Journal of Thermal Analysis, Vol. 7 (1975) 187–190

DSC STUDY OF THE EFFECT OF IRRADIATION UPON THE GLASS TRANSITION TEMPERATURE (T_g) OF POLYETHYLENE

J. SIMON,* C. L. BEATTY** and F. E. KARASZ

Polymer Science and Engineering, University of Massachusetts, Amherst, Massachusetts, USA.

(Received January 29, 1973)

The glass transition of an irradiated, ultra-high molecular weight, linear polyethylene was investigated by means of the Perkin–Elmer DSC-2 differential scanning calorimeter. The experimental specific heat data were compared with those of the non-irradiated sample, obtained by DSC and adiabatic calorimetry.

The glass transition temperature (T_g) is an important parameter of both amorphous and semi-crystalline polymers, as many solid-state physical properties are related to it.

The glass transition of polymers can be considered in terms of a pseudo-second order transition. A true second order transition in the Ehrenfest sense results in discontinuities in the first derivatives of the primary thermodynamic variables, as a function of temperature. The glass transition in polymers exhibits important additional kinetic effects.

Although polyethylene is the simplest and perhaps most widely investigated polymer, its glass transition temperature continues to be a matter of controversy; this is primarily due to the relatively high crystallinity of polyethylene, which results in a small overall change in the thermodynamic properties of the polymer at T_g.

Many methods are known for determining T_g. A convenient "thermodynamic" definition of the glass transition is the point in the temperature range where the specific heat changes more or less abruptly. In the present case, with regard to the basic features of polyethylene, only the more sensitive measurement techniques can be considered.

A well-defined transition detected in linear polyethylene (LPE) by various methods occurs near −125°, another at −40° [1–5]. Recently, a considerable number of publications have appeared which involve the use of the DSC for the determination of the specific heats of different polymers [6–10]. Stehling and Mandelkern [11] determined the T_g of linear polyethylene by DSC experiments. A slight change was found at around −120° and was attributed to the T_g of LPE.

---

* *Institute for General and Analytical Chemistry of the Technical University, Budapest, Hungary*

** Xerox Corporation, Rochester, New York, USA.

Fyans [12] studied this effect with the Perkin – Elmer DSC-2 and found a small increase in the C_p value of LPE between – 123 and – 128°, which is in good agreement with data on ultra-high molecular weight (UHMW) LPE measured by Beatty and Karasz [13].

As a continuation of this work [12, 13] a sample of irradiated UHMW LPE has been investigated. The aim of this work was to attempt to increase the size of ΔC_p by reducing crystallinity at the apparent T_g to get additional confirmation of the second order transition in question. The effect required some changes in the sample and the experimental procedure.

Experimental

An ultra-high molecular weight linear polyethylene with a viscosity average molecular weight of about eight million and initially approximately 50% crystalline, was enclosed in an evacuated sealed ampule at 175° and irradiated with Co^{60} γ-radiation at this temperature at a dose rate of 5.63×10^6 rad. h^{-1}; the sample used received a total dose of about 100 megarad.

The heat capacity of this sample was then measured in a differential scanning calorimeter, model DSC-2, manufactured by the Perkin – Elmer Corporation, with a modified sample container permitting an enlarged sample to be used [14]. The programmed temperature was calibrated using the melting point of indium and transition temperature of cyclopentane. Measurements were performed as reported previously [15]. For the reference side high-purity benzoic acid was used instead of the usual sapphire, the heat capacity of the latter being strongly temperature-dependent in this temperature range. The C_p values for the benzoic acid were taken from the data of Ginnings and Furukawa [16].

A sample of irradiated polyethylene (ILPE) of about 30 – 35 mg was weighed into an aluminum pan and crimped. A scanning rate of 10° min^{-1} was used to cover a 50° scanning interval at a sensitivity setting of 0,2 $mcal.sec^{-1}$. The samples investigated were held in the melt at 190° for 5 min prior to quenching in liquid nitrogen for 2 min. Immediately after quenching the samples whose crystallinity was now reduced to about 20 – 25% were placed in the platinum sample container of the instrument, which was at – 163°. A few attempts were made to cool down the quenched sample at a cooling rate of 320° min^{-1}. It could be established that this program of the instrument was followed only until about – 50°, depending on the size of the sample. All these manipulations were performed in the dry box sub-ambient accessory of the DSC-2.

Results and discussion

The results of specific heat determination by adiabatic calorimeter and differential scanning calorimeter are presented graphically in Figure 1. The results of our measurements represent the average of three separate runs. The scatter in the observed values of the specific heat of ILPE was found to be about 1%. There is no appreciable difference between the data obtained by adiabatic calorimetry and DSC using the same molecular weight sample with the same thermal history. On the other hand, the precision of the scanning method approaches that of adiabatic calorimetry in spite of the sample being three orders of magnitude smaller and the heating rate considerably higher.

