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### The Role of Oxygen in Solid State Polymerization. II. The Effect of Oxygen and Other Reactive Gases on the Polymerization of Methacrylamide

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## **The Role of Oxygen in Solid State Polymerization. II. The Effect of Oxygen and Other Reactive Gases on the Polymerization of Methacrylamide**

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### **SUMMARY**

Methacrylamide polymerizes in the solid state in a manner analogous to acrylamide; i.e., the polymer nucleates as a second phase during reaction. However, in this case, the reaction is sensitive to the presence of reactive gases. These gases are presumed to diffuse along surfaces, lattice defects, and the monomer-polymer interface. Nitric oxide and sulfur dioxide inhibits both the in-source and postirradiation polymerization. Oxygen behaves anomalously. It inhibits the postirradiation reaction, but accelerates the in-source one. It apparently does this by shortening the induction period. A possible mechanism is suggested.

### **INTRODUCTION**

Acrylamide polymerizes in the solid state under irradiation by a two-phase mechanism. After the addition of one or perhaps two monomer units, usually in a given crystallographic direction, the initiating radical becomes "out-of-phase" with the lattice. It then carries on the polymerization by choosing at random between neighboring monomer

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molecules. As a consequence the polymer formed is amorphous and nucleates as a separate phase during the course of the polymerization [1-3]. Methacrylamide shows a similar behavior. If a sample of powdered methacrylamide is irradiated under vacuum and at low temperature and then is allowed to warm up at room temperature, a relatively slow postpolymerization occurs (0.1–0.5% of polymer after 24 hr at room temperature using  $\gamma$  doses in the range 10-50 MR). In this substance, unlike pure acrylamide, a number of gaseous reagents will react with the radicals, affording the opportunity of studying the reactions of gaseous reagents with the growing chain radicals trapped in the rigid matrix of the monomer. For these reactions to occur, the gaseous molecules must be capable of reaching the nucleation sites either by diffusing along defects and surfaces of various kinds or through the lattice or both. This diffusion through a crystal and not just at the surfaces is a relatively rare phenomenon and depends on the crystal lattice, the size of the diffusing gas molecules, and, to some extent, the distribution of nucleation sites. Oxygen and nitric oxide are reactive gases with a relatively small molecular size. They seem capable of reaching and reacting with the radicals in methacrylamide. In this paper we will refer to the results thus far obtained by studying the reactions of these gases and their effects on the kinetics of the solid-state polymerization of methacrylamide.

### EXPERIMENTAL

Methacrylamide, Eastman Kodak, twice recrystallized from acetone, was used. All samples were ground in a mortar and sieved between 0.04 and 0.06 mm mesh opening sieves before use. The ESR measurements were made with an X band Varian spectrometer equipped with a rectangular cavity. For the ESR vacuum measurements, about 0.5 g of powdered amide were sealed under vacuum ( $10^{-5}$  mm Hg) in suitable sample tubes and irradiated at  $-196^{\circ}\text{C}$ . For the ESR measurement made under gas atmospheres the tubes were connected through ground joints and break seals to glass ampoules filled with the proper gas. The irradiations were made in a  $^{60}\text{Co}$   $\gamma$  source at dose rates ranging from 1 to 8 MR/hr.

The gas uptake measurements were made using a conventional manostatic apparatus connected with a vacuum rack. The samples were irradiated under vacuum at  $-196^{\circ}\text{C}$  to total  $\gamma$  doses ranging from 5 to 50 MR. After the irradiation, the samples were attached to the vacuum rack and put under the vacuum for about 20 min at room temperature before admission of the reactive gas in order to eliminate the radiolytic gases. Then the active gas was

admitted to the samples. After the determination of the gas uptake, the samples were submitted to polarographic analysis and analyzed for hydroperoxides, dialkylperoxides, and carbonyl compounds. For the polarographic analysis a Mechrom polarograph was employed using neutral 0.1 N KCl solution as the supporting electrolyte.

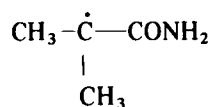
Hydroperoxides were also determined by iodometry under a nitrogen atmosphere. Dialkylperoxides were determined by using the method of Dickey et al. [4]. Carbonyl groups were determined by the following procedure: a 1-g sample was dissolved in 50 ml of standard 2,4-dinitrophenylhydrazine in  $H_2SO_4$ , 2 N solution. The precipitated phenylhydrazone derivative was filtered out and the unreacted 2,4-dinitrophenylhydrazine determined by precipitation with acetone. The difference between the initial and residual amount of 2,4-dinitrophenylhydrazine gave the moles of carbonyl compounds present in the sample.

The extent of polymerization was determined by dissolving the sample in acetone and then filtering and weighing the precipitated polymer. Polymerization was also followed by infrared spectroscopy by observing the decrease in intensity of the double-bond band. For this a Perkin-Elmer Model 501 spectrometer was used. The sample was pressed into pellets with KBr.

