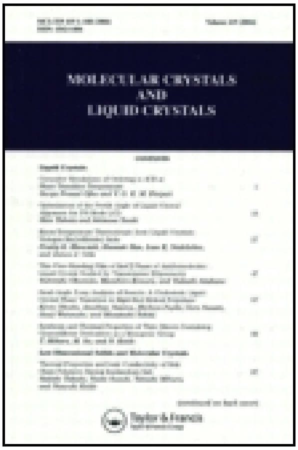

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On the Solid-State Polymerization of Acrylic and Methacrylic Acids Initiated by Ultraviolet Radiation

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On the Solid-State Polymerization of Acrylic and Methacrylic Acids Initiated by Ultraviolet Radiation

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Abstract—This paper brings together the results of our recent studies on various aspects of UV initiated solid-state polymerizations of acrylic and methacrylic acids. The use of polarized UV radiation to initiate the polymerization of acrylic acid at 4 °C is consistent with the initial formation of mobile excitons which are subsequently trapped at the imperfections where radicals are eventually formed. Differences in the electron spin resonance spectra and radical concentrations obtained by irradiating samples of methacrylic acid under various conditions in the temperature range − 50 °C to − 20 °C demonstrate the existence of a range of imperfections in the crystalline monomer, the nature of which is sensitive to the presence of trace impurities. The molecular mobility in the imperfections is seen to increase with increasing temperature in a manner consistent with broad-line n.m.r. studies on the monomer. These results give information on the mechanisms of initiation and termination. The effect of small applied stresses on the polymerizations is sensitive to both temperature and trace impurities; i.e., factors which affect molecular mobility in the bulk material and in imperfections. The mechanism of the polymerization of crystalline acrylic and methacrylic acids is discussed in terms of these results.

Introduction

The polymerization of crystalline vinyl monomers usually results in the formation of amorphous polymer, and it is, therefore, obvious that considerable molecular reorientation must accompany polymerization. From a simple consideration of the crystal structures of organic molecules it may be assumed that reaction probably occurs in lattice imperfections and at temperatures where the molecular mobility in the imperfections is sufficiently great to allow the necessary processes to take place. As a result of studies on a number of solid-state polymerizations there is now a considerable body of evidence supporting the idea that lattice imperfections, probably dislocations, are the preferred sites for reaction.[1–4]

In earlier papers we reported that during the UV initiated polymerizations of crystalline acrylic and methacrylic acids, which proceed by a radical mechanism, birefringent monomer crystals are converted into isotropic polymeric pseudomorphs.[3,5] The rates of polymerization of these monomers are very sensitive to small stresses (~ 10 atm.) applied to the crystals, and on the basis of such evidence it was proposed that mobile dislocations are the preferred sites of reaction.[3,5] Recently, we have investigated molecular motions in crystalline acrylic and methacrylic acids,[6] and various aspects of the solid-state polymerization of these monomers initiated by ultraviolet radiation.[7–10] Experimental details are given in the relevant references. These investigations have allowed the identification of factors which we believe are important in determining the detailed course of the reactions. Each aspect of the polymerization has been studied in detail using one monomer, but it is considered that both monomers undergo reaction by essentially the same mechanism and that the concepts arrived at are applicable to the polymerizations of both monomers. In the present paper we outline a possible reaction mechanism for the UV initiated solid-state polymerizations of acrylic and methacrylic acids over a wide temperature range, based on the conclusions of these studies, together with evidence from related systems and on the assumption that reaction occurs only in imperfections.

