JOURNAL OF MATERIALS SCIENCE **22** (1987) 2079–2082

Thermal expansion of irradiated polystyrene

H. N. SUBRAHMANYAM, S. V. SUBRAMANYAM
Department of Physics, Indian Institute of Science, Bangalore 560 012, India

A three-terminal capacitance technique has been used in the temperature range 80 to 340 K to measure the thermal expansion coefficient of γ-irradiated polystyrene. Below 290 K the expansion coefficient decreased with radiation dose due to the predominant effect of radiation-induced crosslinking. Above 290 K, however, the coefficient increased with radiation dose, due to the predominant effect of degradation which also occurred on irradiation of polystyrene in air.

1. Introduction

Information concerning the thermal properties of irradiated polymers is useful from both scientific and technological points of view. While there have been a few studies on the specific heat and thermal conductivity of irradiated polymers, no information is available on their thermal expansion [1]. We have investigated the thermal expansion of some technologically important polymers, such as polymethyl methacrylate, polystyrene, polytetrafluoroethylene and polyoxymethylene, as a function of gamma-radiation dosage. This paper presents our results of the thermal expansion of irradiated polystyrene in the temperature range 80 to 350 K.

Polystyrene is a highly radiation-resistant polymer whose radiation chemistry has been extensively reviewed [2–4]. When irradiated in vacuum, polystyrene is found to undergo crosslinking [5–12]. When irradiated in air, it has also been found to undergo simultaneous degradation [12–15]. The thermal conductivity of irradiated polystyrene at low dosages and at high temperatures has been studied by Bondarev *et al.* [16], and at high dosages and low temperatures by Reese *et al.* [17] who also studied the specific heat of irradiated polystyrene in the temperature range 1 to 4 K and 30 to 200 K. A similar study was made by Savina *et al.* [18].

2. Experimental details

2.1. Irradiation procedure

Commercial grade polystyrene (crosslinked polystyrene, Q200.5, Polypenco Ltd, UK) was used for our investigation. Samples ~0.01 m long and 0.01 m diameter cut from a rod, were irradiated in air and at room temperature with gamma rays from a ^{60}Co source at a rate of 0.26 Mrad h^{-1} at the Cotton Technological Research Laboratory, Bombay. Because polystyrene is known to be highly radiation resistant, the samples were irradiated to high dosages, from zero to 500 Mrad, in steps of 100 Mrad. The samples became pale yellow in colour on irradiation.

2.2. Infrared spectrum

The infrared spectra of powdered samples containing nujol were taken using the "Schimatzu" infrared spectrophotometer. The infrared spectrum for an unirradiated sample and for the sample irradiated to 500 Mrad are shown in Fig. 1 to facilitate comparison and to indicate the extent of crosslinking in our samples. The intensity of various bands (540 cm^{-1} band due to ring C–C bending, out of plane [19] 750 cm^{-1} band due to the phenyl group [20]; 1020 cm^{-1} band due to C–C stretch, in plane, symmetrical [19]; 1380 cm^{-1} band due to CH_3 deformation; 1460 cm^{-1} band due to CH_2 deformation [20]; 1490 cm^{-1} band due to C$=$C in plane skeletal vibration [21], decrease due to radiation-induced crosslinking.

2.3. Thermal expansion apparatus

The thermal expansion coefficient of the samples was measured using the three-terminal capacitance technique described in detail elsewhere [22]. In this technique, changes in the length of the sample are converted into changes in electrical capacitance which is then measured by using a ratio transformer bridge to a resolution of one part per million [23]. The three-terminal capacitance cell used for the purpose is shown in Fig. 2. Capacitor plate 2 is surrounded by a guard ring, 6, which is earthed. Capacitor plate 1 is connected to the "high" side of the ratio transformer bridge and capacitor plate 2 to the "low" side. Plate 1 rests on the top of the sample, 3, by means of three symmetrically placed springs, 4. By raising or lowering the sample platform, 5, the capacitance gap can be varied. By adjusting the nuts, 7, the parallelism of the capacitor gap can be adjusted. Mica sheets, 0.05 mm thick, are used to insulate plate 2 from the guard ring, 6, and also plate 1 from the body of the cell. The cell is suspended inside a copper chamber, 8, which is filled with helium exchange gas at a pressure of about 1 torr. The copper chamber is mounted inside another evacuated metal chamber which is immersed in a liquid nitrogen dewar.

