E.s.r. study of the reaction of gases with the free radicals produced by u.v. radiation on the surfaces of acrylamide and some crystalline materials: 2. Results of H_2, SO_2 and Cl_2 admission to acrylamide, propionamide, methacrylamide and polyacrylamide

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The differences in reactivity of various gases such as hydrogen, chlorine and sulphur dioxide with the radicals of irradiated acrylamide, propionamide and methacrylamide monomers and polyacrylamide were studied. The free radicals produced in acrylamide as well as in polyacrylamide were not affected significantly by the addition of hydrogen and sulphur dioxide. These gases diffuse through the interface between the monomer and polymer phases rather than reacting with the radicals produced in the locations where crystalline structure is defective. Gas chromatographic analysis of irradiation products indicates that the mechanism proceeds on a radical produced by hydrogen atom scavenging. The hydrogen atoms result only from radiolysis. Chlorine gas was found to be an agent for slowing down the radical decay rather than becoming a radical initiator. Consequently, irradiation in the presence of chlorine gas results in higher polymerization yields.

(Keywords: electron spin resonance; gas reactivity; free radicals; u.v. radiation; acrylamide)

Since u.v.-initiated reactions are mostly radical reactions occurring on the surface of the samples, it is very important to observe the effects of various gases on these samples. The reaction of the radicals formed with these gases can give an idea about the type of radical structure. Electron spin resonance (e.s.r.) provides a convenient method for this purpose. An understanding of the primary process of radical formation and effects of some gases such as oxygen, sulphur dioxide, hydrogen and chlorine, and effect of crystallinity on reaction mechanism, can lead to a better understanding of solid-state chemistry. The type of radicals formed and the changes occurring in these radicals with the admission of gases and the effect of heat on the shape and decay of the radical can be examined by means of e.s.r. spectroscopy. The results were compared with the radicals obtained by γ-irradiated samples under similar conditions[1-7].

It was interesting to observe that the free radicals produced in acrylamide as well as in polyacrylamide sampes were not affected significantly by the addition of hydrogen and sulphur dioxide. However, when acrylamide is irradiated in the presence of chlorine, chlorine atoms act as a radical stabilizing agent. Chlorine gives much more remarkably changes in the polyacrylamide signal, which can be explained by the crystalline structure of acrylamide and the amorphous structure of polyacrylamide.

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 thrice from warm chloroform. The melting point was 110°C.

Chloroform and acetone were obtained from E. Merck A.G. Methanol was a product of Rieede–De Haën A.G., Seelze–Hannover Co.; they were both used directly without any further purification. Triple-distilled water was obtained by redistilling laboratory distilled water

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first over acidic dichromate; then the oxygen mixed vapour was condensed and distilled for a second time over alkaline potassium permanganate.

Hydrogen gas was chemically pure and used at 680 mmHg pressure. Sulphur dioxide had commercial grade purity. Chlorine was obtained from the Matheson Co. Inc. and used at 1 atm pressure. They were all used directly without any further purification.

The gas was admitted to the system either before or after irradiation. Therefore, two types of processes were employed for gas admission.

Gas admission before irradiation was applied to the system primarily to study the catalytic ability of the gases to initiate polymerization. For this purpose the type of tube shown in *Figure 1a* was used. The tubes containing purified and dried monomer samples in section E were connected to the vacuum line at point A and degassed. First the gas was introduced into the manifold of the vacuum line. To provide atmospheric pressure in the system, gas flow was maintained by observing bubbles in a washing bottle. Then the gas was introduced into the system by opening the stopcock where the tube was connected to the vacuum line. The gas was collected at the bottom by immersing the tube in liquid nitrogen. The tube was then sealed off at point B. The sample was transferred to the middle section of the tube D, and irradiated in a horizontal position at constant temperature under a u.v. lamp (Philips, 300 V, 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 taken at room temperature with a Varian E-12, 9.5 GHz, X-Band e.s.r. spectrometer.

For the case of gas admission after irradiation, the powdered samples were immersed in a test tube of the type shown in *Figure 1b* and were first connected to the vacuum line at point A. After evacuation, they were sealed at point B and irradiated. The first e.s.r. signal was taken immediately after completion of the irradiation period. The tube was then again connected to the vacuum line, this time at point G and evacuated. First the manifold of the vacuum system was swept by the gas and the gas was vented out via a gas washing bottle which was connected to the manifold. Then the gas was introduced into the tube by breaking the breakseal H, with a magnet I, which was placed inside and held with another magnet bound to the outside of the tube. Then Teflon stopper J was closed. Gas diffusion into the system was provided by immersing the tube in liquid nitrogen. The tube was removed from the vacuum system at point G and the e.s.r. signal of the sample was taken right after gas admission.

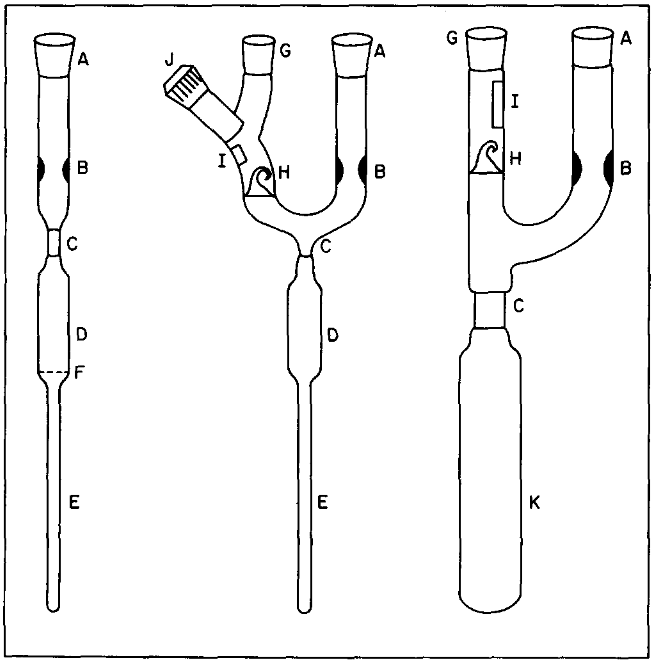


Figure 1 Irradiation tubes for e.s.r. study: (left) irradiation tube; (middle) tube for gas admission; (right) tube for gas chromatographic analysis