Molecular Mobility

The variations of molecular mobility in acrylic and methacrylic acid crystals (melting points, 12.6 °C and 16 °C respectively) with increasing temperature have been investigated by nuclear magnetic resonance.[6] Both monomers were found to exhibit similar behavior, in that three distinct temperature regions could be identified; (i) below about − 60 °C the lattices are effectively rigid, apart from methyl-group rotation in methacrylic acid, (ii) between − 60 °C and about 0 °C certain specific molecular motions, which increase in magnitude with increasing temperature, become observable, (iii) above about 0 °C there is a marked increase in molecular mobility, when a narrow line, which can be partially resolved into the resonances of the individual protons, appears in the centre of the spectrum. This narrow line indicates that a fraction of the monomer molecules are undergoing extensive reorientation. At any temperature the results reflect the general level of molecular mobility in the lattice, and it is anticipated that the mobility of some molecules in the neighborhood of imperfections is higher, ultimately restricted by the structure of the defect and by specific intermolecular forces, e.g. hydrogen bonds. In this discussion we shall be concerned with the two latter temperature regions. In region (ii), particularly at the lower temperatures, very little polymerization is observable, while in region (iii) polymerization is relatively rapid and proceeds readily to complete conversion. It is apparent, therefore, that a close correlation exists between molecular mobility in the lattice and the rates of processes involved in reaction.

Initiation

In view of the extensive molecular motions present in the high temperature region, it might not be expected that the course of the

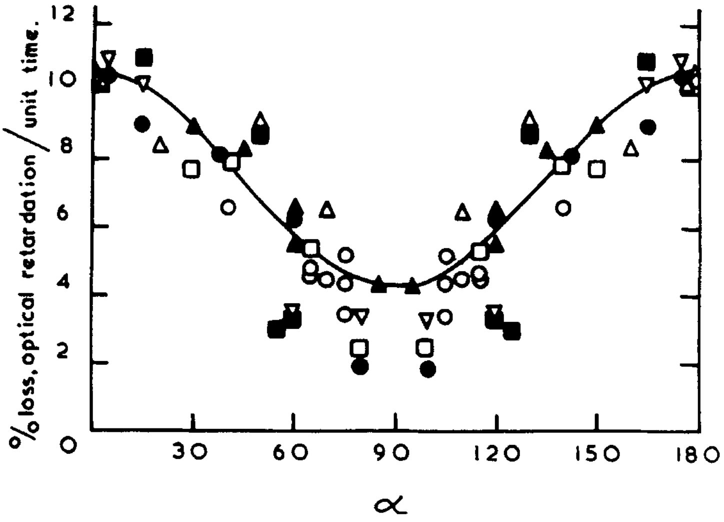

Figure 1. Normalized percentage loss of optical retardation in unit time as a function of α, the angle between the plane of the electric vector of the initiating radiation and the *a* axis of the monomer crystal. Each symbol represents results obtained from a set of individual crystals in a single experiment.

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polymerization would show any relation to the crystal structure of the monomer, especially since reaction is assumed to proceed in imperfections. However, when the polymerization of acrylic acid at 4 °C is initiated by polarized UV radiation there is a marked dependence of rate of loss of optical retardation, in the early stages of reaction, on the angle α between the plane of the electric vector of the polarized radiation and the *a* axis of the monomer crystal,[10] Fig. 1 (Fig. 1 is symmetrical about $\alpha = 90°$). The orientations of the monomer molecules in the crystal lattice, according to the data of Chatani *et al.*,[11] are shown in Fig. 2. The curve in Fig. 1 is calculated assuming that the initiating radiation is absorbed by the vinyl groups, with

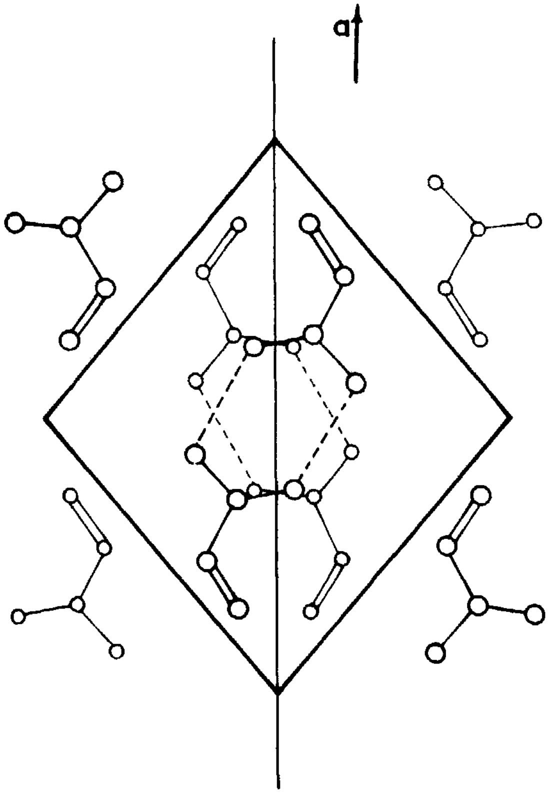
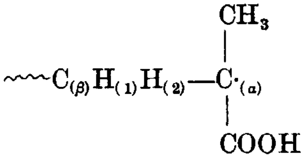


