

Segmental Motions and Associated Dynamic Mechanical Thermal Properties of a Series of Copolymers Based on Poly(hexamethylene terephthalate) and Poly(1,4-cyclohexylenedimethylene terephthalate)

Young Gyu Jeong and Sang Cheol Lee

School of Advanced Materials and Systems Engineering, Kumoh National Institute of Technology, Kumi 730-701, Korea

Won Ho Jo*

Hyperstructured Organic Materials Research Center and School of Materials Science and Engineering, Seoul National University, Seoul 151-742, Korea

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Abstract: The dynamic mechanical thermal properties of poly(hexamethylene terephthalate) (PHT), poly(1,4-cyclohexylenedimethylene terephthalate) (PCT) and their P(HT-co-CT) random copolymers in the amorphous state were examined as a function of temperature and frequency. All the samples exhibited two main relaxation processes in the plot of $\tan \delta$ versus temperature: the primary α -relaxation associated with the glass transition and the secondary β -relaxation attributed to the local segmental motions of mostly cyclohexylene rings for PCT and to cooperative motions of methylene, carboxyl, and phenylene groups for PHT. Both α - and β -relaxation temperatures increased with increasing CT content. The activation energy of the α -relaxation increased with increasing CT content, whereas that of the β -relaxation decreased. The sub-glassy secondary β -relaxation processes of PCT and PHT were investigated in terms of the cooperativity of main-chain segmental motions.

Keywords: dynamic mechanical thermal property, segmental motion, activation energy.

Introduction

The crystal structure, crystallization, melting, and mechanical properties of poly(hexamethylene terephthalate) (PHT) (Figure 1(A)), a member of semicrystalline poly(alkylene terephthalate)s, have been studied for its application to engineering plastics.¹⁻⁷ Poly(1,4-cyclohexylenedimethylene terephthalate) (PCT) (Figure 1(B)) has also attracted considerable attention from academia and industry because of its high potential to be used for fiber, film, and engineering plastic.⁸⁻¹⁵

Copolymerization is very often used for tailoring the macroscopic properties of polymers through variation of the copolymer composition. The copolymer properties may differ markedly from those of the corresponding homopolymers because of specific interactions between different monomers. We have recently prepared a series of copolymers based on PHT and PCT, and investigated their chain structure, thermal property, and cocrystallization behavior.¹⁶ The poly(hexamethylene terephthalate-co-1,4-cyclohexylenedimethylene terephthalate) [P(HT-co-CT)] copolymers synthesized were

identified to be statistically random copolymers. Nevertheless, they show clear melting and crystallization peaks in DSC thermograms and sharp diffraction peaks in X-ray dif-

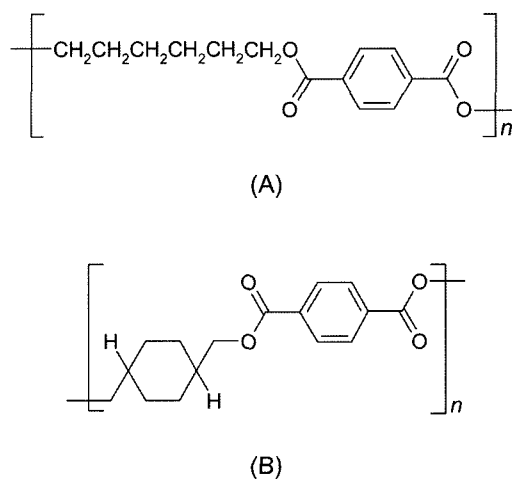


Figure 1. Chemical structures of (A) poly(hexamethylene terephthalate) (PHT) and (B) poly(1,4-cyclohexylenedimethylene terephthalate) (PCT).

*Corresponding Author. E-mail: whjpoly@plaza.snu.ac.kr.

fraction patterns over all the copolymer compositions. When the melting and crystallization temperatures of P(CT-co-HT)s as well as the *d*-spacings of all the X-ray reflections are plotted against the copolymer composition, there exists a eutectic composition, where the crystal transition from PCT-type to PHT-type occurs. These results strongly support the fact that P(HT-co-CT) copolymers exhibit isodimorphic cocrystallization. Thus, it is expected that the cocrystallization of P(HT-co-CT) copolymers provides a possibility to control thermal and mechanical properties as well as processibility through variation of the copolymer composition. In order to understand the processibility and end-use performance of P(HT-co-CT) copolymers, the time- and temperature-dependent viscoelastic property needs to be pursued specifically on the basis of molecular dynamics.

