E.s.r. study of the reactions of gases with the free radicals produced by u.v. radiation on the surfaces of acrylamide and some crystalline materials: 1. Primary results of oxygen exposure to acrylamide, propionamide, methacrylamide and mixed crystals of these materials

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Several aspects of an e.s.r. spectroscopic study of the free radicals induced by u.v. light on the surfaces of acrylamide, propionamide, methacrylamide and on solid solutions of these monomers are studied. The differences in reactivity of various gases such as oxygen, hydrogen, chlorine and sulphur dioxide with the radicals produced in irradiated samples have been investigated. However, in this work only the differences in reactivity of oxygen with the radicals, produced in irradiated samples have been investigated. Evidence obtained from e.s.r. spectra indicates that oxygen can diffuse into these semicrystalline compounds and reach the radical sites easily, indicating chain reactions which are influenced by crystal structure and diffusion rate.

(Keywords: ultra-violet; e.s.r. spectra; gas reactivity; free radicals)

INTRODUCTION

Acrylamide and various acrylic salts can be polymerized by u.v. light to high conversions in the solid state[1]. The interaction of u.v. radiation with organic solids causes the production of free radicals, mainly on the surface of the crystal, which persist for long periods of time at room temperature[1]. The reactions of the radicals formed with oxygen can provide useful information concerning the structure of the radicals and lead to a better understanding of solid state chemistry.

Oxygen cannot diffuse into γ-irradiated acrylamide[2]. However, the formation of peroxy radicals after oxygen exposure for u.v.-irradiated monomeric crystals provides definite proof for the surface character of these reactions. E.s.r. spectra indicate that the free radicals produced at the surface are stable at room temperature and decay rather slowly at elevated temperatures (40°C–72°C). Only about 25% of the originally produced acrylamide radicals decay at 60°C. However, at 60°C, radicals produced on propionamide surface decay much more rapidly and completely, which can be attributed to its crystal structure being rather different to acrylamide.

EXPERIMENTAL

The acrylamide used was an Eastman Organic Chemical product. It was recrystallized several times from chloroform and dried under vacuum before use. The melting point was 84°C.

Propionamide was obtained from the same source and crystallized twice from acetone. The melting point was 81°C.

Methacrylamide was also an Eastman product. It was recrystallized three times from warm chloroform. The melting point was 110°C.

DPPH standard: α-α'-Diphenyl-β-pitrylhydrazyl was a product of Fluka A.G. and used directly in solid form without any further purification.

Oxygen was provided by the direct introduction of air into the samples.

Solid solutions of acrylamide and propionamide were prepared by weighing the two components in the required proportions, melting them together in a Pyrex tube in a 90°C water bath and cooling the melt quickly under tap water. It is known that mixtures prepared in this fashion are isomorphous and form solid solutions over a complete composition range[3].

Acrylamide–methacrylamide solid solutions were prepared by considering the fact that they are isomorphous and form solid solutions in all proportions[4,5]. In given weight proportions the monomers were carefully weighed and the mixtures melted together in hot chloroform and recrystallized.

The purified monomers and crystallized mixed solutions were dried under vacuum to constant weight and ground in an agate mortar then placed (1–2 g portions) in the Vycor end (E) of one of the test tubes shown in *Figure 1*. Each was connected to the vacuum line through point (A) and evacuated to 10^{-5} mmHg for 24 h,

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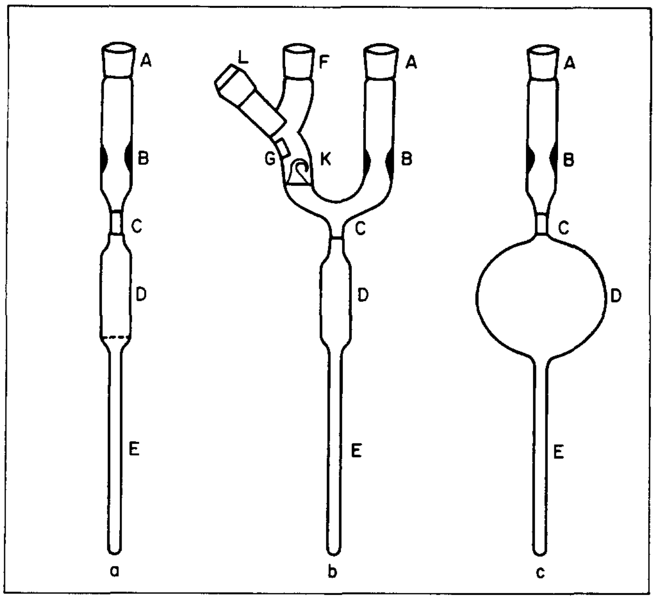


