, although it is impossible to judge its morphology due to lack of higher-order lattice peaks. On the other hand, almost no discernible scattering intensities were observed for both 981116 and 990121, which were a diblock POM–PE with DP = 288 and $n = 18$ and a triblock PE–POM–PE with DP = 280 and each end PE chain bearing $n = 18$, respectively. Thus, no microphase separation is confirmed for these samples.

It is needless to say that the microphase separation observed for POM–PE(C38) results from strong segregation between the polar POM and non-polar PE chains. Since the chain length of the POM block is almost the same in these copolymers and much longer than the PE block chains, comparison between POM–PE(C38) and POM–PE(C18) enables us to discuss the effect of composition for a similar chain length of the entire molecule, and comparison between POM–PE(C38) and PE(C18)–POM–PE(C18) to discuss the effect of chain architecture, diblock versus triblock, at a similar composition. Generally, the micro-

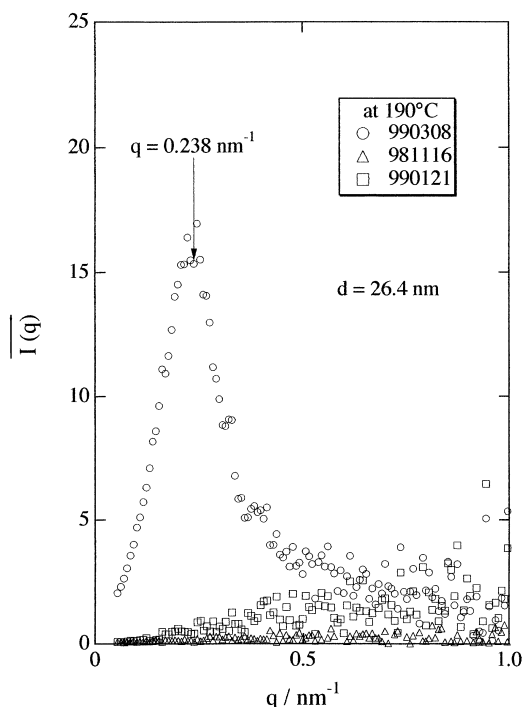


Fig. 3. Normalized SAXS profiles at 190°C, where the normalized scattering intensity, $\bar{I}(q)$, is plotted versus q . To obtain $\bar{I}(q)$, the scattering intensity, $I(q)$, is divided by that for sample-7000. (990308) POM–PE(C38), (981116) POM–PE(C18), (990121) PE(C18)–POM–PE(C18).

phase-separation transition can be discussed with the product χN_t , where χ denotes the Flory interaction parameter and N_t is the total degree of polymerization of the entire chain molecule [15,36,37]. When the value of χN_t exceeds a critical one, $(\chi N_t)_c$, the block copolymer undergoes a microphase separation transition. The critical value of $(\chi N_t)_c$ has strong dependence on the composition such that it drastically increases in the limit of zero composition. The fact that the microphase separation was confirmed for POM–PE(C38) while not for POM–PE(C18) clearly indicates that the composition of POM–PE(C18) locates in the vicinity of the phase boundary between the ordered and disordered states at 190°C. Here upper-critical solution temperature type temperature dependence of χ is assumed, namely χ is expected to decrease with an increase of temperature for POM/PE segmental interaction. As for the effect of chain architecture, the critical value of $(\chi N_t)_c$ is larger for the triblock type than for the diblock type at a same composition [36]. The fact that POM–PE(C38) undergoes microphase separation while PE(C18)–POM–PE(C18) does not again suggests that the composition for these samples locates in the vicinity of the critical condition in terms of the chain architecture. It is reasonable when considering the small fraction of PE moieties in POM–PE(C38), i.e. ~ 0.05 . Although the exact values of the χ parameter are not available, the strong segregation between the polar POM and non-polar PE chains can be confirmed in the present study because the microphase separation even

took place at 190°C in the POM–PE(C38) sample having a significantly low composition.

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