The capacitance is measured by using a six-decade ratio transformer bridge developed in our laboratory to a resolution of one part per million [24]. The Brookdeal lock-in amplifier, model 9503, used as a null detector of the bridge, had a sensitivity of 1 μV and incorporated an oscillator which provided a sinusoidal signal of 10 V r.m.s. and 5 Hz to excite the bridge.

0022-2461/87 $03.00 + .12

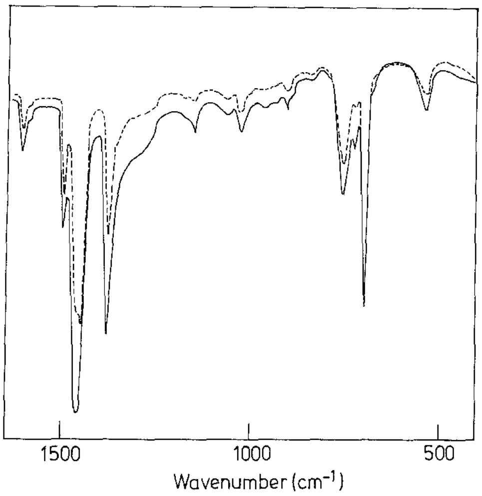

Figure 1 Infrared spectrum. (——) PSTY (0 Mrad), (– – –) PSTY (500 Mrad).

The temperature of the sample was measured and controlled to a resolution of 0.1 K by using Lake Shore Cryotronics digital thermometer/controller Model DRC-84C. The platinum resistance thermometer, P_1, mounted just below the sample platform, measured the sample temperature. Another platinum resistance thermometer, P_2, mounted on the copper chamber served as a sensor for the controller. A 25 Ω heater element was wrapped around chamber 1.

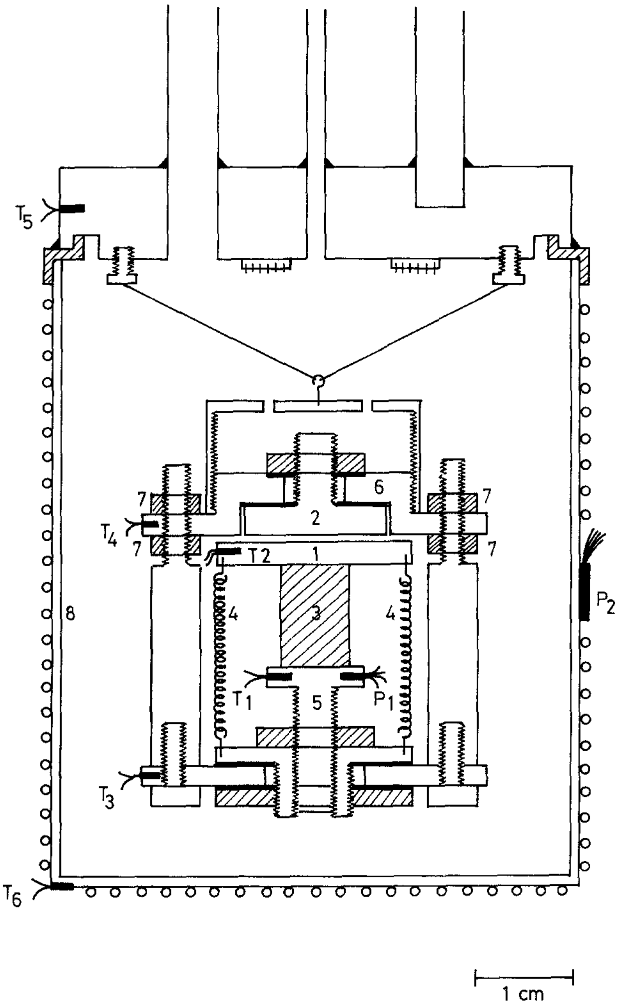

Figure 2 Three terminal capacitance cell. 1, 2, Capacitor plates; 3, sample; 4, symmetrically placed springs; 5, sample platform; 6, guard ring; 7, nuts; 8, copper chamber; T_1 to T_6, copper–constantan thermocouples; P_1, P_2, platinum resistance thermometers.