Figure 1 Irradiation tubes for e.s.r. study: (a) irradiation tube, (b) tube for gas admission, (c) Pyrex bulb

then the tube was sealed at point (B). The sample was then transferred to the quartz or Pyrex middle section of the tube (D) and irradiated at horizontal position at constant temperature (42°C–70°C) under a u.v. lamp (Philips, 300 W, 2534 Å) for different time intervals. After irradiation the sample was transferred to the Vycor end (E) once more, and the e.s.r. spectrum was recorded at room temperature with a Varian E-12, 9.5 GHz, X-Band ESR spectrometer. Using (b) types of tubes (*Figure 1b*) various gases have been admitted on the samples. After irradiation, tubes were connected to the vacuum line through (F) and by breaking the break seal (K) with a magnet (G), gas was introduced into the system. For oxygen exposure only (a) and (c) types of tubes were used and atmospheric oxygen was admitted into the irradiated crystals simply by breaking their seals (B).

RESULTS AND DISCUSSION

The solid state polymerization by ionizing radiation of acrylamide and its mixed crystals with propionamide and methacrylamide have been studied previously, both for in-source and post-irradiation reactions[3,6]. The solid state polymerization of acrylates and methacrylates initiated by γ-irradiation has been studied in detail[7–9]. The u.v.-initiated solid state polymerization of acrylamide and various acrylic acid salts have been also investigated previously and it was found that the u.v.-initiated samples can also be polymerized to high conversions[1,10]. The molecular weights of these polymeric materials reduce under irradiation[1].

Two similar spectra of the radicals were obtained for γ-irradiated single crystals of acrylamide and propionamide at liquid nitrogen temperature[7]. The radical obtained $C_\beta H_3\text{–}\dot{C}_\alpha H\text{–}CONH_2$ is formed by hydrogen atom scavenging of acrylamide and the propionamide monomeric molecules losing one proton. This radical is observed up to −125°C and gives a 5 peak spectrum with two overlapping quartets each with 1:3:3:1 peak height ratio. At higher temperatures a dimeric radical, $CH_3\text{–}CH(CONH_2)\text{–}CH_2\text{–}\dot{C}H(CONH_2)$ is obtained by addition to a monomer molecule and can be seen up to −80°C. Above −20°C, a 3-line signal is observed due to the following growing polyacrylamide radical[7,8,11]:

$$\sim\sim\sim\; C_\beta H_2-\dot{C}_\alpha H-CONH_2$$

Above −20°C, and at room temperature, the 3-line e.s.r. spectrum obtained indicates that polymerization occurs, molecular motions are increased, and the radical has lost all of its orientation dependencies with respect to the lattice. The polymer nucleates as a second amorphous phase with further reactions taking place at the monomer–polymer interface. This 3-line signal of the growing polyacrylamide radical is relatively stable with respect to time at room temperature, but decays very rapidly at elevated temperatures. At 60°C the e.s.r. signal decays rapidly and within one hour all radicals disappear[3,8,11].

For the growing polyacrylamide radical

$$\sim\sim\sim\; C_\beta H_2-\dot{C}_\alpha H-CONH_2$$

the values for the coupling constants are given as $a_\alpha^H = 20.3$ G, $a_\beta^{H_1} = 27.5$ G, and $a_\beta^{H_2} = 2.6$ G. The coupling constants of the α and β protons of the radicals for the vinyl monomers are given by the following expressions[11]; $a_\alpha = 23.7\,\rho_\alpha\,G$, and $a_\beta = 58.6\,\rho_\alpha \cos^2\theta\,G$, where ρ is the spin density carried by α carbon (0.88) and θ is the angle between the axis of the 2p orbital of the unpaired electron and the projection of the C_β–H bond on C_α–C_β plane. Owing to α and β carbon atom splittings a 3-line spectrum with intensity ratio 1:2:1 is observed.

(i) U.v.-irradiated acrylamide gives a spectrum similar to the previously obtained γ-irradiated acrylamide and corresponds to the 3-line spectrum for the growing polyacrylamide radical at room temperature. E.s.r. spectra of the polycrystalline acrylamide irradiated with u.v rays are given in *Figures 2A*, *3A* and *5A*, under various experimental conditions.

