

Title	Thermal Expansion Behavior of Antiplasticized Polycarbonate
Author(s)	Miyagawa, Azusa; Nobukawa, Shogo; Yamaguchi, Masayuki
Citation	日本レオロジー学会誌 (Journal of the Society of Rheology, Japan), 42(4): 255-260
Issue Date	2014
Type	Journal Article
Text version	publisher
URL	<a href="http://hdl.handle.net/10119/12869">http://hdl.handle.net/10119/12869</a>
Rights	本著作物は日本レオロジー学会の許可のもとに掲載するものです。This material is posted here with permission of the Society of Rheology, Japan. Copyright (C) 2014 日本レオロジー学会. Azusa Miyagawa, Shogo Nobukawa, Masayuki Yamaguchi, 日本レオロジー学会誌 (Journal of the Society of Rheology, Japan), 42(4), 2014, 255-260. <a href="http://dx.doi.org/10.1678/rheology.42.255">http://dx.doi.org/10.1678/rheology.42.255</a>
Description	

# Thermal Expansion Behavior of Antiplasticized Polycarbonate

Azusa MIYAGAWA, Shogo NOBUKAWA, and Masayuki YAMAGUCHI<sup>†</sup>

School of Materials Science,  
Japan Advanced Institute of Science and Technology  
1-1 Asahidai, Nomi, Ishikawa 923-1292 JAPAN  
(Received : May 7, 2014)

Thermal expansion behavior and viscoelastic properties of antiplasticized polycarbonate (PC) are studied employing *p*-terphenyl (*p*-tPh) as an antiplasticizer. The rheological characterization reveals that the free volume fraction at the glass transition temperature and thermal expansion coefficient of the free volume in the rubbery region are unchanged by the *p*-tPh addition. However, the linear coefficient of thermal expansion in the glassy region is found to be reduced, which can be attributed to the reduction of free volume in the glassy state. Since the antiplasticized PC exhibits high modulus with a low thermal expansion coefficient, its suitability as a replacement for inorganic glasses will be considered.

**Key Words:** Polycarbonate / Antiplasticization / Mechanical properties / Viscoelastic properties / Thermal expansion

## 1. INTRODUCTION

Because of its excellent transparency, mechanical toughness and high heat-distortion temperature, polycarbonate (PC) is widely employed in optical applications such as plastic glasses, optical disks, and optical films.<sup>1-3)</sup> A lightweight replacement for an inorganic glass is being developed due to strong demand in the automobile industry to reduce the weight of electric vehicles. In order to serve as a replacement for an inorganic glass, however, rigidity and the dimensional stability under temperature change need to be improved.

The role of a conventional plasticizer is, in general, to increase the flexibility in the solid state and flowability in the molten state.<sup>4-12)</sup> A plasticizer weakens the intermolecular topological interaction between neighbor polymer chains, leading to low viscosity in the flow region. Furthermore, the glass-to-rubber transition occurs at low temperature because the relaxation time of the segmental motion is shortened. Even in the glassy state, a plasticizer usually enlarges the free volume fraction, which has been revealed by the positron annihilation lifetime spectroscopy,<sup>4,5,8)</sup> proton spin-lattice relaxation at nuclear magnetic resonance<sup>13,14)</sup> and pressure-

volume-temperature diagram.<sup>15)</sup> Because of the enlarged free volume, the modulus decreases and the thermal expansion increases.<sup>11)</sup>