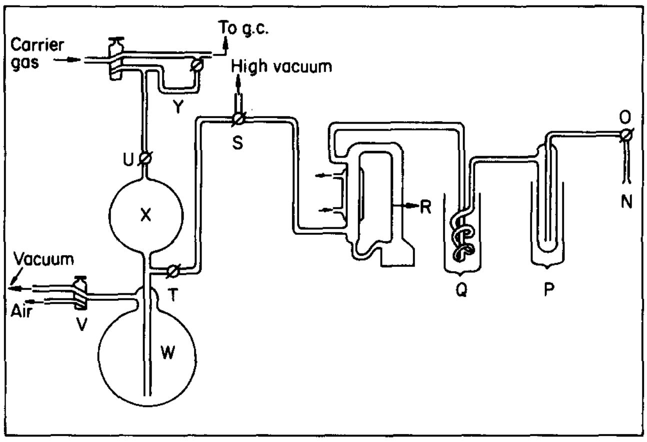


Figure 2 Microgas analysis system

A Varian model-920 gas chromatograph was used for the analysis of radiolysis products. For these determinations a 2.5 m long, coiled, stainless-steel column with inner diameter of 4 mm, packed with Porapak Q (80–100 mesh) was used. The carrier gas was helium with a flow rate of 24 ml $\min^{-1}$. The microgas analysis line was designed to collect micromole amounts of gaseous compounds, as shown in *Figure 2*. The system was connected to a high-vacuum line via a three-way stopcock S. The sample to be analysed was admitted to the system at point N. The shape of the tube connected to N is given in *Figure 1c*. After evacuation, the system was isolated from the vacuum line and the breakseal H of the tube broken by means of a magnet I. High-boiling compounds were trapped in traps P and Q as shown in *Figure 2*. With the aid of a single-stage diffusion pump R, the gaseous products were pumped to the cell Y. In order to pump all of the gases into cell Y, mercury in reservoir W was pumped into X by means of a two-way stopcock V, and stopcock U was closed. Mercury was then collected in part W again. This operation was repeated at least six times. Finally, mercury was pumped up to Y. The contents of the cell Y were then passed into the gas chromatograph, which was equipped with a dual thermal conductivity detector operating at 75°C.

RESULTS AND DISCUSSION

It has been shown previously by means of e.s.r. spectroscopy that acrylamide scavenges hydrogen atoms at low temperature (−196 to −125°C) during γ-radiolysis[1–3]. At this temperature, acrylamide scavenges the hydrogen atom liberated during radiolysis, forming radicals equivalent to those produced from propionamide by loss of a hydrogen atom: $CH_3\text{–}\dot{C}H\text{–}CONH_2$ (P radical). Above −20°C the acrylamide spectrum loses all of its orientation dependence and a propagating polymer radical $\sim\!\sim\!\sim CH_2\dot{C}H\text{–}CONH_2$ is obtained[1].

The gaseous decomposition products for a wide range of solid solutions of acrylamide and propionamide irradiated by γ-rays were measured and G values for hydrogen, carbon monoxide and methane determined[1]. The results indicate that either energy transfer reactions or hydrogen atom scavenging are important in determining yields. In our previous work it was shown in detail that u.v.-irradiated acrylamide and propionamide, at room temperature, gave spectra similar to the spectra obtained for γ-irradiated samples[4–7].

To find out if the mechanism proceeds on a P-type radical by hydrogen atom scavenging, it was necessary to determine if hydrogen is produced as a radiolysis product or is formed due to the vapour pressure of the sample only, when irradiated at 40°C by u.v. rays. For this purpose, two sample tubes were prepared and the identification of hydrogen was attempted for both irradiated and non-irradiated samples. If hydrogen exists in non-irradiated acrylamide it will thus be shown not to be a radiolysis product.

For the gas analysis of the irradiation products of acrylamide and propionamide, the samples were irradiated by u.v. rays in tubes shown in *Figure 1c*. Gas chromatographic analysis was accomplished by comparing the spectra with those given in 'Atlas of Gas Analysis by Gas Chromatography'[8]. Helium was used as a carrier gas. When 5 μl air was injected into the system the peak height was 29 mm, as shown in *Figure 3b*. At attenuation 2, the gas flow was 24 ml min^{-1} and the hydrogen gas calculated by using *Figures 3a* and *3b* was found to be 48.6 μl in 50 ml air and hydrogen mixture; 48.6 μl hydrogen produced a peak of 8 mm height, as shown in *Figure 3a*.

For irradiated acrylamide (evacuated and irradiated at 40°C for 16 h) the hydrogen produced a 5 mm peak height, as shown in *Figure 4a*, with an attenuation of 1. By simple proportion, 15.2 μl hydrogen was obtained when 1.44 g of acrylamide was irradiated initially by u.v. rays. Non-irradiated acrylamide at the same conditions (evacuated and kept at 40°C for 16 h) did not produce any hydrogen, as shown in *Figure 4b*. This indicates that hydrogen is a radiolysis product and can be produced by irradiation only.

The propionamide sample was irradiated in the same way. Hydrogen produced from propionamide gave a peak height of about 5 mm, as shown in *Figure 3c*, with attenuation held at 2. By proportion, 30.4 μl hydrogen was obtained from 1.58 g of irradiated propionamide.