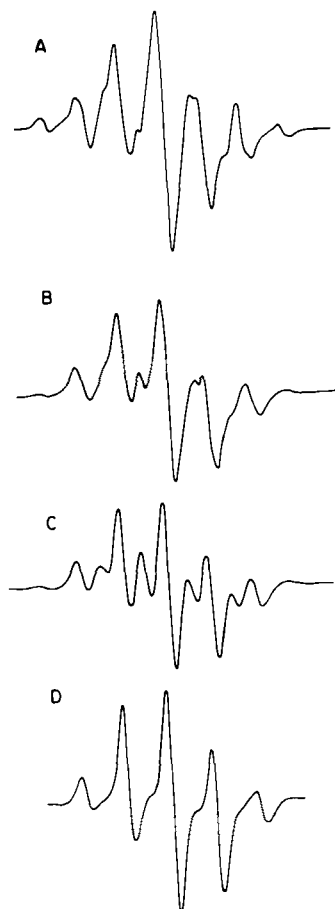
## RESULTS AND DISCUSSION

### ESR Measurements

The main feature of the  $-196^\circ C$  EPR spectrum of powdered methacrylamide irradiated at  $-196^\circ C$  under vacuum consists essentially of seven equally spaced lines with an almost binomial distribution of intensities (Fig. 1). This pattern has been attributed to the radical



[5, 6] formed by addition of hydrogen atoms to the double bond of the monomer. In some samples, especially at a lower dose, an additional sharp peak is seen near the central peak. Annealing of the sample at different temperatures between  $-196$  and  $-50^\circ C$  results in many complex changes of the ESR pattern which we will not attempt to analyze here since they are not relevant to this work. They are probably analogous to the changes



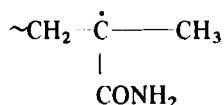
**Fig. 1.** ESR spectra of  $\gamma$ -irradiated powdered methacrylamide. (A) After the irradiation at  $-196^{\circ}\text{C}$ . (B) After 9 min annealing at  $-10^{\circ}\text{C}$ . (C) After 10 min annealing at room temperature. (D) After 15 hr annealing at  $60^{\circ}\text{C}$ . All spectra recorded at  $-196^{\circ}\text{C}$ .  $\gamma$  Dose = 5 MR.

occurring in barium methacrylate, methacrylic acid and other methacrylates [7, 8]. After a minute annealing at  $-10^{\circ}\text{C}$ , the spectrum changes into a weak quartet (Fig. 1) with a superimposed strong five peak signal and with two very small outside peaks. The very small side peaks are probably due to residual traces of the original radical. The intensity of the quartet increases as the annealing temperature is increased from  $-10^{\circ}\text{C}$  to room

temperature and reaches a limiting value after a few minutes at room temperature. At this point we have a nine line pattern that, aside from the relative intensities of the two components, is very similar to the ESR spectrum observed after irradiation of several polymethacrylate systems. Further annealing at 60°C results in a relatively fast polymerization, the extent of conversion to polymer for a given annealing time depends on the  $\gamma$  dose previously given to the sample. For example, a total dose of 30 MR and an annealing time of 15 hr at 60°C results in polymer conversion of about 50%. In the ESR spectrum the quartet structure disappears, but the quintet previously observed remains (Fig. 1). If the sample is given a smaller dose, however, the quartet may not disappear completely no matter how long the annealing time is. It reaches a limiting intensity whose magnitude decreases with increasing initial dose. This suggests the change observed might be a function of the concentration of polymer in the system and, only indirectly, of the temperature. These results are perhaps best explained in terms of conformational isomerism of the growing chain radical [9-14] rather than in terms of the presence of different radical species [5, 6, 15].

The quintet observed at low temperature may be attributed to low molecular weight (presumably dimer) growing chain radicals (A radicals). This is suggested by the fact that this pattern is practically the major feature in the spectrum at -40°C before extensive polymerization starts. On the other hand, the quintet, which is the only pattern observed after annealing at 60°C, must correspond to much higher molecular weight growing chain radicals (B radicals), since extensive polymerization has already occurred and is still occurring, though at a very low rate. It is after anneal at intermediate temperatures that the nine peak (five peak plus four peak) signal is seen. A conformation therefore must exist [13, 14] for very low and for high molecular weight growing chain radicals with 3 methyl protons and 1 methylene proton having an equal coupling of 23 G and the other methylene proton having a coupling constant smaller than the line width. The experiments also suggest that the nine line pattern is generated in some way by growing chain radicals of intermediate size since, before it begins to show up, essentially only the low temperature quintet is present in the spectrum. This possibly occurs by a conformational change in the A radical, presumably following further addition to the double bond. We are inclined to accept this hypothesis since we found we could approximate the nine line pattern, using the method of Bulloch and Sutcliffe [15], by assuming a conformation with 3 equivalent methyl protons and with the methylene protons having

coupling constants of 9 and 14 G corresponding to angles of 63.5 and 56.5° between the symmetry axis of the p-orbital formally carrying the unpaired spin and the plane carrying the respective C—C—H angle and therefore the C—H bond. It can also be shown that all the spectra occurring between -10°C and room temperature can be obtained by simply mixing different percentage of the five and nine line patterns. On this basis we will therefore assume that when oxygen and nitric oxide are admitted over the samples previously irradiated and annealed for 20 min at room temperature, only growing chain radicals of the type



are present.

