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STRESS-INDUCED CRYSTALLINE PHASE TRANSITION IN BLOCK COPOLYMERS OF POLY(TETRAMETHYLENE TEREPHTHALATE) AND POLY(TETRAMETHYLENE OXIDE) (I) DEPENDENCE OF TRANSITIONAL BEHAVIOR ON HARD/SOFT SEGMENTAL RATIO

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ABSTRACT

Stress-induced solid-state transition has been found to occur in the multi block copolymers of poly(tetramethylene terephthalate) [PTMT] and poly(tetramethylene oxide) [PTMO]. In the crystalline regions of PTMT hard segments, the reversible structural change has been observed when the uniaxially-oriented sample is stretched along the draw direction. This is essentially the same phenomenon as that observed in PTMT homopolymer, although the transition in the block-copolymer requires appreciably larger tensile strain than the homopolymer case because of the coexistence of the PTMO soft segments with very low Young's modulus. In the PTMO soft segments, which are in the amorphous state at room temperature under free tension, there has been found to occur the stress-induced crystallization into the fully extended trans-zigzag conformation. At lower temperature below the glass transition point, these transitions in the hard and soft segments can be observed more clearly and sharply. The transitional behaviors have been compared among a series of samples with different molar fractions of PTMT hard segments and interpreted semiquantitatively based on a simple mechanical series model coupled with the crystalline phase transition in the PTMT hard segment. By measuring the temperature dependence of the critical stress at which the phase transition occurs abruptly, the transitional enthalpy and entropy have been evaluated.

1. INTRODUCTION

Multiblock copolymers of poly(tetramethylene terephthalate) [PTMT] and poly(tetramethylene oxide) [PTMO] are thermoplastic elastomers in which the PTMT hard segments act as physical cross-links and the PTMO soft segments as rubber components.¹⁾

There have been published many numbers of reports concerning the macroscopic mechanical properties of this elastomer.¹⁻⁶⁾ But some factor is still remained not to be taken into consideration in analysing such basically important mechanical

properties as stress-strain curves. In the previous paper⁷⁾ we reported the stress-induced phase transition of PTMT homopolymer and discussed the transitional mechanism based on the thermodynamic point of view. The transition occurs between the α and β crystalline phases as shown in Figure 1, in which the main structural difference between these two phases is in the methylene conformational sequence; GGT $\bar{\text{G}}$ (α form) and TTTTT (β form).^{8,9)} The macroscopic stress-strain curve of the uniaxially-oriented PTMT homopolymer exhibits the characteristic plateau region of almost constant stress, at which the crystalline phase transition occurs abruptly and the relative amounts of the α and β phases are

Fig. 1. Crystal structures of α and β forms of poly(tetramethylene terephthalate) homopolymer (PBT).⁸⁾

almost proportional to the applied strain.⁷⁾ The stress-strain curves of the uniaxially oriented PTMT-PTMO block copolymers exhibit also such plateau of constant stress in some strain region and the above-mentioned solid state transition has been found by the present authors to occur also in these copolymer samples.

In the present paper we will describe the characteristic features of this phase transition and the difference in the transition behavior among the various copolymer samples with different PTMT hard segmental contents. Through the theoretical interpretation of these phenomena based on some mechanical model, it will be suggested necessary in general to take into account any possibility of structural phase transition whenever the mechanical properties of copolymers are analysed.

2. EXPERIMENTAL

The copolymer samples utilized here were supplied by Toyobo Co. Ltd., the chemical compositions of which were estimated as shown in Table 1 based on the analytical results by Wegner et al.³⁾ and Dröscher et al.⁴⁾ and also on the elemental analysis made by the present authors. In reference to another name of PTMT, i.e., poly(butylene terephthalate) [PBT], these samples will be called "BT n " hereafter, where n denotes the average number of monomers in the PTMT

Table 1. Averaged Block Lengths (No. of Monomers) of Hard and Soft Segments.

	PBT	BT15	BT7	BT4
Hard	∞	15	7	4
Soft	0	14	14	14

hard segments. The uniaxially oriented samples were utilized in the experiments, which were prepared by cold-drawing the melt-quenched samples at room temperature to about 5 times the original length followed by the heat treatment at 130°C for about 1 hour under tension.

Stress-induced phase transition was monitored by the infrared spectral measurement under tension. The optical cell for measuring the infrared spectra at the various temperatures under constant stress condition was just the one reported in the previous paper.⁷⁾ The infrared spectrophotometer used was of a Japan Spectroscopic Company (JASCO) A-III type.