To counter this normal behavior of plasticization, additives known to enhance the modulus are used, which is called antiplasticization. According to previous studies,<sup>3,15-27)</sup> the decrease in the free volume is believed to be the origin of the modulus enhancement. Therefore,  $\beta$ -relaxation of an amorphous polymer, *i.e.*, local relaxation mode, is strongly affected by an antiplasticizer, because the mobility in a local mode is suppressed by loss of the free volume. This anomalous but well-known behavior has been reported for various polymers including poly(vinyl chloride),<sup>17-19)</sup> poly(methyl methacrylate),<sup>15,18,24)</sup> and cellulose esters.<sup>18,26,27)</sup> PC is also known to show antiplasticization when combined with various materials.<sup>3,16-18,20,22)</sup> The addition of an antiplasticizer enhances the modulus and reduces the  $\beta$ -relaxation mode located around at  $-100$  °C, which is attributed to mechanisms such as ring-flip process of phenyl groups<sup>28,29)</sup> and rotation of the phenylene rings.<sup>30)</sup>

Although numerous researches have been carried out on antiplasticization, to the best of our knowledge, the thermal expansion behavior of an antiplasticized glass has not yet been reported; this phenomenon should be clarified to improve our understanding of antiplasticization. Considering the mechanism of antiplasticization, it can be predicted that

<sup>†</sup> Corresponding to Masayuki Yamaguchi  
School of Materials Science, Japan Advanced Institute of Science and Technology  
1-1 Asahidai, Nomi, Ishikawa 923-1292 Japan  
Tel: +81-761-51-1621, Fax: +81-761-51-1621, E-mail: m\_yama@jaist.ac.jp

thermal expansion will be reduced because of the decrease in the free volume.

In this paper, thermal expansion behavior and viscoelastic properties of PC are investigated using several blends of PC with *para*-terphenyl (*p*-tPh). Since large thermal expansion is a serious problem for glassy polymers used in various applications instead of an inorganic glass, the results will have important implications for industrial applications.

## 2. EXPERIMENTAL

### 2.1 Materials

The polymeric material used in this study was a commercially available bisphenol A polycarbonate (PC) (Teijin Chemicals, Panlite L-1225Y). The number and weight-average molecular weights, which were characterized by a gel permeation chromatography (Tosoh, HLC-8020) with TSK-GEL/GMHXL, were 19,000 and 97,000, respectively, as a polystyrene standard.

*Para*-terphenyl (*p*-tPh), purchased from Tokyo Chemical Industry, was employed as an antiplasticizer in this study without further purification.

Melt-mixing of PC with *p*-tPh was performed using a 60 cm<sup>3</sup> batch-type internal mixer (Toyoseiki, Labo-plastmill) at 240 °C. The rotational speed of the blades was 30 rpm, and the mixing time was 3 min. The mixture obtained was compressed into a flat sheet with a thickness of 300 μm or 3 mm by a compression-molding machine (Tester Sangyo, Table-type-test press SA-303-I-S) for 3 min at 240 °C under 10 MPa, and subsequently quenched at room temperature. The films obtained were annealed for 20 min at  $T_{\alpha} + 15$  °C, where  $T_{\alpha}$  is the peak temperature of tensile loss modulus  $E''$  at 10 Hz ascribed to  $\alpha$ -relaxation, to remove the residual strain.

### 2.2 Measurements

The temperature dependence of oscillatory tensile moduli in the solid state, such as storage modulus  $E'$  and loss modulus  $E''$ , was measured from -150 °C to 180 °C using a dynamic mechanical analyzer (UBM, Rheogel-E4000). The frequency and heating rate were 10 Hz and 2 °C/min, respectively. The rectangular specimen, in which the width is 5.0 mm, the length is 10 mm, and the thickness is 300 μm, was employed.

The angular frequency dependence of  $E'$  and  $E''$  was also measured at various temperatures using the dynamic mechanical analyzer.

Thermal analysis was conducted by a differential scanning calorimeter (DSC) (Mettler, DSC820) under a nitrogen atmosphere. The samples were heated from room temperature to 160 °C at a heating rate of 10 °C/min. The sample amount

in an aluminum pan was approximately 10 mg in weight.

