

A Thermomechanical Investigation of Highly Cold-Drawn Polycarbonate

T. KATO, *Utsunomiya University, Utsunomiya-shi*, and H. KAMBE,
Institute of Space and Aeronautical Science, University of Tokyo,
Tokyo, Japan

Synopsis

A new technique detecting molecular motions in drawn polymers was applied to highly cold-drawn polycarbonate of bisphenol A. It is shown that the sample exhibits thermal shrinkage in three steps with the temperature increase up to above the glass transition temperature. The molecular relaxation at the highest temperature is due to the glass transition. The other two molecular motions at the lower temperature are those of main chain in the glassy state and they correspond to the molecular motions as revealed in dielectric measurement by Sacher.¹ By using the general theory of the thermal analysis by Ozawa,² the apparent activation energies of these molecular motions were obtained: for the highest temperature 110 kcal/mole, and for the lowest temperature, 33.5 kcal/mole. The impact strength and the cold workability of this polymer are also discussed in relation to these molecular motions.

INTRODUCTION

Polycarbonate of bisphenol A shows an excellent impact strength over a wide range of temperature and a high ductility. It is therefore one of the most useful engineering plastics. Some investigators have reported that a fairly large molecular relaxation is found below room temperature for this polymer, but there still remains some confusion about the mechanism of this molecular relaxation.³⁻⁷ Heijboer⁸ suggested that if a polymer showed dynamic mechanical dispersion below room temperature originating from the movements within the main chain, the polymer should have good impact strength at room temperature. Along this suggestion, Locati and Tobolsky⁹ pointed out that the above molecular relaxation is a result of the superposition of two molecular processes, which plays an important role in the high impact strength of this polymer. Robeson and Faucher,¹⁰ Sacher,^{1,11,12} and Stefan and Williams,¹³ however, attributed the good impact property of this polymer to the small molecular motions observed above room temperature.

The authors reported in previous papers^{14,15} a new method for detecting molecular motions of main chains by measuring thermal shrinkage of cold-drawn polypyromellitimide under various rates of temperature increase. The apparent activation energies of these molecular processes were calculated by analyzing the experimental data.

In this report, this method was applied to highly cold-drawn polycarbonate of bisphenol A, and the relation of molecular motions with the impact strength and cold workability of this polymer is discussed to confirm the inferences of Sacher and others.

EXPERIMENTAL

The sample of polycarbonate of bisphenol A was Panlite, supplied by Teijin Kasei Co. Ltd. Viscosity measurements in tetrahydrofuran gave a weight-average molecular weight of 4.6×10^4 . Samples were cold drawn with a tensile machine at room temperature and under a strain rate of 0.02 min^{-1} . The sample begins to show necking above 7% strain, and the strain reaches 90% when the necking part extends to the whole sample under these conditions. But almost all strain seems to be recovered by thermal treatment up to above the glass transition temperature to this polymer, i.e., 153°C .

Thermal expansion of an annealed sample and thermal shrinkage of cold-drawn samples were measured with a thermomechanical analyzer manufactured by the Rigaku Denki Co. Ltd. The details of the instrument were described elsewhere.¹⁵ By using a derivative circuit, the rate of shrinkage was recorded simultaneously as a function of temperature (Fig. 1).

The sample was 70μ thick, 5 mm wide, and 10 mm long. The applied load was kept constant to 5 g. The tensile stress during shrinkage was about 10^6 dynes/cm^2 , and the strain caused by this stress was negligible in the glassy state.

RESULTS AND DISCUSSION

Figure 2 shows the thermal expansion of a sample annealed up to 140°C . The applied stress is about $1 \times 10^6 \text{ dynes/cm}^2$, and the strain caused by this stress can be neglected in the glassy state; but above the T_g , the sample shows a remarkable stretching even by this small stress. There are two inflection points in thermal expansion curve below the T_g . To show these clearly, a straight tangent line is also drawn in the figure. The two inflection points, one near 75°C and the other slightly above 120°C , correspond to the temperature regions where some kind of molecular motion takes place, as Millar¹⁶ and Boyer¹⁷ suggested. This result means that excess free volume is introduced by these molecular motions.

