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## Studies On Uniaxial Tensile Behaviour Of Poly(Ester-Ester) Thermoplastic Elastomers



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### ABSTRACT

Tensile properties of poly(ester ester) elastomers with different content of hard segments were investigated. The tensile tests were performed in the temperature range of 313 to 453 K. The elastomers having a higher content of the hard segments show a higher Young's modulus because the hard segments are crystallized to form a hard domain which acts as crosslinks. The number density of the crystalline domains decreased with increasing temperature. There is no marked difference in the activation energy to form the crystalline domains between samples with different contents of hard segments. © 2007 Trade Science Inc.

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### KEYWORDS

Poly(ether ether)  
thermoplastic elastomer;  
Uniaxial tensile properties;  
Elastic modulus;  
Yield behaviour;  
Plastic flow

### INTRODUCTION

Most thermoplastic elastomers (TPEs) have been produced as multi-block copolymers consisting of repeated hard and soft segments. Hard segments of the TPEs form crystalline domains with a melting temperature higher than room temperature while the soft segments are amorphous. The TPEs are expected to behave as rubbers at room temperature. The crystalline domains act as cross-links and restrict the mobility of the soft segments. At a higher temperature than the melting temperature of the hard seg-

ment domains, the hard segment domains cannot act as cross-links, and thus in that temperature range the TPEs behave as viscous liquids.

Poly(ether ester) elastomers consisting of aromatic ester units as hard segments and aliphatic polyether glycol units as soft segments have attracted much attention in industry because of their high thermal stability and high tensile toughness<sup>[1,2]</sup>. There are many studies on structures<sup>[3-6]</sup> and mechanical properties<sup>[7-9]</sup> of the poly(ether ester) elastomers that aim to reveal the origin of the high mechanical performance of the elastomers.

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In this work, we investigated the tensile properties of TPEs consisting of aromatic and aliphatic polyesters [poly(ester ester) elastomers] which have recently been developed to improve thermal stability. The temperature and strain-rate dependence of tensile properties of the novel poly(ester ester) elastomers was investigated.

### EXPERIMENTAL

#### Materials

Two kinds of poly(ester ester) elastomers (PELPRENE S-1002 and S-2002) were provided from Toyobo Co., Ltd., Japan. The hard and soft segments of the PELPRENE consist of poly(butane-1,4-diyl terephthalate) (PBT) and poly(6-hydroxyhexanoic acid) (PCL), respectively. The number average and weight average molar masses ( $M_n$  and  $M_w$ , respectively) are 63.4 kg/mole and 131.4 kg/mole for S-1002, and  $M_n = 60.3$  kg/mole and  $M_w = 123.0$  kg/mole for S-2002. The average sequence length of PCL units is about 12 units for both samples, while that of PBT units is different; 9.1 units for S-1002 and 15.2 units for S-2002. The pellets of the elastomers were press-molded at 493 K for S-1002 and at 533 K for S-2002 for 5 minutes to obtain sheet samples.

#### Measurements

Plots of tensile engineering stress ( $\sigma_E$ ) against elongational ratio ( $\lambda$ ) of S-1002 and S-2002 were measured with a Tensilon AGS-1kNG (Shimadzu Co., Japan) at two initial strain rates ( $\dot{\epsilon}_0$ ;  $\dot{\epsilon} = v/l_0$ , where  $v$  is the cross-head speed and  $l_0$  is the initial length)  $2.8 \times 10^{-3} \text{ s}^{-1}$  and  $2.8 \times 10^{-2} \text{ s}^{-1}$ . The elongational ratio was calculated by  $l/l_0$ , with  $l$  being the length. The stress  $\sigma_E$  was evaluated from the load divided by the initial cross-sectional area. The width and thickness of the samples were 5.0 mm and 0.80 mm, respectively. The initial length between clumps was ca. 30 mm. The tensile tests were performed in the temperature range of 313 to 453 K.

