side of the cellular boundary give the same zone axis pattern orientation. This indicates that the $[2\bar{1}\bar{1}0]$ crystal direction of each phase is maintained but that the (0001) habit plane is lost in the vicinity of the cell boundary being replaced, in this particular case, by a $(02\bar{2}\bar{5})$ habit.

It is obvious from Fig. 2 that as the solid–liquid interface of the Cd–Zn eutectic becomes cellular the interpenetrating Cd- and Zn-rich crystals continue to grow with a direction $[2\bar{1}\bar{1}0]$ parallel to the specimen axis. However, in those regions near a cell wall, the fanning-out of the lamellae destroys the common (0001) habit. This view is supported by the absence of any appreciable dislocation substructure near the boundary.

Thus it would appear that the cell walls should not provide any appreciable obstruction to dislocation movement during deformation. However, the reason why the deformation twins appear to be halted by cell walls, Fig. 1c and [9], is unclear but the fact that they are implies that there is sufficient mismatch at a cell wall to provide the necessary dislocation "pins". Thus, in the absence of further evidence, it is presumed that the principal cause of the increased strength consequent upon the more rapid solidification of the Cd–Zn eutectic is the decreased interlamellar spacing, but that the minor mismatch associated with cellular growth also contributes to the strengthening.

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Received 11 September
and accepted 13 October 1980

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Effect of co-polymerization on the relaxation time and molar free energy of activation of polyacrylonitrile

In the previous paper [1], the dielectric relaxation study of polyacrylonitrile (PAN), whose structure is known through X-ray diffraction studies, was reported. The discrepancies in the dielectric relaxation data on PAN in the same range of temperature and frequency were reported by others and have been discussed. A comparative study [2] of relaxation time and molar free energy of activation has also been performed.

In another study [3], the effect of co-polymerization on the crystalline structure of polyacrylonitrile was observed by wide-angle X-ray diffraction studies and a two-phase structure was found to be more suitable to explain the results. A dielectric relaxation study [4] of polyacrylonitrile and its co-polymers with poly-2-hydroxyethyl methacrylate, P(HEMA), also favours the presence of an amorphous phase in polyacrylonitrile.

In this communication the effect of co-polymerization of PAN with HEMA on relaxation time and molar free energy of activation is reported. Homopolymers of PAN and HEMA and random co-polymers, P(AN – HEMA)–I (10% HEMA by weight) and P(AN – HEMA)–II (25% HEMA by weight) were prepared by the method already described [5] with dimethylformamide as solvent and 0.5 mol% α, α' azobis – isobutyronitrile at 60° C in an inert atmosphere.

0022–2461/81/082316–02$02.20/0

TABLE I Relaxation time (τ) and molar free energy of activation for dipole relaxation (ΔG^*) of PAN and its co-polymers at 127° C

Polymer	$f_{\max}$ (Hz)	τ (sec)	ΔG^* (kcal mol^{-1})
PAN	1679	9.47×10^{-5}	16.22
P(AN–HEMA)–I	10^5	1.59×10^{-6}	12.78
P(AN–HEMA)–II	15 848.9	1.0×10^{-5}	14.44

Dielectric measurements were performed using a G.R. Capacitance Bridge type 716 CS using a two-terminal connection cell in the frequency range 10^2 to 10^5 Hz and temperature range 30 to 150° C.

The relaxation times, $\tau = (1/2\pi f_{\max})$, where $f_{\max}$ is the frequency for which ϵ'' is a maximum, were calculated from the experimental curves. The molar free energy of activation (ΔG^*) for dipole relaxation at a particular temperature was determined using the relation reported in the literature [2, 6, 7]. The variation of dielectric loss, ϵ'', with frequency for each co-polymer of PAN with HEMA showed a definite maxima at a frequency which was different for different co-polymers. The values of relaxation time (τ) and (ΔG^*) and $f_{\max}$ for different co-polymers and of polyacrylonitrile at (127° C) are summarized in Table I. The temperature of 127° C was chosen because this is an approximate temperature at which all the measurements of ϵ'' at all the frequencies for all the co-polymers and for polyacrylonitrile can be conveniently compared. P(HEMA) measurements are highly affected by d.c. conductivity [4]. So for P(HEMA) no calculations were possible.

From Table I it is seen that the frequency for the maximum value of dielectric loss (ϵ'') for the different co-polymers of polyacrylonitrile has different values, which indicates that τ and hence ΔG^* depend upon the HEMA content.

At low HEMA content, P(AN – HEMA)–I, the influence of HEMA groups on dipole–dipole interaction of nitrile groups is predominant. In PAN, the nitrile groups (– CN) owing to their strong dipole–dipole interaction, would restrict the mobility of the molecular chain and decrease the relaxation time and hence decrease the molar free energy of activation.

At high HEMA content P(AN – HEMA)–II, the effect of bulky substituent groups of HEMA in making the chain heavier predominates. Thus the introduction of HEMA groups on the PAN chain in larger numbers would decrease the chain mobility than in P(AN – HEMA)–I and hence there is a further increase in τ and in (ΔG^*).

Acknowledgement

The author wishes to thank Dr A. Mansingh, University of Delhi for allowing the measurements to be carried out.

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Received 13 November
and accepted 12 December 1980

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