Figure 2. The crystal structure of acrylic acid, showing the orientation of the vinyl groups with respect to the *a* axis of the monomer crystal.

maximum absorption when the plane of the electric vector is parallel to the direction of the double bond, and that the rate of polymerization is proportional to the intensity absorbed. The results in Fig. 1 are taken to indicate that the mechanism of initiation involves the initial formation of excitons, produced by the absorption of UV radiation in the more ordered regions of the lattice. The excitons then travel through the crystal and become localized in imperfections.[12] These localized excitons may decay thermally, or, alternatively, may give rise to radical formation, and, hence, initiate polymerization in the imperfections. On the basis of this argument the variation in rate of polymerization shown in Fig. 1 is evidence for the formation of mobile excitons in these crystals, with the excitons acting as a means of transporting energy to suitable reaction sites.

Radical Conformations

It is difficult to detect free radicals in crystals of acrylic acid after ultraviolet irradiation, but high concentrations of radicals are detectable during the solid-state polymerization of methacrylic acid. The electron spin resonance (ESR) spectrum of radicals formed by irradiating polycrystalline methacrylic acid at high temperatures (region (iii)) consists of 9 lines (Fig. 3a), while irradiation at low temperatures (below about − 20 °C), for short times, produce radicals which exhibit a 13-line spectrum,[13] (Fig. 3b). Radicals giving rise to 9- and 13-line spectra are denoted N and T, respectively. Both spectra are interpreted in terms of different conformations of the same radical species, the normal propagating radical



$$\sim\sim C_{(\beta)}H_{(1)}H_{(2)}-\overset{\displaystyle CH_3}{\underset{\displaystyle COOH}{C^{\cdot}_{(\alpha)}}}$$

An identical 9-line ESR spectrum, obtained during the liquid-phase polymerization of methyl methacrylate, has been interpreted in terms of preferred conformations of the corresponding radical, resulting from hindered rotation about the $C_{(\alpha)}-C_{(\beta)}$ bond, such that the methylene protons ($H_{(1)}$, $H_{(2)}$) interact unequally with the unpaired electron on $C_{(\alpha)}$.[14] The 13-line spectrum of the T radical

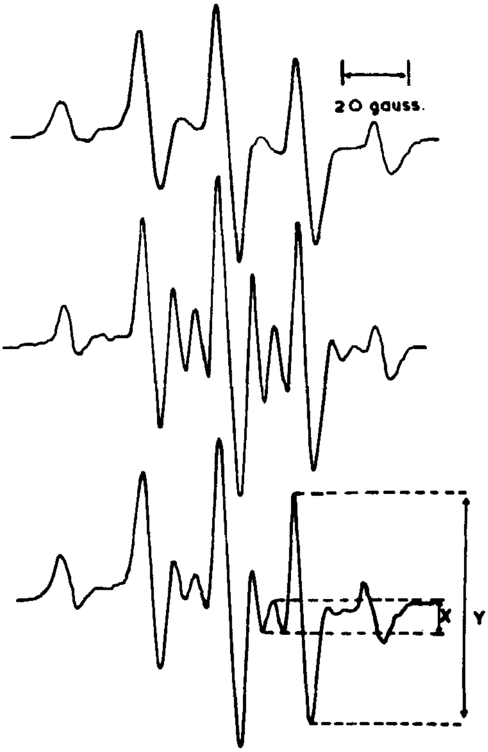


Figure 3. ESR spectra from irradiated methacrylic acid crystals. (a) The 9-line spectrum, (b) The 13-line spectrum, (c) A typical spectrum comprised of a mixture of the 9-line and 13-line spectra, showing the definition of parameters X and Y.