This characteristic signal is stable under vacuum conditions at room temperature, but if the samples are stored at 60°C a rather slow decay is observed. The signal decays at 60° with first order kinetics with rate constant 2.3×10^{-2} h^{-1} in quartz tubes. The activation energy of this decay was calculated as 19.2 kcal mol^{-1}. However, this decay is not continuous, but reaches a limiting value, and becomes constant after a certain time as seen in *Figures 2B* and *3B*. This is attributed to the existence of some radicals isolated within the amorphous polymer matrix.

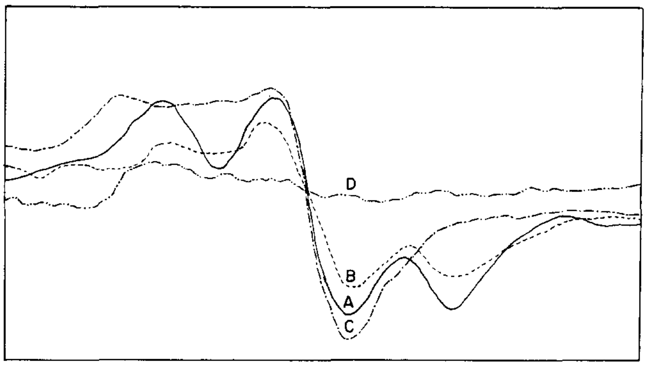


Figure 2 E.s.r. spectrum of acrylamide irradiated in Pyrex tube at 40°C for 6 h: (A) signal taken at room temperature after irradiation, (B) sample stored at 60°C for 163 h, (C) sample opened to air for 2.35 h, (D) sample opened to air for 165 h

When this sample is exposed to atmospheric oxygen, the sudden formation of the 2-line asymmetric peroxidic radical was observed in a time period as short as one hour (*Figure 2C, 3C*). The peroxidic radical is not stable at room temperature, but decays with second order kinetics with rate constant 6.0×10^{-4} ht^{-1} h^{-1} in quartz tubes. After one week complete decay was observed (*Figure 2D, 3D*).

Since it has been observed that γ-irradiated acrylamide is not influenced by oxygen[2], the formation of peroxy radicals after oxygen exposure for u.v.-irradiated crystals, provides definite proof of the surface character of the reactions.

The peroxidic radical formed decays more rapidly than the macroradical itself by bimolecular termination reaction, due to the fact that peroxidic radicals are more active in the hydrogen abstraction process. Consequently, at first, the 3-line spectrum of the growing polyacrylamide radical turns into an asymmetric 2-line spectrum of the peroxidic radical and then disappears completely in a short time due to the following reactions:

$$R\cdot + O_2 \rightarrow ROO\cdot$$

$$ROO\cdot + R'H \rightarrow ROOH + R'\cdot$$

Here, the asymmetry of the signal arises from g-anisotropy, which depends on spin-orbit coupling and the absence of contact hyperfine interactions, which indicates the unpaired spins are located mainly on the oxygen atom as given below:

$$\sim\!\sim\!\sim\; CH_2-CH(CONH_2)-[O]-O\cdot$$

If one electron is lost from an oxygen atom, there will be a small displacement. This distortion (defect) causes a 4-fold axis of symmetry and the system is described as having an axial symmetry which is due to $g_{\|} < g_{\perp}$[12]. For these systems, the X and Y axes are equivalent. The unique axis is usually designated as Z, and the value of g for $H \| Z$ will be called $g_{\|}$, where H is the applied magnetic field. The g factor for H in the XY plane is then $H_{\perp}Z$ and will have the constant value $g_{\perp}$. The system becomes anisotropic with a new g value defined as:[12]

$$g_{\text{eff}}^2 = g_{\|}^2 \cos^2\theta + g_{\perp} \sin^2\theta$$

where θ is the angle between H and the symmetry axis of the defect. However, in isotropic systems, such as dilute liquid solutions of low viscosity, their isotropic behaviour is the result of rapid random reorientation of solute molecules. Any isotropic system has 3 mutually perpendicular directions where:

