Microscopic Origin of Elastic and Plastic Deformation in Poly(Ether-Block-Amide) Elastomers under Various Conditions

Takumitsu Kida*, Keisuke Hamasaki, Yusuke Hiejima*, Shuichi Maeda***, and Koh-hei Nitta*†

*Department of Chemical and Materials Science, Kanazawa University, Kakuma, Kanazawa 9201192, Japan
**Graduate School of Engineering, Department of Applied Chemistry, Hiroshima University, 1-1 Kagamiyama, Higashi-Hiroshima 7398527, Japan
***Advanced Science and Innovative Research Center, Organization for Research Initiatives, Yamaguchi University, 2-16-1, Tokiwadai, Ube, Yamaguchi 7558611, Japan

(Received : February 18, 2020)

Microscopic deformation behavior of polyamide (PA) elastomers (PAE) with various PA contents has been elucidated using various structural analyses including in situ infrared spectroscopy under cycle tests. Below the glass transition temperature (Tg), the stress–strain curves showed an obvious yielding point irrespective of the soft-segment content. The plastic deformation under tension is interpreted by irreversible morphological transformation observed in semi-crystalline polymers, such as the collapse of the spherulites and the fragmentation of the lamellar crystals. Above Tg, whereas the stress–strain curve is dominated by the temperature distance from Tg, PAE with higher soft-segment contents shows more elastic deformation in its supermolecular structure, which is essentially reversible up to the highly-strained region. The microscopic origin of high tunability for the elasticity of PAE is assigned to the mobility of interlamellar amorphous chains dominated by Tg.

Key Words: Polyamide elastomer / Tensile deformation / Morphology

1. INTRODUCTION

Polyamide (PA) elastomer (PAE) is a class of thermoplastic elastomers composed of a hard segment of PA (generally PA6 or PA12) and a soft segment of polyether (PE)1). The hard segment forms strong crystalline structure which acts as the junction of flexible amorphous PE network. It has been established that the physical network is responsible for its excellent strength and drawability1). Therefore, PAE has recently been applied various application fields such as sport and medical supplies1, 2).

The relationship between structure and mechanical properties of PAE has been extensively studied for PEBAX® 3), which is one of the PAE grades developed by Atochem, and some PAEs by using various structural analyses such as infrared (IR)4–5), and Raman spectroscopy6, 7), small- and wide-angle X-ray scattering (SAXS and WAXS)8–10), small-angle light scattering (SALS)9, 10), and microscopies7, 10). In general, the mechanical response of PAE under a uniaxial stretching drastically varies depending on the hard-segment fraction:

the Young’s modulus and strength increase with increasing the hard-segment fraction10). Moreover, it is demonstrated that PAEs with moderate hard-segment fraction show significantly high elasticity up to the highly-strained region with maintaining sufficient strength7).

In this study, we combined a cyclic test and polarized IR spectroscopy for in situ measurements of the microscopic deformation of PAEs at various temperatures. It is demonstrated that the unloading process, as well as the stretching process, provides essential insights for its microstructural origins of the elasticity and plasticity. In addition to the molecular orientation, mesoscopic deformation of lamellar crystals and spherulites was revealed by the SALS and SAXS measurements of drawn PAEs. Based on these observations, a consistent mechanism of microscopic deformation is proposed for various PAEs showing elastic to plastic characters.

2. EXPERIMENTAL

We used PAEs composed of PA12 and poly(ether diamine) as the hard and soft segments, respectively, supplied by Ube Industries, Ltd. The details of the polymerization process of PAEs are described elsewhere13). The chemical
structure of PAE used is shown in Fig. 1. The characteristics of PAEs including the weight-average molecular weight $M_w$ and polydispersity index $M_w/M_n$ are listed in Table I. Here, the number attached to the sample code represents the weight fraction of the soft segment. The pellets of the PAEs were melt-pressed at 503 K and 20 MPa for 5 min, followed by a slow cooling to room temperature to give sample sheets with 1 mm or 10 μm thickness. PA12 supplied by Ube Industries, Ltd. with $M_w = 3.5 \times 10^4$ and $M_w/M_n = 2.8$ was also molded to sample sheets with the same procedure for comparison. It is noteworthy that these pellets were vacuum dried at 353 K for 10 h to remove moisture in prior to the sample preparation.

