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MELTING BEHAVIOR OF POLY(OXYTETRAMETHYLENE)-*alt*-(AROMATIC OLIGOAMIDE) BLOCK COPOLYMERS

M. Tsuchiya[*], *A. Inomura and T. Kojima*

Department of Applied Chemistry, National Defense Academy 1-10-20 Hashirimizu, Yokosuka 239-8686, Japan

Using temperature-modulated differential scanning calorimetry, the melting behaviour of poly(oxytetramethylene)-*alt*-(aromatic oligoamide) (POTM-*alt*-AOA) has been studied in comparison with that of polyoxytetramethylene glycohols (POTMGs). The apparent melting temperature of the block copolymers is found to be less than that of the corresponding POTMGs by approximately 30°C. The relaxation time of melting of a POTM segment has been estimated and compared with that of POTMG. The relaxation time of POTM-*alt*-AOA is slightly shorter than that of POTMG when the molar mass of the POTM segment is 2900; however, it is longer when the molar mass is 1400.

Keywords: *block copolymer, melting behaviour, poly(oxytetramethylene), TM-DSC*

Introduction

Block copolymers and multiblock copolymers have been extensively studied for various applications [1–4]. They are composed of hard and soft segments; therefore, information on the interactions between the different segments is important for predicting new materials. Ukielski *et al.* have studied the influence of the chemical composition of an amide block on the thermal properties of multiblock terpolymers and confirmed the importance of compatibility between the different blocks [4]. A polyether block amide, commercially available as PEBAX®, has been studied in the last decade as a new family of engineering thermoplastic elastomers [2, 3]. In this family of block copolymers, poly(oxytetramethylene) (POTM) serves as the soft segment and poly(aliphatic amide) serves as the hard segment. We have studied the thermal properties of poly(oxytetramethylene)glycols (POTMGs) and chemically crosslinked polymer networks [5–9].

Aromatic polyamides have a rigid structure and poor compatibility with most simple homopolymers. Copolymers of segmented aramide with three aromatic rings in the hard segment and POTM have been studied by Niesten *et al.* [10–12]. It is expected that the size and symmetry of aromatic polyamides affect the melting of POTM in the block copolymer. It is also expected that the interaction between an aromatic amide segment and POTM will influence the relaxation time of melting for POTM crystals. We have studied the melting behaviours of poly(oxytetramethylene)-*alt*-(aromatic oligoamide) (POTM-*alt*-AOA) with five aromatic rings in the hard segment by temperature-modulated differential scanning calorimetry (TM-DSC) in order to determine the influence of AOA on the melting of POTM in the block copolymer.

Experimental

Materials

Polytetrahydrofurans with molar masses of 650, 1400, and 2900 were purchased from Sigma Aldrich Co. Poly(oxytetramethylene)-*alt*-[1,4-phenylenebis(iminoxo-1,3-phenyleneiminoxo- 1,4-phenyleneoxo)] (POTM-*alt*-AOA) was prepared from polytetrahydrofuran, terephthaloyl chloride, and *N*,*N*'-1,4-phenylenebis(1,3-aminobenzamide). The product was precipitated from water by pouring a N,N-dimethylacetamide (DMAc) solution of it, and dried under reduced pressure.

The products were identified by FTIR, ^{1}H-NMR, 2D ^{1}H-NMR, and elemental analysis. The degree of polymerization X was determined by ^{1}H-NMR: POTM(650)-*alt*-AOA, X=16; POTM(1400)-*alt*-AOA, X=51 and POTM(2900)-*alt*-AOA, X=34. The intrinsic viscosities (denoted by η) of POTM(650)-*alt*-AOA, POTM(1400)-*alt*-AOA, and POTM(2900)-*alt*-AOA in DMAc were 0.15, 0.20 and 0.21, respectively.

