

# ESR Study and Copolymer Analysis of Acrylamide-Methacrylamide Solid Solutions

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## Synopsis

When acrylamide-methacrylamide mixed crystals are irradiated by ultraviolet (UV) rays, a copolymeric sample is obtained containing both monomeric constituents. For identification and quantitative analysis of these copolymers, a modified form of UV spectroscopy was used. The greatest advantage of UV spectroscopy for copolymer analysis lies in its rapid application. A comparison of the spectrum of the unknown compositions with spectra of known systems by using a calibration curve and the shifts in absorption maxima in different concentrations are valuable aids in establishing the composition. Electron spin resonance (ESR) provides a correlation between the obtained copolymer composition and the shape of the signal of the responsible radical. ESR spectra obtained for UV-irradiated acrylamide-methacrylamide mixed crystals reveal that during polymerization both radicals are present. As methacrylamide percentage increases in the mixture, the signal becomes similar to the 9-line spectrum of pure methacrylamide. When there is 90% methacrylamide present in the original mixture, a 5-line signal is observed, with even-numbered peaks in the methacrylamide signal appearing now as shoulders. When the methacrylamide percentage is about 16%, a characteristic 3-line signal of acrylamide is dominant. As the methacrylamide percentage increases in the original mixture of the copolymers, ESR signals indicate a decrease in the rate constant values for second-order decay at 60°C. The stability of the formed radicals was studied by admitting oxygen to the copolymeric samples as well as to the homopolymeric systems. Since the peroxidic radicals are more active in the hydrogen abstraction process, they decay more rapidly than the macro radical itself by a bimolecular termination reaction. As the methacrylamide percentage increases in the copolymeric mixtures, the peroxide radical formation becomes more difficult. This indicates that poly-methacrylamide brings more stability in copolymerization reactions with acrylamide. The polymerization rate of both monomers and their mixed crystals were enhanced by adding chlorine gas before irradiation. Chlorine acts as an agent for slowing down the radical decay as well as accelerating the radical initiation reactions.

## INTRODUCTION

In spectroscopic analysis, the amount of unpolymerized monomer in polymerized sample is determined by the following equation:<sup>1</sup>

$$A = [x/100]wE_m + [(100 - x)/100]wE_p \quad (1)$$

where  $x$  is the percent of unreacted monomeric sample in the polymerizing mixture,  $w$  is the weight of the sample,  $E_m$ ,  $E_p$ , and  $A$  are the extinction

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coefficients of monomeric sample, pure polymer, and optical density of the monomer-polymer mixture, respectively. This equation is used by taking individual ultraviolet (UV) absorption spectra of monomeric sample, monomer free polymer and monomer-polymer mixture.

The mole fraction  $x$ , of the unreacted monomeric sample present in copolymer is determined by the following equation:<sup>2,3</sup>

$$E = xE_1 + (1 - x)E_2 \quad (2)$$

where  $E$ ,  $E_1$ , and  $E_2$  are the specific extinction coefficients of copolymer and homopolymers of first and second constituents of the copolymer, respectively. The results obtained in this method for the copolymer analysis, calculated from Eq. (2) and by the calibration curves are in close agreement. The results certainly indicate that this method can be developed in the future even for high conversions considering one of the models presented by other workers.<sup>4,5</sup> However, it should be pointed out that there are some restrictions to the use of this method for copolymer analysis.

The copolymer and the pure homopolymer of only one constituent must show absorption bands at the same wavelength. However, the homopolymer of the other constituent should not give an absorption band at this wavelength. The solvent should not dominate the absorption band of one of the homopolymers. This fact limits the general application of the UV absorption method.

## 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.

The methacrylamide was also a product of Eastman Organic Chemicals Company. It was crystallized thrice from warm chloroform. The melting point was 110°C.

The chloroform and acetone were obtained from E. Merck A. G. The methanol was a product of Riede-deHaen A. G., Seelze-Hanover Company and they were all used directly without any further purification.

An SP800 UV Unicam spectrophotometer was used.

Electron spin resonance (ESR) spectra were taken at room temperature with a Varian E-12, 9.5 GHz, x-band ESR spectrometer.

Acrylamide-methacrylamide solid solutions were prepared considering the fact that these monomers are isomorphous and form solid solutions in all proportions.<sup>7,8</sup>

In given weight proportions the monomers were weighed and melted together in hot chloroform and crystallized. The crystals were filtered and dried under vacuum. The mixture was powdered and put into the tubes either shown in Figure 1(a) for ESR measurements only or in the tubes shown in Figure 1(b) for copolymer analysis:

For ESR measurements only, the mixtures prepared in desired weight proportions were put into the test tube given in Figure 1(a) and degassed to  $10^{-5}$  mmHg pressure for one day. After sealing off at point B, the mixture was

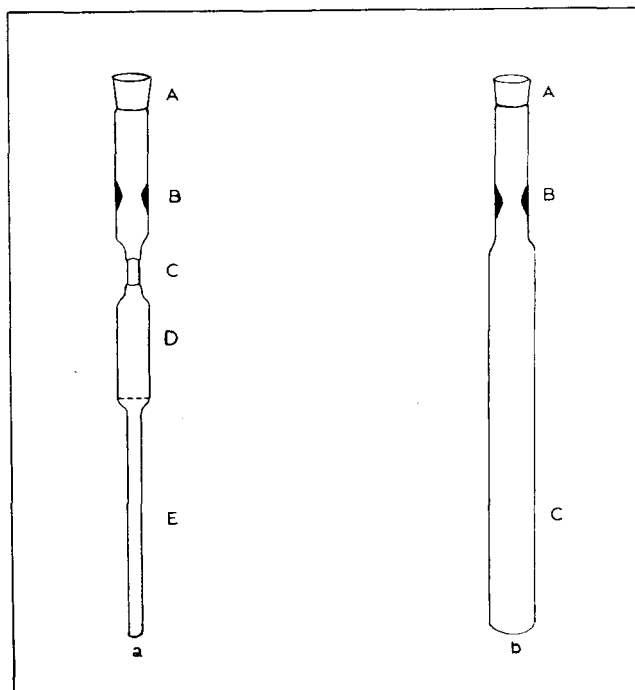


Fig. 1. (a) Irradiation tubes for ESR study. (b) Tube for copolymer analysis.

then transferred to the quartz section of the tube, D, and irradiated at horizontal position at  $42^{\circ}\text{C}$ , under a UV lamp (Philips, 300V,  $2534 \text{ \AA}$ ) for 17 h. After irradiation the mixture was transferred to the Vycor end, E, once more and the ESR spectrum was taken at room temperature with an ESR spectrometer. Different solid solutions were prepared in given weight percentages of methacrylamide in the original mixture: 16.6%, 50.0%, 75.0%, 90.0%. The shape of the signal for each mixture was examined by ESR and the decay was studied at  $60^{\circ}\text{C}$  at different time intervals.