Differential scanning calorimetry (DSC) was conducted to evaluate the crystallinity of PAEs using a Diamond DSC (Perkin Elmar, MA, USA) from 303 to 503 K at a heating rate of 10 K min$^{-1}$ under a nitrogen atmosphere. A circular specimen with about 3 mg was used. The weight-average crystallinity was calculated using the following equation:

$$X_c = \frac{\Delta H}{\Delta H_0},$$  

where $\Delta H$ is a heat fusion of samples and $\Delta H_0$ is a heat fusion of the perfect crystals of PA12 (209.02 J g$^{-1}$)$^{12}$. Dynamic mechanical analysis (DMA) was performed to evaluate the viscoelastic properties of PAE samples using a DVE-V4 (UBM Co., Ltd., Kyoto, Japan) from 123 to 373 K at 10 Hz at a heating rate of 2 K min$^{-1}$. Rectangular specimens with 5 mm width and 30 mm gauge length were cut out from the PAE and PA12 sheets.

The stress–strain curves of PAEs were measured using a custom-made tensile tester equipped with a heating and cooling chamber at a constant strain rate of 1.0 min$^{-1}$ from 198 to 358 K. Dumbbell-shaped specimen with a width of 4 mm and a gauge length of 10 mm was cut out from the PAE sheet. Cycle tests were performed at various temperatures for a loading-unloading process; the specimens were stretched up to $\varepsilon = 1.0$ corresponding to the neck-propagation region, followed by unloading to $\sigma = 0$ at a strain rate of 1.0 min$^{-1}$. The loading-unloading procedure was repeated for 10 times, where the non-recovery strain at $\sigma = 0$ practically reached a constant value of $\varepsilon_c$.

In situ polarized IR spectroscopy under the cycle test was performed using a FTIR spectrometer (Spectrum100T, Perkin Elmer Inc., Waltham, MA, USA) at an exposure time of 2 s. The cycle test was performed using a custom-made tensile machine at a constant strain rate of 0.1 min$^{-1}$ at various temperatures. Dumbbell-shaped specimens with a width of 4 mm, a gauge length of 10 mm, and a thickness of 20 μm were used. The details of in situ polarized IR spectroscopy during stretching are described elsewhere$^{13}$.

The IR dichroic ratio $D$ is defined by the following equation:

$$D = \frac{A_\parallel}{A_\perp},$$

where $A_\parallel$ and $A_\perp$ are the IR absorbance under polarization parallel and perpendicular to the stretching direction, respectively. The orientation function of molecular chain ($f$) is given by$^{13,14}$:

$$f = \frac{2}{3} (\cos^2 \alpha - \frac{1}{3} D + 2)$$

Here, $\alpha$ is the angle between the molecular chain axis and the

---

**Table I Characteristics of PAE samples.**

| Sample code | $w_s^*$ /wt% | $M_w$ /10^4 | $M_w/M_n$ | $X_c$ /wt% |
|-------------|---------------|-------------|-----------|------------|
| PAE10       | 10            | 6.3         | 2.9       | 19.8       |
| PAE15       | 15            | 7.3         | 2.6       | 17.9       |
| PAE30       | 30            | 12.0        | 2.3       | 14.9       |
| PAE40       | 40            | 13.9        | 3.0       | 12.8       |
| PAE50       | 50            | 13.5        | 3.1       | 10.6       |

$^*$ weight fraction of soft segments

---

![Fig. 1 Chemical structure of PAE used.](image)

