

preferred orientation and also cause a specific conformation to be adopted, as observed with some monomers. It may be possible from information of this type to obtain evidence on the structure of the imperfections. Under these conditions considerable strain must be developed in the vicinity of the radical.

Further propagation is apparently not possible until the thermal motions of the molecules increase sufficiently for this strain to be relieved and to allow addition of the radical to another neighbouring monomer molecule. This further addition may well not occur in a specific crystallographic direction, and the orientation of the radical with respect to the monomer crystal axes may be lost. It is at this stage that the polymer chain is likely to become detached from the monomer lattice, by breaking strained intermolecular bonds, and nucleate an amorphous polymer phase within the monomer crystal.⁽³⁷⁾ The detachment of the growing radical from the lattice allows a relaxation process to occur and the radicals to take up their preferred conformations, within any limitations imposed by the free volume available and any strong residual intermolecular or interionic forces which may still be operative (depending on the nature of the monomer); an isotropic e.s.r. spectrum of the normal propagating radical is generally observed.

At this point it is of interest to consider in detail the change from radicals under restrictions imposed by the lattice to radicals whose conformation and orientation are not controlled by the lattice. This change has been studied in some detail in the polymerization of methacrylic acid during continued u.v. irradiation,^(25, 31) when the e.s.r. spectrum changes from 13 lines to 9 lines. The radicals in the restricted form ($\phi = 5^\circ$, Fig. 1) give the 13-line spectrum and are denoted *T*-type, while the radicals in their unrestricted form and which give the 9-line spectrum are known as *N*-type. Most experimental spectra consist of a mixture of 13- and 9-line spectra and a parameter X/Y was defined ($X/Y = 0$ for 9 lines) which would allow estimation of the fraction of radicals in the restricted conformation. Changes in X/Y under different conditions allow the factors which control the relaxation from *T*-type to *N*-type to be identified.^(25, 31) For samples crystallized at -196°C and irradiated at temperatures in the range -50°C to -20°C (where little polymerization occurs) the value of X/Y decreases with time to a constant value characteristic of the irradiation temperature; lower values are obtained at the high temperatures. As X/Y decreases, the radical concentration increases to a stationary value; the stationary concentration increases with increasing irradiation temperature. It is concluded that at long irradiation times a stationary state is developed, radicals continuously being generated in the *T*-form in the lattice defects, relaxation from *T*-type to *N*-type (by what is believed to be a photo-assisted process⁽²⁵⁾) and termination occurring at the same rate as initiation. Each act of initiation in u.v.-initiated polymerizations must generate two radicals in close proximity, i.e. in the same reaction site.

Initially both radicals are of the T -type. It is visualized that termination involves the relaxation of one of these radicals to a small N radical which can then react with a propagating N radical already present in the defect. Eventually the other T radical can relax to N . Thus, termination takes place during irradiation. The rate of the relaxation process must depend on the mobility of the molecules in the defect, and possibly on the energy introduced into the crystal by absorption of light, with the result that the process $T \rightarrow N$ will occur more readily at the higher temperatures giving rise to a lower limiting value of X/Y , or $[T]/([T] + [N])$.

The stationary radical concentration, at long irradiation times, is taken to indicate that all defects capable of supporting reaction contain radicals.⁽²⁵⁾ Although all the samples were crystallized under the same conditions, and might be expected, on average, to contain the same number of defects, the stationary radical concentration increases with increasing temperature. This demonstrates that the crystalline monomer contains a range of imperfections, in which the monomer molecules have different mobilities. Hence, as the temperature is raised the molecular mobility in each defect increases and the number of imperfections capable of supporting reaction also increases.

Studies of the type outlined above have shown that both the number and nature of imperfections can be varied by changing crystallization conditions.⁽²⁵⁾ Samples of methacrylic acid crystallized at -196°C and irradiated at -20°C give a significantly higher limiting radical concentration than samples crystallized at higher temperatures, presumably as a result of a higher rate of nucleation and a higher concentration of defects. On prolonged irradiation all samples gave the same limiting value of X/Y , but in the initial stages samples crystallized at higher temperatures (-60°C to -20°C) gave lower values of X/Y , indicating a higher level of molecular mobility in the defects. This higher mobility might arise from the concentration of impurities in the defects, since the presence of isobutyric acid in concentrations as low as 0.02 per cent in samples crystallized at -196°C reduces the initial values of X/Y considerably.⁽³¹⁾ In samples containing up to at least 0.1 per cent isobutyric acid the same final value of X/Y is obtained, even though this may require the ratio to increase in the initial stages. The higher molecular mobility in the presence of isobutyric acid accelerates the process $T \rightarrow N$ initially, although ultimately the effect is lost. It may be visualized that the isobutyric acid is concentrated around dislocations in the form of a Cottrell cloud.⁽⁵⁰⁾ The isobutyric acid will exert its maximum influence initially, and as reaction proceeds into more perfect regions of the crystal its effect will decrease. The presence of isobutyric acid brings about a large increase in rate of polymerization at slightly high temperatures, about -14°C , where polymerization is more rapid.⁽³¹⁾

Under conditions where the in-source polymerization is rapid and high conversions are obtained these considerations require some modification,