Dynamic mechanical properties of polymers have been measured as functions of temperature and frequency to establish the relationship between structure and mechanical property.¹⁷⁻²¹ Since analysis on the temperature and time dependence of the dynamic modulus and the loss tangent provides very useful information on segmental motion, transition, and structural or morphological characteristics (molecular orientation, the degree of crystallinity, cross-linking, copolymer configuration, miscibility of polymer blends, etc), a precise analysis of dynamic mechanical properties is of great scientific and practical importance in understating the viscoelastic property of polymers at the molecular level.

Several studies have reported on the segmental motions and associated dynamic viscoelastic properties of PCT.^{11,13,15,22} For an example, Yee *et al.* have reported that PCT exhibits an interesting ductile mechanical property, which arises from the cooperative secondary relaxation process due to the segmental motion of cyclohexylene ring undergoing the chair-to-chair conformational transition.^{15,22} On the other hand, there is only limited understanding about the segmental mobility of PHT.¹ Moreover, dynamic mechanical properties of P(HT-co-CT) copolymers associated with their molecular structures have not been reported yet. The primary objective of the present study is to understand the viscoelastic properties of P(HT-co-CT) copolymers in connection with the segmental mobility. For the purpose, we measure dynamic mechanical properties of a series of P(HT-co-CT) copolymers in the purely amorphous state as functions of temperature and frequency, and then interpret the properties in terms of the cooperativity of segmental motions.

Experimental

Materials. PHT, PCT, and P(HT-co-CT)s with different compositions were prepared by melt-condensation polymerization. The detailed synthesis and characterization of the samples were described well in our previous report.¹⁶ The structural information such as composition, the degree of

Table I. Composition, Number Average Sequence Lengths (L_{CT} and L_{HT}), Degree of Randomness (DR), and Inherent Viscosities (η_{inh}) of P(HT-co-CT) Copolymers

Sample Code	CT Unit (mol%)	L_{CT}	L_{HT}	DR	η_{inh} (dL/g)
PHT	0.0	0.00			0.72
P(HT-co-13 CT)	12.6	1.24	7.91	0.93	0.76
P(HT-co-30 CT)	30.2	1.46	3.35	0.98	0.79
P(HT-co-41 CT)	40.8	1.68	2.52	0.99	0.75
P(HT-co-57 CT)	56.5	2.17	1.91	0.99	0.70
P(HT-co-71 CT)	70.8	3.16	1.53	0.97	0.64
P(HT-co-84 CT)	83.8	5.73	1.30	0.95	0.65
P(HT-co-93 CT)	92.5	11.48	1.28	0.89	0.62
PCT	100.0		0.00		0.60

randomness, the number-average sequence lengths of CT and HT units, and the intrinsic viscosity are summarized in Table I. Here the degree of randomness (DR) of copolymers was evaluated from the number-average sequence lengths of CT and HT units (L_{CT} and L_{HT}) using the following equation

$$DR = 1/L_{CT} + 1/L_{HT} \quad (1)$$

The value of DR was used to describe the randomness of a P(HT-co-CT) copolymer as DR=1 for a random copolymer, DR=2 for an alternative copolymer, and DR=0 for a block copolymer or a homopolymer mixture. Since all the DR values in Table I are almost unity, it is identified that all the copolymers are statistically random copolymers.

Dynamic Mechanical Spectroscopy. Dynamic mechanical thermal measurements were performed with a dynamic mechanical analyzer (DMA 2980, TA Instruments, Inc.). The dynamic storage modulus (E'), dynamic loss modulus (E''), and loss tangent ($\tan \delta = E''/E'$) were recorded as a function of temperature at a given frequency. Five different frequencies of 0.32, 1.0, 3.2, 10.0, and 32.0 Hz were applied with the constant peak-to-peak strain of 0.1% in the tensile mode. Each specimen was run at the isothermal step of every 5 °C from -130 °C to the temperature above which the dynamic storage modulus of the sample was too low to be measured by the instrument.