The thermal expansion behavior was evaluated by a thermo mechanical analyzer (Bruker AXS, TMA4000SA) in a compression mode under a constant stress of 3.2 kPa. The initial length of the specimen was 3 mm and the cross-sectional area was 25 mm<sup>2</sup>. Measurements were carried out from 20 °C to 100 °C at a heating rate of 2 °C/min under a nitrogen atmosphere. The linear coefficient of thermal expansion  $\beta$  was calculated using eq.1.

$$\beta = \frac{1}{L_0} \frac{dL}{dT} \quad (1)$$

where  $L_0$  is the initial length.

## 3. RESULTS AND DISCUSSION

Figure 1 shows the temperature dependence of oscillatory tensile modulus for PC containing 0-20 wt% of *p*-tPh at 10 Hz. As seen in the figure, the storage modulus  $E'$  decreases slightly around at -100 °C. Correspondingly, the loss modulus  $E''$  shows a broad peak at this temperature. This is known as  $\beta$ -relaxation and can be ascribed to the local motion of the main chain.<sup>28-30</sup> In the temperature region beyond the  $\beta$ -relaxation,  $E'$  keeps almost a constant value until the glass-to-rubber transition, although there is a weak peak around at 75 °C. Then, it falls off sharply at 160 °C. This is a typical dynamic mechanical spectrum for a glassy polymer. The samples containing *p*-tPh show a weak  $\beta$ -relaxation peak as compared with the pure PC. As similar to other antiplasticized systems, *p*-tPh only reduces the mobility of local chains by filling the free volume of PC, which has been reported by a number of researchers using various antiplasticizers.<sup>3,16-18,20-22</sup> In fact, there is no peak shift in the infra-red spectra (but not present here) by the *p*-tPh addition.

Moreover, the shoulder peak around at 75 °C is found to be pronounced in the blend. This shoulder peak, called  $\beta'$ -relaxation, is often observed in blends with a diluent. According to Belfiore *et al.*,<sup>20</sup> this is attributed to the local motion of an entire PC repeat unit by chain co-operativity with diluent molecules. Furthermore,  $E'$  around at room temperature is enhanced by the addition of *p*-tPh, demonstrating that *p*-tPh acts as an antiplasticizer. Finally, the peak temperatures of  $\alpha$ -relaxation  $T_{\alpha}$ 's of the blends are lower than that of the pure PC. The height and half-width of the  $E''$  peak for the blend are almost the same as those for PC. The result suggests that the distribution of relaxation time is not changed greatly by *p*-tPh, although the blends demonstrate shorter relaxation time. Considering that most plasticizers

broaden the relaxation peak owing to the broad distribution of relaxation time, *p*-tPh shows good miscibility with PC. However, the blend with 20 wt% of *p*-tPh is not transparent but opaque, whereas the blends with less than 15 wt% of *p*-tPh are transparent, as shown in Figure 2. Even for the blend with 20 wt% of *p*-tPh, the compressed film, prior to exposure to annealing procedure at  $T_{\alpha} + 15$  °C, is transparent. The results indicate that the maximum amount of *p*-tPh to show the miscibility with PC is approximately 15 wt% at the annealing temperature.

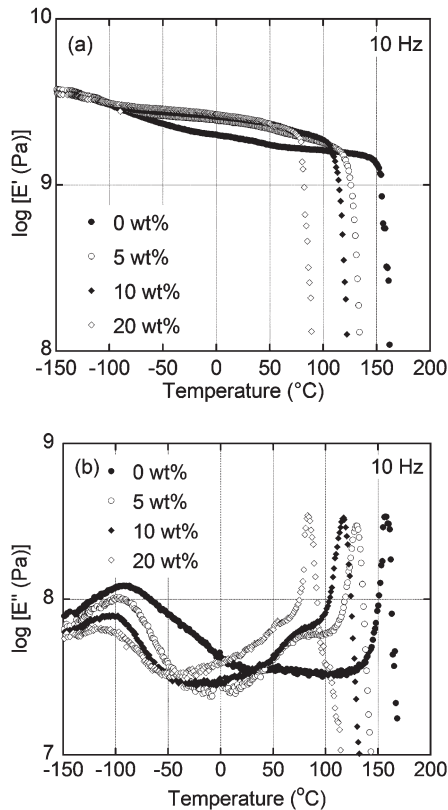


Fig. 1. Temperature dependence of (a) tensile storage modulus  $E'$  and (b) loss modulus  $E''$  at 10 Hz for (closed circles) PC, (open circles) PC/*p*-tPh (5 wt%), (closed diamonds) PC/*p*-tPh (10 wt%), and (open diamonds) PC/*p*-tPh (20 wt%).