![Fig. 2 Polarized IR spectra of PAE15 in (a) 1110 cm$^{-1}$ and (b) 3300 cm$^{-1}$ ranges. The red line represents the fitting curve by a sum of Voigt functions (blue lines).](image)
transition moment of the vibrational mode. The value of $f$ ranges from $-0.5$, corresponding to the perpendicular orientation to the stretching direction, to 1, corresponding to the perfect orientation in the stretching direction. For PAE, the 3300 cm$^{-1}$ band assigned to the N–H stretching mode $(\alpha = 90^\circ)$ of the hard segment and the 1115 cm$^{-1}$ band assigned to the C–O–C stretching mode $(\alpha = 90^\circ)$ of the soft segment were used to obtain the orientation functions for the hard and soft segments ($f_h$ and $f_s$), respectively. The polarized IR spectra were fitted with a sum of Voigt functions using a nonlinear Levenberg–Marquardt method to determine the peak area. Typical fitting results are shown in Fig. 2. We confirmed that the error was less than 7 %.

SAXS measurements were performed using a Nano-Viewer (Rigaku, Tokyo, Japan) with Cu Kα radiation $(\lambda = 0.154 \text{ nm})$. The two-dimensional SAXS pattern from a drawn specimen was detected using an imaging plate at an exposure time of 30 min. The drawn specimens were prepared as follows: dumbbell-shaped specimens with a gauge length of 10 mm and a width of 4 mm were uniaxially drawn up to certain strains, and the applied strain was held by fixing the drawn specimen by a custom-made jig. The long period $L_p$ was calculated using the following equation:

$$L_p = \frac{2\pi}{q_{\text{max}}},$$

(4)

where $q_{\text{max}}$ is the location of the peak maximum of the one-dimensional SAXS profile.

SALS measurements were performed to observe a uniaxial deformation behavior of spherulites. A laser diode module (CPS532, Thorlabs Japan Inc., Tokyo, Japan) at a wavelength of 532 nm and a power of 4.5 mW was used as an incident light. A pair of crossed wire-grid polarizers (WP50L-VIS, Thorlabs Japan Inc., Tokyo, Japan) was inserted in the incident and scattered paths as the polarizer and detector, respectively. The scattered light from the drawn specimen was detected using a CMOS camera (DCC1545M, Thorlabs Japan Inc., Tokyo Japan). The drawn specimen for the SALS measurements was prepared by the same method for the SAXS measurements as described above. Each PAE sheet showed a clear four-leaf clover pattern, indicative of the spherulitic structure. The radius of the spherulites was determined with the following equations:

$$R = 4.1 \frac{\lambda}{4\pi n \sin \theta_{\text{max}}},$$

(5)

where $\lambda$ is the wavelength of the incident light, $\theta_{\text{max}}$ is the scattered angle at which the intensity of four-leaf pattern shows a maximum, and $n$ is the refractive index of the samples assumed to be $n = 1.53^{17}$ as the typical value of PA.

3. RESULTS AND DISCUSSION

The weight-average crystallinity for PAEs are listed in Table I. The crystallinity decreased from 20 to 10 % with increasing the weight fraction of soft segments $w_s$. It has been demonstrated that the crystalline region for these PAEs is solely formed by the hard segment, and about 20 % of the hard segment resides in the crystalline region irrespective of $w_s$. Then, the decrease of the crystallinity is owning to the decreases of the hard-segment content.

The dynamic mechanical spectra of PAEs along with that of PA12 are shown in Fig. 3. For PA12, two relaxation processes called $\alpha$ and $\beta$ relaxations were observed around 328 and 203 K, respectively. The former and the latter are assigned to the main chain motion (glass transition) and the local motion of amide groups, respectively. These two relaxation peaks were also observed for each PAE. The relaxation temperatures are listed in Table II, where the relaxation temperatures of the glass transition and the $\beta$ relaxation are denoted as $T_g$ and $T_\beta$, respectively. It is noteworthy that $\gamma$...
relaxation assigned to the local motion of CH₂ groups for the both segments has been observed at around 138 K for PAEs. It is reasonable that the β-relaxation is located at appreciably higher temperature than the γ-relaxation without affected by ws. A single peak assigned to the glass transition was observed for each PAE, and Tg drastically shifted to lower temperature with increasing ws. Moreover, the ws dependence of Tg was successfully described by the Fox equation as shown in Fig. 4.