For copolymer analysis a UV spectrometer was used. The prepared mixtures in different weight percentages were immersed in tubes shown in Figure 1(b) and were irradiated by UV rays in the presence of chlorine gas. The solid solutions were prepared in given weight percentages of methacrylamide in the original mixture: 16.6%, 25.0%, 50.0%, 75.0%, 100%. The monomers and all of the crystalline mixtures were first degassed to  $10^{-5}$  mmHg pressure in the type of Pyrex tubes shown in Figure 1(b). Chlorine gas was then introduced into the system at 1 atmosphere pressure. The tubes were immersed into liquid nitrogen and sealed at mark B. Then they were all irradiated at  $60^{\circ}\text{C}$  for 25 h. After irradiation the tubes were broken to extract the sample. They were dissolved in a small amount of hot water which is a good solvent for both the monomer and the polymer. The water solution was added dropwise to a large volume of methanol (or acetone) which is a good solvent for the monomer only. The polymerized mixture was precipitated. Then it was filtered with a Gooch crucible and dried in a vacuum at room temperature to constant weight. Long irradiation times caused formation of cross-links and

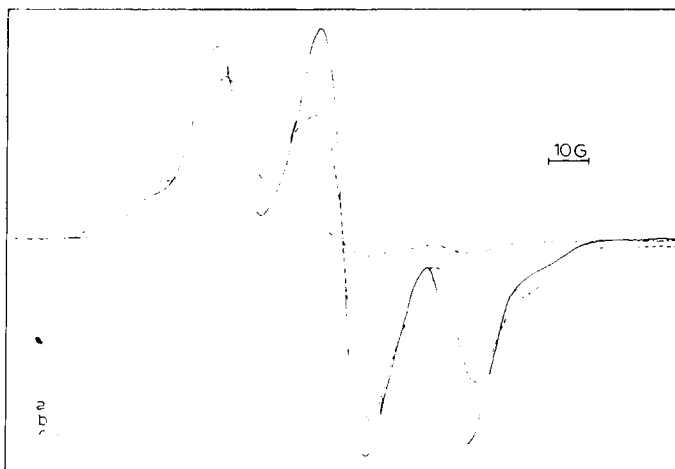


Fig. 2. ESR spectrum of acrylamide irradiated in a quartz tube at 40°C for 16 h. (—) Signal taken at room temperature after irradiation; (---) sample opened to air at room temperature for 5 h without heating; (-·-·-) sample opened to air for 649 h.

the copolymer could not dissolve in hot water (e.g., the formation of gel was observed when the system with 16.6% methacrylamide in monomer mixture was irradiated for 123 h at the same temperature, 60°C).

### RESULTS AND DISCUSSION

Ultraviolet-irradiated acrylamide crystals when irradiated at 42°C for 17 hours give a 3-line spectrum at room temperature<sup>9,10</sup> as shown in Figure 2. Methacrylamide crystals when irradiated at the same conditions show a 9-line signal (Fig. 3). The radicals responsible for these signals were defined in detail in previous papers.<sup>9,10</sup>

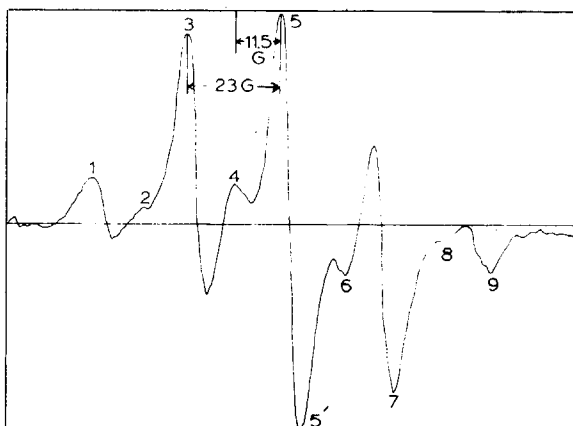


Fig. 3. ESR spectrum of methacrylamide irradiated at 42°C for 17 h. Signal taken at room temperature after irradiation.

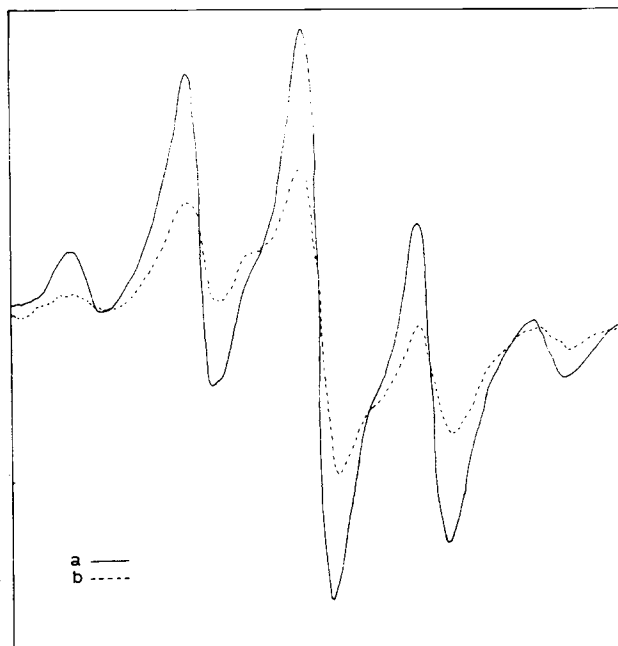


Fig. 4. ESR spectrum of 10% acrylamide (AAM)-90% methacrylamide (MAA) mixed crystals irradiated at 42°C for 17 h. (—) Signal taken at room temperature after 2.5 h of irradiation; (---) sample stored at 60°C for 155 h.