Method

DSC and TM-DSC were performed using a Perkin–Elmer DSC 7 equipped with a DDSC kit. Approximately 10 mg of the sample was placed in an aluminium pan

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[*] Author for correspondence: masahiro@nda.ac.jp

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Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

Table 1 DSC results for the POTM-*alt*-AOAs

Sample*	First heating curve				Second heating curve	
	$T_{m,obs}$/°C	ΔH_m/J g^{-1}	T_{exo}/°C	ΔH_{exo}/J g^{-1}	$T_{m,obs}$/°C	ΔH/J g^{-1}
650	–	–	138.9	– 73.2	–	–
1400	–13.8	3.2	131.3	–206.8	–10.4	9.6
2900	– 1.07	19.3	133.3	–307.5	2.02	20.3

*The numbers denote the molar mass of a POTM block in POTM-*alt*-AOA

and covered with an aluminium lid. All samples were preheated at 50°C (above the melting temperature of POTMGs) and subsequently cooled to –50°C at a cooling rate of 50 K min^{-1} in DSC. In the TM-DSC experiments, the temperature was controlled by sawtooth modulation without cooling. The average heating rate was 2.0 K min^{-1} and the amplitude of modulation was 0.2 K. By using our equipment, the modulation periods, which are a combination of the programming rate and the amplitude, were selected as 24, 48, 60, and 96 s. Baseline files for the modulations were obtained using an empty pan.

Data analysis

TM-DSC provides the complex heat capacity $C^*(\omega)$ at the modulation frequency ω [13–15].

$$C^*(\omega)=C'(\omega)-iC''(\omega) \tag{1}$$

The tangent of the phase angle δ, which is related to the relaxation time τ, is obtained by dividing $C''(\omega)$ by $C'(\omega)$.

$$\tan\delta=\omega\tau \tag{2}$$

The necessity of multicomponent analysis can be easily determined by plotting the tanδ values obtained from the TM-DSC experiments *vs.* the measured frequency ω.

When the observed relaxation phenomenon consists of multiple components, Eqs (1) and (2) are expressed as follows:

$$\begin{aligned} C'(\omega)&=\sum_i\frac{\alpha_i\tau_i}{(1+\omega^2\tau_i^2)}\Big/\sum\alpha_i\tau_i\,, \\ C''(\omega)&=\sum_i\frac{\alpha_i\omega\tau_i^2}{(1+\omega^2\tau_i^2)}\Big/\sum_i\alpha_i\tau_i \end{aligned} \tag{3}$$

$$\tan\delta=\frac{C''(\omega)}{C'(\omega)}=\sum_i\frac{\alpha_i\omega\tau_i^2}{(1+\omega^2\tau_i^2)}\Big/\sum_i\frac{\alpha_i\tau_i}{(1+\omega^2\tau_i^2)} \tag{4}$$

where, α_i is the fraction of component *i*.

If the number of components is assumed as 2, then

$$\tan\delta=\frac{\alpha_1\omega\tau_1^2(1+\omega^2\tau_2^2)+\alpha_2\omega\tau_2^2(1+\omega^2\tau_1^2)}{\alpha_1\tau_1(1+\omega^2\tau_2^2)+\alpha_2\tau_2(1+\omega^2\tau_1^2)} \tag{4a}$$

where, $\alpha_1+\alpha_2=1$. By performing 2-ingredient non-linear least-squares analysis based on Eq. (4a), the relaxation times τ_1 and τ_2 and their respective fractions α_1 and α_2 are estimated from the tanδ values determined by TM-DSC.

Results and discussion

DSC curves of block copolymers

DSC curves of POTM-*alt*-AOAs are shown in Fig. 1, and the DSC results are summarized in Table 1. An endothermic peak, which can be attributed to the melting of the POTM crystal, is observed in the DSC curves of POTM(1400)-*alt*-AOA and POTM(2900)-*alt*-AOA; however, it is not observed in the DSC curve of POTM(650)-*alt*-AOA. The apparent melting temperature of POTM-*alt*-AOAs is less than that of the corresponding POTMG by approximately 30°C, and less than that of the segmented aramide studied by Niesten *et al.* by 10°C [10–12]. An exothermic peak is observed around 130°C in the DSC curve of the block copolymers during the first heating run. This peak is not observed in the real and imaginary C_p curves (Fig. 2). The amount of exothermic heat ΔH_{exo}