### Measurements under O<sub>2</sub> and NO Atmospheres

Powdered samples of methacrylamide irradiated under vacuum at -196°C and then allowed to warm up for 20 min at room temperature (type A sample) show the typical nine line pattern. Under vacuum and at room temperature the intensity of this signal remains practically unaltered for weeks. If O<sub>2</sub> is admitted to the sample (P<sub>O<sub>2</sub></sub> = 500 mm Hg) the rate of decay becomes faster, but no change in the shape of the signal is observed. The annealing under vacuum for 7 hr at 60°C of samples previously irradiated with a dose of 30 MR results in a 50% conversion to polymer. The ESR spectrum is now a quintet as reported above. However, now admission of oxygen results in a change of the shape of signal caused by the buildup of the characteristic asymmetric singlet of peroxyradicals (Fig. 2) superimposed on the previous signal. This new signal reaches a limiting intensity and then the whole spectrum decays without further change of the shape. A possible explanation of this behavior is based on the increased polymer content in the system. The polymer nucleates as a second phase, principally near defects. The O<sub>2</sub> molecules can diffuse more rapidly at the polymer—monomer interface than through the lattice, resulting in an increase of the rate of movement of the O<sub>2</sub> towards the radical sites. The average concentration of peroxy radicals therefore increases beyond the lower limit of detection. Admission of nitric oxide over type A samples results in a decay of the ESR signal intensity at a rate faster than under vacuum or under oxygen. After a period of time which is of the order of 24 hr but whose length depends on the particle size and

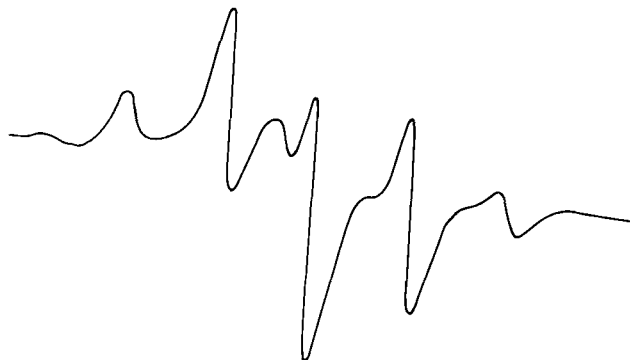
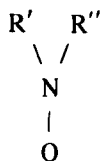


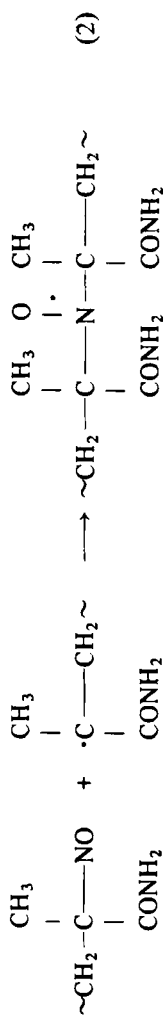
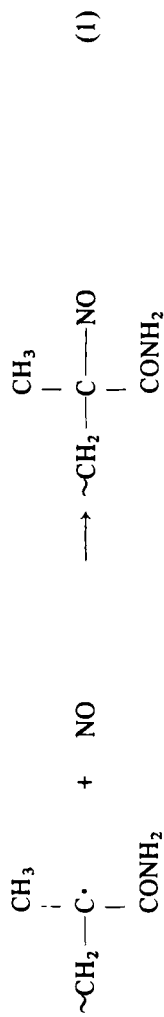
Fig. 2. Effect of oxygen on the EPR spectrum of  $\gamma$ -irradiated powdered methacrylamide sample irradiated under vacuum at  $-196^{\circ}\text{C}$  and then annealed 15 hr at  $60^{\circ}\text{C}$  before admission of oxygen.  $\gamma$  Dose = 35 MR.  
 $P_{\text{O}_2} = 500$  mm Hg.

nitric oxide pressure, the growing chain radicals have disappeared and been replaced by radical whose ESR spectrum is shown in Fig. 3. The new signal is a highly asymmetric broad triplet with a line splitting of approximately 15 G. This spectrum is quite different than the one observed on the addition of NO to propionamide or butyramide [16] but similar in some respects to the one experimentally observed by Stryer and Griffith [17] for dansyl nitroxide radicals and to the one calculated for the same radical by Itzkowitz [18]. On this basis we tentatively suggest that the radical observed is a nitroxyl radical of the type



Such a radical might be formed by scavenging of growing chain radicals by nitroso compounds by a reaction similar to that suggested by Lagercrantz and Forshult [19]. To occur, this type of reaction must involve the approach of two radicals towards each other as well as the diffusion of NO. Migration involving mass transfer is certainly restricted in the solid state, especially for polymer radicals. However, if the polymer radicals were concentrated near defects or surfaces, as seems likely, and the polymer radicals





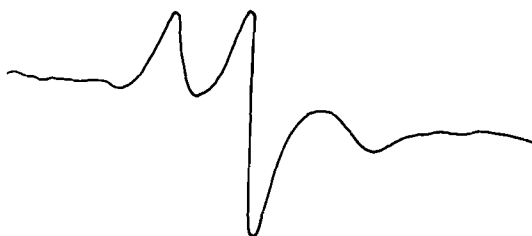


Fig. 3. ESR spectrum of  $\gamma$ -irradiated methacrylamide after reaction with nitric oxide.

grow until they overlap, a small amount of nitroxy radical might be formed in this fashion. It is suggestive that the nitroxy radicals are found in amounts of less than 1% of the growing chain radicals initially present. Alternatively, a type of radical migration, such as that involving H atom abstraction, might be considered.