3. RESULTS AND DISCUSSION

3.1 Crystalline Phase Transition at Room Temperature

In Figure 2 is reproduced the infrared spectral change induced by the external strain applied to the BT7 sample at room temperature. Figure 3 shows the polarized infrared spectra of the BT7 sample measured at the strains of 0 and 100%. As seen in these figures, with an increase of tensile strain, the intensity of the infrared bands characteristic of the PTMT crystalline α form decreases and that of the β form increases.⁷⁾ At the same time some new infrared bands begin to appear at 1488, 995, and 565 cm^{-1} (asterisks in Figure 3) which are intrinsic of the trans-zigzag conformation of the PTMO crystalline state.^{10,11)} It should be noted here that these PTMO trans bands exhibit high degree of dichroic polarization character; i.e., the PTMO segments orient along the draw direction under tension.

These observations of Figures 2 and 3 indicate that, as the sample is tensioned, the phase transition occurs in the crystalline hard block parts and the crystallization with the fully extended molecular conformation is induced in the amorphous soft segmental parts. By estimating the relative absorbances of the α and β bands,⁷⁾ we can

Fig. 2. Strain dependence of polarized infrared spectra (300–900 cm^{-1}) of BT7 sample measured at room temperature. —: the electric vector of the incident infrared beam perpendicular to the orientation direction, ----: the electric vector of the incident infrared beam parallel to the orientation direction.

obtain the stress and strain dependences of the molar fraction of PTMT β form (X_β) for a series of samples with different PTMT contents. The results are shown in Figures 4 and 5. In these figures the X_β is reduced so that the maximal and minimal values are 1 and 0, respectively, in order to make the comparison among the samples easier. In Figure 6 are shown the stress-strain curves measured at the same time with the infrared spectral experiments at room temperature. From these figures we can notice the following characteristic behaviors of the phase transition in the copolyesters.

- (i) With the decrease in the hard-segmental length the transitional region shifts to the higher strain side.
- (ii) The phase transition occurs rather abruptly in the stress region nearly common to all the samples. That is to say, there exists a critical stress at which the transition occurs.
- (iii) The plateau of the stress-strain curves becomes less clear with the decrease in the hard segmental content, but the stress value of the plateau region is found to correspond well to the critical stress.

It should be noticed here that the stress values in Figures 4 and 6 are based on the initial cross-

Fig. 3. Polarized infrared spectra of BT7 sample measured under tension of 0 and 100% strains. —: the electric vector of the incident infrared beam perpendicular to the orientation direction, ----: the electric vector of the incident infrared beam parallel to the orientation direction.

Fig. 4. Stress dependence of reduced molar fraction of the crystalline β phase X_β^r for BT 4, 7, 15, and PBT samples (at room temperature).

Fig. 5. Strain dependence of reduced molar fraction of the crystalline β phase X_β^r for BT 4, 7, 15, and PBT samples (at room temperature).

Fig. 6. Stress-strain curves of the uniaxially oriented BT 4, 7, 15, and PBT samples measured at room temperature. The arrow indicates the stress where the molar fraction X_β^r changes most steeply.

sectional area of the samples. In the present cases of large deformation, however, we must employ the so-called "true stress" which is evaluated by dividing the applied force by the cross-sectional area at each stage of strain.¹²⁾ If ν_a and ν_b are defined as the Poisson's ratios of the sample width and thickness against the tensile deformation along the draw direction, respectively, then the true stress f^* (true) is obtained as

$$f^*(\text{true}) = f / [1 - (\nu_a + \nu_b)\epsilon]$$

where f is the stress evaluated for the initial cross-sectional area and ϵ is the strain. The measured Poisson's ratios ν_a and ν_b were found to change with strain. For example, in the case of BT 15 sample, ν_a , ν_b , and $\nu_a + \nu_b$ are as follows.

strain	ν_a	ν_b	$\nu_a + \nu_b$
0 – 30%	0.25	0.74	0.99
30 – 40%	0.50	0.35	0.85
40 – 50%	0.70	0.08	0.78

Similarly, for BT 4 sample, $\nu_a + \nu_b$ is about 0.8 (0–30% strain) and 0.4 (30–150%), and for BT 7 sample, 0.7 (0–45%) and 0.6 (45–100%). Using these values, the true stress f^* (true) can be estimated from the stress f . In Figure 7 is plotted

Fig. 7. Dependence of the reduced molar fraction of the crystalline β phase X_β^r on the true stress, measured at room temperature. The vertical scale of each curve spans 0 to 1 and the origin is shifted arbitrarily along the vertical axis.