Fig. 2. Sample specimens with 300  $\mu\text{m}$  thickness; (top) 10 wt% and (bottom) 20 wt% of *p*-tPh.

That the antiplasticizing effect is observable when the chain mobility in a local mode is reduced by loss of the free volume is well known.<sup>22,31)</sup> Therefore, the modulus enhancement has a close relationship with the intensity of  $\beta$ -relaxation mode.

Figure 3 shows  $E'$  at room temperature of the blends as a function of *p*-tPh content. The modulus increases monotonically with increasing *p*-tPh and seems to reach a plateau value beyond 10 wt%. The result indicates that the filling effect of free volume is saturated around 10 wt% of *p*-tPh. This is expected because the free volume fraction in the glassy state is believed to be around 2.5 vol%. The excess amount of *p*-tPh, which does not fill the free volume, will act as a conventional plasticizer, leading to the decrease in  $T_{\alpha}$ , as shown in Figure 4.

In Figure 4, the calculated values following the Gordon-Taylor equation<sup>32)</sup> (eq.2) are represented by the solid line, assuming that  $T_{\alpha}$  of *p*-tPh is  $-28$  °C, which is similar to that of *ortho*-terphenyl ( $-30$  °C).<sup>33)</sup>

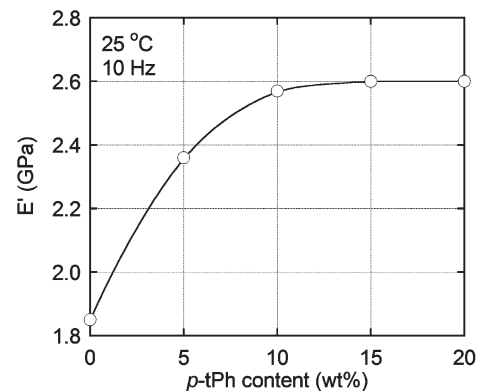


Fig. 3. Tensile storage modulus at 25 °C for PC/*p*-tPh.

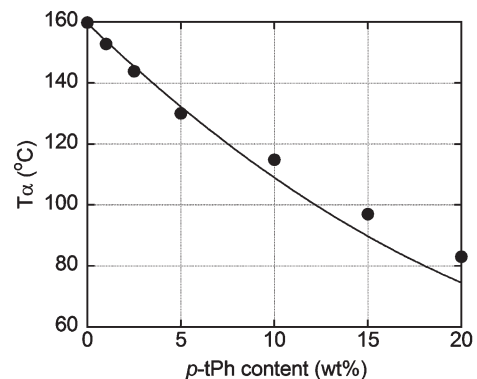


Fig. 4. Peak temperature of  $E''$  ascribed to  $\alpha$ -relaxation,  $T_{\alpha}$ , for PC/*p*-tPh.

$$T_{\alpha} = \frac{w_{PC}T_{\alpha-PC} + kW_{tPh}T_{\alpha-tPh}}{w_{PC} + kW_{tPh}} \quad (2)$$

where  $w_i$  and  $T_{\alpha i}$  are the weight fraction and  $T_{\alpha}$  of  $i$  component, respectively, and  $k$  is a constant evaluated from the experimental data.

The experimental data track the solid line with a slight upward deviation for the blends containing more than 15 wt% of  $p$ -tPh. Since  $T_{\alpha}$  decreases monotonically with increasing  $p$ -tPh in the experimental range with a small deviation from the solid line, it is suggested that only a small amount of  $p$ -tPh is segregated from the matrix for the blend with 20 wt% of  $p$ -tPh.