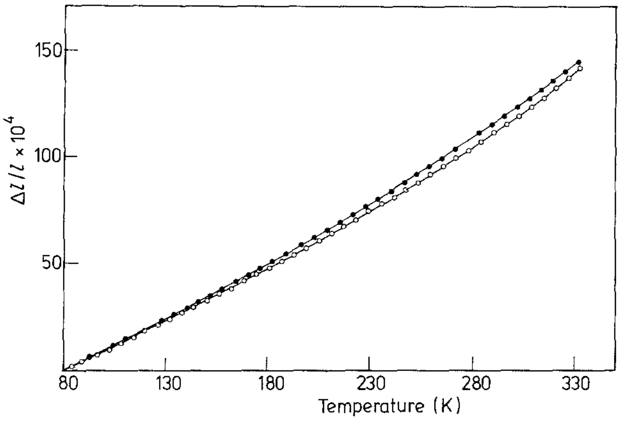

Figure 3 Variation of $\Delta l/l$ with temperature. (●) 0 Mrad, (○) 500 Mrad.

Thermal gradients across the sample were measured by two differential copper–constantan thermocouples, T_1, T_2, that cross the capacitance cell by T_3 and T_4, and that cross the copper chamber by T_5 and T_6.

2.4. Measuring procedure

The two circular ends of the cylindrical polystyrene samples were polished to render them flat and parallel to each other. The sample was mounted in the capacitor cell and slowly cooled to liquid nitrogen temperature over a period of 12 h. Heating was carried out in steps of 6 to 8 K using the temperature controller. For every stabilized temperature (stable for at least 45 min, indicated by no thermal gradients across the sample and the cell) the ratio transformer bridge was balanced and the reading taken which gives $1/C$ directly. Thus values of T and $1/C$ were recorded in the temperature range 80 to 340 K for polystyrene samples irradiated to 0, 100, 200, 300, 400 and 500 Mrad. The thermal expansion coefficient was calculated from the formula

$$\alpha_s = \left(\frac{L_c}{L_s}\right)\alpha_c - \left(\frac{0.156\,25}{L_s}\right)\frac{d}{dT}(1/C) \qquad (1)$$

where L_s is the length of the sample, L_c the length of the cell which contributes to the variation of the capacitance gap, α_c is the expansivity of the cell which is determined in a calibration experiment using aluminium and germanium as standard reference samples and which has been described elsewhere [22]. The derivative $(d/dT)(1/C)$ was determined by fitting the data of T against $1/C$ into a cubic spline with two equispaced knots and then differentiating by using a computer program. The expansivity of the sample, α_s, is then determined in accordance with Equation 1. The accuracy in the measurement of α_s is about 4%. The relative expansion $(\Delta l/l)$ of the sample is calculated from the formula

$$\left(\frac{\Delta l}{l}\right)_s = \left(\frac{L_c}{L_s}\right)\left(\frac{\Delta l}{l}\right)_c - \left(\frac{0.156\,25}{L_s}\right)\Delta(1/C) \qquad (2)$$

3. Results and discussion

The variation of $\Delta l/l$ with temperature for polystyrene irradiated to 0 and 500 Mrad is shown in Fig. 3. The thermal expansion coefficients for the samples irradiated to 0, 100, 300 and 500 Mrad are plotted together as a function of temperature in Fig. 4.