Fig. 8. Polarized infrared spectra of oriented BT4 sample measured under free tension at 25°C and -155°C. —: the electric vector of the incident infrared beam perpendicular to the orientation axis, ----: the electric vector of the incident infrared beam parallel to the orientation axis. The asterisks indicate the bands characteristic of PTMO crystalline trans-zigzag conformation.^{10,11)}

the reduced molar fraction X_{β}^f against the true stress. For all the samples of BT4, 7, and 15 and PBT, the X_{β}^f changes drastically in the vicinity of the similar stress value, indicating the critical stress $f^*(\text{true})$ is almost common to all these samples and confirming the above-mentioned item (ii).

3.2 Phase Transition at Low Temperature

Figure 8 shows the polarized infrared spectra measured at 25°C and -155°C for BT4 sample under free tension. At low temperature most of the bands increase their intensities largely and the PTMO crystalline trans bands indicated by asterisks begin to appear below the glass transition temperature T_g of about -30°C (see Figure 9).⁶⁾ These trans bands show a clear infrared dichroism, suggesting that the soft PTMO chain segments are not so random but rather oriented along the draw direction even under free tension at room temperature in the uniaxially oriented samples, and crystallize into oriented aggregation state below T_g . In order to investigate the effect of these structural changes within the sample onto the

Fig. 9. Temperature dependence of relative absorbance of infrared 564 cm⁻¹ band measured for BT4 sample under free tension.

$\alpha \rightleftharpoons \beta$ phase transition, we measured the infrared spectra under tension at the various low temperatures. In Figure 10 are shown the stress-strain curves at -80°C, which should be compared with those measured at room temperature; the curves at low temperature are almost overlapped with each other independently of the content of the hard segments. The plateau region is more clearly

Fig. 10. Stress-strain curves measured at 25°C and -80°C for uniaxially oriented BT 4, 7, 15 and PBT samples.

detected and shifts to the lower strain and higher stress side. In Figures 11 and 12 are shown the dependences of X_β^f on the stress and strain, respectively, measured at the several temperatures for BT4 sample. At lower temperature, corresponding to the shift of the plateau region in the stress-strain curve (Figure 10), the phase transition occurs in the lower strain region and the critical stress increases largely.

In the previous paper⁷⁾ we treated the phase transition of PBT sample thermodynamically and indicated a suitability of applying the Clausius-Clapeyron equation for the one-dimensional tensile stress;

$$[\partial(f^*/T)/\partial(1/T)]_p = \Delta H / (A_\alpha \Delta L) \quad (1)$$

where ΔH is the enthalpy change between the α and β phases ($\Delta H = H_\beta - H_\alpha$), ΔL is the change in the fiber identity period, A_α is the effective cross-sectional area of the molecular chain in the α phase, and T is an absolute temperature. As shown in Figure 13, the above equation (1) is found to be useful also to the cases of the elastomers; the plot of $f^*(\text{true})/T$ against $1/T$ fits well the straight line for all the samples, where the true stress $f^*(\text{true})$ was evaluated under the assumption that the summation of the Poisson's ratios $\nu_a + \nu_b$ is almost unchanged with temperature as reported for polyethylene sample.¹⁵⁾ The

Fig. 11. Stress dependences of X_β^f measured for BT4 sample at the various low temperatures.

Fig. 12. Strain dependences of X_β^f measured for BT4 sample at the various low temperatures.

Fig. 13. Plots of $f^*(\text{true})/T$ against $1/T$ for BT 4, 7, 15, and PBT samples. The true stress $f^*(\text{true})$ was evaluated under the assumption that the summation of the Poisson's ratios $\nu_a + \nu_b$ in eq 1 of the text is almost unchanged with temperature as reported for polyethylene sample.¹⁵⁾

Table 2. Transition Enthalpy and Entropy of $\alpha \rightleftharpoons \beta$ Phase Transition in the Block Copolymers.

	PBT	BT15	BT7	BT4
ΔH (kJ/mol m.u.)	5.1	4.4	4.8	3.7
ΔS (J/K mol m.u.)	12.6	12.3	12.2	10.4

transitional enthalpy and entropy estimated from the slope of these lines are listed in Table 2. Taking into consideration the experimental errors, we may say, in the first approximation, that the transitional enthalpy and entropy are not so affected by the difference in the samples with the various hard segmental lengths. We should notice that the extrapolated temperature into the zero value of f^*/T , about 150°C, is common to all the samples, where the α to β transition would be expected to occur under free tension.⁷⁾

3.3 Interpretation of Stress-Strain Curves by a Simple Mechanical Series Model

The phase-transitional behavior and the stress-strain curve described in the previous sections suggest an applicability of the mechanical series model to the present system of the PTMT-PTMO block copolymers just as likely as in the case of the PTMT homopolymer.⁷⁾ We assume here the structural model consisting of three components of the crystalline and amorphous regions of PTMT and the amorphous PTMO,^{1,13)} which is coupled with the phase transition in the PTMT crystalline part. The crystallization in the soft PTMO part is neglected here for simplicity.