For dynamic mechanical thermal measurements, the melt-quenched films with 0.2 mm in thickness were prepared by heating the samples to the temperature 30 °C higher than their respective melting temperature, holding for 3 min to melt crystals completely, and rapidly transferring into cooling water. The films were dried in a vacuum oven for several days at room temperature. All the melt-quenched films were optically transparent, indicating that the films are purely amorphous, which was also confirmed from X-ray diffraction data. The sample for dynamic mechanical thermal measure-

ment was cut into the dimension of $15.0 \times 5.0 \times 0.2 \text{ mm}^3$. Since the moisture in polymer alters the dynamic mechanical properties by lowering the transition temperature as well as by changing the transition peak shape,²³⁻²⁵ the melt-quenched amorphous films under investigation were desiccated before used for dynamic mechanical measurements to minimize the influence of water adsorbed in the sample.

Results and Discussion

Effect of Copolymer Composition on Dynamic Mechanical Properties. The dynamic storage modulus (E') and the loss tangent ($\tan \delta$) are plotted as a function of temperature in Figure 2, where the sample was measured at the frequency of 1.0 Hz. Before examining dynamic mechanical properties of each of the copolymers, it is informative to review the dynamic mechanical properties of PCT and PHT homopolymer. Changes in the dynamic storage modulus and loss tangent of PCT with temperature are quite different from those of PHT. The dynamic storage moduli of PCT and PHT decrease dramatically at the glass transition temperature. Here the glass transition temperature (T_g) is defined as the temperature corresponding to the peak temperature (T_α) of α -relaxation in the plot of the loss tangent versus temperature. The glass transition temperatures of PCT and PHT were ~ 91 and $\sim 36^\circ\text{C}$, respectively. Just above the glass transition temperature, PCT exhibits cold-crystallization, yielding a substantial increase in the dynamic storage modulus. The increased dynamic storage modulus is maintained up to the melting temperature. Similarly, the dynamic storage modulus of PHT in the glassy state decreases remarkably at the glass transition, but the reduced dynamic storage modulus remains unchanged up to the melting temperature of PHT, without showing cold-crystallization. Indeed, it was observed in DSC thermogram of PHT that an exothermic peak corresponding to cold-crystallization was hardly recognized with very small change in the heat capacity at the glass transition as compared with PCT.¹⁶ In the dynamic storage modulus (Figure 2(A)), the cold-crystallization of PHT is not discernible, and the intensity of α -relaxation of PHT corresponding to the glass transition is much smaller than that of PCT, as can be seen in Figure 2(B). This behavior has been found in other polymers with fast crystallization, which undergoes around the glass transition.²⁶

In the loss tangent versus temperature plots shown in Figure 2(B), both PCT and PHT exhibit the secondary β -relaxation below their respective glass transition temperature. It is known that the β -relaxation of PCT is closely related with segmental motions of cyclohexylene rings undergoing the chair-to-chair conformational transition.^{11,13,15,27} However, unlike other poly(alkylene terephthalate)s such as poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT),^{1,2,24,28-32} the dynamic mechanical properties of PHT associated with segmental motions have not been investigated