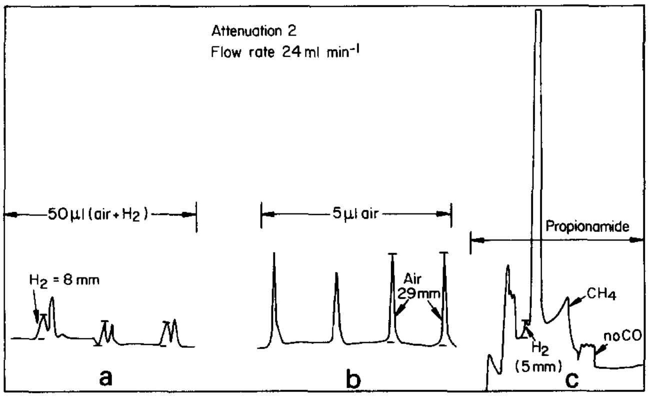


Figure 3 Gas chromatographic analysis of air and propionamide: (a) 50 μl (air $+H_2$); (b) 5 μl air; (c) propionamide irradiated at 40°C for 16.5 h (30.4 μl H_2 in irradiated propionamide)

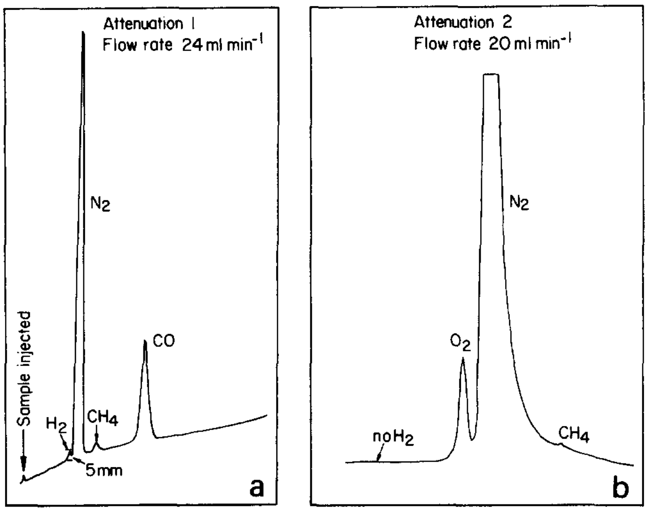


Figure 4 Gas chromatographic analysis of: (a) acrylamide (irradiated at 40°C for 16.5 h); (b) non-irradiated acrylamide (stored at 40°C for 16.5 h without irradiation)

The hydrogen yield from γ-irradiated propionamide was found to be higher than that from γ-irradiated acrylamide[1]. In the γ-irradiated solid solutions studied, as the percentage of acrylamide increased in the mixture, the hydrogen yield decreased. However, the hydrogen yield was found to be higher than carbon monoxide and methane yields. Factors of molecular size of products and lattice dimensions may effect the diffusion and recombination reactions; as a result the small size of the hydrogen molecule would produce a higher yield. The decrease of G_{H_2} while increasing acrylamide percentage in the solid solutions can be explained by the unsaturation in the acrylamide molecule where hydrogen is scavenged more easily by this molecule due to the double bonding. Methane and carbon monoxide have greater physical size so their ability to diffuse through the cage formed by the lattice is less than that of hydrogen; consequently their G values are much smaller[1].

The results obtained from the gas chromatographic analysis of u.v.-irradiated acrylamide and propionamide samples agree with the data given for γ-irradiated samples[1]. A sample of 1.44 g of u.v.-irradiated acrylamide produces only 15.2 μl hydrogen, while almost the same amount of propionamide (1.58 g) after irradiation produces about 30.4 μl hydrogen, or about twice the amount. This can be explained by the same reason given above. Gas chromatographic analysis of u.v.-irradiation products of acrylamide and propionamide samples indicate that hydrogen is a radiolysis product produced by irradiation only.

The nature of the e.s.r. spectra of the radicals obtained by u.v.-irradiated acrylamide, propionamide and methacrylamide were explained briefly in previous work[7,8]. E.s.r. spectra of u.v-irradiated acrylamide and polyacrylamide samples exhibit different shapes. The spectrum of the radicals was attempted by an analysis of polyacrylamide signal using a simulation method. γ-Irradiated polyacrylamide at -196°C gives a poorly resolved quintet[9,10]. This is identical with the u.v.-irradiated polyacrylamide spectrum obtained at room temperature as seen in *Figure 5* (trace A). Here the spectrum lines are broadened by the inhomogeneities of the local fields acting on unpaired electrons with a corresponding poor resolution. The nature of the radicals

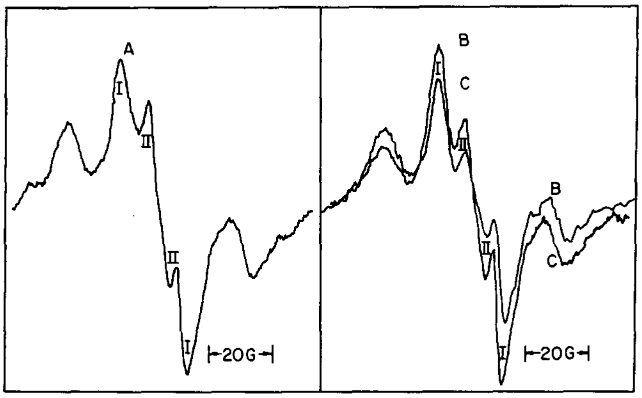
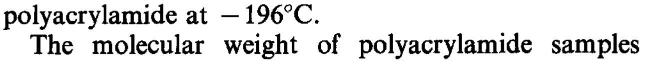