### RESULTS AND DISCUSSION

#### Stress-strain curves obtained from experiments

Figure 1 shows the  $\sigma_E$ - $\lambda$  curves of S-1002 measured

**Figure 1: The elongational ratio ( $\lambda$ ) dependence of engineering stress ( $\sigma_E$ ) for S-1002 at  $\dot{\epsilon}_0 = 2.8 \times 10^{-3} \text{ s}^{-1}$ . The symbols stand for the experimental temperature as  $\diamond$ : 453 K,  $\square$ : 433 K,  $\Delta$ : 413 K,  $\times$ : 393 K,  $*$ : 353 K,  $\circ$ : 313K**

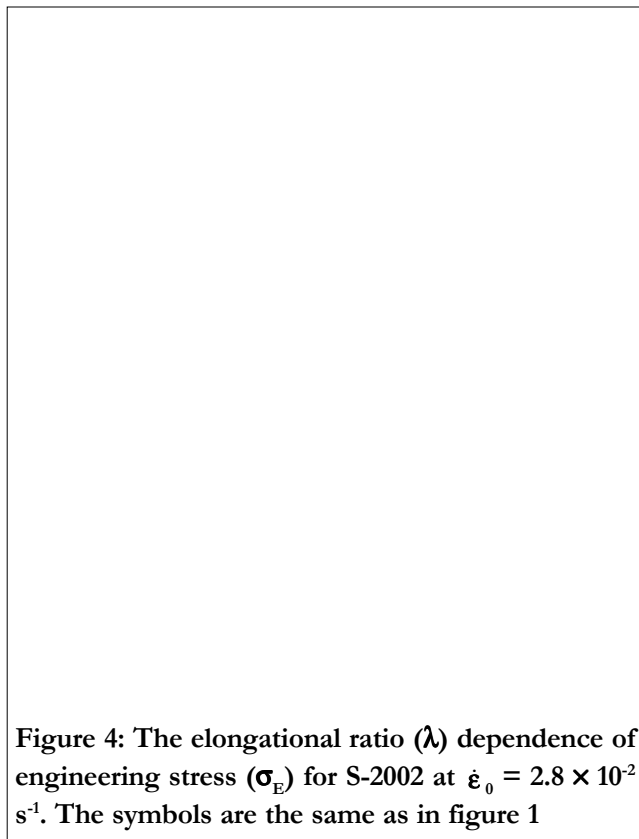
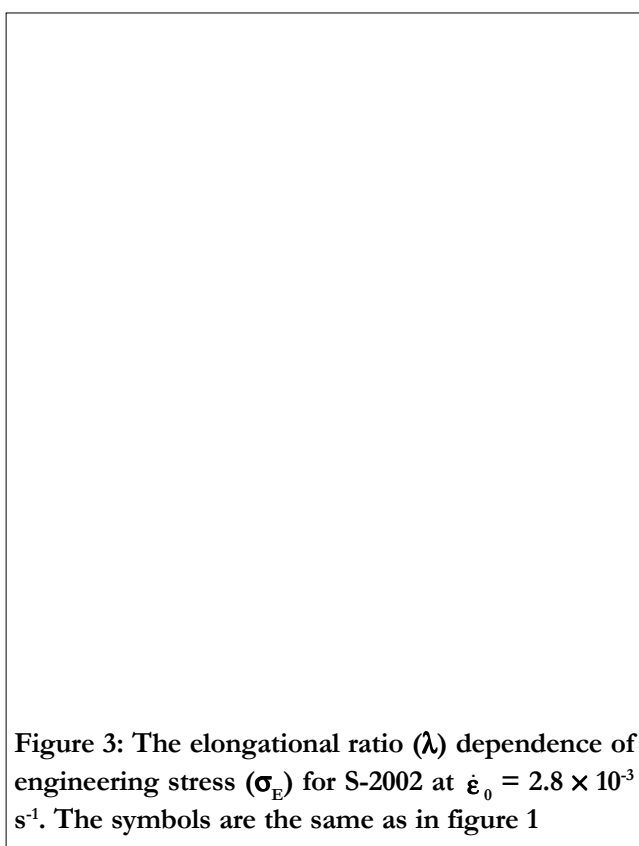
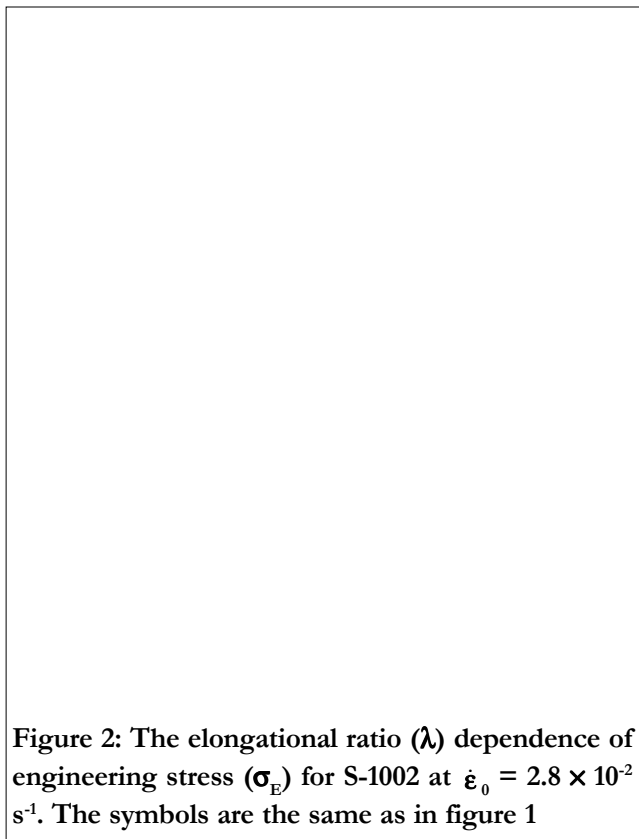
at  $\dot{\epsilon}_0 = 2.8 \times 10^{-3} \text{ s}^{-1}$ . At small strains, the  $\sigma_E$  values increase linearly with  $\lambda$ . The stress  $\sigma_E$  at large strains also increases with increasing  $\lambda$  but the slope of the curves is much smaller than that of the curves at small strains. The overall stress level increases with decreasing temperature ( $T$ ). An inflection point appears at about  $\lambda = 1.1$  on the  $\sigma_E$ - $\lambda$  curve at  $T = 393$  K while yielding behavior becomes complicated for the curves at  $T > 393$  K.