### Gas Uptake Measurements

When oxygen is admitted over type A samples of powdered methacrylamide, a large amount of gas absorption takes place. The ratio of moles of oxygen absorbed to the moles of radicals disappearing clearly indicates that a long-chain oxidation reaction is occurring (Table 1). The  $O_2$  uptake curves (Fig. 4) show a relatively rapid initial uptake followed by a steadier and slower rate of uptake. The latter presumably involves radicals more deeply buried in the lattice. The rate of uptake increases with decreasing particle size (Fig. 4). Since all the radicals seem eventually to react with oxygen, the situation here is similar to that observed in the reaction of oxygen with other irradiated amides, i.e., the kinetics of the reaction is affected by the rate of diffusion of the  $O_2$  into the particle and therefore the particle size is a factor [16]. The rate is also increased with the dose given to the sample (Fig. 5).

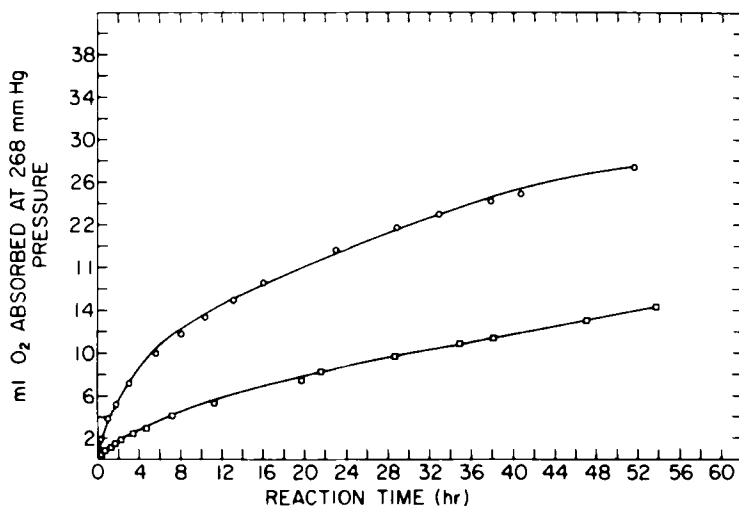
Samples that had been allowed to partially polymerize under vacuum before admitting oxygen show a faster rate of gas absorption (Fig. 6). This may be related to the ease of diffusion of the gas at the monomer-polymer interface.

### Nitric Oxide Absorption

Unlike what has been observed in the saturated amides [16, 20], a large amount of nitric oxide is absorbed by type A samples of methacrylamide

Table 1. Postirradiation Oxidation of Methacrylamide

Dose (MR)	Initial radical concn (No. of rad/g) $\times 10^{-18}$	O <sub>2</sub> absorbed (moles/g) $\times 10^{-4}$	Moles of O <sub>2</sub> absorbed/ moles of radicals reacted
3.6	0.187	0.526	295
9	0.52	0.861	177
32.3	1.3	1.56	133
43	2.1	1.98	57



**Fig. 4.** Effect of particle size on the rate of oxygen uptake. Dose = 15 MR.  $P_{O_2} = 268$  mm Hg. Measurements made at room temperature.  
 (○) Ground sample. (□) Unground sample.

(Fig. 7). Furthermore, the uptake goes on steadily even after no more growing chain radicals are detected in the ESR spectrum. Blank runs performed by using unirradiated methacrylamide show that a thermal reaction takes place between the monomer and the gas (Fig. 7). The presence of the growing chain radicals as a consequence of the irradiation results in an increased rate of NO uptake. It seems likely, therefore, that when irradiated samples are used, two chemical processes superimpose, the thermal reaction with monomer molecules and the reaction initiated by growing chain radicals.

The first process, although it must involve radical intermediates, does not result in initiation of polymerization. In fact, no polymer was found in samples on unirradiated methacrylamide left under a nitric oxide atmosphere for prolonged periods of time. The second process causes a faster rate of decay of growing chain radicals and is therefore responsible for the observed inhibition by NO of methacrylamide solid-state polymerization.

### Oxidation Products

After 24 hr of postirradiation reaction with oxygen ( $P_{O_2} = 500$  mm Hg), type A samples of powdered methacrylamide give a polarogram with two

