

Short-Time Annealing Behavior of Polytetrafluoroethylene Subjected to γ -Irradiation

It has been reported¹⁻³ that, when polytetrafluoroethylene was irradiated with γ -rays, backbone chains are broken and thereby the average molecular weight decreases. In addition, chain scission caused by γ -irradiation results in a change in the degree of crystallinity w^c , which increases as the radiation dose r is increased. The crystallization with chain scission occurs without further thermal treatment.

A relation between the amorphous fraction ϕ ($= 1 - w^c$) and the radiation dose r has been proposed².

$$\log(\phi/\phi_0) = -f \log(r/r'_0 + 1) \quad (1)$$

where ϕ_0 is the amorphous fraction of the initial sample, r'_0 is the characteristic radiation dose, at which on the average one chain breaks at one site, and f is a rate constant, which is dependent on temperature; after chain scission due to γ -irradiation, the motion of segments at the scission region becomes active on account of the liberty of strain energy and the degree of freedom of chain ends. When any number of segments is rearranged cooperatively, stable structure at that region is formed.

The original PTFE, molded in 1 mm thick sheets, was irradiated with a ⁶⁰Co source. The γ -irradiation for the samples in the glass vessels was performed at room temperature in air. The radiation dose is 1×10^5 roentgens (R).

The degree of crystallinity was estimated by the density method. The density was measured at 298.2K by means of gradient tubes with the precision of 0.0005 g/cm³. Two liquids were used, bromoform and carbon tetrachloride.

The irradiated sample within the glass capillaries of 1.6 mm diameter were annealed at different temperatures ranging from 298K to 623K. The annealing temperature was controlled with the precision of ± 0.01 K. All the samples were quenched into an ice-water mixture after each annealing procedure. The time periods of annealing were 0.1, 0.3, and 1 min at various temperatures. The annealing time was taken as the elapsed time after the sample reached its desired temperature. No appreciable change in the crystallinity was observed for annealing times below about 1 min. It should be noted, however, that at long times the crystallinity varied with annealing time, although this was not considered in this investigation.

Figure 1 shows the dependence of the crystallinity on annealing temperature in a fixed annealing time of 1 min. The crystallinity increased up to a temperature of 598K, and a peak was observed

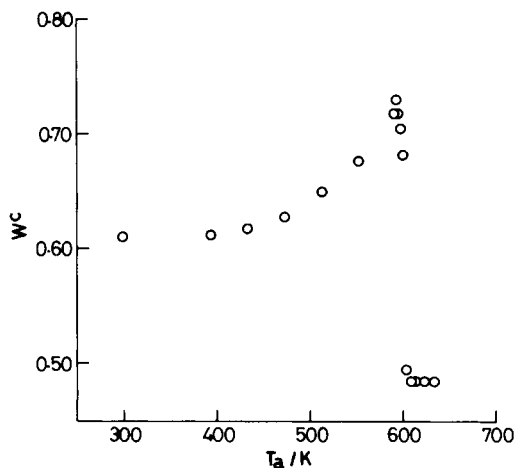


Fig. 1. Degree of crystallinity against annealing temperature for PTFE irradiated with 1×10^5 R. Annealing time is 1 min.

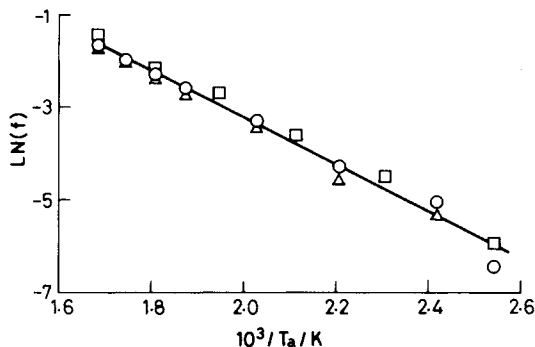


Fig. 2. Values of f in eq. (1) against the inverse annealing temperature of the irradiated PTFE; annealing times (min): (Δ) 0.1; (\circ) 0.3; (\square) 1.

in the vicinity of the melting point; the crystallinity above 608K stayed constant at a value of 0.485. It appears that the constant crystallinity is due to the quenching process from the melt. Similar behavior was observed in the irradiated samples annealed for times of 0.1 and 0.3 min.

Values of f in eq. (1) were calculated from the crystallinity obtained at annealing temperatures T_a between 373K and 598K by using $r'_0 = 2.7 \times 10^4$ R and $\phi_0 = 0.61$. Figure 2 shows the logarithm of f against the reciprocal of T_a for annealing times $t_a = 0.1, 0.3,$ and 1 min. The plots of $\log f$ against $1/T_a$ fitted onto a straight line, although some scatter is seen at lower temperatures. The apparent activation energy obtained from its slope was 42.5 kJ/mol.

Although the crystallinity of the unirradiated PTFE did not change during annealing for short times, the irradiated sample gave rise to crystallization in the same annealing condition. It seems that further crystallization is associated with the increase in molecular mobility caused by scission of constraint chains. Such radiation damage may facilitate transport of segments at ambient temperatures. Furthermore, the activation energy obtained thus is consistent with that of transport phenomena,⁴ and the process holds over the wide temperature range below the melting point of PTFE.

The radiation effect of crystallization at elevated temperatures may be predicted from the temperature dependence of f ; the value of f at 593K is about 0.32, compared to 0.12 at room temperature. In other words, if PTFE is irradiated at high temperature below the melting point, rearrangement of chain segments takes place at high rate.

The crystallinity at long-time annealing for PTFE as-irradiated increases linearly with the logarithm of annealing time.

References

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