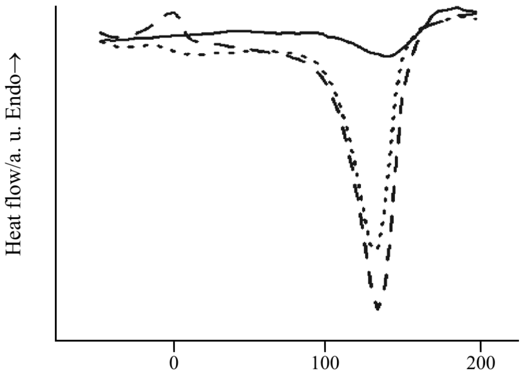

Fig. 1 DSC curves of POTM-*alt*-AOAs: – – POTM(650)-*alt*-AOA; ——POTM(1400)-*alt*-AOA; · ·· –POTM(2900)-*alt*-AOA. The heating rate was 5.0 K min^{-1}

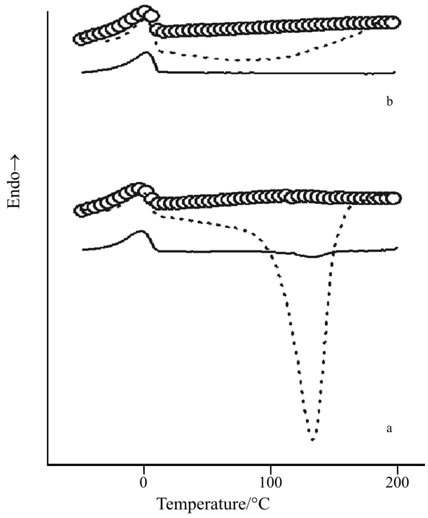

Fig. 2 TM-DSC curves of POTM(1400)-*alt*-AOA: a – the first heating run; b – second heating run. The curves represent total ······–C_p, O–C' and —–C''. The average heating rate was 2.0 K min^{-1} and the amplitude of modulation was 0.2 K. The modulation period was 60 s

apparently increases with the molar mass of POTM in the block copolymer. After annealing at 180°C, which is lower than the expected melting temperature of the AOA crystal and higher than the exothermic peak temperature, the curve of POTM-*alt*-AOAs changes; the melting peak temperature increases by approximately 4°C and the exothermic peak at 130°C is suppressed. Moreover, in the case of POTM(1400)-*alt*-AOA, the heat of melting ΔH_{exo} increases threefold, while in the case of POTM(2900)-*alt*-AOA, it changes only slightly.

A remarkable exothermic peak is observed in the curve of POTM-*alt*-AOAs at 130°C; this suggests that the microphase separation is incomplete. Although POTMG thermally decomposes at 353 K [6], the above-mentioned exothermic peak is not observed in the DSC curves of POTMG and poly(oxytetramethylene)dimethacrylate-*net*-poly(methylmethacrylate). If this exothermic peak were to correspond to the pyrolysis of POTMs, the endothermic heat of melting would disappear or the exothermic peak would be visible until the complete decomposition of POTM. As in the case of other block copolymers, it is considered that POTM-*alt*-AOAs are physically crosslinked at the AOA segments. The smaller the mass of the hard segment in comparison with the mass of the soft segment, the greater the compatibility between them. Therefore, the degree of aggregation of the hard segment before annealing is expected to decrease with increasing molar masses of the POTM. The heat of the exothermic peak at 130°C probably corresponds to the amount of AOA free from the aggregate before the annealing. It is expected that a block chain of the copolymer behaves like a homopolymer in a well separated microphase. The increase in both the melting temperature and ΔH_{m} suggests the probability of an increase in the POTM crystallinity in the block copolymer.

As mentioned above, solid POTM-*alt*-AOA is considered to have a cross-linked structure. The motion of the polymer segments in a network polymer is affected by the flexibility of the cross-linking points. We have reported that the mesh size of a POTM network polymer affects the melting temperature of a POTM segment [5]. The symmetry of the chemical structure of the hard segment in this study is lower than that of the block copolymer studied by Niesten *et al.* [10–12]. Therefore, the low melting temperature of the POTM-*alt*-AOAs is probably due to the physically cross-linked structure and the tightness of the cross-linking domain.