Figure 2 shows the  $\sigma_E$ - $\lambda$  curves of S-1002 at  $\dot{\epsilon}_0 = 2.8 \times 10^{-2} \text{ s}^{-1}$ . The shape of the curves is almost similar to that of the curves at  $\dot{\epsilon}_0 = 2.8 \times 10^{-3} \text{ s}^{-1}$  (Figure 1). The overall stress level is also lowered as  $T$  is elevated.

As shown in figures 3 and 4, the stress-elongation curves measured at different elongation rate are almost similar at the same  $T$ . The  $\sigma_E$ - $\lambda$  curves of S-2002 at  $\lambda < 5$  are almost similar in shape to those of S-1002, but the large enhancement of  $\sigma_E$  in the  $\sigma_E$ - $\lambda$  curves of S-2002 is observed at  $\lambda > 5$ .

#### Mechanical properties at small strains

The Young's modulus ( $E_y$ ) of S-1002 decreases



at the same  $T$  shows that the values of  $E_0$  measured at a higher strain rate are slightly larger than those at a lower strain rate. The  $E_0$  of S-2002 is almost twice as high as that of S-1002 at the same  $T$ . The hard segments aggregate to form the crystalline domains because the melting temperature ( $T_m$ ) of the elastomers used in this study is reported to be 473 K for S-1002 and 479 K for S-2002, according to the data sheets prepared by the manufacturer. The crystalline domains must be harder than the amorphous matrix consisting of the soft segments; hence,  $E_0$  is expected to increase by a filler reinforcement effect. The increase of  $E_0$  is assumed to be described by the following equation<sup>[10]</sup>