$$g_{xx} = g_{yy} = g_{zz}$$

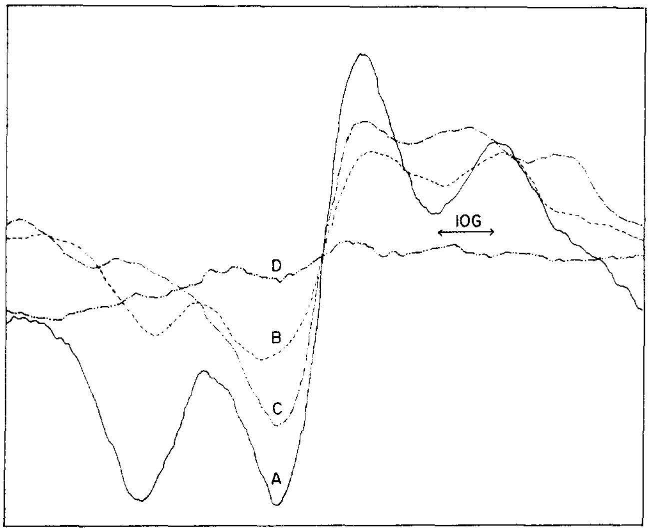


Figure 3 E.s.r. spectrum of acrylamide irradiated in a quartz tube at 60°C for 6.5 h: (A) signal taken at room temperature after irradiation, (B) sample stored at 60°C for 144 h, (C) sample opened to air for 2.5 h, (D) sample opened to air for 213 h

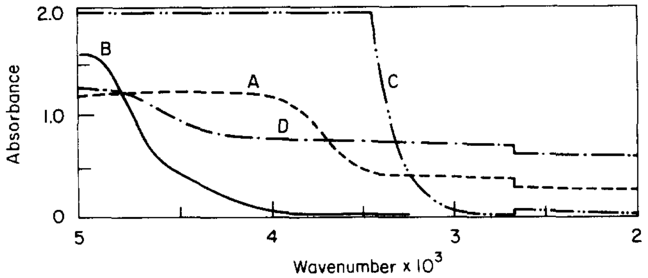


Figure 4 U.v. absorption spectra of: (A) solid acrylamide, (B) 2.2 mg acrylamide/100 ml water, (C) Pyrex tube empty, (D) quartz tube empty

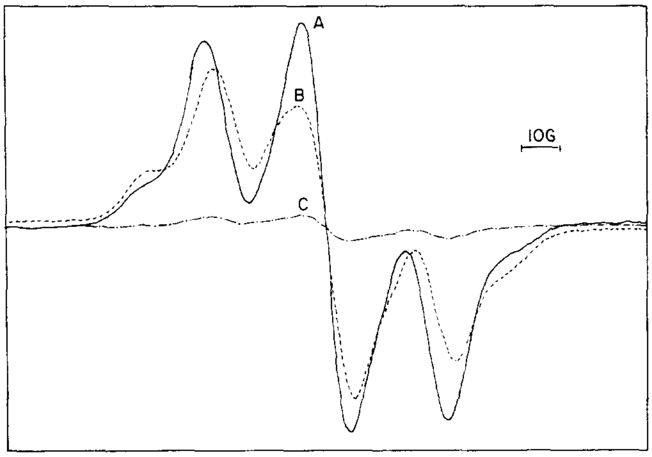


Figure 5 E.s.r. spectrum of acrylamide irradiated in quartz tube at 40°C for 16 h: (A) signal taken at room temperature after irradiation, (B) sample opened to air at room temperature for 5 h without heating first to elevated temperatures, (C) sample opened to air for 648 h

The two types of experiments described above were performed either by using quartz or Pyrex tubes. By using DPPH standard the initial radical concentrations were calculated for each case. With quartz tubes the radical concentrations achieved were 37 times larger than with the Pyrex tubes. (The initial radical concentration calculated in quartz tubes was 3×10^{-7} mol/g of acrylamide.) This was attributed to the fact that Pyrex absorbs u.v. light at the absorption region of acrylamide, as shown in *Figure 4*.

If oxygen is introduced into irradiated acrylamide samples without heating the sample first, the formation of peroxidic radicals occurs very slowly since oxygen can react only with the radicals at the surface (*Figure 5B*). The asymmetric signal of the peroxidic radical overlaps with the triplet of growing polyacrylamide radical. This signal shows a slow decay at room temperature (*Figure 5C*).

Figure 6 shows the decay curves of the peroxidic radical for the system given in the previous Figure where it was

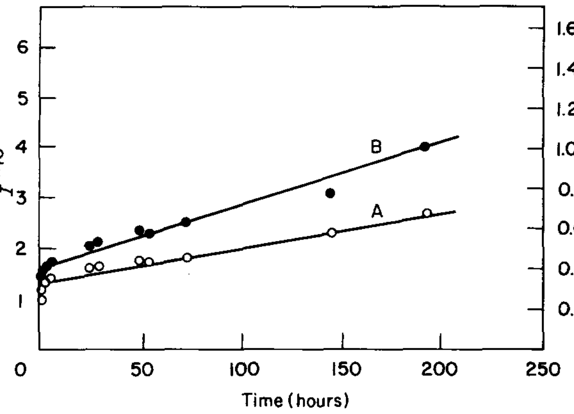


Figure 6 Second order decay of the peroxy radical at room temperature (acrylamide irradiated in quartz tubes at 40°C for 16 h opened to air without heating): (A) ○ : peroxy radical decay measured as peak to peak height 1/[*I*] vs. time (hours), (B) ● : peroxy radical decay measured as radical concentration 1/[R·] vs. time (hours)