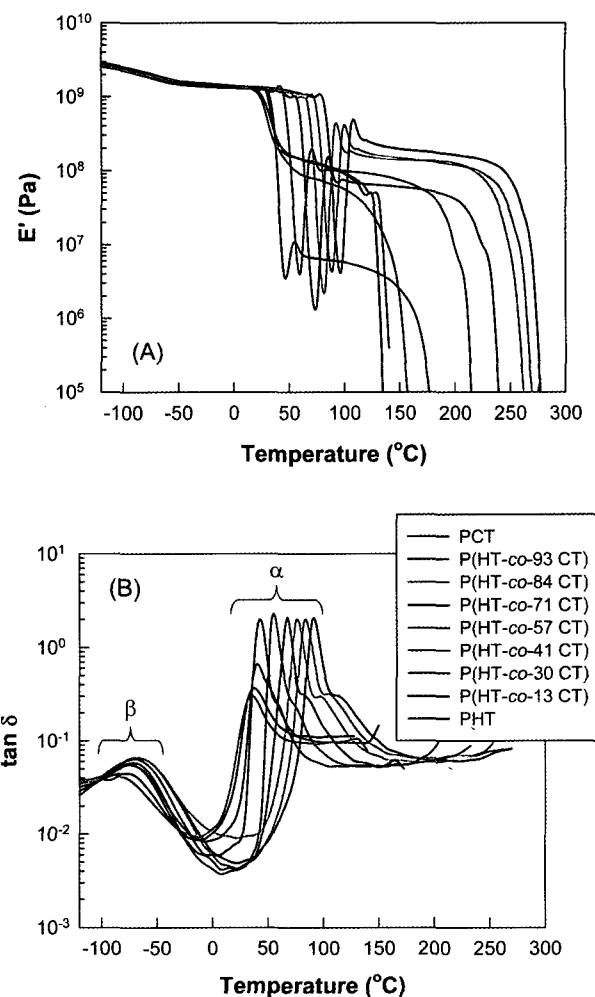


Figure 2. (A) The dynamic storage modulus E' and (B) the loss tangent $\tan \delta$ as a function of temperature at the frequency of 1 Hz for PHT, PCT, and their random copolymers.

extensively.¹ It was reported that the dynamic mechanical spectra of poly(alkylene terephthalate)s have the same pattern exhibiting two main α - and β -relaxation processes, except for the fact that both relaxation peaks shift to lower temperature with increasing the number of methylene groups in poly(alkylene terephthalate)s.¹ The α - and β -relaxation processes of poly(alkylene terephthalate)s are ascribed to the glass transition and the sub-glass segmental motions, respectively. It was found that the secondary β -relaxation peak of poly(alkylene terephthalate)s is asymmetric and might be composed of two relaxation processes due to the segmental motions of carboxyl and methylene units.^{1,28} Recent dynamic mechanical and dielectric analysis has suggested that the secondary β -relaxation of PET consists of two different relaxation processes, showing that the high temperature side of the peak is due to phenylene ring flips and the low temperature side is due to the motion of carboxyl groups.³²

Solid-state NMR relaxation spectra of PBT have also revealed that large amplitude segmental motions of phenylene rings as well as methylene units undergo at the temperatures below the glass transition temperature.³¹ As can be seen in Figure 2(B), the β -relaxation peak of PHT is highly asymmetric, indicating that the low temperature side (around -100 °C) of the secondary β -relaxation of PHT arises from the segmental motions of methylene and carboxyl units, and the high temperature side (around -83 °C) stems from the motions of phenylene units. In short, the symmetric β -relaxation process of PCT is originated from segmental motions of mostly cyclohexylene units, whereas the asymmetric β -relaxation of PHT arises from cooperative motions of methylene, carboxylic, and phenylene units.

For a series of P(HT-co-CT) copolymers, the dynamic storage modulus is almost equal at the glassy state, drops at the glass transition followed by a steep increase due to cold-crystallization, showing a sharp minimum, and then remains unchanged up to the melting transition, as can be seen in Figure 2(A). Here, it is worthy to note that the dynamic storage modulus after cold-crystallization is dependent on the copolymer composition, i.e., the modulus decreases and then increases with increasing the CT monomer content, showing the existence of a eutectic composition. As mentioned in the introduction section, P(HT-co-CT) random copolymers exhibits isodimorphic cocrystallization,¹⁶ in which the degree of crystallinity decreases with increasing the comonomer content in the copolymers.³³ Therefore, it is reasonable to conclude that the dynamic storage modulus after cold-crystallization is roughly proportional to the degree of crystallinity developed by cocrystallization. The plot of the loss tangent versus temperature shows that all the copolymers have two dominant α - and β -relaxation processes, as shown in Figure 2(B). When the peak temperatures of the α - and β -relaxations (T_α and T_β) are plotted against the CT content, both T_α and T_β increase with increasing the CT content in copolymers, as can be seen in Figure 3. When the T_α corresponding to the glass transition temperature (T_g) of P(HT-co-CT) copolymers is plotted against the CT content, the experimental T_g 's are in good agreement with the values predicted by the Fox equation (the solid line),³⁴ as shown in Figure 3. It is noted here that the T_g values from dynamic mechanical thermal measurements in this study are very consistent with the ones obtained from DSC measurements within experimental error.¹⁶

Frequency Dependence of Dynamic Mechanical Properties. Dynamic mechanical measurements were carried out as the frequency is varied from 0.32 to 32.0 Hz. When the dynamic storage modulus and the loss tangent of PCT and PHT are measured at different frequencies, it is observed that the peaks of α - and β -relaxations for all the samples shift to higher temperatures with increasing the frequency applied, as shown in Figures 4 and 5. This is because the samples have less time to relax against the applied strain or