$$E_0 = E_{00}(1 + 2.5\phi + 14.1\phi^2) \quad (1)$$

Here,  $E_{00}$  is the modulus without filler particles (crystalline domains),  $\phi$  being the volume fraction of the domains. The  $E_0$  can be determined by the two factors: one is the contribution from the increase of the number density of the elastically effective chain (namely,  $E_{00}$ ) and the other is the contribution originating from the mixing the fillers with the higher modulus than matrix. The values of  $\phi$  are necessary to discuss the details of the latter contribution, but

with increasing  $T$  (see TABLE 1). The comparison

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**TABLE 1: Initial Young's modulus ( $E$ ), Elongational ratio at yield ( $\lambda_Y$ ) and Yield Stress ( $\sigma_Y$ ) for the sample at initial strain rate ( $\dot{\epsilon}_0$ ) at various temperatures ( $T$ )**

Sample	$10^3 \dot{\epsilon}_0 / \text{s}$	$T / \text{K}$	$E / \text{MPa}$	$\lambda_Y$	$\sigma_Y / \text{MPa}$		
S-1002	2.8	313	88	1.1	8.3		
		353	61	1.1	5.0		
		393	41	1.1	3.8		
		413	36	1.1	3.3		
		433	25	1.1	1.9		
		453	12	1.1	1.0		
		313	86	1.1	9.1		
	28	353	65	1.2	6.5		
		393	39	1.1	4.1		
		413	33	1.1	3.3		
		433	24	1.2	2.6		
		453	11	1.1	1.1		
		S-2002	2.8	313	160	1.1	11
				353	120	1.1	8.7
393	83			1.1	6.3		
413	61			1.1	4.7		
433	52			1.1	3.6		
28	453		38	1.1	2.5		
	313		130	1.1	11		
	353		110	1.1	8.8		
	393		76	1.1	6.6		
	413		66	1.1	5.3		
433	50	1.1	3.9				
453	38	1.1	2.6				

the content of the hard segments is unknown at present. It has been reported for poly(ether ester) elastomers containing PBT units that  $T_m$  decreases as the content of hard segments decreases<sup>[2]</sup>. If this is also applicable to our systems, a little difference in  $T_m$  between S-1002 and S-2002 suggests that only a little difference exists in the content of the hard segments, or equivalently, only a little difference in the contribution originating purely from the reinforcement effect exists for S-1002 and S-2002. This indicates that the large difference in  $E_0$  must be attributed to the difference in  $E_{00}$  rather than in the reinforcement effect.

According to the classical theory of rubber elasticity<sup>[11]</sup>, the modulus  $E_0$  of incompressible materials is related to the number density of cross-links ( $\nu$ ) and  $T$  in K as

$$E_0 = 3\nu RT, \quad (2)$$

where  $R$  is the gas constant. Assuming that  $\nu$  is the number density of crystalline domains, this equation leads to the conclusion that the values of  $\nu$  of S-2002 becomes almost twice as high as those of S-1002 at the same  $T$  because the ratio of  $E_0$  of S-2002 to that of S-1002 at the same  $T$  lies around 2, as stated previously. The hard domains melt at  $T_m$ ; namely,  $\nu$  vanishes at  $T = T_m$ . The quantity,  $\nu$ , is a decreasing function of  $T$ . These imply that  $\nu$  can be written by a following form.