In order to investigate the glass-to-rubber transition in detail, the master curves of the frequency dependence of oscillatory tensile moduli are obtained as exemplified in Figure 5. The glass transition temperature  $T_g$  evaluated by the DSC measurement is employed as the reference temperature; 150 °C for PC and 105 °C for the blend containing 10 wt% of  $p$ -tPh.

As is well known, the shift factor  $a_T$  follows the WLF (Williams-Landel-Ferry) equation as follows;

$$\log a_T = \frac{-c_1(T-T_r)}{c_2+(T-T_r)} \quad (3)$$

where  $c_1$  and  $c_2$  are the constants, and  $T_r$  is the reference temperature ( $T_r = T_g$  in Figure 5).

Further, the constants  $c_1$  and  $c_2$  are expressed by the free volume fraction at  $T_g$ , *i.e.*,  $f_g$  and the thermal expansion coefficient of the free volume in the rubbery region  $\alpha_f$  as follows;

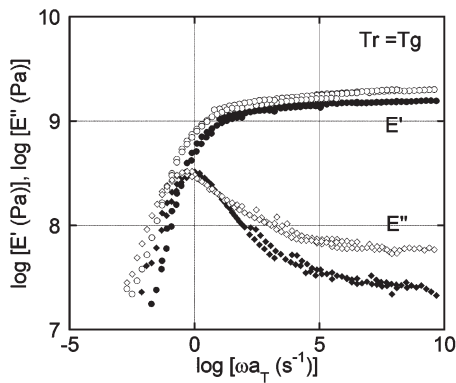


Fig. 5. Master curves of (circles) tensile storage modulus  $E'$  and (diamonds) loss modulus  $E''$  for (closed symbols) PC and (open symbols) PC/ $p$ -tPh (10 wt%). The reference temperature is  $T_g$  determined by DSC measurements.

$$c_1 = \frac{B}{2.303f_g}, \quad c_2 = \frac{f_g}{\alpha_f} \quad (4)$$

where  $B$  is a constant and generally considered to be unity.

The values of  $f_g$  and  $\alpha_f$  are summarized in Table I. It is found that neither parameter, *i.e.*,  $\alpha_f$  or  $f_g$ , was affected by the  $p$ -tPh addition considering the experimental error, which suggests that the glass-to-rubber transition occurs when the free volume fraction reaches a constant value even for antiplasticized systems. Moreover, the thermal expansion beyond  $T_g$  is expected to be independent of the  $p$ -tPh content.

Figure 6 shows the temperature dependence of the linear coefficients of thermal expansion  $\beta$  for PC and the blend with 5 wt% of  $p$ -tPh in the glassy state. The value of PC at room temperature is approximately  $70 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ , which is in harmony with the data reported previously.<sup>34,35</sup> It is demonstrated by the figure that  $p$ -tPh effectively reduces the thermal expansion of PC in the glassy state. Moreover, the blend shows a steep slope. Consequently, the reduction of the thermal expansion is not obvious at high temperatures. This is predictable because the free volume fraction at  $T_g$  that shifts to a lower temperature is not changed by the antiplasticizer.

Figure 7 shows the linear coefficients of thermal expansion at various temperatures as a function of  $p$ -tPh content. It is

Table I. Thermal expansion coefficients of free volume in the rubbery region and free volume fractions at  $T_g$  for PC and PC/ $p$ -tPh.