If the volume fraction of the soft PTMO segment is m and the degree of crystallinity in the PTMT hard segment is denoted as x and the Young's moduli of each component are defined as E_α (E_β), E_{am}^h , and E_{am}^s for the crystalline PTMT, amorphous PTMT, and amorphous PTMO parts, respectively, then we may express the strain of the sample ϵ as follows.⁷⁾

(i) For the applied stress f below the critical stress f^* , the crystal and amorphous regions are deformed elastically. If we neglect the effect of viscosity as an approximation and treat the amorphous part as a purely elastic body, then for $0 < f < f^*$,

$$\epsilon = \epsilon_c + \epsilon_{am} = (x/E_\alpha + (1-x)/E_{am}^h)(1-m)f + fm/E_{am}^s \quad (2)$$

$$L = L_0(1 + \epsilon) \quad (3)$$

where L and L_0 are the long periods of the system. (ii) When the stress f reaches the critical value f^* , the $\alpha \rightarrow \beta$ transition takes place in the crystalline region of the PTMT hard segments. The length of the amorphous region is kept unchanged because the stress remains constant during the phase transition. At the terminal point of the phase transition, the sizes (or the lengths) of the crystalline and amorphous regions are expressed as follows.

$$L_{cry}^* = (1-m)xL_0(1+0.117) \quad (4)$$

$$L_{am}^* = [1 - (1-m)x]L_0(1+f/E_{am}) \quad (5)$$

$$1/E_{am} = [(1-x)(1-m)/E_{am}^h + m/E_{am}^s]/[1 - x(1-m)] \quad (6)$$

Here the α crystal transforms into the β form with the extension of 11.7%.⁷⁾ Then, from eqs. (4) and (5), we can express the strain ϵ at the terminal point of the phase transition as

$$\begin{aligned} \epsilon^* &= (L_{cry}^* + L_{am}^* - L_0)/L_0 \\ &= 1.117(1-m)x - 1 + [1 - (1-m)x][1 + f^*/E_{am}] \end{aligned} \quad (7)$$

(iii) When the stress f is beyond the critical value f^* , the elastic deformation of the β form and amorphous phase takes place again. For $f > f^*$,

$$f = f^* + (\epsilon - \epsilon^*)E_{sys} \quad (8)$$

$$1/E_{sys} = (1-m)x/E_\beta + (1-m)(1-x)/E_{am}^h + m/E_{am}^s \quad (9)$$

where E_{sys} is the Young's modulus of the whole system.

Using the eqs. of (2)–(9), we can calculate the stress-strain curves of the block copolymer. In Figure 14 are illustrated the calculated results of the stress-strain curves for the various values of the soft-segmental fraction m at room temperature and -80°C , where the numerical values of the parameters are assumed as follows.⁷⁾

At room temperature

$$E_{sys} = 8 \times 10^{-2} \text{ GPa (observed)},$$

$$E_\alpha = 10.1 \text{ GPa}, \quad E_\beta = 269 \text{ GPa},$$

$$E_{am}^h = 3.9 \text{ GPa}, \quad E_{am}^s = 0.062 \text{ GPa},$$

$$f^* = 7.48 \times 10^7 \text{ Pa (PBT)}, \quad x = 0.8$$

Fig. 14. Stress-strain curves at room temperature and -80°C calculated for the various m values, where m denotes the volume fraction of the soft PTMO segment. Refer to Fig. 10.

At -80°C

$$\begin{aligned} E_{\text{sys}} &= 1.8 \text{ GPa (observed)}, \\ E_a &= 10.1 \text{ GPa}, \quad E_\beta = 26.9 \text{ GPa}, \\ E_{\text{am}}^h &= 3.9 \text{ GPa}, \quad E_{\text{am}}^s = 1.5 \text{ GPa}, \\ f^* &= 15.5 \times 10^7 \text{ Pa}, \quad x = 0.8 \end{aligned}$$

From Figure 14 we may say that the characteristic features of experimental stress-strain curves are well reproduced; (i) the plateau region shifts toward the higher strain side and becomes more obscure with an increment of m or the relative amount of the soft segment, but (ii) at low temperature, the plateau is not so dependent on m but shifts to the lower strain region and becomes appreciably definite. Strictly speaking, however, we must introduce more positively an idea of rubber elasticity and the effect of crystallization occurring in the soft segments. But the essential feature of the mechanical behaviors of the uniaxially oriented PTMT-PTMO multi-block copolymers can be understood based on the above-mentioned mechanical model.