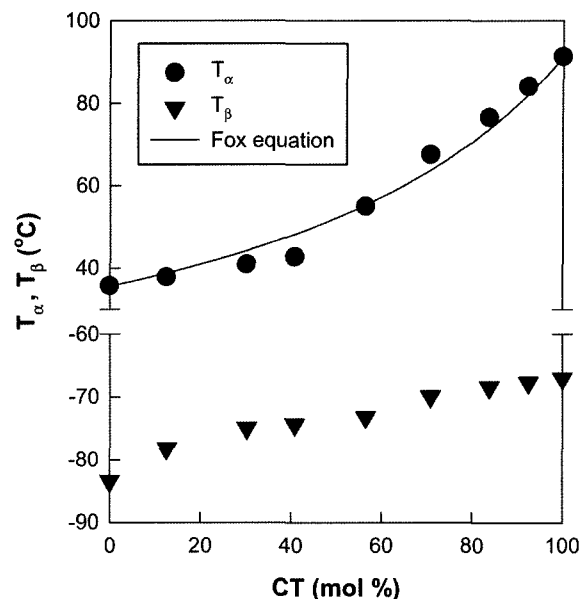


Figure 3. Peak temperatures, T_α and T_β , of the α - and β -relaxations as a function of copolymer composition. The solid line indicates the glass transition temperatures predicted by the Fox equation.

stress with higher frequency.

The frequency dependency of the α - and β -relaxations, which are thermally activated processes, is analyzed by the Arrhenius equation:

$$f = f_0 \exp\left[-\frac{E_a}{RT}\right] \quad (2)$$

where f is the frequency applied, f_0 the pre-exponential factor, E_a the activation energy, R the gas constant, and T the temperature. For both α - and β -relaxation processes, the logarithm of frequency applied is in good linear relationship with the reciprocal of relaxation peak temperature, as shown in Figure 6. Therefore, the activation energies, $E_{a,\alpha}$ and $E_{a,\beta}$, of the α - and β -relaxation processes are calculated from the linear slopes and summarized in Table II. It is interesting to note that the activation energy of α -relaxation increases with increasing the CT content in the copolymer, whereas that of β -relaxation decreases. It should be mentioned that the activation energy and peak temperature (14.2 kcal/mol and -67 °C) of β -relaxation of PCT at 1 Hz in this study are quite consistent with the values reported by others within experimental error,^{13,15} indicating that the dynamic mechanical data obtained in this study are reliable.

It is generally known that the primary α -relaxation process corresponding to the glass transition originates from the cooperative molecular motions rearranging some tens to hundreds of repeating units,^{35,36} whereas the secondary β -relaxation in the glassy state stems from the segmental