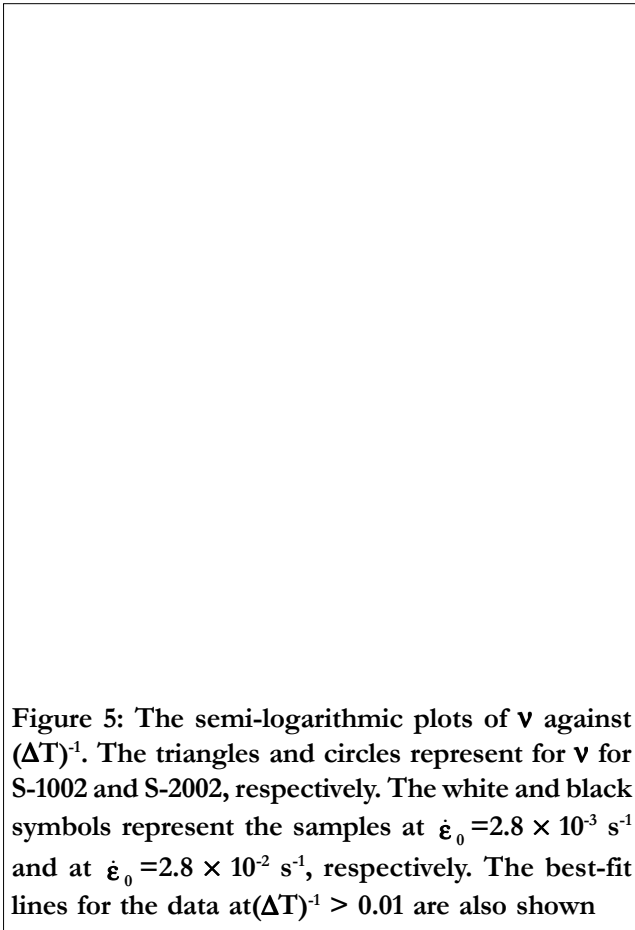
$$\nu = \nu_0 \exp(-\Delta E_m / R\Delta T) \quad (3)$$

where  $\Delta T = T_m - T$  and  $\Delta E_m$  might be a kind of activation energy,  $\nu_0$  being  $\nu$  at  $\Delta T \rightarrow \infty$ . Although in an actual case, the value of  $n$  must level off with decreasing temperature, this cannot be reflected in equation 3.

Figure 5 shows the semi-logarithmic plots of  $\nu$  against  $(\Delta T)^{-1}$  for S-1002 and S-2002. Although the values of  $\log n$  do not change linearly with  $(\Delta T)^{-1}$ , the  $\log \nu - (\Delta T)^{-1}$  curve is approximated by a straight line at  $(\Delta T)^{-1} > 0.01$ . At  $(\Delta T)^{-1} < 0.01$ , the data points deviate upward from the line. There is no marked difference in the curves between the different strain rates for both samples. The curve of S-2002 exhibit a similar behavior to that of S-1002 but the values of  $n$  is higher than those of S-1002 over the entire range of  $(\Delta T)^{-1}$ . The soft segments will be crystallized at 323-333 K because the melting points of the crystalline domains of poly(6-hydroxyhexanoic acid) is reported around 328 K<sup>[12]</sup>. This is the major reason for the upward deviation of  $\nu$  from the straight line. The values of  $\Delta E_m$  and  $\nu_0$  can be estimated from the best-fit line of the  $\log \nu - (\Delta T)^{-1}$  curves at  $(\Delta T)^{-1} > 0.01$  on the basis of equation 3. The values obtained for both samples are tabulated in TABLE 2. The  $\Delta E_m$  value of S-1002 is close to that of S-2002, implying that the size of the crystalline domains in S-1002 is similar to that in S-2002.

### Mechanical properties at large strains

The permanent residual strain, not observed at the applied strains smaller than the strain at the inflection point ( $\lambda \approx 1.1$ ), occurred at all temperatures examined when the sample was stretched to the strains beyond the inflection point. The inflection point appearing at  $\lambda \approx 1.1$  corresponds to the onset of the plastic deformation. The permanent residual strain reflects a structural change caused by the ap-



**Figure 5:** The semi-logarithmic plots of  $v$  against  $(\Delta T)^{-1}$ . The triangles and circles represent for  $v$  for S-1002 and S-2002, respectively. The white and black symbols represent the samples at  $\dot{\epsilon}_0 = 2.8 \times 10^{-3} \text{ s}^{-1}$  and at  $\dot{\epsilon}_0 = 2.8 \times 10^{-2} \text{ s}^{-1}$ , respectively. The best-fit lines for the data at  $(\Delta T)^{-1} > 0.01$  are also shown

**TABLE 2:** Estimated  $\Delta E_m$  and  $v_0$  in equation 3

Sample	$\Delta E_m / \text{J} \cdot \text{mol}^{-1}$	$10^3 v_0 / \text{mol} \cdot \text{m}^{-3}$
S-1002	290	5.8
S-2002	270	10

plication of the large strain. It has been reported for poly(ether ester) elastomers containing PBT units that the hard segment PBT domains are fractured when the applied strain is larger than the yield strain<sup>[6]</sup>. This strongly suggests that the PBT hard domains in the elastomers used in this study are also fractured at the strains beyond the yield strain.