\[
\frac{1}{T_g} = \frac{w_s}{T_g^s} + \frac{1 - w_s}{T_g^h},
\]

where \( T_g^s = 195 \text{ K} \) and \( T_g^h = 328 \text{ K} \) are the glass transition temperatures for the soft and hard segments, respectively. Note that Tg for PA12 is plotted as \( w_s = 1 \). These results indicate that the soft and hard segments of the PAEs form well-mixed morphology. Then, Tg is assigned to the glass transition of the interlamellar amorphous layer composed of a mixture of the hard and soft segments.

The stress–strain curves at various temperatures of PAE15 and PAE40 are exemplified in Fig. 5. Because the temperature distance \( \Delta T = T - T_g \) between the test temperature T and the glass transition temperature \( T_g \) strongly affects the mechanical properties for polymeric materials, the tensile tests were conducted at given temperature distance of \( \Delta T \). For both samples, the overall stress level decreased with increasing temperature accompanied by a broadening of the yielding region. For PAE15, the stress–strain curves showed a clear yielding region below \( T_g (\Delta T < 0) \), but the yielding became broader at higher temperatures. Above \( T_g (\Delta T > 0) \), the yielding was unclear, which is similar to typical elastomers. Although the overall stress level for PAE40 was lower than that for PAE15, the temperature dependence of the stress–strain curves in the yielding region for PAE40 was essentially the same as that for PAE15: The yielding point was obscured above \( T_g \), while broad yielding was observed below \( T_g \). Moreover, the macroscopic shape of the test specimen during yielding was also dominated by \( \Delta T \) irrespective of \( w_s \), as shown in Fig. 6. Although both samples showed an obvious necking below \( T_g (\Delta T = -45 \text{ K}) \), the necking became broad and unclear above \( T_g (\Delta T = 30 \text{ K}) \). These results suggest that the glass transition is relevant for determining the plasticity and elasticity of PAEs irrespective of the PA content.

Stress–strain curves under the cyclic tests for PAE15 and PAE40 are presented in Fig. 7. For PAE15, the shape of the stress–strain curves in the loading–unloading processes were elliptical in the entire temperature range, while the

![Fig. 4 Soft-segment fraction dependence of glass transition temperatures of PAEs. The solid line is calculated by Fox equation (Equation (6)).](image)

![Fig. 5 Stress–strain curves at various temperatures for (a) PAE15 and (b) PAE40.](image)

| Sample code | \( T_g^s / \text{K} \) | \( T_g^h / \text{K} \) |
|-------------|----------------|----------------|
| PA12        | 328            | 214            |
| PAE10       | 313            | 213            |
| PAE15       | 308            | 211            |
| PAE30       | 278            | 221            |
| PAE40       | 263            | 223            |
| PAE50       | 246            | 219            |

Table II Relaxation temperatures for PA12 and PAEs estimated from the peak position of the loss modulus.
hysteresis loop reflecting its plasticity was smaller at higher temperatures. For PAE40, whereas the elliptical loops were observed below $T_g$, the shape changed above $T_g$ to inverse S-shaped curves which are commonly observed for elastomers$^{21-23}$. In Fig. 8, the non-recovery strain $\varepsilon_n$ is plotted against the test temperature for PAEs. The non-recovery strain $\varepsilon_n$ linearly decreased with increasing temperature below $T_g$, indicating enhancement of elasticity. Above $T_g$, $\varepsilon_n$ remained unchanged even at higher temperatures. Then, it is suggested that the chain mobility in the interlamellar amorphous region is responsible for the mechanical response.