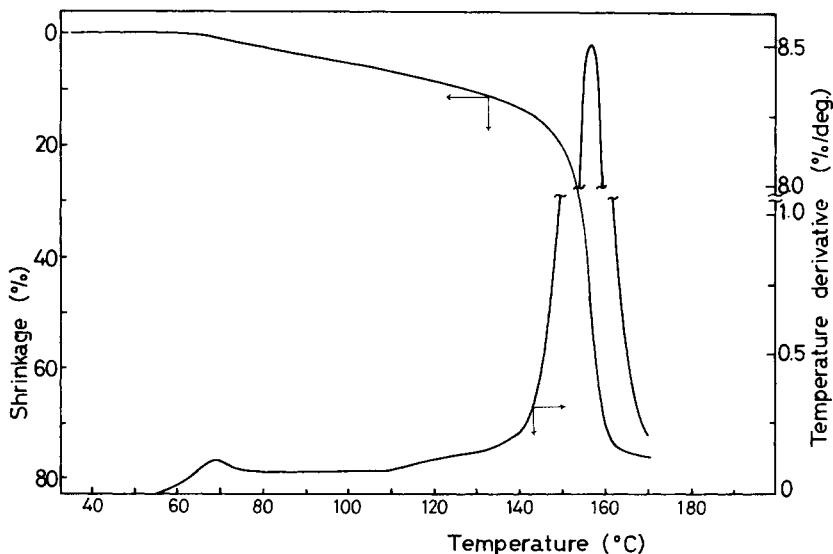


Fig. 1. Thermal shrinkage and temperature derivative curves of 80% cold-drawn polycarbonate, 5.2°C/min in air.

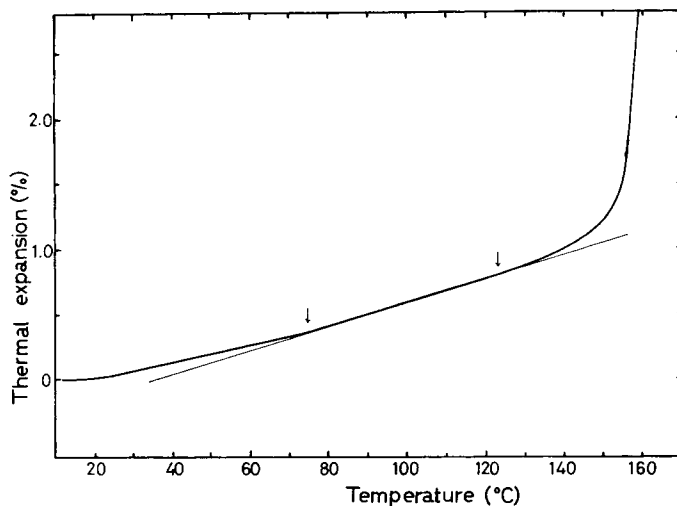


Fig. 2. Linear thermal expansion of an annealed, undrawn polycarbonate film, 2.5°C/min in air.

Figure 1 shows the thermal shrinkage curve and its temperature derivative curve of an 80% cold-drawn sample under uniform rate of heating. As seen from the figure, the sample shrinks gradually from about 50°C following an abrupt shrinkage at the glass transition region, and finally almost all strain seems to be recovered within experimental error. The temperature derivative of the shrinkage, $d(\Delta L)/dT$, gives more detailed informations about the thermal shrinkage of highly cold-drawn polycarbonate. There are two peaks and one shoulder shown in the temperature derivative curve. The peak at the highest temperature originates from a molecular motion at the glass transition. The second peak appears as a shoulder of the glass transition peak in the temperature derivative curve.