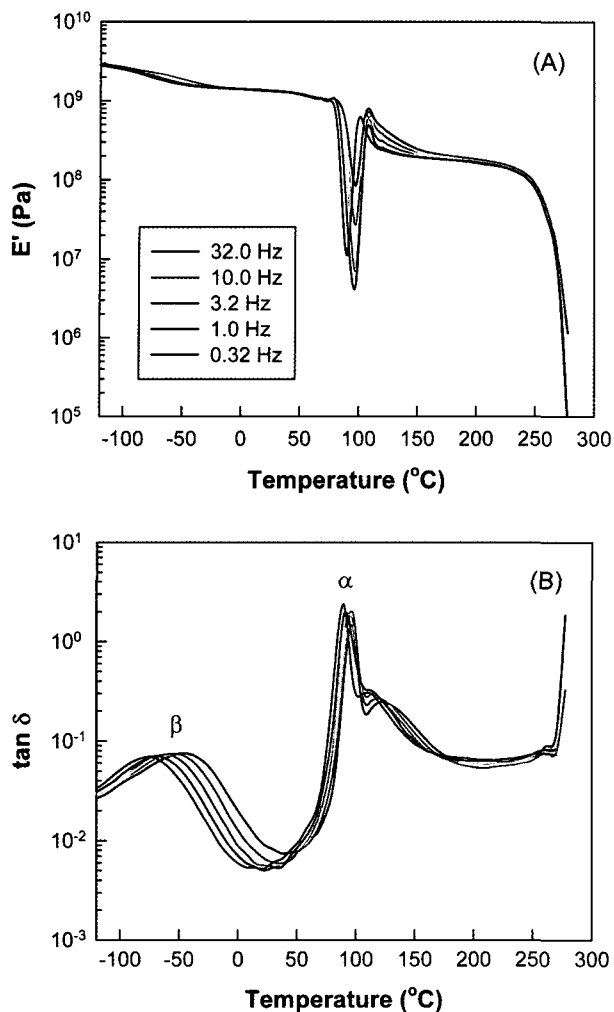


Figure 4. (A) The dynamic storage modulus E' and (B) the loss tangent $\tan \delta$ as a function of temperature measured at the various frequencies for PCT.

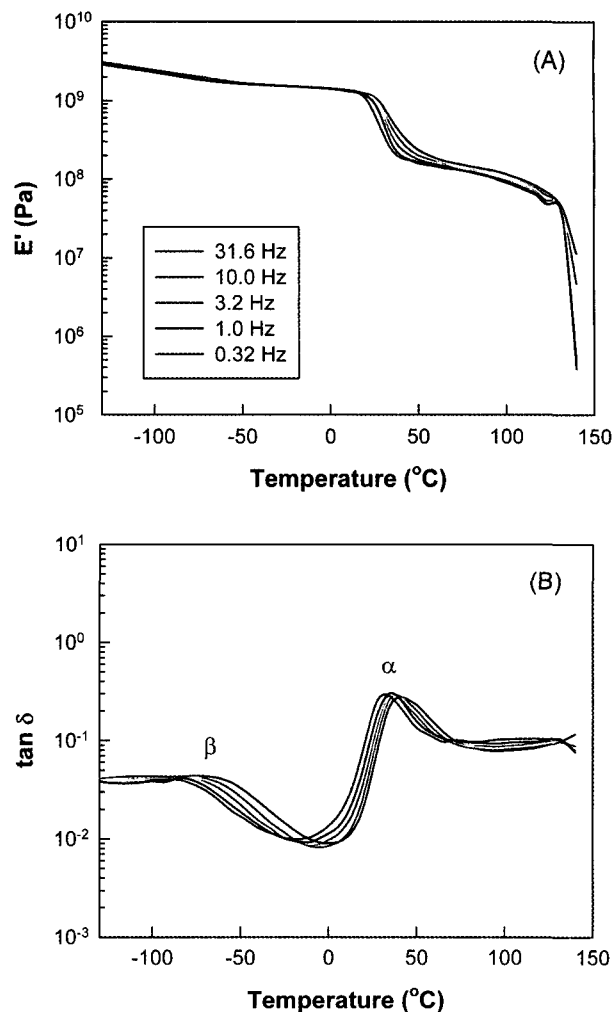


Figure 5. (A) The dynamic storage modulus E' and (B) the loss tangent $\tan \delta$ as a function of temperature measured at the various frequencies for PHT.

motions of shorter range than those of the α -relaxation.^{17,37} This concept is confirmed by the above results that the activation energy of α -relaxation for all the samples under investigation is much higher than that of β -relaxation, as can be seen in Table II. It has been recognized that the macroscopic mechanical properties are strongly correlated with the secondary sub-glass relaxation behavior.^{15,22,26,38} It was known that the large-scaled main-chain cooperative motion of the secondary β -relaxation is beneficial for shear yielding or ductile deformation. Considering that P(HT-co-CT) copolymers are used mostly below their glass transition temperatures, it is important to understand the secondary relaxation process in connection with the cooperative segmental motions.

An alternative equation, derived from the Eyring's theory of absolute reaction rate, also expresses the relationship between frequency and temperature:³⁹

$$f = \frac{RT}{2\pi h} \exp\left[\frac{\Delta S}{R}\right] \exp\left[-\frac{\Delta H}{RT}\right] \quad (3)$$

where h , ΔS , and ΔH are the Plank constant, the activation entropy, and the activation enthalpy, respectively. By combining the general thermodynamic relation of $E_a = \Delta H + RT$ with eq. (3), the activation energy in eq. (2) can be expressed as