opened to the air before heating up to 60°C. Decay was examined both in terms of the charge of peak to peak height [*I*] and the change in radical concentration [R·]. Second order rate constants calculated at room temperature as 6.9×10^{-5} ht^{-1} h^{-1} in terms of change of [*I*] or 3.2×10^{4} g mol^{-1} h^{-1}, in terms of [R·], are about 10 times slower than is the case when the system was opened to the air after heating (6.0×10^{-4} ht^{-1} h^{-1}) [ht ≡ height]. This can be attributed to the system being opened to atmosphere without heating, before reaching high radical concentrations.

(ii) U.v.-irradiated polycrystalline propionamide gives a 5-line signal which is identical with the signal obtained with γ-irradiated propionamide[7,13]. This spectrum is attributed to a system of two overlapping quartets each with 1:3:3:1 peak height ratio which could be expected from $C_\beta H_3$–$\dot{C}_\alpha$H–CONH$_2$ radical (*Figure 7A*). This radical is stable at room temperature, but decays very fast at 60°C. As seen in *Figure 7B*, *7C*, it decays continuously without reaching a limiting value with second order kinetics with rate constant being 5.5×10^{-3} ht^{-1} h^{-1}. Since no radical was left at the end of this decay, when the sample is exposed to oxygen no peroxy radical was observed as seen in *Figure 7D*.

This continuous decay can be explained by the crystal structure of propionamide which is rather different from acrylamide. Other than chemical saturation, the principle differences between acrylamide and propionamide crystals is that the distance between planes is 11% greater in propionamide which provides freer diffusion. The planes are held together by hydrogen bonding between >C=O and >N– bonds.

For the propionamide radical $C_\beta H_3$–$\dot{C}_\alpha$H–CONH$_2$, the coupling constant for the α proton is $a_\alpha = 20.9$ G and for 3 equivalent β protons are $a_\beta = 25.8$ G resulting a 5-line signal with an intensity ratio of 1:4:6:4:1.

(iii) Three different solid solutions of acrylamide and propionamide were prepared containing 10%, 50%, 90% (by weight) acrylamide. These two molecules are isomorphous. In all cases, u.v.-irradiated mixtures show similar spectra to those obtained with pure acrylamide. This result indicates that propionamide radicals formed by u.v.-irradiation easily add monomeric acrylamide and consequently only the characteristic signal of the growing polymeric acrylamide radical is observed. This can be explained by the high chain transfer constant of propionamide. At 25°C chain transfer constants for propionamide and acrylamide are 2.2×10^{-2} and 2.0×10^{-5}, respectively. At 60°C, these values are, respectively, 6.4×10^{-3} and 6.0×10^{-5}.[9] The high chain transfer efficiency of propionamide in solid solution with acrylamide strongly suggests an important degree of control of the polymerization by the crystal lattice. Fadner and Morametz[9] suggested that propionamide acts as a chain transfer agent to decrease the molecular weight of the polymer in solid solutions. Once the polymer nuclei are formed, propionamide and acrylamide molecules can diffuse along the polymer–monomer interface and possibly along crystal defects. There is probably some recrystallization taking place at the interface. The polymer is denser than the solid solution and its formation produces a net shrinkage and therefore lattice strain. This explains the higher polymerization rates in the presence of propionamide[3,14].

Figure 8A shows the spectra of the u.v.-irradiated samples of acrylamide-propionamide mixed crystals (50% acrylamide). The spectra obtained from solid solutions of acrylamide and propionamide show a slow decay at 60°C. The rate of decay increases with the increasing ratio of propionamide in these mixtures. However, at this temperature (60°C) decay of the signal measured as peak to peak height stops at certain limiting values after which there will be no further decay (*Figure 8B*). The same behaviour was observed for pure acrylamide, whereas only 25% of the original signal decays at this temperature and reaches a limiting value. On the other hand, for u.v.-irradiated propionamide the complete decay of the original signal, without reaching a limiting value, was observed at the same temperature (*Figure 7C*). For a solid solution containing 10% acrylamide, the signal decays by 45%. If the acrylamide ratio increases and exceeds 50% in the solid mixtures, the limiting value of the decay will be about 25–30% of the original signal. The percentage decay increases with the increased propionamide percentages in the mixture.