Ozawa² has shown that the peak temperatures T_m of the temperature derivative curves of the general thermal analysis could be linearly plotted with the logarithms of the uniform heating rate $\log v$, and the apparent activation energy of the process could be evaluated approximately from the slope of the straight line as follows:

$$\Delta E = - \frac{R}{0.4567} \frac{d \log v}{d(1/T_m)} \quad (1)$$

where ΔE and R are the apparent activation energies of the process and the gas constant, respectively.

Figure 3 shows the rate dependence of the temperature derivative curve for molecular motion at the lowest temperature range. Figure 4 shows the plot of the reciprocal peak temperature versus the logarithmic heating rate. As shown in the figure, the data give a straight line, and according to eq. (1) the apparent activation energy of this molecular motion was calculated from the slope of this line as 33.5 kcal/mole.

This molecular motion was first found by Krum and Müller³ and Illers and Breuer¹⁸ dielectrically for cold-drawn polycarbonate. They reported that this molecular motion disappeared by thermal annealing. For undrawn, nonannealed samples, Hara and Okamoto⁴ first observed this motion dielectrically, and

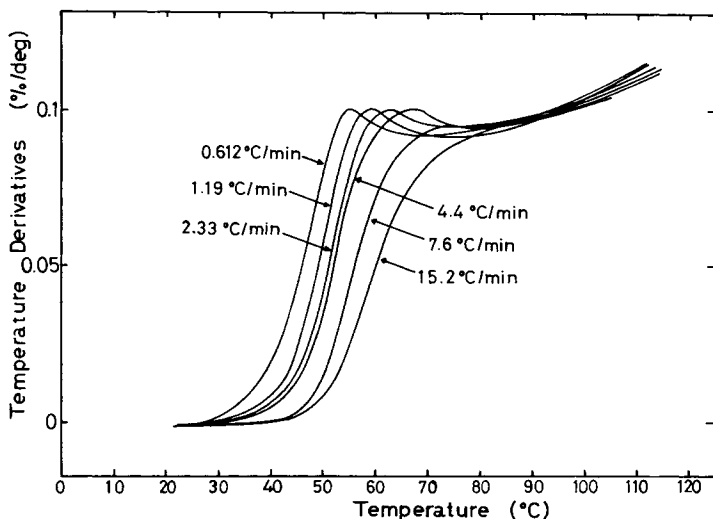


Fig. 3. Heating rate dependence of temperature derivative curves of 80% cold-drawn polycarbonate, low-temperature part.

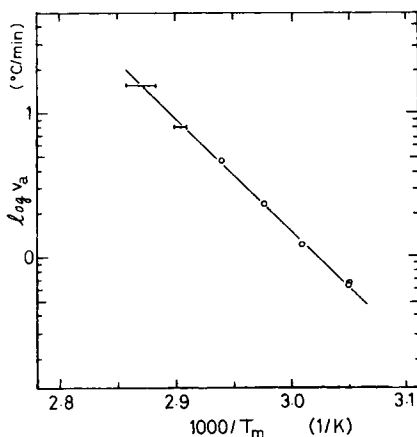


Fig. 4. Arrhenius plot of inverse maximum temperature vs logarithmic heating rate for 80% cold-drawn polycarbonate.

Miller¹⁶ also found this by several kinds of thermal analysis. For samples annealed up to T_g , Tomikawa and Fujimoto⁷ observed this dielectrically. Sacher^{1,11} and Stefan and Williams¹³ ascribed this molecular motion to a large-scale restricted rotation of the β -cumyl group moving as a unit, with cooperative motions of the adjacent phenylene and carbonyl groups, or to a restricted reorientation of phenylene and carbonate groups. But Ito et al.¹⁹ estimated that this might be closely associated with a molecular motion in the region having a good regularity. With our experimental results it is safe to say that this molecular motion is that of main chain because a motion of side groups does not cause thermal shrinkage. But this molecular motion is rather restricted because it recovers only about 10% of the strain frozen at cold drawing.