$$E_a = RT[1 + \ln(RT/2\pi hf)] + T\Delta S \quad (4)$$

For a relaxation with zero activation entropy ($\Delta S=0$), corresponding to the lower limit of the activation energy of viscoelastic relaxations, eq. (4) with $\Delta S=0$ can be simplified as

$$E_a = RT[22.92 + \ln(T/f)] \quad (5)$$

Starkweather has suggested that this lower limit of activation

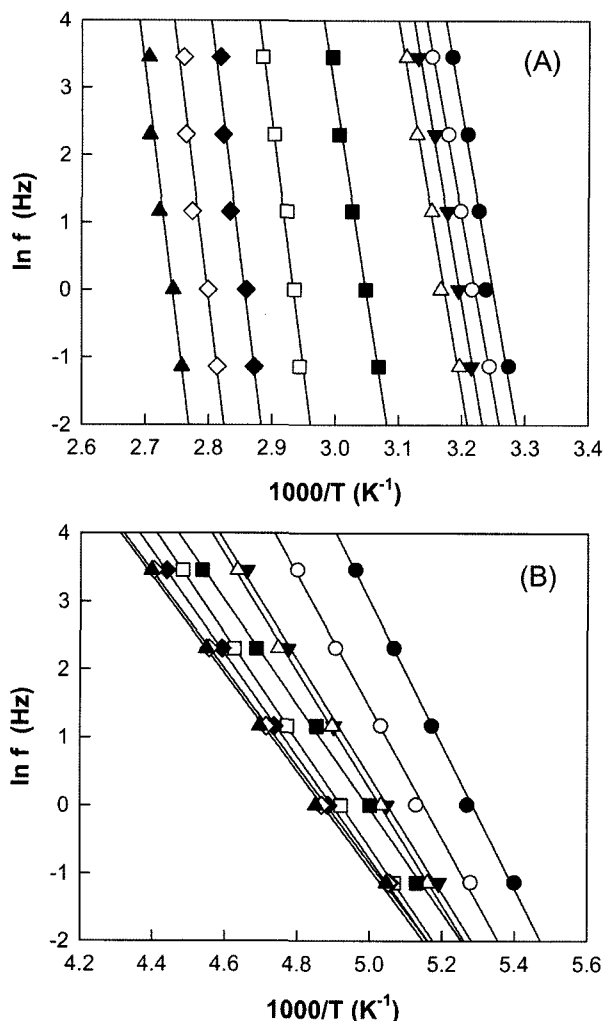


Figure 6. Frequency dependence of the (A) α - and (B) β -relaxations on the inverse of relaxation peak temperature for PHT (●), P(HT-co-13 CT) (○), P(HT-co-30 CT) (▼), P(HT-co-41 CT) (△), P(HT-co-57 CT) (■), P(HT-co-71 CT) (□), P(HT-co-84 CT) (◆), P(HT-co-93 CT) (◇), and PCT (▲).

Table II. Activation Energies, $E_{a,\alpha}$ and $E_{a,\beta}$ of α - and β -Relaxation Processes for PHT, PCT, and Their Copolymers

Sample Code	$E_{a,\alpha}$ (kcal/mol)	$E_{a,\beta}$ (kcal/mol)
PHT	106.2	19.4
P(HT-co-13 CT)	102.8	18.3
P(HT-co-30 CT)	109.6	17.0
P(HT-co-41 CT)	108.6	17.0
P(HT-co-57 CT)	119.3	15.2
P(HT-co-71 CT)	146.3	15.6
P(HT-co-84 CT)	149.9	14.9
P(HT-co-93 CT)	150.9	14.2
PCT	152.4	14.2

energy corresponds to the relaxation process characterized by local and non-cooperative motions.³⁹⁻⁴¹ In such a non-cooperative relaxation process, the molecular motions are of short range without considerable interaction between the relaxing molecule and the neighboring ones (simple relaxations). On the other hand, the activation energy far above the zero activation entropy condition is attributed to the relaxation process with cooperative motions (complex relaxations). Therefore, the zero activation entropy criterion of eq. (5) can be used as a comparative method for estimating the extent of cooperativity for different relaxation.