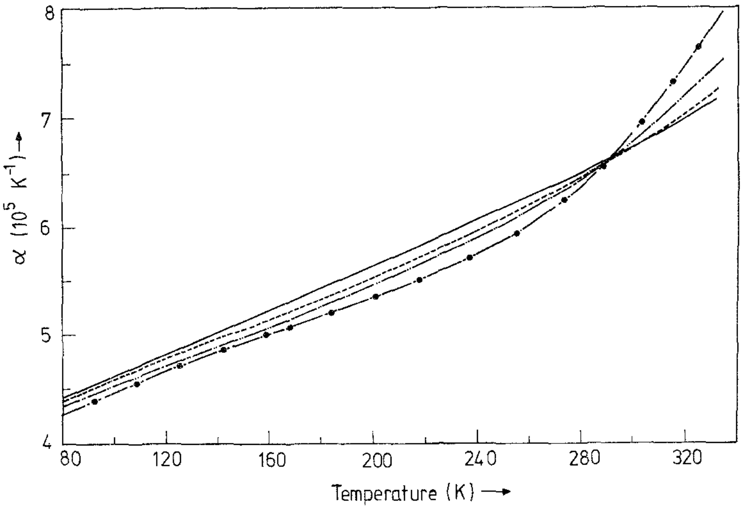

Figure 4 Variation of α with temperature. (——) 0, (– – –) 100, (– · · –) 300, (–●–) 500 Mrad.

Variation of α with radiation dosage at a few representative temperatures (e.g. 80, 240, 300 and 330 K) is shown in Fig. 5. It may be seen from these figures that α of polystyrene decreases with radiation dose in the temperature range 80 to 290 K. Around 290 K, this trend reverses and α begins to increase with radiation dose. The decrease in α is about 3.4% at 80 K and about 5.5% at 240 K; the increase in α is about 2% at 300 K and 9.6% at about 330 K.

The decrease in α with radiation dose in the temperature range 80 to 290 K is due to the crosslinking of polymer chains. With every crosslinking, a strong covalent bond is formed between the two polymer chains which are otherwise held by weak Van der Waal bonds. The thermal expansion coefficient of a solid depends on the strength of interaction of its constituent units. For a solid whose molecules are held by Van der Waal forces, the thermal expansion coefficient is larger by two orders of magnitude than that for a covalently bonded solid. Thus the relative increase in the covalent bonds caused by radiation-induced crosslinking is responsible for a decrease in α with increasing dose.

This conclusion is supported by similar results obtained during the study of thermal expansion of oriented polymers [25]. As the draw ratio is increased, the expansivity in the draw direction, $\alpha_{\parallel}$, decreases while the expansivity in the perpendicular direction, $\alpha_{\perp}$, increases. With an increase in the draw ratio, polymer chains become aligned along the draw direction, so that the relative increase in the interchain covalent bonds causes a decrease in $\alpha_{\parallel}$. Radiation-induced crosslinks play a similar role in decreasing expansivity.

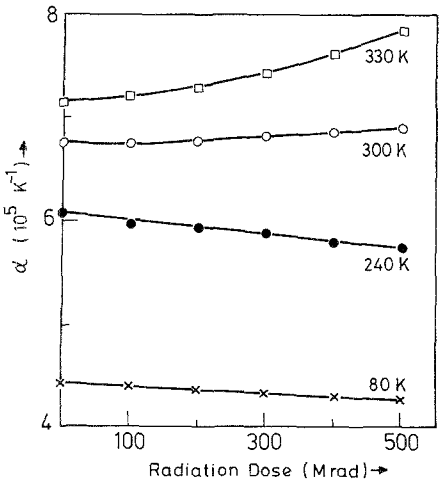

Figure 5 Variation of α with radiation dose.

The increase in thermal expansion coefficient with radiation dose above 290 K is a surprising observation. This is probably the result of the simultaneous degradation of polystyrene due to irradiation in air. When bulk polystyrene is irradiated in air, values of G for crosslinking and chain scission have been found to be the same [13]. When both crosslinking and degradation occur simultaneously, the effect of one on thermal expansion is opposed by the effect of the other. Further, crosslinking and degradation may have different temperature dependences so that they predominate in different temperature regions. The thermal expansion results indicate that the effect of crosslinking predominates in the low temperature region from 80 to about 290 K, whereas above 290 K, the effect of degradation predominates.

The thermal expansion studies on oriented amorphous polymers support the above conclusion [25, 26]. When an amorphous polymer is drawn, the decrease in $\alpha_{\parallel}$ is much more than the corresponding decrease in $\alpha_{\perp}$. Hence, by analogy, crosslinking should have a much more dominant effect on thermal expansion than degradation, so that the net effect of both of them is to decrease the thermal expansion coefficient. $\alpha_{\parallel}$ has also been found to have a weaker temperature dependence than $\alpha_{\perp}$, so that the anisotropy parameter $\alpha_{\perp}/\alpha_{\parallel}$ is larger at higher temperatures. Again, by analogy, crosslinking has a weaker temperature dependence than degradation, so that it predominates at lower temperatures while degradation predominates at higher temperatures.