Figure 5 E.s.r. spectrum of polyacrylamide irradiated at 40°C for 6 h. The effect of H_2 admission: A, signal taken after keeping irradiated sample at room temperature for 115 h; B, signal taken at room temperature after 211 h of H_2 admission; C, sample opened to air for 193 h

produced by the γ-irradiation of polyacrylamide has been analysed earlier[10]. At −196°C it gives the $-CH_2-\dot{C}(CONH_2)-CH_2-$ radical[10]. The quintet with a splitting of 22 G in the spectrum is caused by the radical shown above in which the unpaired electron is localized in the carbon sp^3 orbital. At low temperature the radical may maintain the conformation of the initial chain due to the presence of hydrogen bonds and the $-CONH_2$ side-chain groups. Transition of a radical to the planar form involves overcoming an energy barrier. Upon heating to room temperature, the spectra of γ-irradiated polyacrylamide gives a triplet with a splitting of 26 G, which is due to the same radical with $a_\beta^{H_1} = 26$ G and $a_\beta^{H_2} = 0$–5 G[11]. Upon heating, the e.s.r. spectrum quintet transforms irreversibly into a triplet with the splitting of 26 G. It is assumed that illumination and heating cause reversible radical conversion by the following reaction:



$$\begin{array}{c} -\dot{C}- \\ | \\ O{=}C{-}NH_2 \end{array} \underset{kT}{\overset{h\nu}{\rightleftharpoons}} \begin{array}{c} -C- \\ \| \\ {}^{\bullet}O{-}C{-}NH_2 \end{array}$$

When polyacrylamide is exposed to light, the charged radicals are evidently converted into neutral radicals. Since u.v.-irradiated polyacrylamide gives a spectrum at room temperature as shown in *Figure 6*, with a splitting of 22 G, as a result of a poorly resolved quintet, it can be concluded that the radical $-CH_2-\dot{C}(CONH_2)-CH_2-$ is identical to the one obtained by γ-irradiation of polyacrylamide at −196°C.

The molecular weight of polyacrylamide samples before and after extensive u.v. irradiation was found to be the same (2.0×10^6). Intrinsic viscosity in aqueous solution at 30°C determined by using the Scholton equation[12] ($\eta = 6.31 \times 10^{-5}\, M^{0.8}$) was found to be 8.1 dl g^{-1} prior to and after the irradiation. This indicates that the molecular weight of polyacrylamide does not change upon irradiation.

The polyacrylamide spectrum is stable at room temperature and decays according to second-order kinetics at elevated temperatures with a rate constant $k_2 = 3.4 \times 10^{-3}$ height^{-1} h^{-1}. When the sample was opened to air, no peroxy radical was observed, in contradiction to the acrylamide radical as shown in *Figure 5* (trace C).

Dole *et al.* showed the catalytic effect of hydrogen molecules on the formation of allyl radicals from alkyl radicals[13]. They produced alkyl radicals ($-CH_2\dot{C}HCH_2-$) by electron beam irradiation of polyethylene at liquid-nitrogen temperature. When alkyl radicals are heated to room temperature, they convert to allyl free radicals: ($-\dot{C}HCH{=}CH-$). The decay of the alkyl radicals is accurately first order and markedly catalysed by molecular hydrogen[13]. The rate constant for the uncatalysed reaction is smaller than for similar gas reactions by a factor of 10^7. Free radicals usually decay by a second-order recombination process, but in this case alkyl radicals decay with first order because the rate-determining step is a first-order hydrogen jump mechanism[13,14]. A small number of alkyl radicals that are regenerated from the allyl by u.v. irradiation at −196°C have no measurable decay at room temperature in the absence of molecular hydrogen. In the presence of hydrogen they decay by a second-order process but do not re-form to the allyl radical.

The catalytic effect of hydrogen on the decay rate of the radicals formed by u.v. irradiation of acrylamide and polyacrylamide was studied at room temperature. Addition of hydrogen does not change the shape of the signal of u.v.-irradiated acrylamide, as shown in *Figure 7* (trace B). However, this signal decays rather fast at first, then relatively slowly at room temperature. A slow second-order kinetic with rate constant $k_2 = 7.8 \times 10^{-4}$ height^{-1} h^{-1} is obtained. Upon oxygen admission into this system another peak appears as a shoulder; the signal decays with $k_2 = 1.5 \times 10^{-4}$ height^{-1} h^{-1}, but the characteristic shape of the peroxy radical does not appear (*Figure 7* (trace C)).

Hydrogen admission does not cause significant changes in the shape of the polyacrylamide signal, as shown in *Figure 5* (trace B). Only a slight change in the intensity of the central peak is observed. Peak I increases while peak II decreases in peak-to-peak height; this is probably caused by one type of radical at II turning into the other one at I. When this system was opened to air, the peroxy radical did not form, but the intensities of both peaks I and II were reduced. This suggests that oxygen cannot interact easily in the presence of hydrogen. It was interesting to observe that free radicals produced in acrylamide as well as in polyacrylamide samples were not affected significantly by the addition of hydrogen gas.

The shape of the signal of the u.v.-irradiated acrylamide does not change when sulphur dioxide

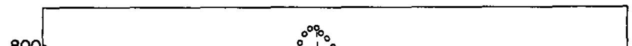


Figure 6 Absorption e.s.r. spectrum of irradiated polyacrylamide (experimental points) obtained by baseline correction of absorption spectrum of polyacrylamide (by numerical integration of the first derivative spectrum)