The apparent activation energy of this molecular motion, 33.5 kcal/mole, compares with the activation enthalpy, 20–37 kcal/mole reported by Sacher,²⁰ because the activation enthalpy is nearly equal to the apparent activation energy

in the Arrhenius equation measured in the solid state under low pressure. Ito et al.¹⁹ estimated the apparent activation energy to be about 20 kcal/mole, and Kochi et al.²¹ reported that the activation energy of this molecular process was around 14 kcal/mole.

Molecular motion just below the glass transition was reported by Kochi et al.²¹ for cold-drawn polycarbonate, and they found that this disappeared by thermal treatment. Lunn and Yannas^{22,23} found this by measuring the change in infrared dichroism and ascribed this to limited backbone motion, less extensive than the glass transition molecular motion. The activation enthalpy obtained for this molecular motion was scattered from 49 to 460 kcal/mole with annealing condition.²⁰ Our experimental results could not give an apparent activation energy because the temperature derivative curves did not give a peak in this temperature region, but it is obvious by the same reason as before that this molecular motion is also that of main chains.

We found that in annealed polypyromellitimide samples, three kinds of inherent molecular motion are restrained by strong intra- or intermolecular interactions, but in cold-drawn samples, they appear again with the aid of frozen strain energies.¹⁵ Polypyromellitimide is well known by its excellent thermal stability, but it also shows characteristic mechanical properties by not losing its toughness over a wide range of temperature, and it can be stretched to a high degree without showing necking at low temperature. Molecular motions are responsible for these characteristic mechanical properties of polypyromellitimide. According to the above considerations and our experimental results of cold-drawn polycarbonate, the conditions are quite the same for polypyromellitimide and this polycarbonate.

The two molecular motions below T_g of polycarbonate, named β and γ by Sacher,¹ are the large-scale and inherent molecular motions of this polymer in these temperature regions, but they seem to be restrained by intra- or intermolecular interactions and become small in an annealed sample. Therefore there was some confusion about the existence of these molecular motions. As Sacher reported,¹ they can be observed only by highly sensitive measurements for annealed samples. In the case of cold-drawn samples, they can be easily detected by the aid of frozen strain energy.

When an impact force is applied to this polymer, these molecular motions are activated easily by the impact energy, and the energy is dissipated into heat because of the large degree of motional freedom of these molecular motions. Therefore these motions are responsible for the good impact property of this polymer above room temperature. This explanation confirms those reported by Robeson and Faucher,¹⁰ Sacher,^{1,11,12} and Stefan and Williams.¹³ It was also reported by Vincent²⁴ that some kind of impact strength of polycarbonate increased significantly with temperature in these temperature regions.

Polycarbonate is one of the engineering plastics expected to be worked in the cold. The cold workability of this polymer has been ascribed to the δ relaxation detected around -100°C . According to the above discussion, however, it is natural to consider that these "restrained" or "stress-induced" molecular motions above room temperature are also responsible for the cold workability of this polymer, because the impact deformation and cold working are essentially the problems of large deformation under high stress. Robertson²⁵ reported that yield stress of this polymer decreased rather rapidly with temperature increase from 30° to 120°C and abruptly above 120°C .

Figure 5(a) and 5(b) show the heating rate dependence of thermal shrinkage and temperature derivative curves around T_g for 80% cold-drawn polycarbonate. Figure 6 shows the relation of the reciprocal peak temperature versus the logarithmic heating rate. Neglecting the small deviation at higher heating rate, the data also give a straight line, and an apparent activation energy of the glass transition of 110 kcal/mole can be obtained coincident with the values 115 ± 5 kcal/mole by Krum and Müller³ and 103–110 kcal/mole by Matz et al.^{26,27} However, a very large value, 333 kcal/mole,²⁸ and a very small value, 22.5 kcal/mole,²⁹ were also reported.