The effects of irradiation are observed as (1) an increase in the heat capacity change, ΔC_p, in the −133 to −128° interval, (2) a depression of the glass transition temperature, and (3) a slight shift to higher heat capacities at all temperatures.

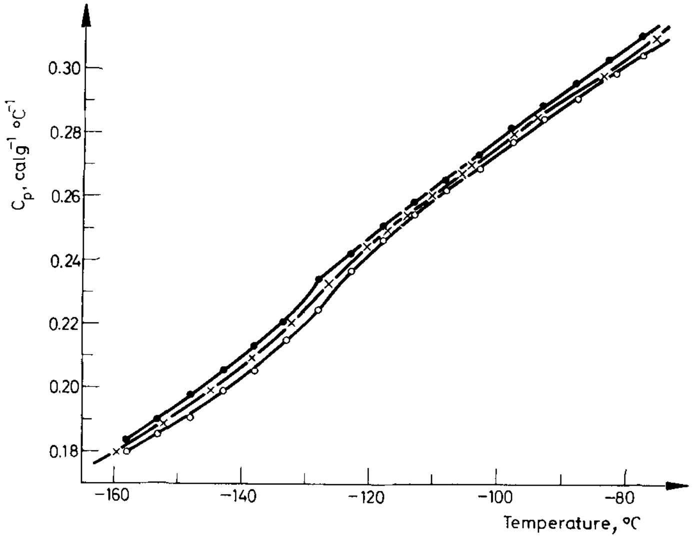

Fig. 1. Specific heat value of LPE, and ILPE as a function of temperature. × Data obtained by adiabatic calorimeter for LPE. Sample size: 40.882 g. Heating rate: 0.25°/min; ○ Data obtained by DSC-2 Perkin–Elmer for LPE. Sample size: 27 mg. Heating rate: 10°/min; of ● Data obtained by DSC-2 Perkin-Elmer for ILPE. Sample size: 34 mg. Heating rate: 10°/min

The increase in the heat capacity change glass transition is expected [17, 18] as the crystallinity of the polymer is reduced to 20–25% as measured by the DSC technique [19]. The slight absolute increase in heat capacities may be due to a forced reduction in density of the amorphous phase, due to the restraints imposed by cross-linking in the melt phase, which would also account for the lowering of the glass transition.

The results thus confirm the identification of the transition in the vicinity of −125° in linear polyethylene with the glass transition for this polymer.

*

The UMHW LPE sample was kindly donated by A. F. Margolies of Allied Chemicals Corporation. The irradiation was performed at the Brookhaven National Laboratory through the courtesy of Dr. D. Metz. The authors thank both for their valuable assistance. The work was supported by the Materials Research Laboratory and by Grant AFOSR 68–1434.

References

1. V. L. Bohn, Kolloid-Z., 194 (1964) 10.
2. W. V. Pechhold and G. Knauss, Kolloid-Z., 196 (1964) 27.
3. K. H. Illers, Rheol. Acta, 3 (1964) 202.
4. A. H. Willbourn, Trans. Faraday Soc., 5 (1958) 4717.
5. R. F. Boyer, Macromolecules, 6 (1973) 288.
6. S. Ichihara, A. Komatsu and Y. Tsujita, Polym. J., 2 (1971) 530.
7. S. Ichihara, A. Komatsu and T. Hata, Polym. J., 2 (1971) 640.
8. ibid, Polym. J., 2 (1971) 644.
9. G. W. Miller, J. Appl. Polym. Sci., 15 (1971) 2335.
10. D. Vučelić, V. Vučelić and N. Juranić, J. Thermal Anal., 5 (1973) 459.
11. F. C. Stehling and L. Mandelkern, Macromolecules 3 (1970) 24.
12. R. L. Fyans, personal communication.
13. C. L. Beatty and F. E. Karasz, to be published.
14. J. Simon and F. E. Karasz, Thermochim. Acta, 8 (1974), 97.
15. M. J. O'Neill, Anal. Chem., 38 (1966) 1331.
16. D. C. Ginnings and G. T. Furukawa, J. Am. Ceram. Soc., 75 (1933) 522.
17. C. M. Guttman, J. Chem. Phys., 56 (1972) 627.
18. S. S. Chang and A. B. Bestul, J. Chem. Phys., 56 (1972) 503.
19. A. P. Gray, Thermochim. Acta, 1 (1970) 563.