Relaxation time of melting

In most cases in this study, data cannot be analyzed by Eq. (2). Figure 3 shows the phase angle spectra of POTMG2900 at different temperatures. The data at 40°C may be analysed by Eq. (2) to obtain τ=0.1 s. By assuming that this is the relaxation time for one of the ingredients, data at several temperatures are analysed by assuming a 2-ingredient system. The calculated curves approximately fit the experimental data. Figure 4 shows the phase angle spectra of POTM-*alt*-AOAs at the melting peak temperatures and the results of the 2-ingredient analysis. Table 2 summarizes the results of the 2-ingredient analysis of τ for the block copolymers and the corresponding POTMGs by the non-linear least-squares method. Fractions of the fast relaxation

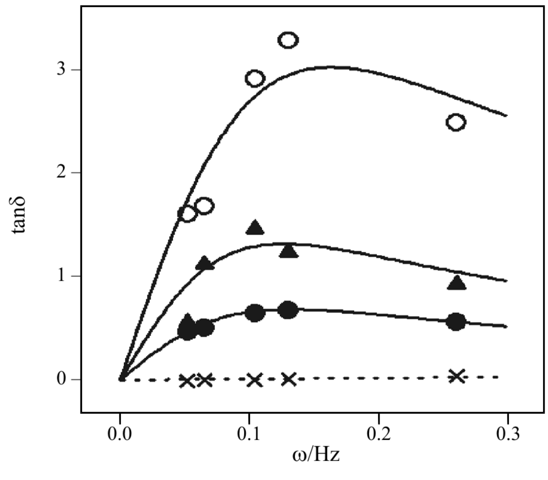

Fig. 3 Phase angle spectra of POTM2900 at different temperatures: ●–20; ○–25; ▲–28; ×– 40°C. Solid lines represent the results from 2-ingredient analysis using the non-linear least-squares method. Data at × 40°C fits a ······ straight line that passes through the origin with a gradient of 0.1 s

Table 2 2-ingredient analysis results of relaxation time τ at the endothermic peak temperature

Sample*	Thermal history	$T_{m,p}$/°C**	α_1	τ_1/s	α_2	τ_2/s
POTM(1400)-*alt*-AOA	50°C, 5 min	–12	0.002	15	0.998	0.12
	180°C, 5 min	–10	0.004	10	0.996	0.12
POTM(2900)-*alt*-AOA	50°C, 5 min	0	0.01	12	0.99	0.12
	180°C, 5 min	3	0.02	9	0.98	0.14
POTMG1400	50°C, 5 min	20	0.10	17	0.90	0.09
POTMG2900	50°C, 5 min	26	0.09	35	0.91	0.09

* The numbers represent the molar mass of POTM and POTMG, **Endothermic peak temperature

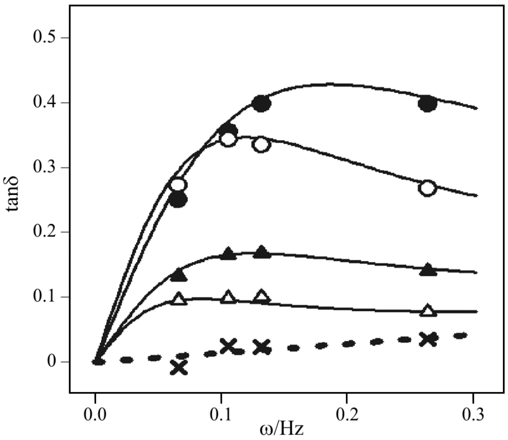

Fig. 4 Phase angle spectra of POTM-*alt*-AOAs at the endothermic peak temperature:
○–POTM(2900)-*alt*-AOA annealed at 50°C;
●–POTM(2900)-*alt*-AOA annealed at 180°C;
△–POTM(1400)-*alt*-AOA annealed at 50°C;
▲–POTM(1400)-*alt*-AOA annealed at 180°C. The plot denoted by (✕) is the data at 30°C of preheated POTM(2900)-*alt*-AOA at 180°C. Solid lines represent the results from the 2-ingredient analysis using the non-linear least-squares method. The dashed line passes through the origin with a gradient of 0.1 s