### ESR Study of Acrylamide-Methacrylamide Mixed Crystals

Acrylamide-methacrylamide mixed crystals were prepared as explained in the Experimental section. Figure 4 shows the signal of the mixture containing 90% methacrylamide in the original mixture. Here the even-numbered peaks as indicated for pure methacrylamide signal are not apparent; however they appear as shoulders due to the overlapping signal of acrylamide in the mixture. Figure 5 shows the signal of 75.0% methacrylamide-containing mixture. Decay at 60°C is continuous and reaches a limiting value after which no further decay was observed in each case. When the system is opened to atmospheric oxygen, asymmetry arises and the spectrum becomes a 4-peak signal. Figure 6 was obtained for the mixture containing 50.0% methacrylamide in monomer mixture initially. Figure 7 was taken for the mixture containing 16.6% methacrylamide in the monomer mixture. Here, since the acrylamide percentage is higher in the mixture, the shape of the acrylamide signal is more predominant. When this system is opened to the atmospheric oxygen, very sudden formation of asymmetric peroxidic radical is observed as shown in Figure 7(c) which was taken 30 min after oxygen exposure. However, as acrylamide percentage increases in the mixture, the characteristic 9-line spectrum of methacrylamide signal overlaps with growing acrylamide radical and even-numbered peaks of methacrylamide disappear gradually.

Signal decay for all mixed crystals were studied at the same conditions. Figure 8 shows the second-order decay of the two of these mixed crystal signals at 60°C.

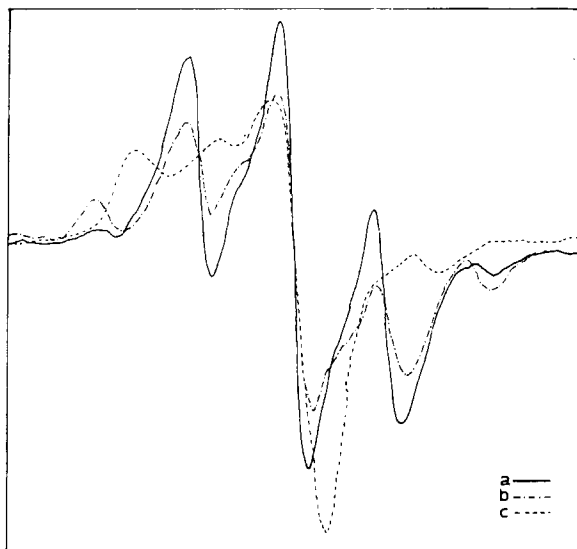


Fig. 5. ESR spectrum of 25% AAm-75% MAA mixed crystals irradiated at 42°C for 17 h. (—) Signal taken at room temperature after 3 h of irradiation; (----) sample stored at 60°C for 259.5 h (R.G.:  $1.6 \times 10^4$ ); (---) sample opened to air for 70 min (R.G.:  $1.0 \times 10^4$ ).

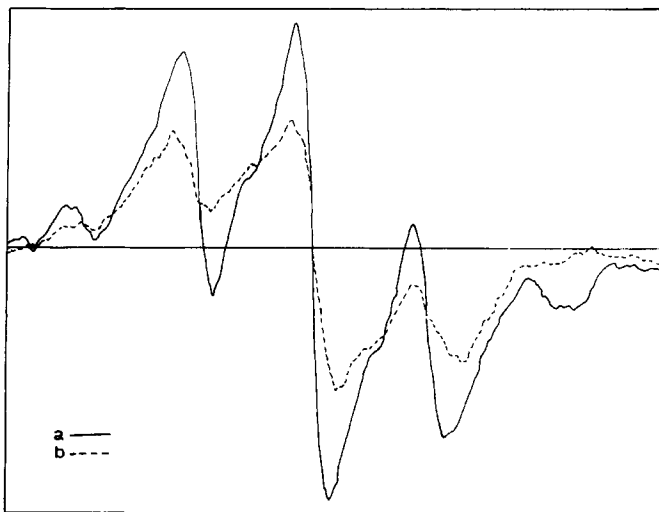


Fig. 6. ESR spectrum of 50% AAm-50% MAA mixed crystals irradiated at 42°C for 17 h. (—) Signal taken at room temperature after 2.5 h of irradiation; (---) sample stored at 60°C for 155 h.

It was not possible to calculate radical concentrations for all of the UV irradiated samples because of the difficulty in adjusting the sample parameters to be the same as the DPPH standard. Therefore, decay of the radicals was not studied in terms of radical concentration  $[R \cdot]$ , but rather by measuring peak-to-peak amplitude  $[I]$  in the first derivative spectrum of the ESR signal which corresponds to maximum peak height in the normalized

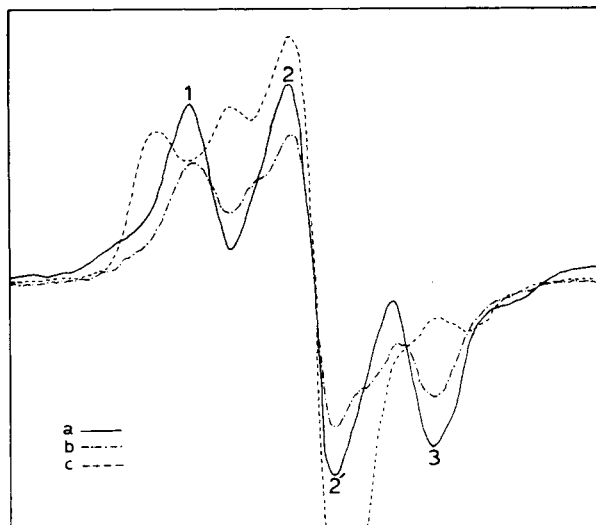


Fig. 7. ESR spectrum of 83.4% AAm-16.6% MAA mixed crystals irradiated at 42°C for 17 h. (—) Signal taken at room temperature after irradiation; (---) sample stored at 60°C for 173 h.; (-·-) sample opened to air for 30 min.