is attributed to a single conformation, adopted as a result of restrictions imposed by the lattice at the lower temperatures.[13] The individual conformations can be identified from Fig. 4, which is a projection along the $C_{(\alpha)}$—$C_{(\beta)}$ bond; R represents the remainder of the polymer chain. According to Symons the 9-line spectrum arises from the presence of two conformations with $\phi = 0°$ and $\phi = 15°$, respectively.[14] The single conformation responsible for the 13-line spectrum of the T radical corresponds to $\phi = 5°$.[13] Similar restricted conformations have been observed on γ-irradiation of barium methacrylate[15] ($\phi = 4°$) and on addition of hydrogen atoms to itaconic acid[16] ($\phi = 10°$).

All the radicals referred to above are effectively the same species,

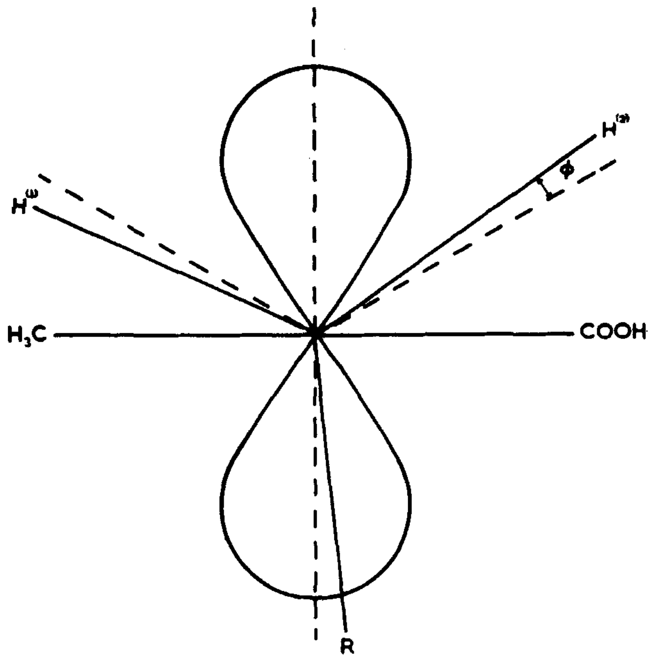


Figure 4. Radical conformations in methacrylic radicals, showing definition of ϕ.

having identical protons available for interaction with the unpaired electron. The individual restricted conformations observed must result from differences in the intermolecular forces between the substituent groups. Thus, in the case of methacrylic acid the hydrogen bonds between the substituent groups on the radical and neighboring monomer molecules must be retained, although probably strained, when T radicals are present.

Under conditions such that a 13-line ESR spectrum is observed (i.e. T radicals are present) the rates of polymerization of methacrylic acid are very low. ESR studies on γ-irradiated acrylamide[17] and acrylic acid[18] have demonstrated that restrictions are also imposed on the radicals derived from these monomers at low temperatures, causing them to be orientated in specific directions in the crystal. Negligible polymerization is observed under these conditions. At higher temperatures, where molecular mobility is greater, the restraints are removed and the ESR spectra become isotropic and characteristic of the normal propagating radicals, i.e. N radicals in methacrylic acid. The loss of the constraints in these cases must represent the breaking of intermolecular bonds, allowing the radicals to relax and adopt their normal conformations. The fact that such changes often take place over a wide temperature range has been attributed, by Adler and Petropoulos,[17] to the existence of a variety of imperfections having a range of properties, so that the behavior of each radical is controlled by its local environment. According to Adler *et al.*,[19] crystallographic considerations suggest that the radicals which adopt a specific orientation in acrylamide at low temperatures are probably dimers, or possibly trimers, and similar considerations probably apply to the T radicals in methacrylic acid.