The stretch ratio at yield point ( $l_y$ ) is defined as the stretch ratio at the inflection point. The point with the smallest values was regarded as the  $\lambda_y$  when several inflection points occurred. The yield stress ( $\sigma_y$ ) is defined as the stress at  $\lambda_y$ ; namely,  $\sigma_y = E_0 \lambda_y$ . The estimated values of  $\lambda_y$  and  $\sigma_y$  are listed in TABLE 1. The values of  $\lambda_y$  of S-1002 are almost the same at any T while  $\sigma_y$  of S-1002 decreases with increasing T. No marked differences in  $\sigma_y$  and  $\lambda_y$  between the samples elongated at the different

strain rate are observed. The values of  $\sigma_y$  and  $\lambda_y$  of S-2002 show a similar behavior to that of S-1002, but the higher values of  $\sigma_y$  in S-2002 as compared with S-1002 are observed at all T examined. Because  $\sigma_y = E_0 \lambda_y$ ,  $\sigma_y$  increases with increasing  $E_0$  if  $\lambda_y$  remains constant; hence, the decrease of  $\sigma_y$  with increasing T is due to the decrease of  $E_0$  since  $\lambda_y$  remained around 1.1 for all T. The higher  $\sigma_y$  for S-2002 than S-1002 is attributed to the higher  $E_0$  since no marked difference in  $\lambda_y$  was observed between S-1002 and S-2002. Because  $E_0$  is in proportion to  $v$ , according to equation, the difference in  $\lambda_y$  is caused only by the difference in  $v$ .

The deformation of the crystalline domains at the strains beyond the yield point ( $\lambda > \lambda_y$ ) can be phenomenologically regarded as the uniaxial plastic flow. Assuming that the samples behave as the Bingham fluid, the relationship between  $\sigma_e$  and the extensional strain rate ( $\dot{\epsilon}_p$ ) can be expressed by the following equation<sup>[13]</sup>.

$$\sigma_e = \sigma_y + \eta_p \dot{\epsilon}_p \quad (4)$$

with  $\eta_p$  being the plastic viscosity. The samples would become difficult to flow as the number density of the crystalline domains increases, that is,  $\eta_p$  would increase with increasing  $v$ ; hence, we assume that  $\eta_p$  can be written as a similar function of T to  $v$ . Thus, ( $\eta_p$ ) can be written by using  $\Delta T$  as