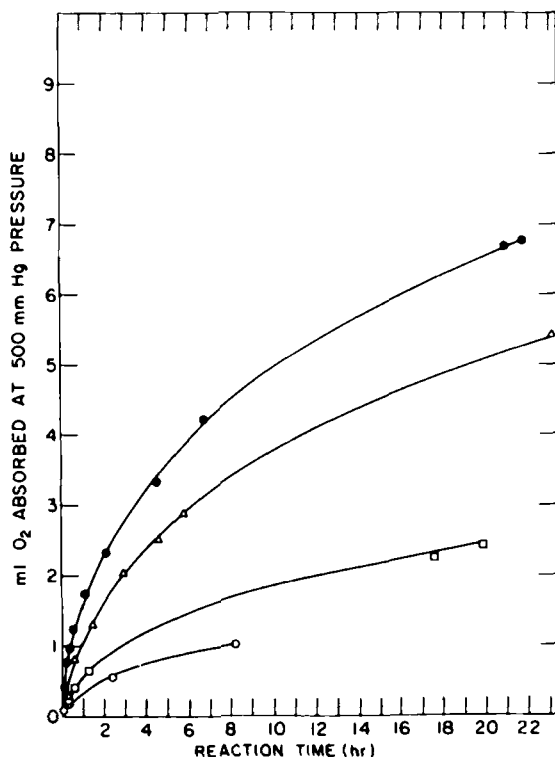
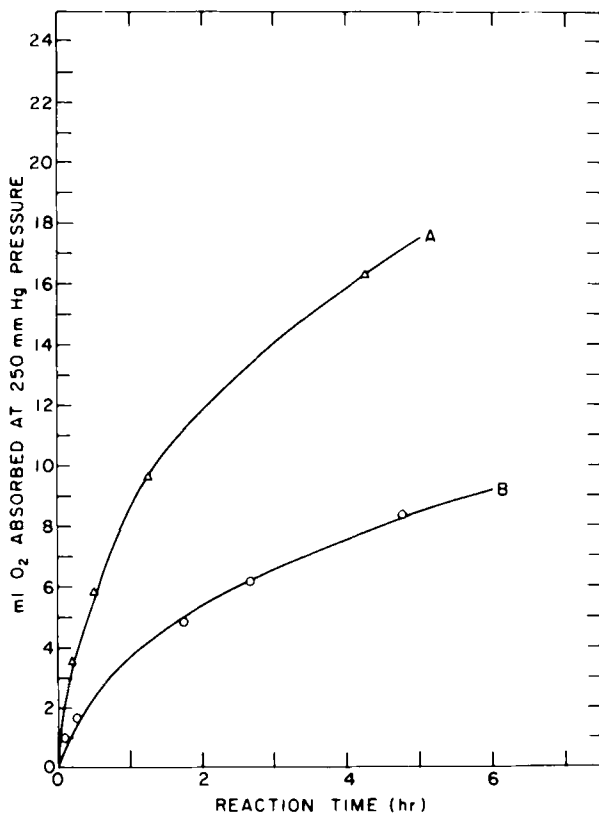


Fig. 5. Postirradiation oxidation of methacrylamide. Effect of  $\gamma$  dose on the rate of oxygen uptake.  $P_{O_2} = 500$  mm Hg. (●) 43 MR, radiation dose, (▲) 32.5 MR, (□) 9 MR, (○) 3.6 MR.

distinct waves having halfwave potentials at  $\sim 0$  and  $-1.25$  V vs. a standard calomel electrode. The first wave corresponds to hydroperoxides since it is completely suppressed by  $SO_2$  and  $Fe^{2+}$  ions. The second wave was attributed to a  $\alpha$ -ketoamides since it has the same halfwave potential as pyruvamide. No waves corresponding to  $H_2O_2$  and dialkylperoxides have been observed. Dialkylperoxides, however, were identified by chemical means.

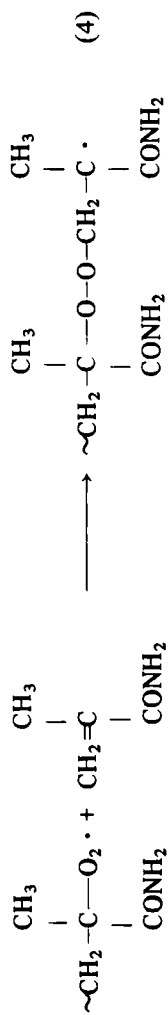
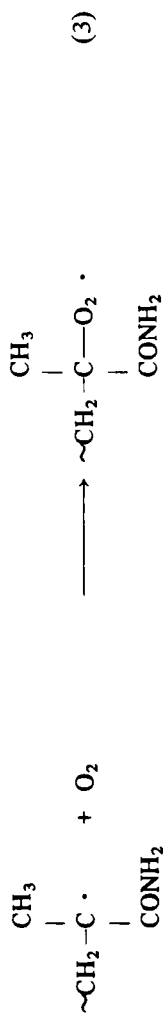
Quantitative analysis of hydroperoxides, carbonyl compounds, and dialkylperoxides shows that these products account for only about 30% of the over-all amount of oxygen absorbed. For example, a sample given a radiation dose of 4.3 MR, then exposed to oxygen at a pressure of 510 mm for 24 hr absorbed  $2.5 \times 10^{-4}$  mole/g of  $O_2$ , but only gave  $2.5 \times 10^{-5}$  mole/g