A study of the relaxation T → N in methacrylic acid as both the temperature and reaction time are increased,[7] and the influence of additives on this process,[8] has allowed additional evidence for the presence of a distribution of imperfections to be obtained, and the factors controlling this distribution to be identified. The ESR spectra normally observed in methacrylic acid crystals at low temperatures are a mixture of the 13-and 9-line spectra (Fig. 3c), and a parameter X/Y ($X/Y = 0$ for 9-lines) was used to indicate the proportion of T radicals present in the sample,[7] $X/Y = 0.35$, approxmately, for " pure " T radicals.

Reactions at Low Temperatures

The variations in X/Y and total radical concentration during continued irradiation have been studied at $-20\,^{\circ}\mathrm{C}$ and lower, where polymerization is so slow that the interpretation of the results is not complicated by polymer formation.[7] The value of X/Y decreases steadily from a high initial value to a limiting value at long irradiation times (Fig. 5); the limiting value is characteristic of irradiation temperature and has a higher value at the lower temperatures.[7] During the same period the radical concentration rises to a limit, which increases with increasing temperature[7] (Fig. 5). The limiting radical concentrations are taken to represent the attainment of a stationary state in which rates of initiation and termination are equal. Conventional bimolecular termination of radicals is negligible in these reactions, since high concentrations of free radicals are stable

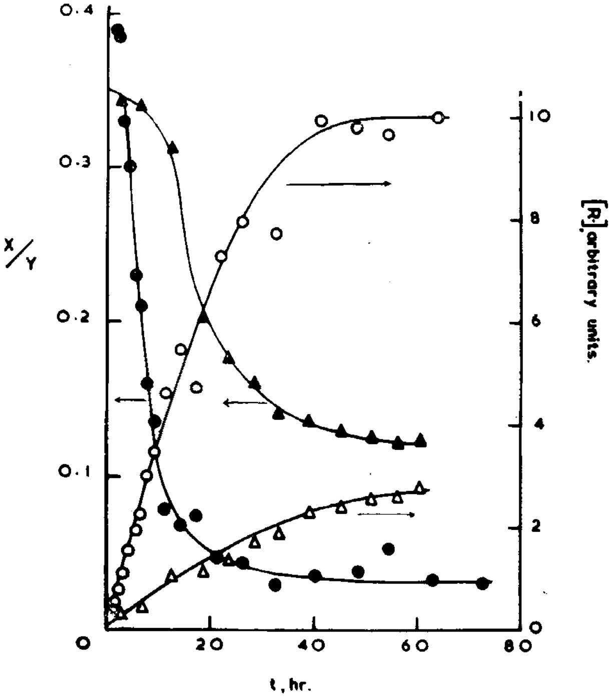


Figure 5. Variations of X/Y and radical concentration in methacrylic acid crystals as a function of time of irradiation at − 50 °C and − 20 °C. Samples crystallized in liquid nitrogen.

Irradiation temp. − 50 °C:	▲ X/Y,	△ radical concentration.
Irradiation temp. − 20 °C:	● X/Y,	○ radical concentration.

indefinitely in the dark. Termination must, therefore, occur during irradiation, and the overall reaction can be considered as a series of processes operating in a " cage ". Such " cages " represent specific reaction sites in which molecular mobility is sufficient for reaction to proceed.

The decrease in X/Y in the early stages of reaction is consistent with the initial formation of T radicals in the reaction sites and the T radicals subsequently becoming detached from the lattice by breaking of hydrogen-bonds, and relaxing to give N radicals.[7] Thus, as irradiation continues the number of sites containing N radicals increases, until at long reaction times all sites capable of supporting reaction contain radicals. The limiting value of X/Y is a result of further initiation in the same reaction sites.[7] Since light must produce radicals in pairs, it has been proposed[7] that the secondary initiation produces two T radicals in the immediate vicinity of an N radical. Relaxation of one of these T radicals produces a small N radical which terminates rapidly with the N radical already present in the same site. Subsequently, the remaining T radical relaxes to an N radical.[7] These processes can be represented by the following equations

$$2\mathrm{S} + h\nu \rightarrow 2\mathrm{T} \rightarrow 2\mathrm{N} \tag{1}$$

$$\begin{tikzcd}\mathrm{N} + h\nu \arrow[r] & \mathrm{N}^{\mathrm{T}}_{\mathrm{T}} \arrow[d] \\ \mathrm{T} \arrow[u] & \mathrm{N}^{\mathrm{T}}_{\mathrm{N}} \arrow[l]\end{tikzcd} \tag{2}$$

where S represents a site capable of supporting reaction. The factor 2 is introduced in Eq. (1) to account for the formation of radicals in pairs and the absence of conventional bimolecular termination. This implies that the radicals formed initially are located in separate sites and capable of independent existence. Eq. (2) represents subsequent reactions occurring in a single site.