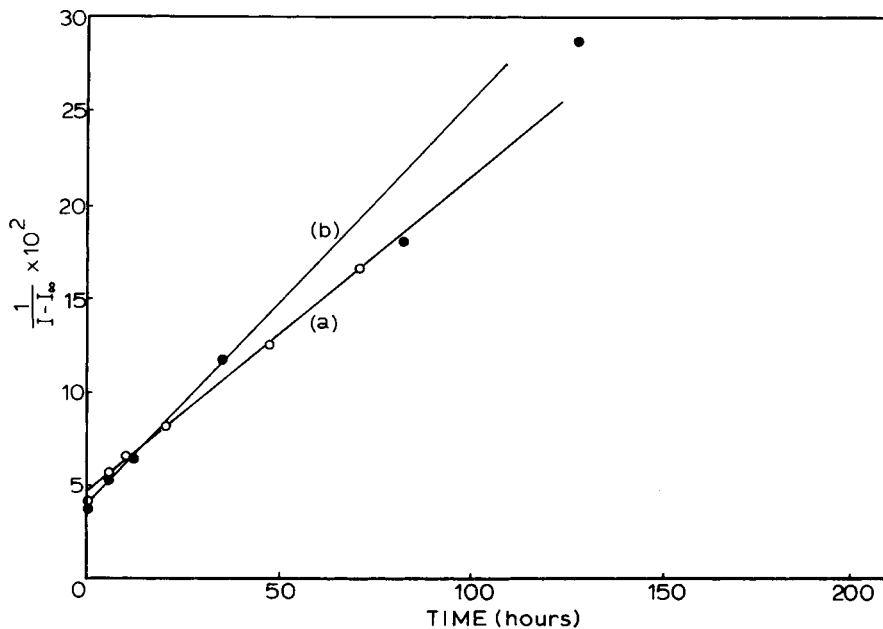


Fig. 8. Decay of the mixed crystal signals at 60°C (AAm-MAA Mixed crystals irradiated at 42°C for 17 h.) (a) ○: 75% MAA-25% AAm; (b) ●: 16.6% MAA-83.4% AAm.

absorption curve. Considering  $[I_0]$  as the initial peak-to-peak height of the first derivative curve, immediately after irradiation (shown as the distance between the peaks 5 and 5' at Fig. 3), and  $[I]$  as the peak-to-peak heights taken after keeping the sample at constant temperature for different time intervals, a kinetic study was applied to the irradiated samples.  $[I]$  values are taken at constant temperature for certain time intervals up to a constant value  $[I_\infty]$ .  $[I_\infty]$  is the value where the peak-to-peak height does not change any further due to the presence of propagating radicals which are assumed to be constant and stabilized by increase in chain length. Due to entanglement of polymer chain, these radicals are buried inside the coils and have no contribution to radical decay.<sup>11</sup> To see the actual radical recombinations,  $[I_\infty]$  must be subtracted from both  $[I_0]$  and  $[I]$  values of the peak heights. The order of the decay was determined by either plotting  $\ln[I_0] - [I_\infty]/[I] - [I_\infty]$  versus time or  $1/[I] - [I_\infty]$  versus time. If a straight line is obtained, it corresponds to a first- or a second-order decay. After finding the decay order from the slope of the line, the rate constant  $k$  was calculated.

Ultraviolet irradiated acrylamide at 60°C decays by first-order kinetics.<sup>9</sup> However, decay is second order in the solid solution of acrylamide and methacrylamide. Figure 8 shows the second-order plots of two of these mixtures (16.6% and 75% methacrylamide in monomer mixture) where decay at 60°C was expressed as  $1/[I] - [I_\infty]$  versus time. Here  $[I]$  indicates the measured peak-to-peak height of the ESR spectrum for the copolymer mixtures at time  $t$ , as the distance between peaks 2 and 2' indicated in Figure 7.  $[I_\infty]$  is the limiting value of peak-to-peak distance due to the isolation of the radicals within the amorphous polymer matrix, where the change reaches a constant value. At this point, propagating radicals are stabilized by increase in chain length. The second-order rate constants calculated from the slopes of these plots are listed in Table I. As shown in this table, as the methacrylamide percentage increases in the monomer mixture, the second-order rate constant values decrease, with the order between  $2.14$  and  $0.90 \times 10^{-3} (\text{height})^{-1} (\text{h})^{-1}$ . This indicates that the polymethacrylamide signal is more stable than that of polyacrylamide.

When the system is opened to atmospheric oxygen, sudden formation of peroxidic radical was observed with a sharp increase in peak-to-peak height [Figs. 5(c) and 7(c)]. However, the peroxidic radical 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

TABLE I  
The Change of Rate Constants of  
Acrylamide-Methacrylamide Mixed Crystals

Wt MAA% in the monomer mixture	Rate constant for second-order decay at 60°C, $\text{ht}^{-1} \text{h}^{-1} \times 10^3$
16.6	2.14
50.0	2.00
75.0	1.71
90.0	0.90



radical formation also increases. When methacrylamide percentage is increased in the solid solutions, formation of peroxide radical becomes more difficult.

### Copolymer Analysis of Acrylamide-Methacrylamide Mixed Crystals

A previous study shows an extensive analysis of copolymers and a rapid method based on UV spectroscopy developed for analysis of styrene-*p*-substituted styrene copolymers.<sup>3</sup> The absorption bands of copolymers and polystyrene or *p*-substituted styrene homopolymers have been investigated and the bands at the same wavelength were compared.<sup>3</sup> In the present work the same method has been applied to the analysis of acrylamide-methacrylamide mixed crystals.