**Fig. 6** Pictures of drawn specimens at $\varepsilon = 1.0$ for (a) PAE15 and (b) PAE40 at $\Delta T = -45$ K and (c) PAE15 and (d) PAE40 at $\Delta T = 30$ K. The scale bar in each picture indicates 5 mm.

**Fig. 7** Stress–strain curves under cyclic tests for PAE15 (a) below and (b) above $T_g$ and PAE40 (c) below and (d) above $T_g$.

**Fig. 8** Temperature distance dependences of non-recovery strain $\varepsilon_n$ for PAEs.

**Fig. 9** Time dependences of orientation functions of hard and soft segments along with stress–time curve at $\Delta T = -45$ K for (a) PAE15 and (b) PAE40 and at $\Delta T = 30$ K for (c) PAE15 and (d) PAE40.
of the PAEs; the elasticity of PAE is ascribed to the chain mobility which is promoted by the increase of $w_s$ and heating until the glass transition. It is interesting to note that the values of $\varepsilon_r$ seem to converge to an identical value for all PAEs at $\Delta T = -70$ K.

Figure 9(a) and (b) shows the temporal changes of the orientation functions for hard and soft segments ($f_h$ and $f_s$) during the cycle tests of PAE15 and PAE40 below $T_g$ ($\Delta T = -45$ K), where the stress–time curves are also shown. In the first loading step, both orientation functions linearly increased with time and the applied strain, suggesting that the hard and soft segments simply oriented into the stretching direction. During the first unloading, both orientation functions appreciably decreased in accordance with the decrease of the stress but not completely recovered to zero. These orientation behaviors were repeated in the second loading–unloading step. Thus, the molecular orientation of both segments can be recovered only partly because of the frozen mobility of the hard segment in the interlamellar amorphous region.

For PAE15 above $T_g$ ($\Delta T = 30$ K) in Fig. 9(c), whereas both orientation parameters showed a similar behavior to the vitrified PAEs during the loading process, the relaxation of the molecular orientation was appreciably pronounced, and $f_i$ reached around zero during unloading. Above $T_g$, both soft and hard segments in the interlamellar region are so flexible that the amorphous chains are prone to recover toward random orientation due to entropic elasticity under the unloading step, resulting in higher reversibility of the molecular orientation. The molecular orientation of PAE40 at $\Delta T = 30$ K shown in Fig. 9(d) was completely different from other PAEs: the soft segment oriented into the stretching direction in the first loading step whereas the hard segment showed perpendicular orientation to the stretching direction. Such an opposite molecular orientation of the soft and hard segments has been interpreted by the affine-like deformation of spherulites for PAEs with relatively high $w_s$, which has been observed by IR$^4$ and Raman spectroscopy$^7$. In the first unloading step, both soft and hard segments completely reverted random orientation, and the opposite and reversible orientation was maintained in the second loading–unloading step, indicating that the affine-like spherulitic deformation is elastic. These elastic deformation behaviors are consistent with our previous results for PAEs with relatively high $w_s$$^3$, where the tensile deformation mainly concentrates in the interlamellar amorphous region without significant fragmentation of the lamellar crystals.

The SALS and SAXS patterns under the cycle tests are shown in Fig. 10. A typical four-leaf clover pattern was observed for each PAE, and the size of spherulites was estimated to be about 20–30 $\mu$m with Equation (5). A circular scattering pattern observed in these SAXS images indicates randomly oriented lamellar alternating structure, where the long period was determined to be about 12 nm from the one-dimensional SAXS profile. We confirmed that the sizes of the spherulites and the lamellar alternating structure remain unchanged irrespective of $w_s$.

Under a uniaxial stretching below $T_g$ ($\Delta T = -45$ K), the clover patterns for PAE15 and PAE40 vanished beyond the yielding point, and no recovery was observed after unloading. The irreversible change in the SALS pattern suggests that the spherulites collapse accompanied with plastic deformation. The SALS and SAXS patterns under the cycle tests are shown in Fig. 10.
deformation. Beyond the yielding point, a circular SAXS pattern transformed into a strong streak pattern in the low-angle region. This streak pattern generally results from formation of voids with the size of a few hundred nanometers, which has been widely observed for semi-crystalline polymers with high crystallinity\(^\text{24, 25}\).