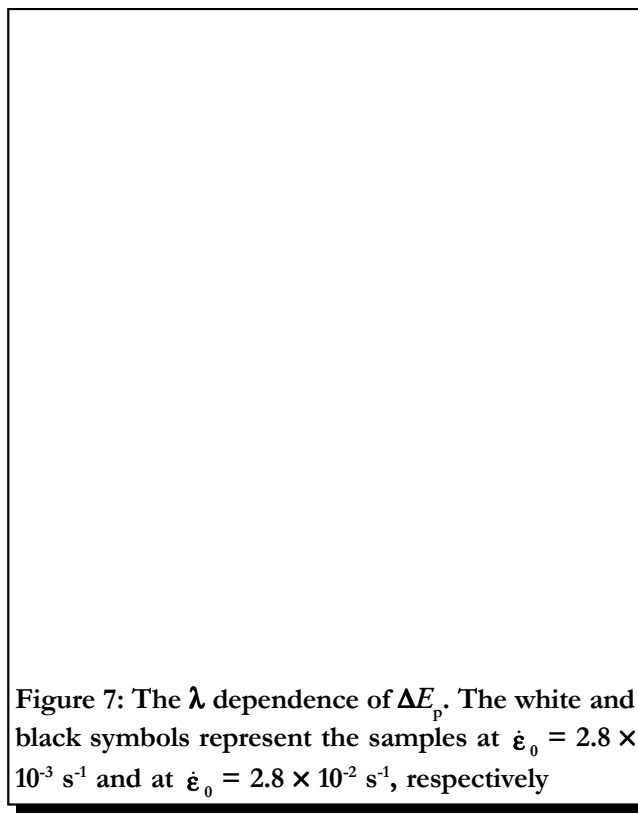
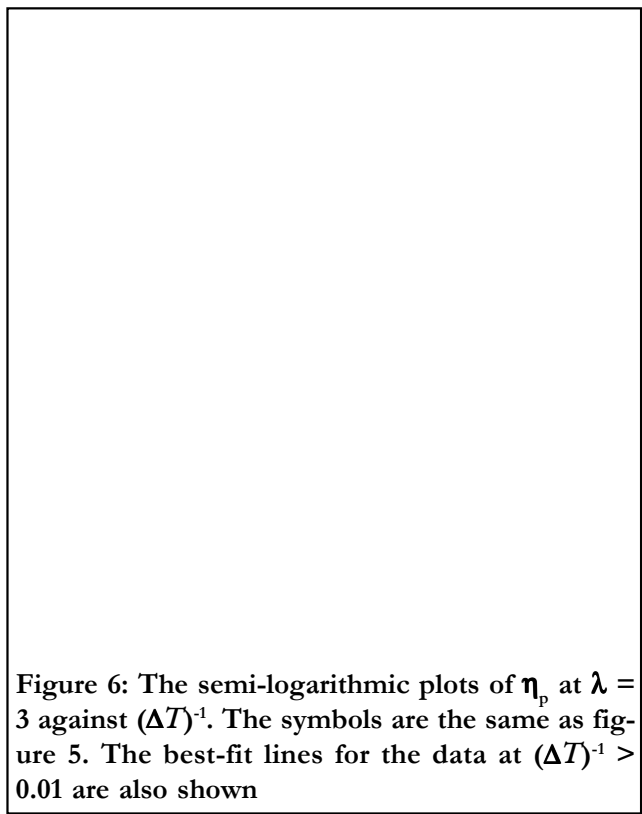
$$\eta_p = \eta_{p0} \exp(-\Delta E_p / R\Delta T) \quad (5)$$

Here,  $\Delta E_p$  is the activation energy of the plastic flow. The quantity  $\eta_{p0}$  is the plastic viscosity at  $\Delta T \rightarrow \infty$ .

Figure 6 shows the  $(\Delta T)^{-1}$  dependence of  $\eta_p$  drawn on semi-logarithmic plots for S-1002 and S-2002 at  $\lambda = 3.0$ . Although  $\log \eta_p$  is not a linear function of  $(\Delta T)^{-1}$ , the  $\log \eta_p - (\Delta T)^{-1}$  curve at  $(\Delta T)^{-1} > 0.01$  can be approximated by a straight line, as in the case of  $v - (\Delta T)^{-1}$  plots. The value of  $\Delta E_p$  can be estimated from the best-fit line of the  $\log \eta_p - (\Delta T)^{-1}$  curves at  $(\Delta T)^{-1} > 0.01$  on the basis of equation 5.

Figure 7 shows the  $\lambda$  dependence of  $\Delta E_p$ . The quantity  $\Delta E_p$  is almost constant around  $2.8 \times 10^2 \text{ J} \cdot \text{mol}^{-1}$ . The estimated  $\Delta E_p$  represents the activation energy of the plastic flow. The flow requires the breakdown of the crystalline domains, of course. As mentioned previously for  $\Delta E_m$ , no large difference in size of the crystalline domains existed between S-1002 and S-2002. As a result, no marked difference in estimated  $\Delta E_p$  was observed for the samples. It is

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natural that  $\Delta E_m$  and  $\Delta E_p$  are close to each other.

### CONCLUSION

Tensile properties of poly(ester ester) elastomers with different content of hard segments at various temperature were investigated. The elastomers having a higher content of the hard segments show a higher Young's modulus because the hard segments are crystallized to form a hard domain which acts as cross-links. The number density of the crystalline domains decreased with increasing temperature. There is no marked difference in the activation energy to form the crystalline domains between samples with different contents of hard segments.

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