Polymer Bulletin 1, 845-848 (1979)

Polymer Bulletin

Calculation of Kinetic Parameters of Phase Transitions in Glassy Polymers

H. Kothandaraman and C. T. Vijayakumar

Department of Physical Chemistry, University of Madras, Madras-600 025, India

When a polymer is heated above T_g and then cooled to a temperature below T_g very slowly or when the polymer is kept at a temperature slightly below the T_g for a preset time interval, it is found that there is greater energy absorption at T_g. The extra energy involved appears as an added peak in the heat capacity versus temperature plot which is more similar to a first order type transition rather than an inflexion type transition. ELLERSTEIN (1) proposed the following expression to obtain the kinetic parameters associated with T_g directly from such data:

$$\left[\frac{\Delta \log (du/dT)}{\Delta \log \text{area III}}\right] = \left[\frac{-E}{2.3o3\ R}\right] \left[\frac{\Delta\ (1/T)}{\Delta \log \text{area III}}\right] + 1$$

Experiments were carried out in a Differential Scanning Calorimeter (Perkin-Elmer DSC-1B), using aluminum as the enthalpy calibrant.

In the present study the results obtained by M.J. RICHARDSON, et al. (2) for anionic polystyrene (PS) ($\bar{M}_n$: 36,000) were employed to test the validity of ELLERSTEIN's equation. The details of the sample history, the values of the intercept and the energy of activation are listed in Table I. The intercept values were found to be nearly zero. Systematic experiments were carried out with poly(ethyleneterephtha-

0170-0839/79/0001/0845/$01.00

late) (PET) (M_n: 22.000) and poly(vinyl alcohol) (PVA) (M: 125.000). The samples were cooled at different cooling rates, viz., 0.5, 1, 2, 4, 8, 16, 32 and 64°/min and reheated subsequently at a constant heating rate of 8°/min. When the PET samples were cooled at different rates of 8°/min and above and reheated at a constant rate (8°/min), it was found that in all these cases there was no endothermal peak in the T_g region. However, at slower cooling rates, a distinct peak appeared in the T_g region, of course, with different peak areas. The parameters calculated are listed in Table I. It was found that E was maximum for the polymer cooled at 1°/min.

Table I shows that the E for PS calculated using RICHARDSON's values in the ELLERSTEIN's equation was 48.17 kcal/mole, for 20°/min cooling. This value is markedly different from the reported value of 80 kcal/mole (3), for the relaxation occuring at the glass transition. Also the E value obtained for the slowly cooled PS is 83 kcal/mole. This value should not be considered as due to molecular relaxation at T_g but should be ascribed mainly due to changes that are taking place in the structural alignment during the slow cooling of the polymer. Further, the fact that the intercept was not unity in both the cases clearly proved the inapplicability of the equation. So it is reasonable to conclude that such processes of slow cooling lead to some increase in the local order of the chain segments in the amorphous phase of the polymer. Further the intercept values obtained in all the cases were zero or nearly zero indicating that there was no induction period for local ordering for PS and PET.

A plot of the logrithm of the cooling rate versus E values for PET clearly indicated that the E goes through a maximum. So the present study showed that the maximum local ordering of the chain segments near the T_g region in PET occurred only at an optimum rate of cooling (1^o/min). Further only those portions of the chain which have matching stereoregularity can align in such a manner as to have a certain percentage of orientation. From the structural aspects of both PET and PS one can explain that PET molecules can easily align themselves to a more ordered form than PS molecules. This is in accord with the experimental observation that E values are less for PET as compared to PS.

The fact that there was no endothermal peak observed in the case of PVA even at 0,5, 1 and 2^o/min cooling rates, clearly showed that in PVA chain alignment did not seem to occur at all near or below the T_g region. This can be ascribed to the fact that in PVA there was hydrogen bonding, leading to a maximum ordering even without annealing. Further the concept of local ordering in glassy polymers in the amorphous phase is supported by a variety of techniques like electron microscopy (4), FT-IR(5), etc.

TABLE I

Energy of activation (E kcal/mole) and intercept values for PS and PET

Sample	Thermal History			
	Heating Rate ($K\ min^{-1}$)	Cooling Rate ($K\ min^{-1}$)	E (k cal/mole)	Intercept
PS	20	20	48.17	0.35
PS	10	0.625	83.20	0
PET	8	0.5	6.36	0
PET	8	1	9.92	0.01
PET	8	2	5.45	0.05
PET	8	4	5.32	0.01

REFERENCES

1. M. ELLERSTEIN, J. Phys. Chem, 69, 2471 (1965)
2. M.J. RICHARDSON and N.G. SAVILL, Polymer, 16, 753 (1975)
3. G.E. ROBERTS and E.F.T. WHITE, 'The Physics of Glassy Polymers', ed., R.N. Haward, Applied Science, London, p. 206 (1973)
4. A. SIEGMAN and P.H. GEIL, J. MACROMOL. Sci., Phys., B4, 239 (1970)
5. L. D'ESPOSITO and J.L. KOENIG, J. Polym. Sci., Polym. Phys. Ed., 14, 1731 (1976)

Received August 26, 1979
Accepted September 6,1979