For copolymerization reactions it was found necessary to admit chlorine gas before applying UV irradiation to the systems: It was observed that methacrylamide crystals after irradiation at 50°C for 70 h and after postpolymerization at 60°C for 96 h gave less than 1% conversion. Acrylamide samples after UV irradiation at 50°C (irradiation thickness about 1 cm) for 70 h and after leaving for postpolymerization at 60°C for 24 h gave only 6.79% conversion. As a result, it was decided that to increase the yield, crystalline monomers of acrylamide and methacrylamide must be polymerized in the presence of chlorine gas under UV irradiation.<sup>12</sup>

It was found that crystalline acrylamide and methacrylamide can be polymerized by Cl<sub>2</sub> under UV irradiation starting from the crystal surface and propagating into the inner part of the crystal without destroying the crystal shape.<sup>12,13</sup> Chlorine molecules separate into atoms under UV irradiation, and the solid-state polymerization of these monomers under UV irradiation seems to be initiated by Cl atoms produced on the surface of the monomer crystal.

Polyacrylamide obtained in the  $\gamma$ -irradiated solid-state polymerization was amorphous.<sup>12,13</sup> Nevertheless, polyacrylamide and polymethacrylamide obtained in the solid-state polymerization by Cl<sub>2</sub> under UV irradiation were oriented and showed crystalline structure. 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. In the UV-irradiated case, the initiation sites are concentrated on the surface of the crystal in the *a* plane; thus propagation proceeds step by step along each *a* plane. Regularity will be obtained by slow surface-initiated solid-state polymerization at the interface between polymer molecules, probably forming 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.<sup>13</sup> The polymerization rate was enhanced by adding Cl<sub>2</sub> during the polymerization of acrylamide. Before Cl<sub>2</sub> admission the conversion was only 10%. After 30 min of Cl<sub>2</sub> admission the conversion increased to 40%.

Monomers and monomer mixtures are first exposed to UV light in the presence of Cl<sub>2</sub>. The chlorination develops nearly on the surface (top 20  $\mu$ m) of the exposed sample leaving the underlying layer unchanged. With further

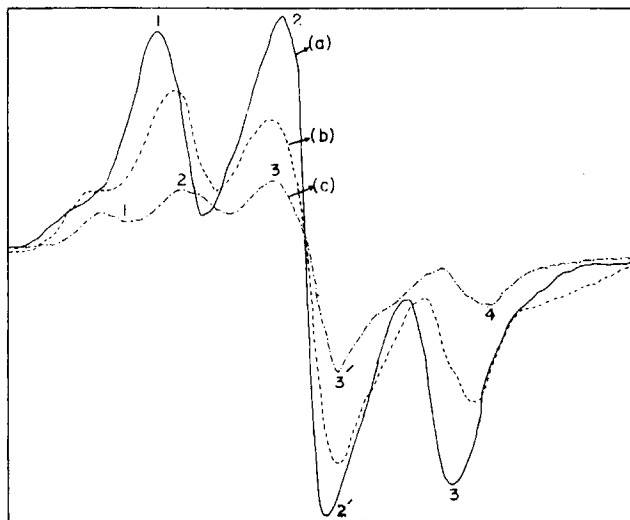


Fig. 9. ESR spectrum of acrylamide irradiated at 40°C for 6 h. Cl<sub>2</sub> admission after irradiation. (—) Signal taken at room temperature after irradiation; (---) signal taken after 6 h of Cl<sub>2</sub> admission; (-·-·-) signal taken after 340 h of Cl<sub>2</sub> admission.

irradiation, the superficially chlorinated polymer surface then develops the chain reaction more efficiently in chlorinated monomers than in the monomers itself and leads to chlorinated polymer sequences that strongly absorb in the UV and visible regions.<sup>14</sup> This explanation has been supported very recently by the introduction of Cl<sub>2</sub> gas for the surface modification of polyvinylchloride (PVC) by photochemical reactions.<sup>14-17</sup>

It was proposed that acrylamide and methacrylamide polymerization cannot proceed without the presence of chlorine gas, which was introduced before UV irradiation.<sup>12</sup> However, when acrylamide was irradiated with UV rays in the absence of chlorine gas, polyacrylamide was obtained; the percentage yield of the polymer was given in our previous work.<sup>18</sup> This fact was also confirmed by the observation of growing acrylamide radical signal in the absence of Cl<sub>2</sub> gas, immediately following irradiation. However, for both monomeric samples the obtained percent conversions were very low in the absence of Cl<sub>2</sub> gas.

When Cl<sub>2</sub> was introduced into UV-irradiated acrylamide, the signal decayed rather fast and asymmetry arose with the appearance of a fourth peak as shown in Figure 9. However, when acrylamide was irradiated in the presence of Cl<sub>2</sub>, the signal decayed much more slowly with very little change in the shape of the signal (Fig. 10). This can be explained by the decomposition of Cl<sub>2</sub> molecules into atoms and the binding effect of these atoms to hold the layers with hydrogen bonding and stabilizing the formed materials. From the obtained spectra (Figs. 9 and 10) it can be concluded that Cl<sub>2</sub> gas acts as an agent for slowing down the radical decay, rather than acting as a radical initiator.