In the case of the uniaxial stretching above \(T_g\) (\(\Delta T = 30\) K), the spherulites for PAE15 are irreversibly collapsed beyond the yielding region because no four-leaf pattern was observed for the unloaded sample. On the other hand, PAE40 were strained along the stretching direction with maintaining the four-leaf SALS and circular SAXS patterns. The strained four-leaf pattern almost completely reverted to the initial isotropic state. Thus, the spherulites for PAE40 at \(\Delta T = 30\) K are highly elastic to the induce reversible deformation. As for the SAXS patterns of PAE15, a circular pattern was transformed into a four-point pattern beyond the yielding point. This four-point pattern has been observed for PEBAX and some thermoplastic elastomers, which is assigned to a formation of a checker-board arrangement caused by a fragmentation of lamellar crystals into small crystallites\(^\text{8, 26}\). The four-point pattern of the unloaded PAE indicates that the fragmented lamellar crystals can no longer recover the initial lamellar crystals. For PAE40, the SAXS patterns were reversibly strained along the stretching direction, which means that the lamellar alternating structure is elongated into the stretching direction without a fragmentation of lamellar crystals, as observed in the SALS results.

Schematics of the deformation mechanism of PAEs with relatively high and low soft segment contents below and above \(T_g\) are presented in Fig. 11. Below \(T_g\), the molecular motion of the interlamellar amorphous chains is frozen so that these amorphous chains cannot fill the interlamellar space under a uniaxial stretching, resulting in an occurrence of voids and cavitation as observed for semi-crystalline polymers\(^\text{24, 25, 27}\). Considering that spherulites are completely collapsed and both segments orient into the stretching direction, the lamellar alternating structure is fragmented into smaller blocks followed by the reorientation into the stretching direction. The soft and hard segments cannot revert random orientation in the unloading process because the molecular motions are frozen. Thus, the spherulites and lamellar crystals also remain fragmented during unloading.

Above \(T_g\), the fragmentation of lamellar crystals was clearly observed from the SAXS measurements for PAEs with relatively low \(w_s\), which is also observed for PA12 under an uniaxial stretching\(^\text{29}\). During the unloading process, mobility and flexibility of the amorphous chains lead to appreciable reversibility of the molecular orientation. However, the deformed spherulites and lamellar crystals cannot revert the initial morphology because of the irreversible mesoscopic transformation from spherulitic to fibrillar structure accompanied by a rearrangement of the fragmented lamellar crystals. In the case of PAEs with relatively high \(w_s\), it is found that the modulus of the interlamellar amorphous chains is low compared with PAEs with relatively low \(w_s\). Thus, the induced deformation mainly concentrates on the interlamellar amorphous chains with sufficiently high mobility, which results in the affine-like deformation of spherulites maintaining the spherulitic morphology with a slight fragmentation of lamellae. Moreover, such affine-like elastic deformation of spherulites leads to the perpendicular orientation of the crystalline chains. The spherulitic morphology and the lamellar crystals are maintained under a uniaxial stretching so that the molecular orientation can be completely recovered to the initial state, resulting in high elasticity.

4. CONCLUSIONS

The mechanical and morphological responses of PAEs under cyclic tests have been elucidated using \textit{in situ} IR spectroscopy, along with the SAXS, and SALS analyses. The tensile properties of PAEs are dominated by the glass transition temperature \(T_g\) of the interlamellar amorphous chains composed of the hard and soft segments: the stress–strain curves show obvious yielding below \(T_g\) while those are elastomeric without a clear yielding point above \(T_g\). The molecular orientation of the amorphous chains is reversible to the applied strain above \(T_g\) although the orientation of both hard and soft segments cannot be recovered to the initial state below \(T_g\). Moreover, for PAEs with relatively lower PA contents, the applied deformation mainly concentrates on the amorphous region because of the low crystallinity and the high amorphous flexibility, which leads to the reversible deformation of morphology and molecular orientation. These microscopic
insights of the mechanical responses for PAEs provide us valuable information for tuning various properties of thermo-plastic elastomers.