The activation energies of the secondary β -relaxation for the samples are plotted against the relaxation peak temperature measured at 1 Hz in Figure 7, where the solid line represents the lower limit of activation energy, i.e., the zero activation entropy ($\Delta S=0$) at 1 Hz as calculated from eq. (5). It is realized from Figure 7 that the β -relaxation processes of P(HT-co-CT) copolymers are all cooperative, although the extent of cooperativity of segmental motions may not be evaluated quantitatively from Figure 7. It has been generally known that the higher activation energy is required, the more segments move cooperatively.¹⁵ As noted above, with increasing the CT content in copolymers, the activation energy of the β -relaxation decreases from 19.4 to 14.2 kcal/mol. This indicates that the extent of cooperativity of the segmental motions in the β -relaxation process of PHT is higher than that of PCT. In other words, PHT exhibits more cooperative segmental motions in the glassy state as compared with

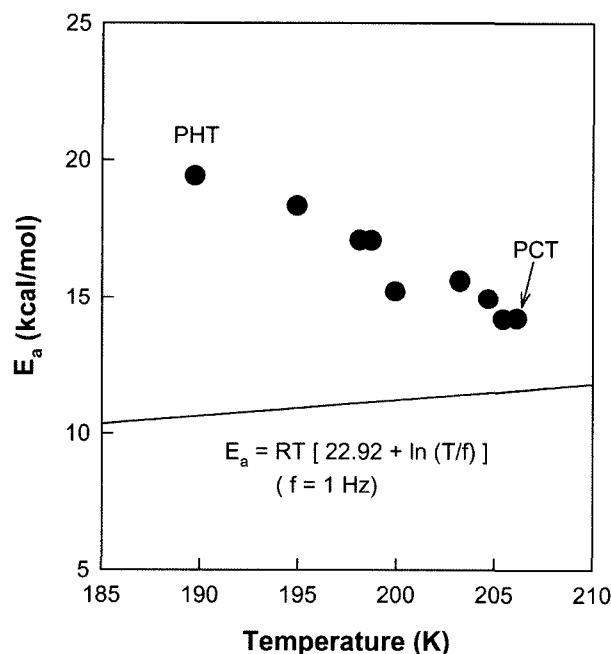


Figure 7. The activation energy of β -relaxation as a function of relaxation peak temperature at 1 Hz for PHT, PCT, and their copolymers. The solid line represents the zero activation entropy criterion calculated from eq. (5).

PCT. This is evidenced by the fact that the segmental motions at the β -relaxation process of PHT are related with combined motions of hexamethylene, carboxyl, and phenylene units, whereas the motions of PCT are associated with mostly cyclohexylene rings of PCT. As reported previously, only the secondary relaxations associated with the cooperative main-chain motions contribute to an increase in ductility and impact strength, whereas the secondary relaxations due to side chains do not contribute significantly.^{15,22,26,38} Although the β -relaxations of both PHT and PCT arise from the cooperative motions of segments in the main-chains, it is expected from comparison of the activation energies of β -relaxation that P(HT-co-CT) copolymer with higher content of HT has more ductile mechanical properties at the service temperature even below the glass transition temperature.

Conclusions

In an attempt to elucidate the relationship between the microstructure of P(HT-co-CT) and its segmental motion, the transition temperature, and modulus, dynamic mechanical thermal properties of P(HT-co-CT) random copolymers with various compositions were measured as a function of temperature and frequency. The dynamic storage modulus of the copolymers drops at the glass transition followed by a steep increase due to cold-crystallization showing a minimum peak, and then maintains a constant value up to the melting temperature. All the samples exhibit two dominant relaxation processes in the plot of $\tan \delta$ versus temperature: the primary α - and the secondary β -relaxations. The α -relaxation is attributed to the glass transition, whereas the sub-glass β -relaxation is associated with segmental motions of cyclohexylene groups for PCT and with combined motions of methylene, carboxyl, and phenylene groups for PHT. It was observed that the α - and β -relaxation processes were noticeably affected by the copolymer composition and frequency. Peaks of both relaxations shift to higher temperatures with increasing the CT content in the copolymer. It was also observed that the activation energy of the α -relaxation increases with increasing the CT content, while that of the β -relaxation decreases. It was found that although the β -relaxation processes of P(HT-co-CT) copolymers are all cooperative regardless of copolymer composition, the extent of cooperativity increases with increasing the HT content in the copolymer. This is because the segmental motions of PHT are related with combined motions of methylene, carboxylic, and phenylene units whereas the segmental motions of PCT are associated with mostly cyclohexylene rings.

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