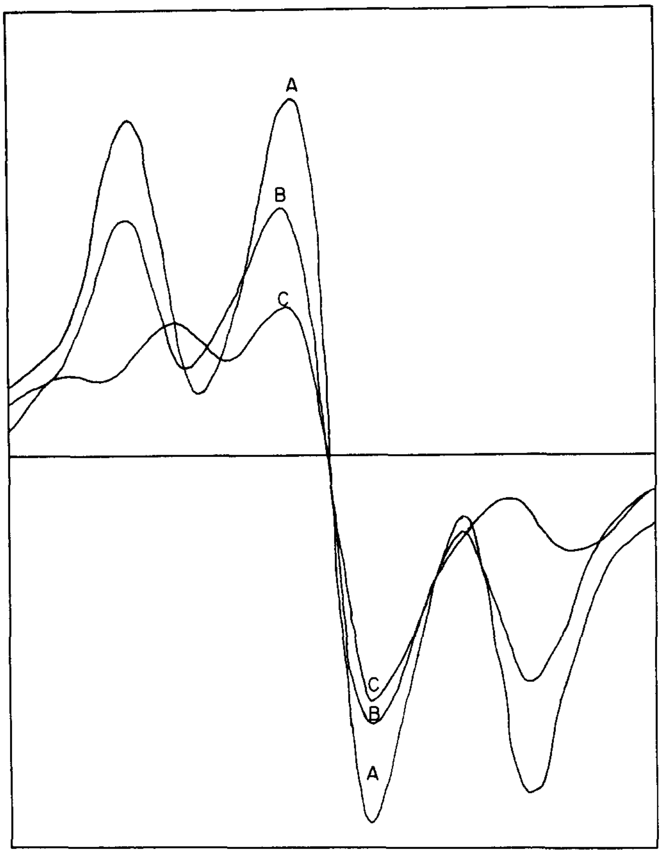


Figure 7 E.s.r. spectrum of acrylamide irradiated at 40°C for 6 h. H_2 admission at room temperature: A, signal taken after irradiation; B, signal taken after 245 h of H_2 admission; C, sample opened to air for 25.5 h

addition is made, but peak-to-peak, height decreases slowly with time (*Figure 8*). However, when sulphur dioxide is added to u.v.-irradiated polyacrylamide, asymmetry arises and $RSO_2^{\bullet}$ radical concentration increases with time (*Figure 9*). The effect of sulphur dioxide on γ-irradiated acrylamide and other amides[15-17] and on various irradiated polymers have been investigated previously, and the following conclusions were given[5,18,19].

(i) In the case of hydroxyl-containing polymers, no reactivity with sulphur dioxide was observed[18]. But γ-irradiated mono- and polyamides do react with sulphur dioxide. The hydrogen bonds formed by the NH_2 groups in acrylamides may be weaker than those formed by hydroxyls.

(ii) Irradiated amides react with sulphur dioxide, giving rise to a new type of radical whose e.s.r. spectrum is an asymmetric singlet. The absence of hyperfine contact interaction and the g anisotropy that results in the asymmetry of the signal suggests a radical with the unpaired spin totally located on a sulphur or oxygen atom.

(iii) The radicals with sulphur dioxide give the following reactions:

$$R^{\bullet} + SO_2 \rightleftharpoons RSO_2^{\bullet}$$

and some radicals are regenerated by hydrogen abstraction:

$$RSO_2^{\bullet} + R'H \rightleftharpoons RSO_2H + R'^{\bullet}$$

The sulphonyl radicals are found to be much more stable than the corresponding peroxy radicals.

(iv) Sulphur dioxide can only diffuse freely along objects such as edge dislocations and more possibly between the layers of the lattice structure[19]. Since its molecules are larger than oxygen or nitrogen monoxide molecules, its diffusion into the lattice should be much slower than that of smaller gases. In all amides the rate of $RSO_2^{\bullet}$ formation increases with decreasing particle size and increasing partial pressure of sulphur dioxide.

(v) The spectra obtained by Ueda and Kuri[20] for γ-irradiated acrylamide and polyacrylamide indicate that with sulphur dioxide addition, only a slight decrease is observed in acrylamide, while the asymmetric sulphonyl radical with corresponding increase in peak-to-peak height is easily observed in the polyacrylamide signal.

In this study it was observed that sulphur dioxide on u.v.-irradiated acrylamide and polyacrylamide causes the same changes as in the spectra of γ-irradiated samples (*Figures 8* (trace B) and *9* (trace B)). The asymmetry in the polyacrylamide spectrum, which may be caused by an anisotropic g-factor associated with incomplete quenching of the orbital angular momentum, indicates that sulphonyl radicals are formed. During the reaction the concentration of the $RSO_2^{\bullet}$ radicals increases until a maximum is reached; then a definite decay is observed.

The slower reaction velocity of sulphur dioxide with acrylamide monomer (u.v.– or γ-irradiated) than with polyacrylamide can be explained by the crystal structure of acrylamide, where sulphur dioxide molecules cannot easily penetrate, and by the amorphous structure of