For the solid solutions containing 20% acrylamide in monomer mixture, when chlorine gas is introduced into the system after degassing, the polymer conversion was found to be 13.14%. When the same procedure was applied to the system containing 50.0% acrylamide in monomer mixture, without degas-

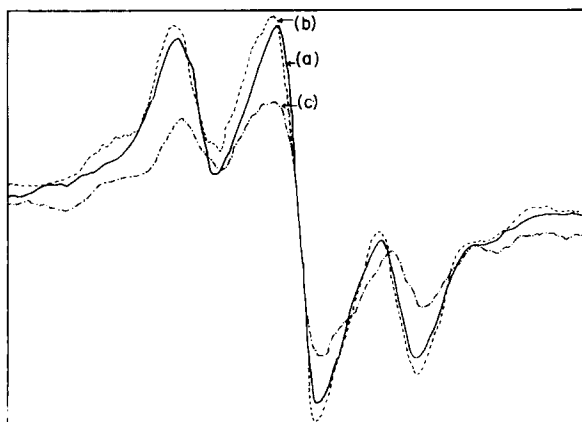


Fig. 10. ESR spectrum of acrylamide after  $\text{Cl}_2$  admission irradiated at  $40^\circ\text{C}$  for 6 h. (—) Signal taken at room temperature after irradiation (R.G.:  $1.6 \times 10^4$ ); (---) (AA +  $\text{Cl}_2$ ) irradiated at  $40^\circ\text{C}$  for 6 h. (R.G.:  $2.5 \times 10^4$ ); (-·-·-) signal taken for (AA +  $\text{Cl}_2$ ) after 449 h. of irradiation (R.G.:  $2.5 \times 10^4$ ).

sing the system and by direct admission of chlorine gas, the polymer conversion was only 9.46%. Consequently, it was found necessary first to admit chlorine gas into the system after degassing, then applying UV irradiation to the chlorinated systems.

By taking ESR signals and measuring the peak-to-peak distances the rate constants were calculated. The first-order decay constant of acrylamide radical was calculated to be  $2.3 \times 10^{-2} \text{ h}^{-1}$  at room temperature.<sup>9</sup> When chlorine gas was added to acrylamide after irradiation the first-order rate constant calculated is  $4.5 \times 10^{-3} \text{ h}^{-1}$ . First-order decay constant for the acrylamide when it was irradiated in the presence of chlorine is calculated to be  $6.2 \times 10^{-3} \text{ h}^{-1}$ . These values indicate the effect of chlorine gas for slowing down the radical decay and resulting high polymerization yields.

For copolymer analysis, the copolymers were dissolved in a proper solvent to obtain solutions in order to have the same initial concentrations of each copolymeric sample. At different concentrations, different spectra were taken for each copolymer as well as its homopolymer. The most convenient concentration was chosen from the spectra of one of the homopolymers to represent 100% concentration of this absorption region. A calibration curve was then obtained by plotting the absorbance values against percent concentration of diluted solutions of the homopolymer. For analysis it was necessary to find an absorption band at which wavelength only one of the homopolymer and all the copolymer samples show a characteristic peak while the other constituent of the copolymer does not absorb. The absorbance values of the copolymeric samples at the same concentration were obtained from the spectra of copolymers and the corresponding percentages of the desired residues were determined from the calibration curve.

The method described in the previous work<sup>3</sup> has been applied to the analysis of acrylamide-methacrylamide mixed crystals. However, in this case, two homopolymers gave absorption bands at the same wavelength, except that one of the homopolymers (polymethacrylamide) gave higher absorption.

TABLE II  
Copolymer Analysis of Acrylamide-Methacrylamide Mixed Crystals by UV Spectrophotometer

1	2	3	4	5	6
100.0	0	1.58	0.40	0	100.0
95.75	16.6	1.65	0.43	29.17	74.41
78.23	25.0	1.71	0.48	54.17	50.32
54.49	50.0	1.75	0.50	70.83	33.03
28.53	75.0	1.77	0.60	79.17	23.96
0	100.0	1.82	0.63	100.00	0

1-Mol% acrylamide in monomer.

2-Wt% methacrylamide in monomer.

3-Absorbance at  $51,000\text{ cm}^{-1}$  (196 nm) ( $c = 2\text{mg}/25\text{ mL}$ ).

4-Absorbance at  $51,000\text{ cm}^{-1}$  (196 nm) ( $2 \times 3/17\text{ mg}/25\text{ mL}$ ).

5-Wt% methacrylamide in copolymer.

6-Mol% acrylamide in copolymer.

Copolymer mixtures show absorption bands between the two absorption limits. The mole percentages of acrylamide and methacrylamide in the copolymers were therefore determined by using Eq. (1).<sup>1,2</sup> Here  $E_m$  and  $E_p$  are calculated from the absorption equation:

$$A = Elc \quad (3)$$

where  $c$  is the concentration,  $l$  is the thickness of the cell which is 1 cm,  $A$  is the absorption at this concentration,  $E$  is the extinction coefficient for polyacrylamide and for polymethacrylamide. The calculated  $E$  value for polymethacrylamide was  $22.75\text{ cm}^2/\text{mg}$  and for polyacrylamide it was  $19.75\text{ cm}^2/\text{mg}$  at  $51,000\text{ cm}^{-1}$  (196 nm).

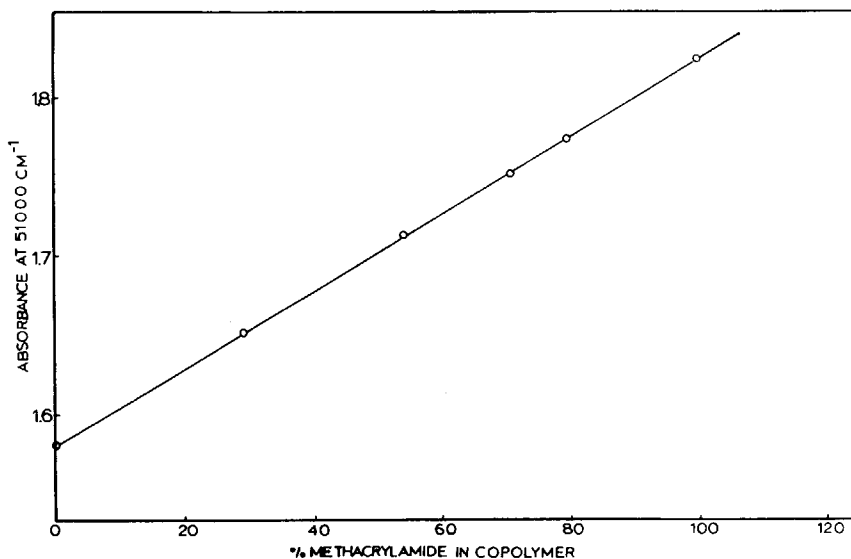


Fig. 11. Absorption values of methacrylamide at  $51,000\text{ cm}^{-1}$  (196 nm) vs. methacrylamide percentage in the copolymer mixture.