ACKNOWLEDGEMENTS

The authors would like to thank Ube Industries, Ltd., Japan for supplying PAE and PA12 samples. T.K. is grateful for a financial support from Grand-in-Aid for JSPS Research Fellow (19J01025).

REFERENCES

1) Drobny JG, “Handbook of Thermoplastic Elastomers”, (1979), Van Nostrand Reinhold Publishers, NY.
2) Fakirov S, “Handbook of Condensation Thermoplastic Elastomers”, (2006), John Wiley & Sons Inc, NY.
3) Deleens G, SPE ANTEC, 417 (1981).
4) Yeh F, Hsiao BS, Sauer BB, Michel S, Siesler HW, Macromolecules, 36, 1940 (2003).
5) Song Y, Yamamoto H, Nemoto N, Macromolecules, 37, 6219 (2004).
6) Schmidt P, Hendra PJ, Spectrochim Acta, 50A, 1999 (1994).
7) Kida T, Sasaki T, Hiejima Y, Maeda S, Nitta KH, Polymer, 189, 122128 (2020).
8) Kamal T, Park SY, Choi MC, Chang YW, Chuang WT, Jeng US, Polymer, 53, 3360 (2012).
9) Kamal T, Park SY, Park JH, Chang YW, Macromol Res, 20, 725 (2012).
10) Sheth JP, Xu J, Wilkes GL, Polymer, 44, 743 (2003).
11) Maeda S, Okushita H, Nihon Reoroji Gakkaishi (J Soc Rheol Jpn), 47, 119 (2019).
12) McFerran NLA, Armstrong CG, McNally T, J Appl Polym Sci, 110, 1043 (2008).
13) Nitta KH, Sawada T, Yoshida S, Kawamura T, Polymer, 74, 30 (2015).
14) Bower DJ, Maddams WF, “The Vibrational Spectroscopy of Polymers”, (1992), Cambridge University Press, NY.
15) Clough S, Van Aartsen JJ, Stein RS, J Appl Phys, 36, 3072 (1965).
16) Wang HP, Chum SP, Hiltner A, Baer E, J Polym Sci Part B Polym Phys, 47, 1313 (2009).
17) Brandrup J, Immergut E, Grulke EA, “Polymer Handbook”, (1999), John Wiley & Sons Inc, NY.
18) Hucher C, Eustache RP, Beaume F, Tekely P, Macromolecules, 38, 9200 (2005).
19) Fox TG, Bull Am Phys Soc, 1, 123 (1956).
20) Hobeika S, Men Y, Strobl G, Macromolecules, 33, 1827 (2000).
21) Al-Hussein M, Strobl G, Macromolecules, 35, 8515 (2002).
22) Hong K, Rastogi A, Strobl G, Macromolecules, 37, 10174 (2004).
23) Men Y, Rieger J, Strobl G, Phys Rev Lett, 91, 095502 (2003).
24) Lu Y, Wang Y, Chen R, Zhao J, Jiang Z, Men Y, Macromolecules, 48, 5799 (2015).
25) Lu Y, Men Y, Macromol Mater Eng, 303, 1800203 (2018).
26) Liu LZ, Hsiao BS, Fu BX, Ran S, Toki S, Chu B, Tsou AH, Agarwal PK, Macromolecules, 36, 1920 (2003).
27) Pawlak A, Gałęski A, Rozanski A, Prog Polym Sci, 39, 921 (2014).
28) Paolucci F, Govaert L, Peters G, Polymers, 11, 1001 (2019).