The limiting radical concentrations at long irradiation times indicate that all sites capable of supporting reaction contain radicals, and the higher limiting radical concentrations observed at the higher temperatures (for samples crystallized at − 196 °C) demonstrate that the density of active sites increases with increasing temperature, i.e. with increasing molecular mobility.[7] Since all samples will, on average, contain the same imperfections on crystallization, it may be concluded, from the changes in limiting radical concentration, that the crystals contain a distribution of imperfections with different properties and associated molecular mobilities.[7]

If a certain threshold value of molecular mobility is necessary for reaction to occur, then, at any given temperature, only a certain fraction of the imperfections will operate as reaction sites. At higher temperatures, when the general level of molecular mobility is greater, the distribution of mobilities in the imperfections will change, with a larger fraction of imperfections capable of supporting reaction.

The limiting value of X/Y represents a balance between the rate of formation of T radicals and the rate of relaxation T → N and will depend on the light intensity. Since the rate of radical formation in a site will be relatively independent of temperature, at constant light intensity, the lower limiting values of X/Y observed at the higher temperatures[7] result from an increase in the rate of relaxation T → N with increasing temperature, i.e. the relaxation, which involves detachment of T radicals from the lattice, is more rapid under conditions of high molecular mobility. A consequence of the radicals being situated in imperfections with different mobilities is that the value of any parameter used to describe the rates of the individual processes must be a mean value.[7]

The distribution of the properties of the sites can be varied by changing the rate of crystallization, i.e. freezing the monomer in baths at different temperatures.[7] Values of X/Y at short irradiation times (at $-20\,°$C) obtained from samples crystallized at higher temperatures ($-60\,°$C to $-20\,°$C) are slightly lower than those obtained by shock-cooling monomer to $-196\,°$C. Thus, slow crystallization produces a fraction of reaction sites in which the molecular mobility is so high that the relaxation T → N is too rapid to allow the initial formation of T radicals in these sites to be observed. Conversely, crystallization at lower temperatures produces a larger fraction of imperfections in which the mobility is low. At long irradiation times the same limiting value of X/Y is obtained, demonstrating that under these conditions relaxation occurs in all sites,[7] since if the mobility in some sites was so low that relaxation of T radicals could not occur it would be expected that different limiting values of X/Y would be observed. Ultimately the average rate of relaxation in all samples is the same and characteristic of the temperature of irradiation. This probably results from the consumption of the more mobile monomer molecules in the site so that eventually the properties of the sites represent the general level of mobility in the crystal. When samples are irradiated at $-20\,°$C and then stored in the dark at the same temperature the value of X/Y decreases to a constant finite value.[7] Under these conditions, therefore, not all T radicals can relax to N, which contrasts with the results obtained during continued irradiation. It must be concluded, therefore, that detachment of a T radical from the lattice, and its subsequent relaxation, is a photo-assisted process. The mechanism of this process is possibly the decay of excitons in the neighborhood of the radicals enhancing the local level of mobility[12] to an extent sufficient to allow the breaking of strained intermolecular hydrogen bonds.