Various samples of acrylamide–propionamide mixtures as well as the pure compounds, were kept at 60°C after u.v. irradiation and the time dependence of the e.s.r.

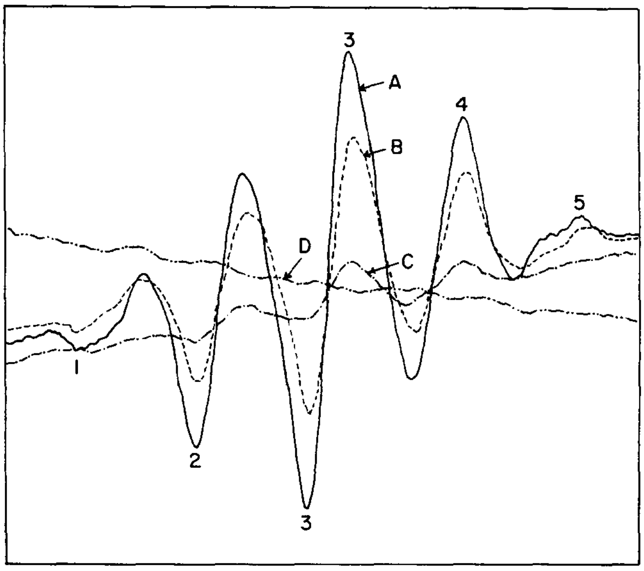


Figure 7 E.s.r. spectrum of propionamide irradiated in a quartz tube at 40°C for 6 h: (A) signal taken at room temperature, (B) stored at 60°C for 60 min, (C) stored at 60°C for 470 min, (D) opened to air for 5 min

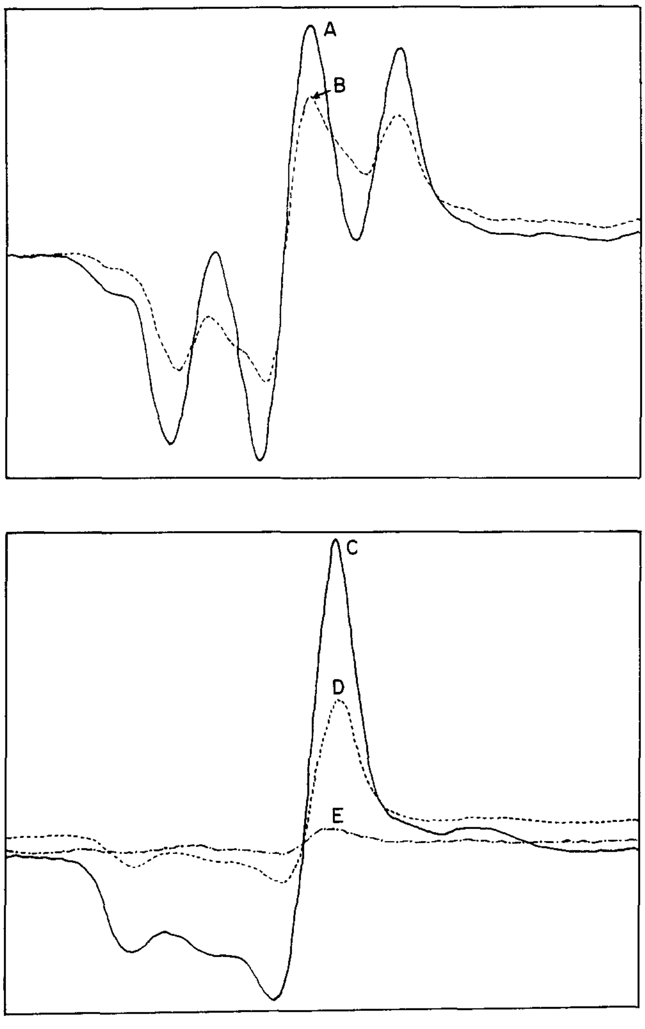


Figure 8 E.s.r. spectrum of 50% propionamide—50% acrylamide mixed crystals irradiated at 40°C for 6 h: (A) signal taken at room temperature after irradiation, (B) sample stored at 60°C for 247 h, (C) sample opened to air for 1.5 h, (D) sample opened to air for 25 h, (E) sample opened to air for 150 h