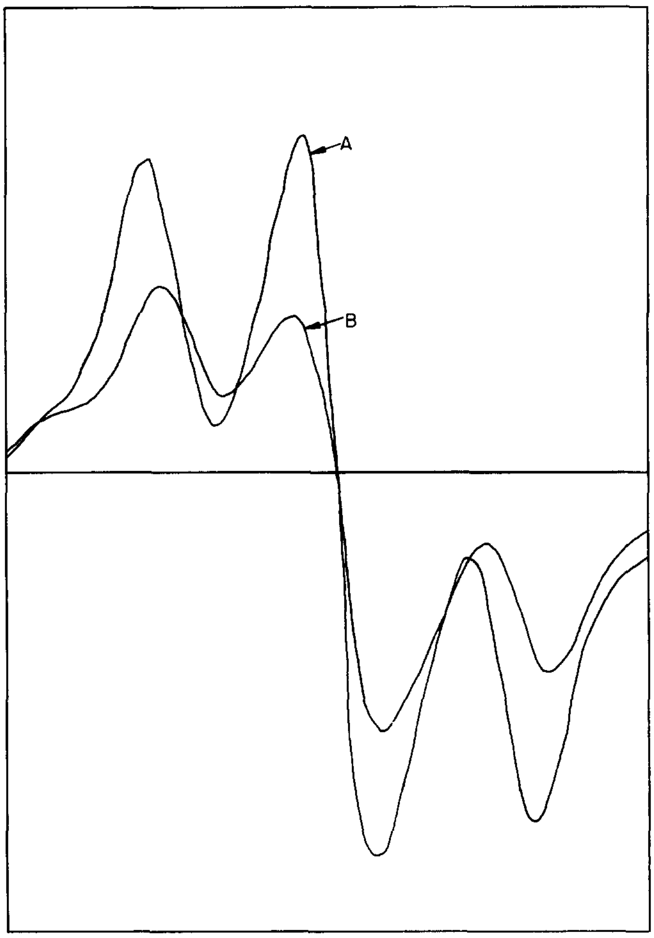


Figure 8 E.s.r. spectrum of acrylamide irradiated at 40°C for 6 h. SO_2 admission at room temperature: A, signal taken after irradiation; B, signal taken after 50 h of SO_2 admission

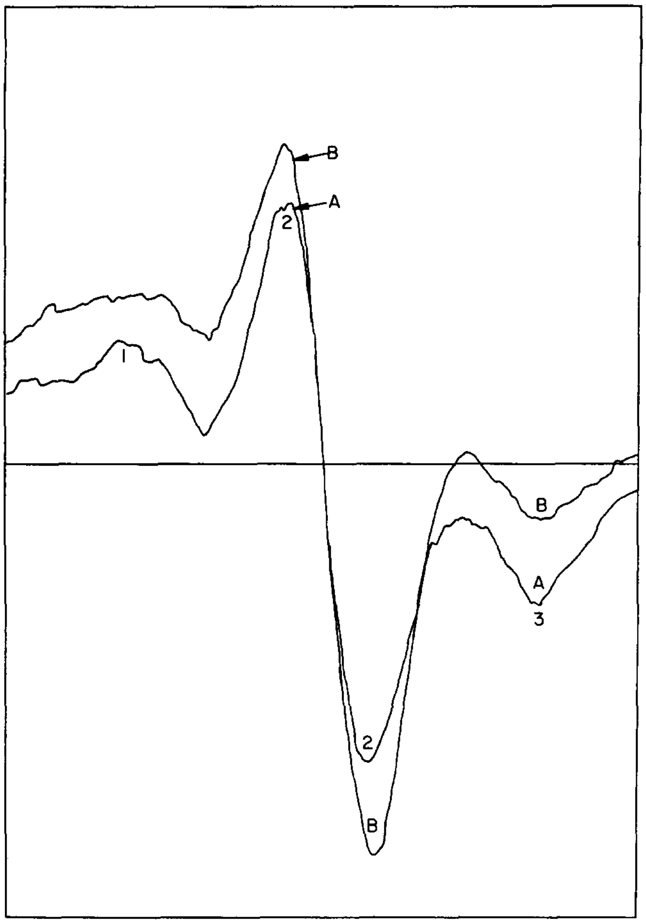


Figure 9 E.s.r. spectrum of polyacrylamide irradiated at 40°C for 24 h. SO_2 admission at room temperature: A, signal taken after irradiation; B, signal taken after 146 h of SO_2 admission

polyacrylamide, which allows freer diffusion. Since sulphur dioxide cannot diffuse into the crystalline structure, it does not react with chain radicals and the shape of the acrylamide signal does not change. Since it can react only with a limited number of radicals, the $RSO_2^\bullet$ radical spectrum was always accompanied and overlapped by the original radical signal of acrylamide. Sulphur dioxide may diffuse through the interface between the crystalline monomer and amorphous polymer phases rather than reacting with the radicals in the locations where crystalline structure is defective. Otherwise, the sulphonyl radicals are expected to be formed very shortly after exposing the sample to this gas. Also, the central peak should reach its maximum height immediately. On the contrary a decrease was observed. In polyacrylamide only a gradual increase in the central peak was observed. The mechanism proposed here has been proved by similar studies of methacrylamide where sulphur dioxide was very slowly diffused[13].

By the introduction of chlorine gas into u.v.-irradiated acrylamide (*Figure 10* and *11*) and polyacrylamide (*Figure 12*), the asymmetric shape of the signals obtained suggests an axial symmetry. When chlorine gas was introduced into the acrylamide before irradiation, as shown in *Figure 11*, the decay was slower than the case when chlorine was admitted after irradiation (*Figure 10*).

It was found that crystalline acrylamide and methacrylamide can be polymerized by chlorine under u.v. irradiation, starting from the crystal surface and propagating into the inside part of the crystal without destroying the crystal shape[21,22]. Polyacrylamide obtained in the γ-irradiated solid-state polymerization was amorphous. Nevertheless, polyacrylamide as well as polymethacrylamide obtained in the solid-state polymerization by chlorine under u.v. irradiation were oriented and showed crystalline structure[21,22]. On the other hand, if the sites for initiation are distributed at random on the crystal, propagation in a random direction to the *a*-plane will make the polymer amorphous[23,24].