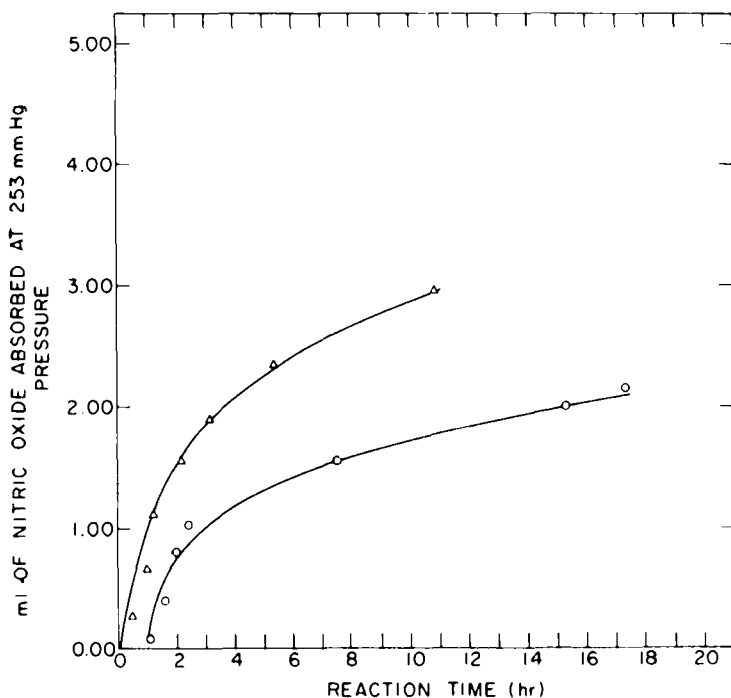


**Fig. 6.** Postirradiation oxidation of methacrylamide. Effect of polymer conversion on the rate of oxygen uptake. (A) Sample allowed to postpolymerize up to 50% conversion before admission of oxygen.  $\gamma$  Dose = 29 MR,  $P_{O_2} = 250$  mm Hg. (B) Oxygen admitted few minutes after irradiation.

hydroperoxide,  $2.3 \times 10^{-5}$  mole/g dialkylperoxide and  $2.0 \times 10^{-5}$  mole/g carbonyl compounds.

Dialkylperoxides, as well as hydroperoxides and carbonyl compounds, are present in amounts higher than expected if they were formed in the termination steps. The ratio of moles of dialkylperoxide to the moles of radicals reacted is approximately 10. A chain reaction, therefore, must be involved. A possible mechanism is based on the addition of peroxyradicals to the monomer double bond:





**Fig. 7.** Reaction of methacrylamide with nitric oxide.  $P_{NO} = 253$  mm Hg. ( $\Delta$ ) Postirradiation absorption.  $\gamma$  Dose = 24 MR. ( $\circ$ ) Unirradiated sample. Measurements made at room temperature with 1 g powdered samples.

This type of reaction is analogous to that suggested for the extensive reaction of styrene with oxygen to form an oxygen copolymer [21]. Besides addition, the peroxy radical probably can also abstract hydrogen from the polymer or from the methyl group of the monomer to form the hydroperoxide. At present we do not have enough information to propose a probable mechanism for the information of carbonyl compounds in amounts comparable to the peroxides. At any rate, the carbonyl compounds are not found in the isolated polymer. This is indicated by the fact that the polymer fraction isolated with methanol or acetone after the reaction with oxygen does not show the polarographic wave of the carbonyl compounds, but only the one due to hydroperoxides.

Radicals of small molecular size, as well as radicals arising from the decomposition of peroxyradicals (e.g., OH or  $HO_2$ ), might afford a mechanism for the oxidation chain termination in the solid matrix. These



radicals should be able to diffuse easily along defects, dislocations, grain boundaries, at the monomer-polymer interface, etc., where most of the reaction seems to occur.

The distribution of some of the products formed during the in-source oxidation reaction appears to differ from that of postirradiation oxidation. The carbonyl compounds are formed in yields almost ten times higher than the hydroperoxides. This is most likely due to the radiation-induced decomposition of hydroperoxide since their yield decreases with increasing radiation dose (Table 2).

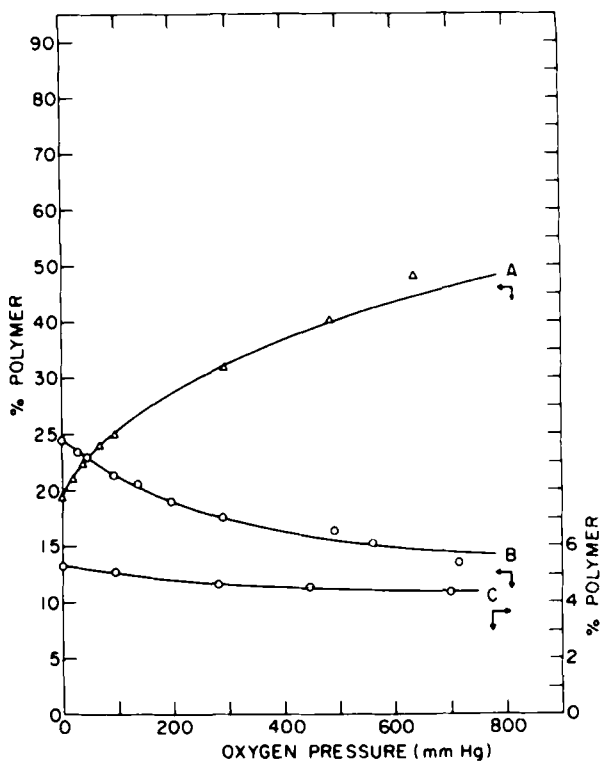
### **Effect of Oxygen and Nitric Oxide on the Solid State Polymerization of Methacrylamide**

