

### Viscosity of Polytetrafluoroethylene Above the Melting Point

The behavior of polytetrafluoroethylene above the melting point is interesting and unusual in several respects. The polymer exhibits an extreme melt viscosity, about  $10^{11}$  poises. The melt exhibits a marked degree of elasticity. The polymer has an extraordinary thermal stability, decomposing at appreciable rates only at about  $400^\circ\text{C}$ . and higher.

The thermal degradation of the polymer has been extensively studied.<sup>1-4</sup> However, the interpretation of the mechanism of degradation is not unambiguous.

The melt viscosity of the polymer has been reported in a brief note.<sup>5</sup> In the note, the data were taken to represent a simple flow process, with an activation energy of about 36 kcal./mole. However, systematic deviations were pres-

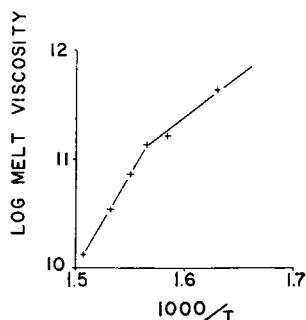
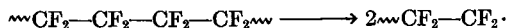


Fig. 1. Melt viscosity vs. temperature.

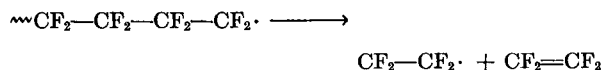
ent in the data. The data are replotted in Figure 1. The data seem to indicate a transition point at about  $365^\circ\text{C}$ . Below this temperature, the activation energy for flow is about 25 kcal./mole. Above this temperature, the value is about 52 kcal./mole. There is also an indication of a transition point in the modulus at this temperature.

This transition in viscous flow is qualitatively consistent with, and required by, the following mechanism of thermal degradation:

Initiation. Random scission of C—C bonds in the chain:



Chain Propagation:



Termination:

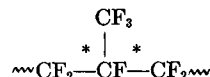


The kinetic chain length of degradation is indeterminant, but is much shorter than the mean chain length in the polymer. This mechanism is essentially the same as that of ref. 1.

Below the temperature at which bond scission begins to occur, viscous flow occurs by simple molecular motion. The activation energy of flow is higher than for normal polymers, because of the extreme stiffness of the chain. At above about  $365^\circ\text{C}$ ., chain scission occurs. Now, the molecular units which undergo flow are shorter and shorter chains with increasing temperature, and one or both ends of the units are free radicals. The energy of activation for flow now includes a contribution from the chain-scission reaction, which has an activation energy of about 80 kcal./mole, and is therefore much higher than that for simple viscous flow. Since the kinetic chain length for degradation is much shorter than the mean polymer chain, there is very little observable degradation of the polymer in this temperature region. However, at about  $400^\circ\text{C}$ ., the kinetic chain length becomes appreciable, and observable degradation begins to occur.

It is not immediately clear what activation energy would be called for by the combination of chain scission and the subsequent viscous flow of the chain fragments. A rather complex relationship exists among random chain scission and recombination, and the flow of fragments.

It is interesting to note that the observed thermal stability of the tetrafluoroethylene-hexafluoropropylene copolymer is considerably lower than that of polytetrafluoroethylene. In view of the above mechanism for thermal degradation of the latter, it is tempting to speculate that the linkage



marked with an asterisk in the former polymer is "weak," and that chain scission preferentially occurs here. If so, it would be noted that the products of degradation of the copolymer are relatively high in hexafluoropropylene, since chain scission preferentially involves the residue of this monomer, and since the recombination of the radical terminated in this monomer residue should be no faster, and should probably be slower than the recombination of the  $\sim\text{CF}_2-\text{CF}_2\cdot$  radical.

### References

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