Additionally we must also take into account the following situation in case of analysing the

mechanical behavior of the copolymers. The actually observed $\alpha \rightleftharpoons \beta$ phase transition in the block copolymers occurs over a very wide stress and strain region, much wider than that expected from the above-mentioned simple and ideal mechanical model where the homogeneous deformation is assumed. That is to say, the critical stress f^* is thought to distribute broadly around the averaged value. So we must take into consideration the inhomogeneous deformation, which may reflect the distribution of segmental lengths in the copolymer samples. The detailed investigation of inhomogeneous deformation will be reported in the next paper of this journal.¹⁴⁾

4. CONCLUSIONS

Just as likely as the case of PTMT homopolymer,⁷⁾ we have found the reversible solid-state phase transition in the uniaxially oriented PTMT-PTMO block copolymers induced by the externally applied tensile stress. In the PTMT hard segments the $\alpha \rightleftharpoons \beta$ crystalline transition is observed and in the soft PTMO segments the crystallization into the fully extended trans conformation. The $\alpha \rightleftharpoons \beta$ transition observed in the copolymers occurs in the higher strain region but almost in the same stress region as in PTMT homopolymer, although the transitional behavior becomes gradually obscure with a decrease in the relative content of the PTMT hard segments. The mechanical characteristic feature of these polymer samples is seen in the existence of plateau region in the stress-strain curves, where the structural transition occurs. By assuming a simple mechanical series model coupled with the phase-transition in the hard segmental parts, we can interpret, though semiquantitatively, this characteristic stress-strain curve. The reason why the transition occurs apparently in the higher strain region may come from the situation that the block copolymer contains the soft segments of very low Young's modulus. At low temperature below T_g , the transition occurs at the higher critical stress and in the lower strain region. The plateau of the stress-strain curve becomes clearer than that at room temperature. These characteristic temperature dependences can be also explained by the above-mentioned mechanical model. As understood from the constancy of the estimated transitional enthalpy and entropy, the essential

features of the phase transition in the PTMT hard segments may be almost the same as those in PBT homopolymer, as long as the averaged value of stress is concerned. But the transition actually occurs in much broader stress/strain region than the ideally expected one, indicating an appreciably inhomogeneous deformation in the block copolymers, especially in the samples with short hard segments. The details of such inhomogeneous deformation will be discussed in the following paper. A variety of block copolymers have been synthesized so far and their mechanical properties have been measured so widely. But, as mentioned in the present paper, it may be always necessary to take some attention onto the possibility of an occurrence of the structural transition when the measurement of the mechanical tensile deformation is made, because such structural change affects more or less the mechanical properties of the bulk samples. In other words, we must not ignore any possibility of structural change whenever we try to interpret the mechanical properties of the polymer samples.

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ポリテトラメチレンテレフタレートとポリテトラメチレン オキシドのブロック共重合体における応力誘起結晶相転移 (I) 転移挙動のハード/ソフトセグメント比に対する依存性

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ポリテトラメチレンテレフタレート (PTMT) とポリテトラメチレンオキシド (PTMO) のマルチブロック共重合体において、応力誘起固相転移の起ることを見出した。一軸配向試料を延伸軸方向に引張った時、PTMTハードセグメントの結晶領域においては、PTMTホモポリマーの場合と本質的に同じ可逆的構造変化が観測される。ただし、この場合、非常に低いヤング率の PTMO ソフトセグメントが共存しているため、相転移発現には、ホモポリマーの場合に比べ、かなり大きな引張り歪が必要となる。一方、室温の未緊張状態では非晶性である PT

MO ソフト部分においては、伸びきった trans-zigzag conformation への結晶化が引き起こされる。これらハードおよびソフト部分の転移現象は、ガラス転移点以下の低温においては、より明瞭に、そして鋭く起こる。

これら相転移挙動を PTMT ハードセグメント分率の異った試料について比較し、結晶相転移と力学的直列模型をカップルさせた単純なモデルを用いて解釈した。また相転移が急激に起こる、いわゆる臨界応力について、その温度依存性を測定し、転移エンタルピーとエントロピーを評価した。