$p$ -tPh content (wt%)	$\alpha_f$ ( $\times 10^{-4} \text{ }^\circ\text{C}^{-1}$ )	$f_g$
0	1.9±1.0	0.017±0.005
5	1.6±0.8	0.016±0.004
10	1.6±0.8	0.015±0.004

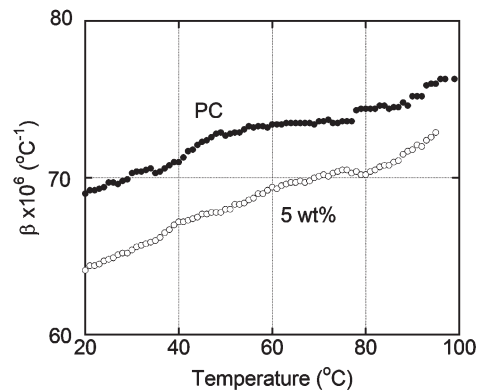


Fig. 6. Temperature dependence of linear coefficients of thermal expansion  $\beta$  for (closed) PC and (open) PC/ $p$ -tPh (5 wt%).

interesting to note that the values of the blend with 10 wt% of *p*-tPh are almost identical to those of PC/*p*-tPh (5 wt%), a similar trend to the modulus at room temperature.

It has been reported that conventional plasticizers enhance thermal expansion due to the increased anharmonicity of the potential function with low modulus.<sup>11)</sup> In this study, however, the opposite phenomenon is observed, which is presumably attributed to the reduction of free volume. Because marked thermal expansion is a severe problem for transparent plastics, the phenomenon should be noted. In fact, the thermal expansion coefficient is still higher than that of a typical inorganic glass (ca.  $7 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ ). However, the result should have an impact on the industrial applications, because it is close to the value of aluminum (ca.  $40 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ ); a material that is often used for frames.

#### 4. CONCLUSION

A small addition of *p*-tPh enhances the modulus in the glassy state, demonstrating that it acts as an antiplasticizer for PC. The  $\beta$ -relaxation mode of PC, attributed to the local motion of the main chain, is reduced due to the decrease in the free volume of PC. The free volume fraction at  $T_g$  is, on the contrary, unchanged by the addition of *p*-tPh.

Furthermore, thermal expansion in the glassy state is found to be reduced by the *p*-tPh addition without loss of excellent transparency when the content is lower than 15 wt%. This result is attributed to the low level of free volume fraction. Reduced thermal expansion will be a great benefit as it will allow a glassy polymer to be employed instead of an inorganic glass, thus potentially leading to the development of a new material design of a plastic glass.

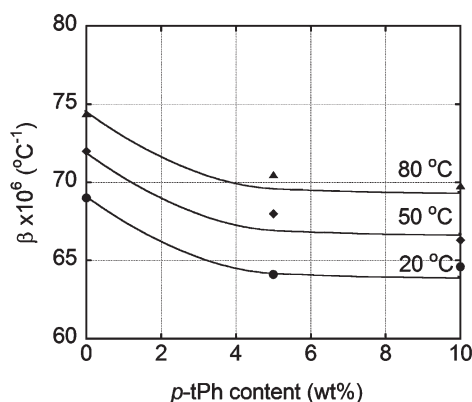


Fig. 7. Linear coefficients of thermal expansion  $\beta$  at various temperatures for PC/*p*-tPh; (circles) 20 °C, (diamonds) 50 °C, and (triangles) 80 °C.