Oxygen causes a decrease in the rate of methacrylamide solid-state post-polymerization, the inhibition being larger the higher the oxygen pressure (Fig. 8, Curves B and C) and the smaller the particle size (Fig. 9) as would be expected in a diffusion-limited reaction. The extent of inhibition is rather small. This is probably due to the fact that the oxidation reaction is a long-chain process where radicals capable of initiating new polymer chains are continuously regenerated in the propagation steps. If the rate of oxygen diffusion was low or if polymer peroxide were formed as in Eqs. (3) and (4), polymerization would proceed to a limited extent, initiated or propagated by the peroxy radicals, thus partially compensating for the increased termination rate. This is suggested by the fact that large amounts of oxygen are absorbed during the polymerization and that gaseous inhibitors having a bigger or approximately the same van der Waals diameter, e.g., sulfur dioxide and nitric oxide, are more efficient as inhibitors than is oxygen.

The effect of oxygen on the rate of the in-source polymerization of methacrylamide is quite different than the one observed for the post-polymerization. In fact, an increased rate is observed (Fig. 10) which is apparently related to a decrease in the initiation period. The rates of polymerization are similar at similar stages of conversion as determined by the amount of polymerization that has occurred. This effect is more pronounced the higher the  $O_2$  pressure (Fig. 8, Curve A) and decreases with increasing radiation dose. It does not seem to be caused by scavenging of impurities, since comparable results have been obtained using samples submitted to different degrees of purification. Samples sublimed several times or recrystallized, preirradiated, and then resublimed showed approximately the same extent of oxygen acceleration as relatively impure samples. This

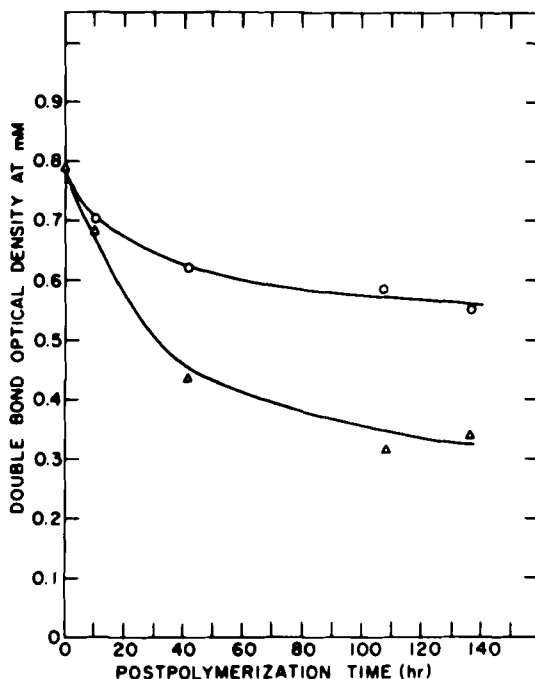
Table 2. In-Source Oxidation of Methacrylamide: Product Yields

Dose (MR)	O <sub>2</sub> absorbed (moles/g) × 10 <sup>-3</sup>	Hydroperoxides (moles/g) × 10 <sup>-3</sup>	Carbonyl compounds (moles/g) × 10 <sup>-3</sup>	Polymer (%)
21.7	0.256	0.020	0	3
81.4	0.717	0.065	0.160	34
101.1	1.010	0.062	0.175	54.3



**Fig. 8.** Effect of oxygen pressure on the rate of the  $\gamma$ -ray induced solid-state polymerization of methacrylamide. (A) In-source polymerization at room temperature. Total  $\gamma$  dose = 72 MR. (B) Postpolymerization at 65°C. Total  $\gamma$  dose = 20 MR. Reaction time = 22 hr. (C) Postpolymerization at room temperature. Total  $\gamma$  dose = 70 MR. Reaction time = 7 days.

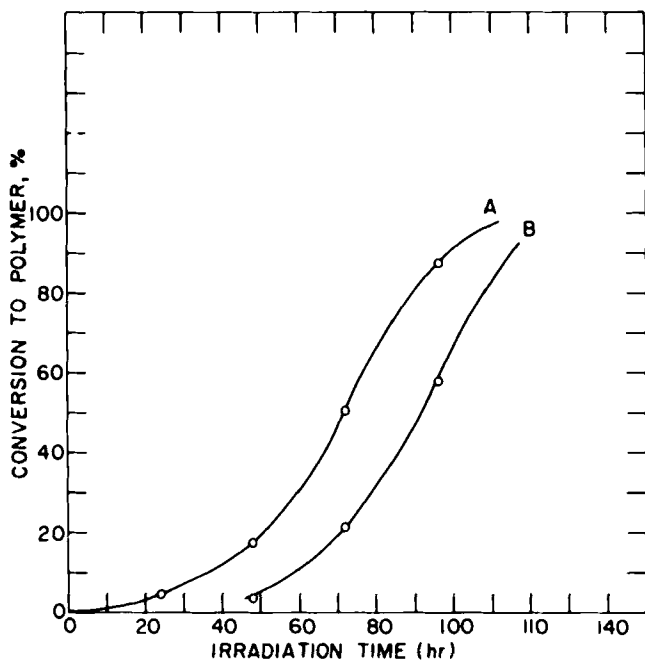
oxygen effect cannot be attributed to increased radical yield. In fact, the radical yield under oxygen, as determined by ESR, is only slightly larger than the vacuum yield and then only in the early stage of the irradiation (0–7 MR). It becomes rapidly smaller than vacuum yield (Fig. 11) while the rate of polymerization under oxygen is still faster by a factor of 2–3. That this acceleration effect is related to the oxygenated radicals or the oxygenated products is indicated by the fact that it does not occur with NO. This probably cannot be explained by an ionic mechanism in which  $O_2$  acts as an electron scavenger. This would not explain why only the initiation period is markedly affected, or why NO and  $SO_2$ , which can also be