If the above samples, after storage in the dark, are irradiated with light of wavelengths greater than 3000 Å there is a small preferential loss of N radicals.[7] Light of these wavelengths does not produce radicals in this monomer. It has been suggested that the longer wavelengths assist the propagation reaction, by increasing the rate of detachment of monomer molecules from the lattice, and allowing a small amount of bimolecular termination between N radicals in sites situated very close together.[7] There is further evidence that light of these wavelengths assists propagation from results obtained in the high temperature region, when the after-effect, or post-irradiation reaction, in methacrylic acid proceeds more rapidly under the influence of such radiation than in the dark.[20]

Influence of Additives on the Sites at Low Temperatures

The addition of small concentrations of isobutyric acid ($< 0.01\%$ v/v) to methacrylic acid before crystallization has a marked effect on the nature of the reaction sites, and is further evidence that reaction proceeds in imperfections. In the initial stages of reaction the presence of isobutyric acid (the saturated analogue of methacrylic acid) causes a marked reduction in the values of X/Y.[8] As reaction proceeds the values of X/Y increase before finally decreasing to their limiting value, which is identical in the presence and absence of isobutyric acid.[8] From these results it is proposed that isobutyric acid increases the mobility in some reaction sites and that radical formation takes place preferentially in the sites associated with high molecular mobility.[8] At longer irradiation times radicals are formed in sites where the mobility is lower but sufficiently high to support reaction. This view is substantiated by changes in radical concentration with increasing reaction time when the presence of 0.1% isobutyric acid brings about at least a threefold increase in the initial rate of radical formation, but at longer times the radical concentration increases at the same rate in all samples.[8] It is also apparent that the presence of isobutyric acid increases the density of reaction sites.

The observation that the same limiting value of X/Y is obtained at long reaction times in all samples shows that the influence of the isobutyric acid is gradually lost and that the properties of the sites change with time.[8] It is proposed that the additive is concentrated around dislocation lines, where the reaction sites are located, in the form of Cottrell clouds.[21] As reaction proceeds in a site containing isobutyric acid the additive becomes detached from the lattice and its influence on the local mobility decreases. Eventually, as reaction progresses into the lattice the effect of the additive is lost and the site adopts the properties characteristic of the sites in pure monomer at that temperature.

Nature of the Reaction Sites

At the present time it is impossible to identify the detailed nature of the reaction sites but, assuming that reaction sites are associated with dislocations, it is easy to see that imperfections with different structures can be formed by generating edge dislocations associated with various slip planes. It is apparent from the crystal structure of acrylic acid (Fig. 2) that the formation of a dislocation with unit Burgers vector requires the removal of two adjacent half-planes of centro-symmetrical hydrogen-bonded dimer units. In the vicinity of the core of such a dislocation some monomer molecules will be significantly displaced from their lattice correct positions, and the free volume available to some molecules for molecular motions will be considerably increased. In a real crystal the missing half-planes may not be adjacent, but the dislocation may be resolved into two half-dislocations separated by a variable distance, and under such circumstances the displacement of the molecules from their lattice positions and the free volumes available for motion could vary. Thus, it can be seen that, considering only dislocations as possible reaction sites, a variety of reaction sites associated with a range of molecular mobilities is possible.

When considering the structure of such defects in more detail, the region in the vicinity of a dislocation core cannot be visualized as a region of disorder. The pairs of monomer units, from which the crystal is constructed are large and flat and their shape and intermolecular interactions will limit the orientations which they may adopt in the defect. An imperfection, therefore, will have a structure, particularly at low temperatures, which will depend on the nature of the dislocation and the proximity of other defects. The structure of the imperfections will also vary with distance from the dislocation core as the displacement of molecules from their lattice positions decreases towards the more perfect regions of the lattice.

In the early stages of reaction it is probably incorrect to think of reaction proceeding at a definite interface between the perfect lattice and a disordered region, but rather through a region of changing structure. When reaction has proceeded to a significant distance from the dislocation core, it may then be possible to consider that further reaction in the defect occurs at an interface, with monomer molecules becoming detached from effectively perfect lattice. It can thus be seen how the property of a reaction site can vary as reaction proceeds, as was concluded from results of ESR studies in the presence of added isobutyric acid, and which probably occurs, to a smaller extent, in pure monomer.