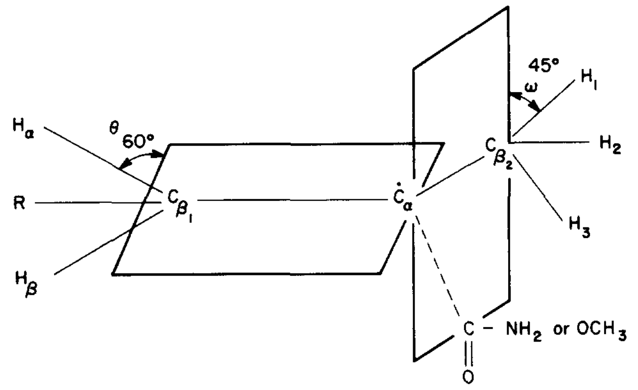
signal was studied at this temperature. Upon reaching the limiting values, these samples were opened to the air and characteristic asymmetric singlet of the primary radical was immediately observed. Thereafter, the decay of the spectrum of the peroxidic radical was studied at room temperature. *Figures 8C, D, E* show the formation and the decay of peroxidic radical for one of the samples (containing 50% acrylamide) and were taken after 1.5, 25 and 150 h of oxygen exposure, respectively. Peroxidic radicals show a second order decay with the following rate constants: 4.2×10^{-4} for 90% AA, 7.6×10^{-4} for 50% AA, 20×10^{-4} for 10% AA, the units being $(\text{height})^{-1}$ $(\text{h})^{-1}$. It will be seen that the rates of decay increase with increasing propionamide percentage in the mixture[10].

(iv) U.v.-irradiated methacrylamide gives a 9-line spectrum which is identical with the one obtained for u.v.-irradiated methacrylic acid[15] and X-ray irradiated methyl methacrylate[16].

Figure 9 shows a 9-line e.s.r. spectrum of the propagating methacrylamide radical at room temperature. This 9-line spectrum is expected from

$$\sim\sim\sim\; C_{\beta_1}H_2-\dot{C}_{\alpha}(C_{\beta_2}H_3)-CONH_2$$

radical. The open structure of this radical is:



where θ is the angle between $C_{\beta_1}H_2$ protons and C_α–C_{β_1} plane. ω is the angle between CH_3 protons and C_α–C_{β_2} plane, ϕ is the projection along the C_{β_1}–C_α bond (angle between the projection of C_{β_1}–H bond on the plane and the 2p orbital axis of the unpaired electron). R represents the remainder of the polymer chain. Since it is perpendicular to the radical plane it makes no contribution to the signal shape.

Similar radical species can have two different conformations: (i) Above 4°C and at room temperature a 9-line spectrum is obtained with projection angle ϕ taking values either 0° or 15° and $\theta = 60°$ resulting in two equivalent $C_{\beta_1}H_2$ protons, each with coupling constant 11.5 G. ω angle is 45° and $C_{\beta_2}H_3$ protons are also equivalent, each having coupling constant values of 23.0 G[16]. The 9-line spectrum results from a distribution of conformations and hindered rotation about the C_α–C_{β_1} bond, such that the methylene protons H_1 and H_2 interact equally with the unpaired electron on C_α. H_α and H_β make 60° angles with C_α–C_{β_1} plane. (ii) Below −20°C the projection angle ϕ is 5° and results in two different angles for C_{β_1}–H_2 protons ($\theta_1 = 55°$ and $\theta_2 = 65°$C). A 13-line spectrum is obtained with two nonequivalent C_β–H_2 protons with two different coupling constants ($a_{\beta_1}^{H_1} = 15.15$ G and $a_{\beta_1}^{H_2} = 8.05$ G). C_{β_2}–H_3 protons are all equivalent, each with coupling constant 23.0 G[17,18]. The 13-line spectrum is attributed to a single conformation adopted as a result of restrictions imposed by the lattice at the lower temperatures[17,18].

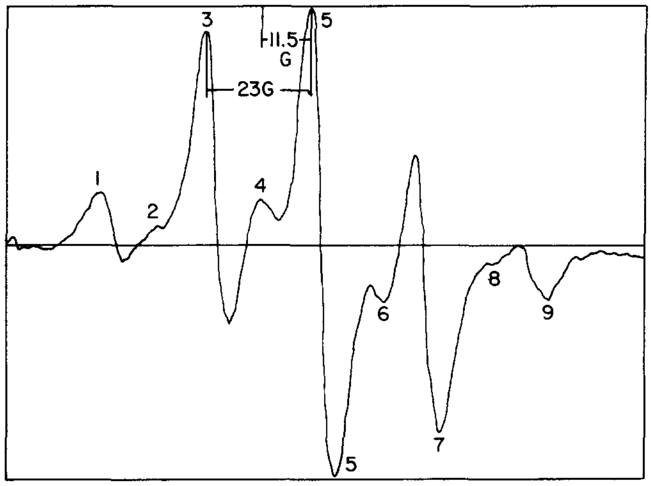


Figure 9 E.s.r. spectrum of methacrylamide irradiated at 42°C for 17 h. Signal taken at room temperature after irradiation