#### REFERENCES

- 1) Claude B, Goron L, Verney V, Gardette JL, *Polym Test*, **20**, 771-778 (2001).
- 2) Uchiyama A, Yatabe T, *Jpn J Appl Phys*, **42**, 6941-6945 (2003).
- 3) Ueda MA, *Polym Eng Sci*, **44**, 1877-1884 (2004).
- 4) Borek J, Osoba W, *J Polym Sci, Part B: Polym Phys*, **34**, 1903-1906 (1996).
- 5) Borek J, Osoba W, *J Polym Sci, Part B: Polym Phys*, **36**, 1839-1845 (1998).
- 6) Xiao C, Wu J, Yang L, Yee AF, Xie L, Gidley D, Ngai KL, Rizos AK, *Macromolecules*, **32**, 7913-7920 (1999).
- 7) Dlubek G, Bondarenko V, Pionteck J, Supej M, Wutzler A, Krause-Rehberg, R, *Polymer*, **44**, 1921-1926 (2003).
- 8) Scott MP, Rahman M, Brazel CS, *Eur Polym J*, **39**, 1947-1953 (2003).
- 9) Yamaguchi M, Okada K, Manaf MEA, Shiroyama Y, Iwasaki T, Okamoto K, *Macromolecules*, **42**, 9034-9040 (2009).
- 10) Manaf MEA, Tsuji M, Shiroyama Y, Yamaguchi M, *Macromolecules*, **44**, 3942-3949 (2011).
- 11) Takahashi S, Okada H, Nobukawa S, Yamaguchi M, *Eur Polym J*, **48**, 974-980 (2012).
- 12) Yamaguchi M, Manaf MEA, Songsurang K, Nobukawa S, *Cellulose*, **19**, 601-613 (2012).
- 13) Liu Y, Roy AK, Jones AA, Inglefield PT, Ogden P, *Macromolecules*, **23**, 968-977 (1990).
- 14) Itagaki H, Ochiai A, Nakamori T, *Eur Polym J*, **42**, 1939-1952 (2006).
- 15) Razinskaya IN, Shtarkman BP, Izvozchikova VA, Averbakh NY, Monich IM, Bubnova LP, Pupukina NI, *Polym Sci U.S.S.R.*, **26**, 1806-1813 (1984).
- 16) Jackson WJ, Caldwell JR, *Adv Chem Ser*, **48**, 185-195 (1965).
- 17) Jackson WJ, Caldwell JR, *J Appl Polym Sci*, **11**, 211-226 (1967).
- 18) Jackson WJ, Caldwell JR, *J Appl Polym Sci*, **11**, 227-244 (1967).
- 19) Mascia L, *Polymer*, **19**, 325-328 (1978).
- 20) Belfiore LA, Henrichs PM, Cooper SL, *Polymer*, **25**, 452-458 (1984).
- 21) Kuz'min VP, Perepechko II, Zvonkova YM, Kerber ML, *Polym Sci U.S.S.R.*, **27**, 141-147 (1985).
- 22) Cais RE, Nozomi M, Kawai M, Miyake A, *Macromolecules*, **25**, 4588-4596 (1992).
- 23) Tiemblo P, Martinez G, Gomez-Elvira JM, Millan J, *Polym Bull*, **32**, 353-359 (1994).
- 24) Goodelle JP, Pearson RA, Santore MM, *J Appl Polym Sci*, **86**, 2463-2471 (2002).
- 25) Teyssedre G, Reinecke H, Corrales T, Navarro R, Tiemblo P, *Macromolecules*, **38**, 10820-10828 (2005).
- 26) Yamaguchi M, Masuzawa K, *Eur Polym J*, **43**, 3277-3282 (2007).
- 27) Yamaguchi M, Masuzawa K, *Cellulose*, **15**, 17-22 (2008).

- 28) Spiess HW, *Colloid Polym Sci*, **261**, 193-209 (1983).
- 29) Perchak D, Skolnick J, Yaris R, *Macromolecules*, **20**, 121-129 (1987).
- 30) Alegria A, Mitxelena O, Colmenero J, *Macromolecules*, **39**, 2691-2699 (2006).
- 31) Fischer EW, Hellmann GP, Spiess HW, Hörth FJ, Ecarius U, Wehrle M, *Makromol Chem Suppl*, **12**, 189-214 (1985).
- 32) Gordon M, Taylor JS, *J Appl Chem*, **2**, 493-500 (1952).
- 33) Chang SS, *J Chem Phys*, **79**, 6229-6236 (1983).
- 34) Gilmour W, Trainor A, Haward RN, *J Polym Sci, Part B: Polym Phys*, **16**, 1277-1290 (1978).
- 35) Seitz JT, *J Appl Polym Sci*, **49**, 1331-1351 (1993).