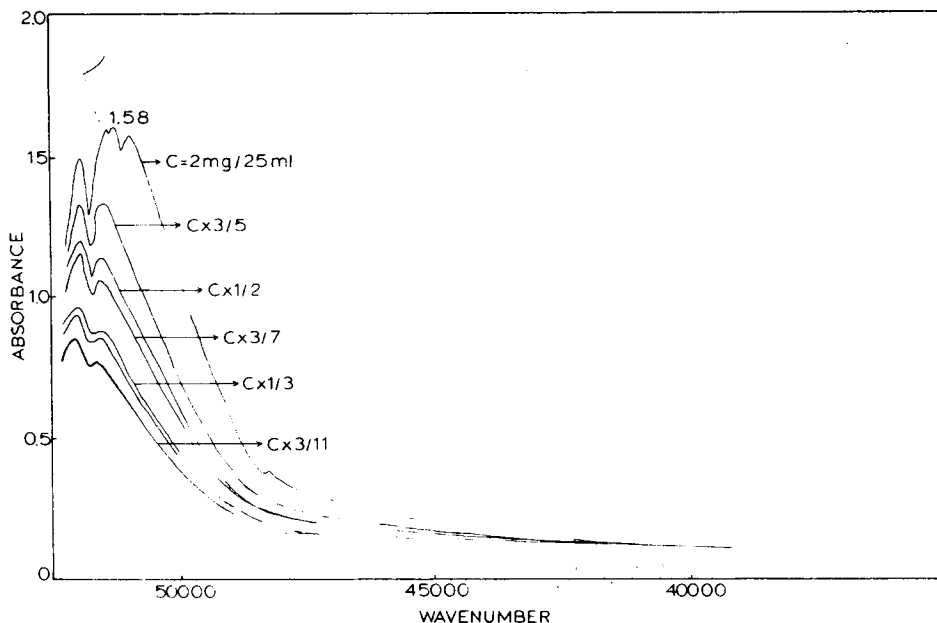


Fig. 12. UV absorption spectrum of polyacrylamide at different concentrations (solvent: water).

When the absorption values given in Table II are plotted against methacrylamide percentage in the copolymer mixture as shown in Figure 11, the obtained straight line showed that the results obey Beer's rule. A UV-absorption spectrum was taken for acrylamide homopolymer at different concentrations as shown in Figure 12. Considering the maximum peaks in aqueous solution at concentration 2 mg/25 mL, corresponding to be 100% concentration and by using the results given in Table III, the absorption values at 196 nm ( $51,000\text{ cm}^{-1}$ ) were plotted against percent concentration as shown in Figure 13. This could be used as a calibration curve; however, for the mixed crystals studied, since the other component (polymethacrylamide) also gives an absorption band at the same wavelength, this reference curve was not used as a calibration curve for the further analysis.

TABLE III  
UV Absorption of Polyacrylamide  
(Solvent: Water; Initial Concentration: 2 mg/25 mL)

Concentration mg/25 mL	Absorption at $51,000\text{ cm}^{-1}$ (196 nm)	Concentration %
2.00	1.58	100.0
1.20	1.16	60.0
1.00	0.96	50.0
0.85	0.86	42.5
0.66	0.60	33.0
0.54	0.50	27.0

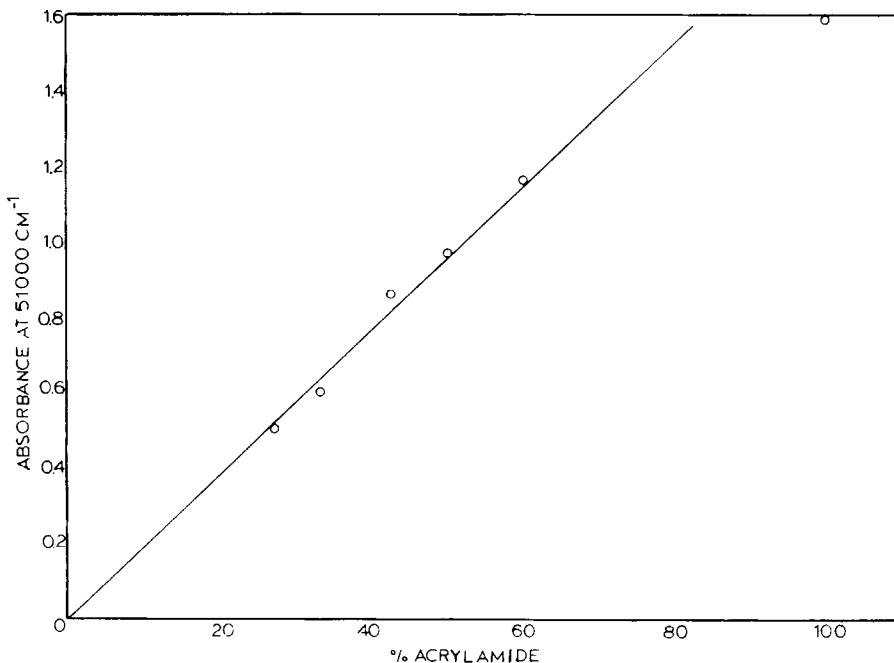


Fig. 13. Absorption values of polyacrylamide at  $51,000\text{ cm}^{-1}$  ( $196\text{ nm}$ ) vs. percent concentration.