It is not clear yet whether the deviation from a straight line at the higher heating rate in Figure 6 may be attributed to the time lag of the sample temperature to that recorded at a higher rate or whether there is an essential cause that makes this theory inapplicable to the shrinkage in the glass transition region. Barton³⁰ has reported that the glass transition of poly(5-ethylresorcinol isophthalate) could be treated as a rate process of first-order reaction kinetics, and he obtained an apparent activation energy of the glass transition. McMillan³¹ has also treated the glass transition of glycerol as a rate process of n th order and obtained an apparent activation energy from an Arrhenius plot. On the other

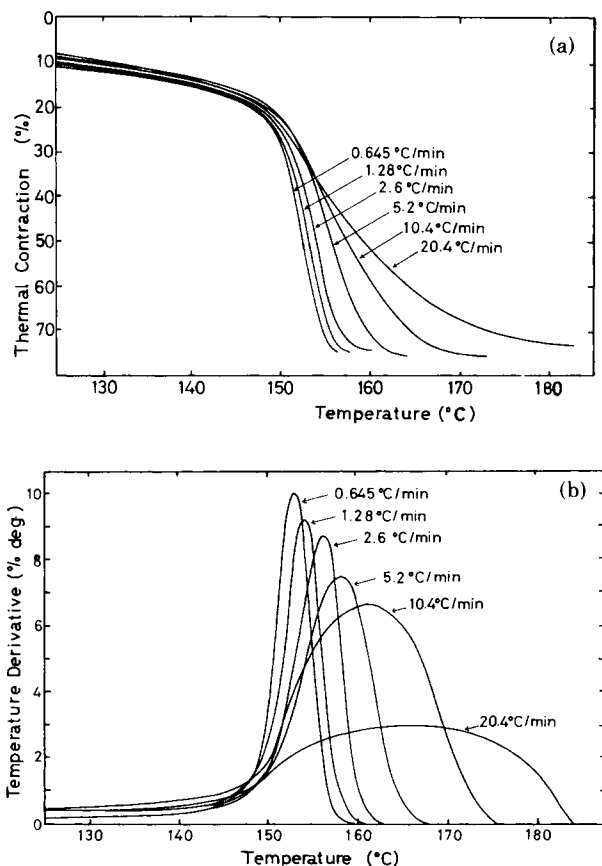


Fig. 5. (a) Heating rate dependence and (b) temperature derivative curves of thermal shrinkage of 80% cold-drawn polycarbonate, high-temperature part.

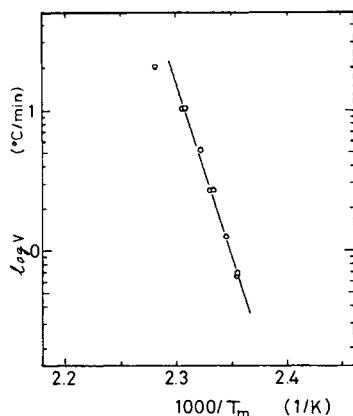


Fig. 6. Arrhenius plot of inverse maximum temperature vs logarithmic heating rate for 80% cold-drawn polycarbonate, high-temperature part.

hand, Ishinabe et al.^{32,33} have reported that thermal shrinkage of hot-drawn poly(methyl methacrylate) and poly(ethylene terephthalate) obeyed the WLF equation above their glass transition temperatures. Rusch³⁴ has also reported that the dimensional recovery of cold-rolled polycarbonate fits well the WLF equation above its glass transition temperature.

If the cause of the deviation from a straight line at the higher heating rate in Figure 6 is the time lag of the sample temperature, the same deviation should be observed in Figure 4. If not, another theory would be necessary to analyze the thermal shrinkage of cold-drawn polymers around their glass transition temperatures.

Part of this work was supported by a grant-in-aid for scientific research of the Japanese Government given to T. Kato in 1975, and this is much appreciated. The sample of the Panlite film was kindly supplied by the Teijin Kasei Co. Ltd.