Acknowledgements

The authors thank the Director of CTRL, Bombay, for providing the irradiation facilities, also DST and ISRO-IISc Space Technology Cell for financial assistance. One of the authors (H.N.S.) is grateful to UGC for the fellowship under Faculty Improvement Programme. The assistance of Messrs Govindaraju, Jayanna and Satish is gratefully acknowledged.

References

1. B. A. BRISKMAN, *Russian Chem. Rev.* **52** (1983) 469.
2. A. CHARLESBY, in "Atomic Radiation and Polymers" (Pergamon, Oxford, 1960) p. 284.
3. A. CHAPIRO, in "Radiation Chemistry of Polymeric Systems" (Interscience, New York, 1962) p. 446.
4. D. O. GEYMER, in "The Radiation Chemistry of Macromolecules", Vol. 2, edited by M. Dole (Academic Press, New York, 1974) p. 57.
5. J. A. SILVINSKAR and J. E. GUILLET, *J. Polym. Sci. Polym. Chem. Edn.* **11** (1973) 3057.
6. A. CHARLESBY, *Radiat. Phys. Chem.* **10** (1977) 177.
7. C. DAVID and D. BAEYENS-VOLANT, *Eur. Polym. J.* **14** (1978) 29.
8. J. H. O'DONNELL, C. A. SMITH and D. J. WINZON, *J. Polym. Sci. Polym. Phys. Edn.* **16** (1978) 1515.
9. J. H. O'DONNELL, N. P. RAHMAN and C. A. SMITH, *J. Polym. Sci. Polym. Chem. Edn.* **17** (1979) 4081.
10. YUICHI SHIMIZU and HIROSHI MITSUI, *ibid.* **17** (1979) 2307.
11. T. N. BOWMAN and J. H. O'DONNELL, *ibid.* **19** (1981) 1167.
12. S. EGUSA, K. ISHIGURE and Y. TOBOTA, *Macromol.* **13** (1980) 171.
13. J. M. NICHOL, J. H. O'DONNELL, N. P. RAHMAN and D. J. WINZOR, *J. Appl. Polym. Sci. Polym. Chem. Edn.* **15** (1977) 2919.
14. T. N. BOWMAN, L. K. COWER, J. H. O'DONNELL and D. J. WINZON, *J. Appl. Polym. Sci.* **24** (1979) 425.
15. M. C. GUPTA, B. S. SRIRAO, B. P. KANPHADE and V. P. BANSOD, *Polym. Commun.* **25** (1984) 334.
16. V. D. BONDAREV, B. A. BRISKMAN and V. P. SAVINA, *Plastmassy* **7** (1973) 7.
17. W. REESE, P. J. HIGGINS and G. W. ROSTINE, *J. Appl. Phys.* **39** (1968) 1800.
18. V. P. SAVINA, B. A. BRISKMAN and V. D. BONDAREV, *Vysokomol Soed.* **A14** (1972) 1180.
19. W. W. PARKINSON and R. M. KEYSTER, in "The Radiation Chemistry of Macromolecules", Vol. 2, edited by M. Dole (Academic Press, New York, 1974) p. 57.
20. H. W. THOMPSON and P. TORKINGTON, *Proc. R. Soc. (Lond.)* **A184** (1945) 3.
21. L. J. BELLAMY, "The Infrared Spectra of Complex Molecules" (Wiley, New York, 1958) p. 72.
22. H. N. SUBRAHMANYAM and S. V. SUBRAMANYAM, *Pramana* **27** (1986) 647.
23. G. K. WHITE, *Cryogenics* **1** (1961) 151.
24. P. P. KRISHNAPUR, S. V. SUBRAMANYAM and E. S. R. GOPAL, *Ind. J. Technol.* **17** (1979) 165.
25. L. H. WANG, C. L. CHOY and R. S. PORTER, *J. Polym. Sci. Polym. Phys. Edn.* **20** (1982) 633.
26. L. H. WANG, C. L. CHOY and R. S. PORTER, *ibid.* **21** (1983) 657.

Received 7 July
and accepted 23 July 1986