Figure 14 was taken for different concentrations of polymethacrylamide. For all of the copolymer mixtures, UV spectra were taken at different concentrations, and in all cases, for comparison the most convenient concentration was chosen as  $2\text{ mg}/25\text{ mL}$  in aqueous solution at  $196\text{ nm}$  ( $51,000\text{ cm}^{-1}$ ). The absorption values of different composition of copolymers are given in Table II for the same concentration and wave number. In Figure 15 the initial mole percentages of acrylamide in monomer mixture are plotted against the calculated mole percentages of acrylamide in the copolymer. The S-shaped curve is the same as given by Tobolsky et al.<sup>19</sup> for styrene percentages in styrene-methylmethacrylate copolymer and the one obtained before for *p*-methoxystyrene-styrene copolymer.<sup>3</sup> This indicates that the reactivity ratios for both monomers are less than 1 and the instantaneous composition of copolymer as a function of monomer composition for the polymerization of acrylamide-methacrylamide proceeds by a free radical mechanism.<sup>20-22</sup>

The values of the reactivity ratios for a given pair of comonomers markedly depend on the polymerization mechanism. It will be recalled for example, that  $r_1$  and  $r_2$  for the radical copolymerization of styrene ( $M_1$ ) and with methylmethacrylate ( $M_2$ ) are 0.52 and 0.46, respectively.<sup>20-23</sup> For cationic polymerization  $r_1 = 10$  and  $r_2 = 0.1$  and for anionic polymerization  $r_1 = 0.1$  and  $r_2 = 6$ .<sup>20-23</sup> Accordingly, the instantaneous copolymer compositions will vary with the monomer feed composition in a manner determined by the particular polymerization mechanism. Instantaneous composition of copolymer as a function of monomer composition for the system of styrene-methylmethacrylate shows different plots when they are polymerized by (a) cationic (with  $\text{SnCl}_4$ ); (b) free radical (with benzoyl peroxide); and (c) anionic (with Na)

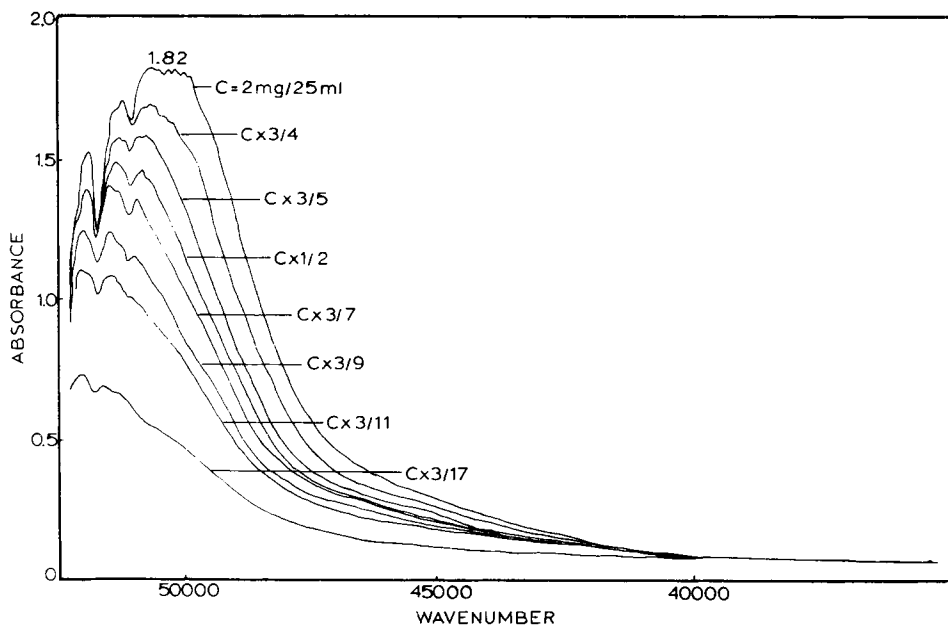


Fig. 14. UV absorption spectrum of polymethacrylamide at different concentrations (solvent: water).

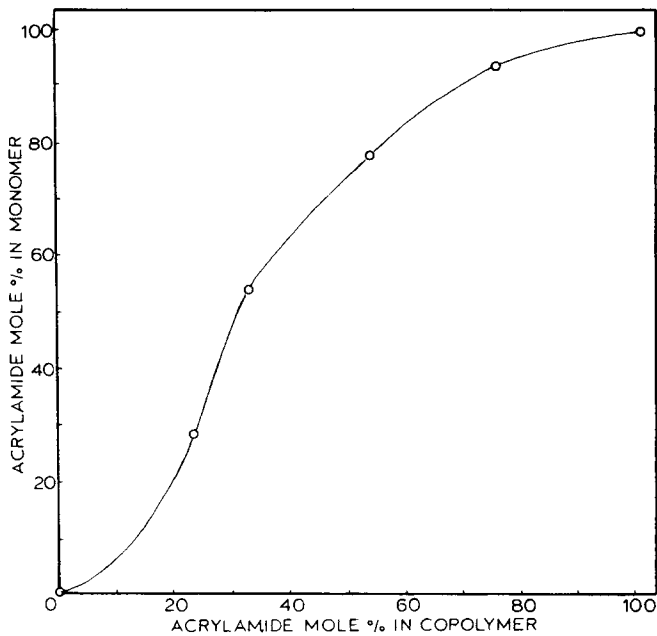


Fig. 15. Mole percentages of acrylamide in monomer mixture vs. mole percentage of acrylamide in copolymer.

mechanisms. The results verify the different polymerization mechanisms and extreme variation of reactivities that monomers exhibit with different types of initiators.<sup>22, 23</sup>

In this work when the initial mole percentage of acrylamide in monomer mixture are plotted against the calculated mole percentage of acrylamide in the copolymer, the obtained S-shaped curve (Fig. 15) represents the same curve (b) as indicated in the example given above and gives a definite proof for a free radical mechanism.<sup>20, 24</sup>

The results of the copolymer analysis are summarized in Table II. As one can see, up to 80% methacrylamide residue in the copolymer can be reached. In addition, plots representing the percent of one of the monomers in initial solution as a function of percent of the same component in the copolymeric mixture are given. In the preparation of copolymers these plots can be used to choose the proper initial monomer composition for any desired final composition of copolymer.

The plot indicating absorbances as a function of percent of homopolymer residue in copolymer would be valuable for compositional analysis of these copolymers prepared from varying composition mixtures of the same monomers.

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