Reaction at High Temperatures

At high temperatures (region (iii)), where polymerization readily proceeds to complete conversion, it is obviously unrealistic to consider reaction restricted to the limited number of defects initially present in the crystals. Since the results of earlier experiments on the effects of small applied stresses indicate that at the higher temperatures dolymerization proceeds in dislocations,[3] we envisage that, as polymerization proceeds, strains are set up in the lattice surrounding the polymer particles and that these strains are relieved by dislocation multiplication (this process has been observed in the decomposition of sucrose[22]). The number of active sites, therefore, increases as polymerization proceeds, giving rise to the autocatalytic behavior observed. The results of Sella *et al.*[4] on the solid-state polymerization of acrylamide suggest that as polymerization proceeds to high conversion there is a steady increase in the number of reaction sites and that the original nuclei do not grow indefinitely.

The effect of small stresses applied to the crystals during polymerization is markedly temperature dependent. At 4°C a unidirectional stress of about 10 atm. stops the reaction completely, while at 7°C the same pressure has no effect.[3] The result at 4°C was taken to indicate that the pressure removes the dislocations from their normal sites to locations where reaction cannot occur, or is not observable.[3] At 7°C the overall molecular mobility is extremely high and the optical retardation of the monomer decreases markedly with increasing temperature; at this temperature the monomer is probably in the pre-melting region.[3] The lack of a pressure effect under these conditions probably results from the increased disorder present and, under these conditions, the concept of a discrete dislocation possibly loses its meaning.

Similar results have been obtained using methacrylic acid, at 7 °C, when it was demonstrated, from the effects of stress on the after-effect, that application of the stress moves the dislocations from the sites containing radicals and stops reaction, and that on removal of the stress reaction recommences as the dislocations return to their original sites.[3] Recent experiments have shown that the effect of the applied stress, in reducing the rate of reaction, decreases steadily as the temperature is lowered[9]; the effect finally disappears at − 14 °C. These results are attributed to a general hardening of the crystals as the temperature is lowered and the molecular mobility decreases, thus making movement of the dislocations more difficult.

The presence of isobutyric acid has a marked effect on these results. At 4 °C the addition of isobutyric acid rapidly reduces the effect of the applied stress, which almost vanishes in the presence of 0.3% (v/v) of the additive.[9] As in the case of reaction at low temperatures the presence of isobutyric acid is considered to increase the mobility and to be equivalent to a local increase in temperature. Although no effect of applied stress is observable in pure monomer at − 14 °C the addition of 0.1% isobutyric acid causes a reappearance of the effect, while the addition of 0.5% of this additive causes the effect to decrease again.[9] These results are again taken to indicate that the addition of isobutyric acid is equivalent to a local increase in temperature.

An alternative explanation for the loss of the pressure effect at 4°C by addition of isobutyric acid could be the localization of isobutyric acid around the dislocations in the form of Cottrell clouds[21] which pin down the dislocations and prevent their movement under small stresses. This explanation, however, is not consistent with the appearance of a pressure effect at − 14 °C in the presence of isobutyric acid. Although the isobutyric acid is probably localized in the region of dislocations, a reason for the failure of the Cottrell cloud mechanism in these experiments is that the molecular mobility is too high at these temperatures; it is known that this mechanism does not operate in metals at high temperatures.[21]

Conclusions

Among the major factors to be considered in photo-initiated polymerizations in the solid-state is the formation of excitons which become localized in imperfections and decay, either to produce radicals or to enhance local thermal motions and, hence, assist the various processes involved in reaction. The reactions at low temperatures, where polymerization is negligible, occur in discrete reaction sites, but at high temperatures, where considerable polymerization occurs the number of reaction sites increases, to relieve the stresses produced, by dislocation multiplication. It is thus necessary to consider the number of reaction sites in the crystal and the distribution of their properties, particularly their associated molecular mobilities. In this connection, factors such as the effects of additives on the nature of the sites and the changes in properties of the sites as reaction proceeds must be taken into account. Although the mechanism outlined in this paper has been developed for photo-initiated solid-state polymerizations of acrylic and methacrylic acids, the ideas proposed are capable of explaining features of a number of other solid-state polymerizations. The relative importance of each factor must vary with the nature of the monomer and when necessary account must be taken of the size and nature of the substituent groups and the strength of the interactions between them.

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