It was proposed that initiation sites are concentrated on the surface of the crystal in the *a*-plane. Thus propagation proceeds step by step along each *a*-plane[21,22]. Regularity will be obtained by slow surface initiation at the interface between polymer molecules, probably by hydrogen bonding between >NH and >C=O groups. The monomers in the first layer will be polymerized into a well oriented polymer layer by hydrogen bonding with the second layer of monomers acting as a bed surface; then the second layer of monomers will be polymerized. The polymerization rate

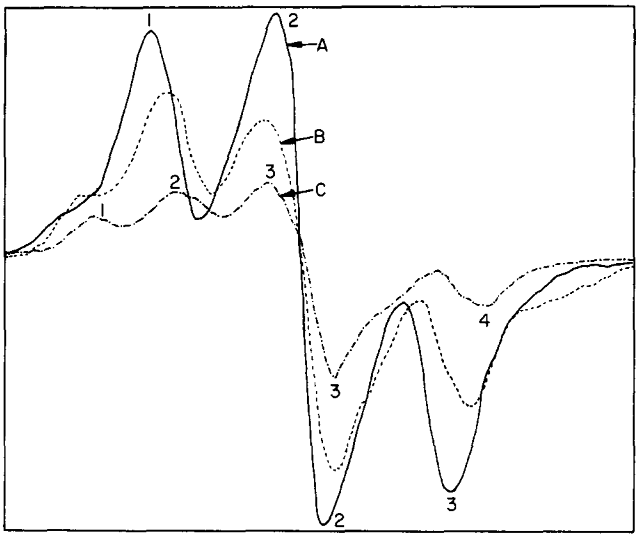


Figure 10 E.s.r. spectrum of acrylamide irradiated at 40°C for 6 h. Cl_2 admission at room temperature: A, signal taken after irradiation; B, signal taken after 6 h of Cl_2 admission; C, signal taken after 340 h of Cl_2 admission

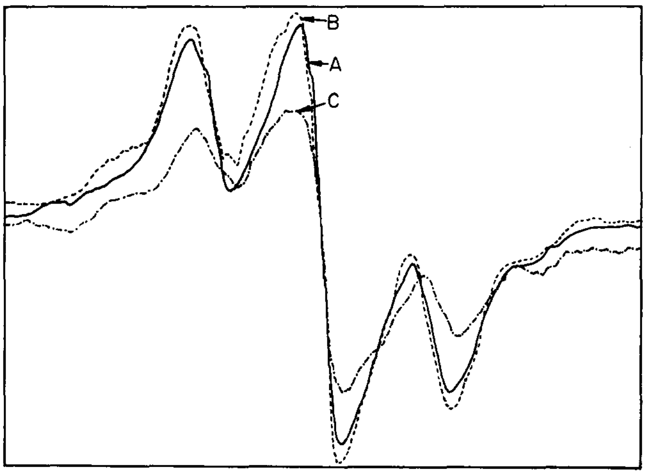


Figure 11 E.s.r. spectrum of acrylamide after Cl_2 admission irradiated at 40°C for 6 h: A, acrylamide irradiated at 40°C for 6 h, signal at room temperature (receiver gain 1.6 × 10^4); B, (acrylamide + Cl_2) irradiated at 40°C for 6 h (receiver gain 2.5 × 10^4); C, (acrylamide + Cl_2) after 449 h of irradiation (receiver gain 2.5 × 10^4)

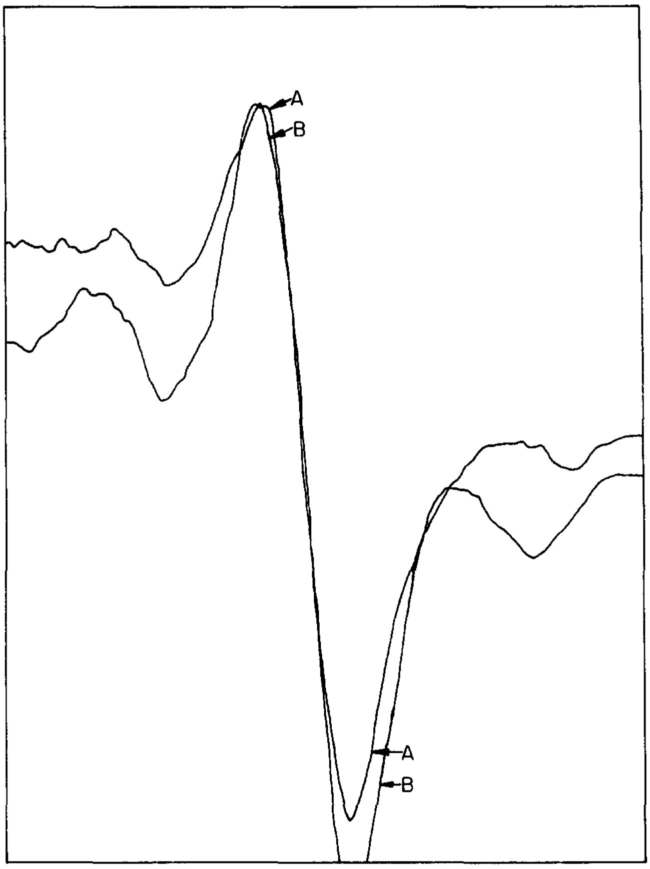


Figure 12 E.s.r. spectrum of polyacrylamide irradiated at 42°C for 25 h. Cl_2 admission at room temperature: A, after 1.5 h of Cl_2 admission; B, after 19 h of Cl_2 admission

was enhanced by adding chlorine during polymerization of acrylamide[21]. Before chlorine admission the conversion was only 10%. After 30 min of chlorine admission the conversion increased to 40%.

Okamura proposed that acrylamide and methacrylamide polymerization cannot proceed without the presence of chlorine gas before u.v. irradiation[21]. However, when acrylamide was irradiated with u.v. rays in the absence of chlorine, polyacrylamide was obtained; and the percentage of the polymer calculated has been given in our previous work[6,7,25]. This fact was also verified by the observation of growing acrylamide radical signal right after u.v. irradiation which causes polymerization (*Figure 10* (trace A)).

When chlorine was introduced into acrylamide after u.v. irradiation, the signal decays rather fast and the three-peak signal of acrylamide turns out to be a four-peak asymmetric signal, as shown in *Figure 10* (traces B and C). When acrylamide was irradiated in the presence of chlorine, chlorine atoms produced by irradiation act as a radical stabilizing agent, causing a much slower decay of acrylamide signal. As a result there is no significant change in the shape of the signal (*Figure 11*). The effect of chlorine on the polyacrylamide signal is more remarkable. When chlorine is introduced into u.v.-irradiated polyacrylamide, asymmetry arises as shown in *Figure 12*. This effect is much more pronounced for the case of polyacrylamide irradiated in the presence of chlorine, where a two-line asymmetric signal arises immediately (*Figure 13*).