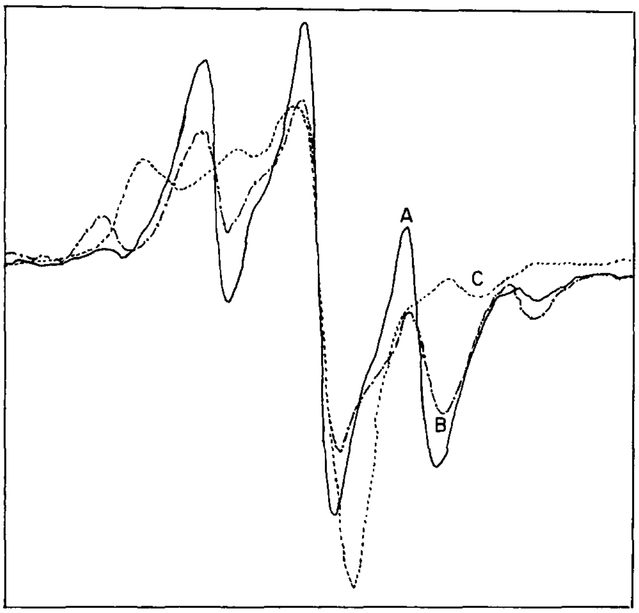


Figure 10 E.s.r. spectrum of 25% acrylamide—75% methacrylamide mixed crystal irradiated at 42°C for 17 h: (A) (———) signal at room temperature after 3 h of irradiation, (B) –·–·–) stored at 60°C for 260 h ($RG = 1.6 \times 10^4$), (C) (– – –) opened to air for 70 min ($RG = 1.0 \times 10^4$)

In this study it was observed that u.v.-irradiated methacrylamide crystals do not yield measurable amounts of polymer. This indicates that the polymerization rate of methacrylamide is much smaller than that of acrylamide.

(v) Five different solid solutions of acrylamide–methacrylamide were prepared with changing methacrylamide percentage between (16–90%) in the mixture. E.s.r. spectra obtained for acrylamide–methacrylamide mixed crystals reveal that during polymerization both radicals are present. As methacrylamide percentage in the mixture increases, the signal becomes similar to the 9-line spectrum for pure methacrylamide. When there is 75% methacrylamide in the original mixture, a 5-line signal is observed with even-numbered peaks in methacrylamide signal appearing as shoulders as seen in *Figure 10A*. When the methacrylamide percentage is about 16%, the characteristic 3-line acrylamide signal is dominant. For the mixed crystals the decay at 60°C is not continuous, but reaches a limiting value for all compositions (*Figure 10B*). When a decay study was applied, the values of the second order rate constants obtained exhibited decreasing values as methacrylamide percentage in the original mixture increased. This indicates that the polymethacrylamide signal is more stable than that of polyacrylamide. When the system was exposed to air, sudden formation of peroxidic radical was observed with a sharp increase in peak to peak heights (*Figure 10C*). However, the signal decays at room temperature within a short time. Also, it is very apparent from these spectra that when the percentage of acrylamide is increased in the mixture, the peroxide radical formation also increases. Formation of peroxide radical is more difficult when methacrylamide percentage is increased in the solid solution.

U.v.-irradiated acrylamide–methacrylamide and their mixed crystals were investigated here for the first time. Previously the solid state polymerizations of acrylates and methacrylates were usually initiated using γ-rays[4,5,7,8].

This work indicates that acrylamide and propionamide and their mixed crystals can be polymerized by u.v. light to high conversions in the solid state.

The u.v.-irradiated acrylamide crystals show a 3-line spectrum which is similar to the one obtained from the γ-irradiated acrylamide at room temperature. This clarifies any doubts concerning the polymerization mechanism of γ-irradiated acrylamide as to whether it proceeds via an ionic or free radical process. This indicates that the free radical initiation mechanism proposed for solid-state polymerization is correct.

Oxygen addition causes a typical change in the e.s.r. spectrum of u.v.-irradiated samples providing a definite proof for the surface character of the reactions. When O_2 is admitted to irradiated amides the e.s.r. spectrum is rapidly quenched and polymerization inhibited.

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