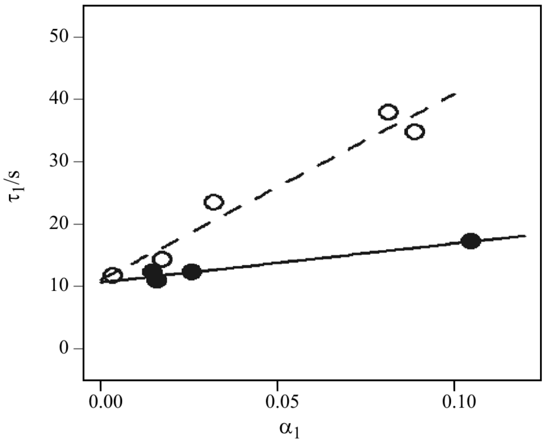

Fig. 5 Plots of relaxation time τ_1 *vs.*the fraction of the component α_1: ○–POTMG2900; ●–POTMG1400

process α_2 exceed 0.9 and their τ_2 values are almost identical. These results suggest that the fast components are independent of the material and can be attributed to the response of the measurement system.

In the case of POTMGs, it appears that the τ_1 obtained at a different temperature is not dependent on the temperature but on a fraction of the slow ingredient α_1 (Fig. 5). We estimated the relaxation time at $\alpha_1 \rightarrow 0(\tau_{1,0})$; the results are summarized in Table 3. The estimated $\tau_{1,0}$ values for POTMG1400 and 2900 are 11 s in both cases. In case of POTM-*alt*-AOAs, the dependency of τ_1 on α_1 is low. This is probably due to the small α_1 of these block copolymers. These results suggest that melting process of a POTM segment is independent of the other POTM segments in POTM-*alt*-AOAs.

Although the molar mass of POTMG does not appear to affect its $\tau_{1,0}$, the $\tau_{1,0}$ value of each block copolymer is different. The temperature dependence

Table 3 Estimated relaxation time $\tau_{1,0}$ at $\alpha_1 \rightarrow 0$

Sample*	Thermal history	$\tau_{1,0}$/s	Slope/10^3s	R^2
POTM(1400)-*alt*-AOA	50°C, 5 min	19	–3.30	0.958
	180°C, 5 min	14	–1.1	0.995
POTM(2900)-*alt*-AOA	50°C, 5 min	10	0.1	0.311
	180°C, 5 min	9	–0.02	0.878
POTMG1400	50°C, 5 min	11	0.06	0.976
POTMG2900	50°C, 5 min	11	0.30	0.975

* The numbers represent the formula mass of POTM and POTMG
The slope and R^2 (correlation coefficient) values are obtained by the linear least-squares method

of τ_1 reveals the different melting behaviours of these two copolymers. Based on the average value of X or the intrinsic viscosity, it is considered that the chain lengths of the two block copolymers in this study are almost comparable. Therefore, the τ_1 value probably reflects the relaxation process of a POTM crystal between AOA segments. The shorter the POTM segments, the larger the fraction of influence of the AOA segments on the motion of the POTM segments. The results of the annealing experiments on the τ_1 of the block copolymers support the hypothesis that the microphase separation had proceeded and the homogeneous POTM domain had increased in the block copolymer solid by annealing at a temperature above 130°C.

Conclusions

The chemical structure of aramide affects the melting temperature of the segmented aramide-POTM copolymer. The influence of the aramide blocks on the relaxation time for the melting of POTM is observed in case of POTM(1400)-*alt*-AOA. The relaxation time mainly depends on the amount of the crystal. The melting behaviour of POTM-*alt*-AOA depends on the molar mass of POTM; this can be explained by the compatibility between the segments of POTM and AOA. In the 2-ingredient analysis of the phase angle dependence on the modulation frequency, the melting relaxation time of POTM in a block copolymer can be isolated from the effects of other phenomena that can be attributed to the response of the measurement system.

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