From the spectra obtained the observations can be summarized as follows:

(i) With chlorine diffusion into the acrylamide system, asymmetry arises and the three-line signal turns out to be a four-line signal. At room temperature this signal decays fast with first-order kinetics with rate constant $k_1 = 4.5 \times 10^{-3}\,h^{-1}$.

(ii) When chlorine was admitted into the acrylamide system, either before or after irradiation, the formation of peroxy radicals was not observed if the system is opened to atmospheric oxygen. Oxygen diffuses very slowly and causes only a slow decay in peak-to-peak height (*Figure 10* (trace C) and *11* (trace C)). This indicates that oxygen cannot diffuse into chlorinated acrylamide easily; however, it has a considerable effect on the chlorinated polyacrylamide system as shown in *Figure 13* (trace C).

(iii) When the sample is irradiated in the presence of chlorine (*Figure 11*), the radical obtained is more stable than the one obtained when chlorine is introduced after irradiation (*Figure 10*).

(iv) When polyacrylamide was irradiated in the presence of chlorine by u.v. rays, the sudden formation of an asymmetric signal (*Figure 13*) suggests an axial symmetry due to g-anisotropy. The anisotropy of the g-factor arises from a coupling of the electron spin angular momentum with a small amount of reduced orbital angular momentum. Systems with n-fold axis of symmetry ($n > 3$) are described as having an axial symmetry, which is due to $g_\parallel < g_\perp$ (refs. 7 and 26). Here, $g_\parallel$ and $g_\perp$ are the g-factors appropriate to the orientations $H_\parallel$ and $H_\perp$ of the magnetic field when it is respectively parallel and perpendicular to the symmetry axis Z. If one electron is lost from an atom, there will be a small displacement. This distortion leaves a four-fold axis of symmetry. If H is parallel to the unique axis Z, and

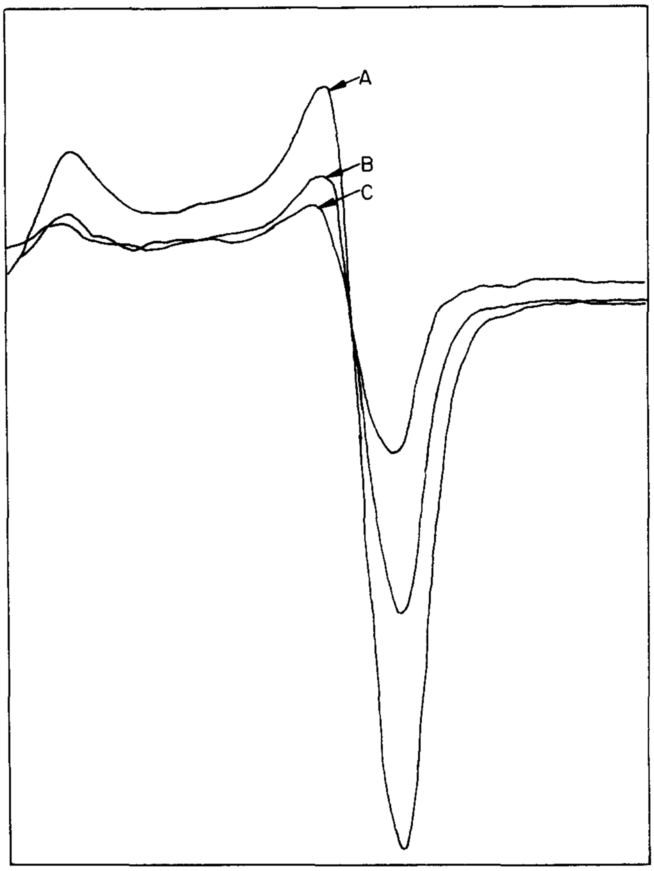


Figure 13 E.s.r. spectrum of polyacrylamide after Cl_2 admission, irradiated at 42°C for 6 h: A, after 0.5 h of irradiation; B, after 70 h of irradiation; C, sample opened to air for 24 h

$v=9.65$ GHz, a line is observed at $H=3233.1$ G. Thus, $g_{\parallel}=hv/\beta H_{\parallel}=2.0033$ is obtained. When the crystal is rotated so that H remains in the YZ plane, the line shifts to $H=3177.1$ G. For this case, $g_{\perp}=hv/\beta H_{\perp}=2.038$. As a result $g_{\parallel}<g_{\perp}$ (ref. 26).

(v) When chlorine was introduced into acrylamide either before or after extensive u.v. irradiation, a slow decay was observed in the signal accompanied by the appearance of a fourth peak. In polyacrylamide this effect is more pronounced as witnessed by an increase in peak-to-peak height and the formation of an asymmetric signal (*Figure 13*). This can be explained by the compact crystal structure of acrylamide and the amorphous structure of polyacrylamide, which allows freer diffusion of chlorine molecules to form new radicals more easily.

From the spectra obtained it can also be concluded that chlorine gas does not have any effect as a radical initiator. However, it acts as an agent for slowing down radical decay since it was observed that chlorine admission into the acrylamide system before irradiation stabilizes the radical and slows down radical decay (*Figure 11*). Here chlorine atoms formed by decomposition of molecular chlorine by u.v. rays slow down the decay rate of the radicals. Chlorine atoms act as an agent for slowing down radical decay rather than becoming a radical initiator. Consequently, irradiation in the presence of chlorine gas results in higher polymerization yields. This will be discussed in future work.

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