References

1. E. Sacher, *J. Macromol. Sci.-Phys.*, **B9**, 163 (1974).
2. T. Ozawa, *J. Thermal Anal.*, **2**, 301 (1970).
3. F. Krum and F. H. Müller, *Kolloid-Z.*, **164**, 81 (1959).
4. T. Hara and S. Okamoto, *Jpn. J. Appl. Phys.*, **3**, 499 (1964).
5. S. Matsuoka and Y. Ishida, *J. Polym. Sci. C*, **14**, 247 (1966).
6. G. Vosskötter and R. Kosfeld, *Kolloid-Z. Z. Polym.*, **216-217**, 85 (1967).
7. M. Tomikawa and N. Fujimoto, *Kobunshi Kagaku*, **25**, 625 (1968).
8. J. Heijboer, *J. Polym. Sci. C*, **16**, 3755 (1968).
9. G. Locati and A. V. Tobolsky, *Adv. Mol. Relax. Proc.*, **1**, 375 (1970).
10. L. M. Robeson and J. A. Faucher, *Polym. Lett.*, **7**, 35 (1969).
11. E. Sacher, *J. Macromol. Sci.*, **B11**, 403 (1975).
12. E. Sacher, *J. Appl. Polym. Sci.*, **19**, 1421 (1975).
13. D. Stefan and L. Williams, *J. Appl. Polym. Sci.*, **18**, 1279 (1974).
14. H. Kambe and T. Kato, *Appl. Polym. Symp.*, **No. 20**, 365 (1973).
15. H. Kambe, T. Kato, and M. Kochi, *J. Macromol. Sci.-Chem.*, **A8**, 157 (1974).
16. G. W. Miller, *ACS Prepr.*, **9**(1), 832 (1968).
17. R. F. Boyer, *Polym. Eng. Sci.*, **8**, 161 (1968).
18. K. H. Illers and H. Breuer, *J. Polym. Sci.*, **18**, 1 (1963).
19. E. Ito, S. Sawamura, and S. Saito, *Colloid Polym. Sci.*, **253**, 480 (1975).
20. E. Sacher, *J. Macromol. Sci.-Phys.*, **B10**, 319 (1974).
21. M. Kochi, T. Sasaki, M. Murakami, and H. Kambe, *Rep. Progr. Polym. Phys. Jpn.*, **17**, 307 (1974).

22. I. V. Yanas and A. C. Lunn, *J. Polym. Sci. B*, **9**, 611 (1971).
23. A. C. Lunn and I. V. Yanas, *J. Polym. Sci.-Phys.*, **10**, 2189 (1972).
24. P. I. Vincent, *Polymer*, **15**, 111 (1974).
25. R. E. Robertson, *J. Appl. Polym. Sci.*, **7**, 443 (1963).
26. D. J. Matz, W. G. Guldmond, and S. L. Cooper, *J. Polym. Sci.-Phys.*, **10**, 1917 (1972).
27. D. J. Matz, W. G. Guldmond, and S. L. Cooper, *Polym. Eng. Sci.*, **13**, 300 (1973).
28. A. F. Lewis, *J. Polym. Sci. B*, **1**, 649 (1963).
29. J. B. Park and D. R. Uhlmann, *J. Appl. Phys.*, **41**, 2928 (1970).
30. J. M. Barton, *Polymer*, **10**, 151 (1968).
31. J. A. McMillan, *J. Chem. Phys.*, **42**, 3497 (1965).
32. T. Ishinabe, Y. Koike, and K. Ishikawa, *Zairyo (J. Mater. Sci.)*, **19**, 387 (1970).
33. T. Ishinabe, K. Shinoda, and K. Ishikawa, *Kobunshi Kagaku*, **29**, 56 (1972).
34. K. C. Rusch, *Polym. Eng. Sci.*, **12**, 288 (1972).

Received July 2, 1976

Revised February 25, 1977