**Fig. 9.** Effect of particle size on the rate of postpolymerization of methacrylamide in air.  $\gamma$  Dose = 36 MR. Measurements made at 45°C. The polymerization is proportional to the decrease in double-bond optical density as determined by IR spectroscopy. (○) Sample unground. (△) Sample ground.

electron scavengers albeit weaker ones than  $O_2$ , reduce the reaction rate.

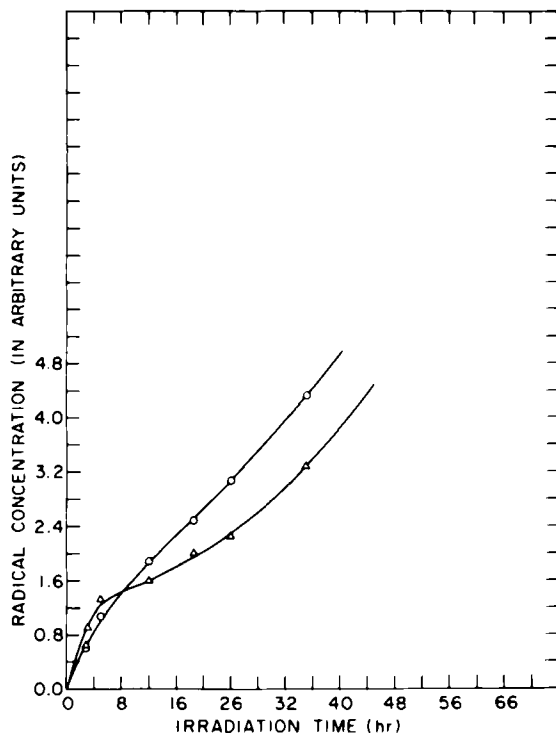
We are at present unable to give a conclusive explanation of this, but can only offer a suggestion. Figure 11 suggests that it cannot be due to an increase in radical population due to radiation decomposition of the already formed peroxides. However, if the long initiation period were due to nucleation phenomena, as seems likely, then perhaps the critical size the nucleus must reach before rapid polymerization is smaller for the peroxy radical. In addition, the peroxy radical may be able to reorient itself more rapidly within the lattice because there are no bulky methyl or amide groups attached to the active end. This would make the initial addition step more rapid. The rate of annealing of the surrounding lattice may also



**Fig. 10.** Effect of oxygen on the in-source solid-state polymerization of methacrylamide. Dose rate = 0.890 MR/hr. Measurements made at room temperature. (A) Under oxygen.  $P_{O_2} = 700$  mm Hg. (B) Under vacuum.

be higher. As a result, the initiation period would be smaller in the presence of oxygen and the apparent rate higher despite the increased termination rate. Nucleation has occurred in postirradiation polymerization prior to the admission of oxygen and only the increased termination rate is effective.

Nitric oxide acts as an efficient inhibitor both in post and in-source polymerization. The rate of in-source polymerization is reduced by a factor of 2 at  $P_{NO}$  around 500 mm Hg (Table 3). In Table 3 the data on in-source inhibition by  $SO_2$  molecules is also reported. This comparison with  $NO$  is interesting since the  $SO_2$  molecules have a bigger van der Waals diameter and are expected, therefore, to diffuse at a lower rate toward the polymerization sites. What is observed is that the inhibiting power of  $SO_2$  is comparable to that of nitric oxide. This behavior can be tentatively explained by assuming that a large fraction of polymer nucleation sites is located at defects which are accessible to the gas from the surface. If the free volume at these sites is large enough, the rate of diffusion of the gas,



**Fig. 11.** Radical build up in irradiated crystalline methacrylamide. (○) Under vacuum. (△) Under oxygen. Dose rate = 0.78 MR/hr.

and therefore the extent of the inhibition, will not be critically dependent on the molecular size provided it is not too large, but rather on the chemical efficiency of the inhibitor. This leads to the conclusion that, with monomers which polymerize in the solid state with a mechanism similar to acrylamide, significant inhibition may sometimes be obtained when gaseous inhibitors which are not able to penetrate the lattice of the monomer, are used. However, this is expected to apply when, as in our case, small particle size samples are used (0.04–0.06 mm). When larger crystals are used, a larger fraction of the polymerization sites will find themselves shielded from the diffusing gas by domains of intact lattice. In order for extensive inhibition to occur, the gas must show real diffusion through the lattice and not just diffusion at defects accessible from the surface [22].

**Table 3.** In-Source Polymerization of Methacrylamide: Effect of Nitric Oxide and Sulfur Dioxide on the Polymer Yield

Inhibitor	Gas Pressure (mm Hg)	Inhibitor/vacuum polymer yield	Total dose (MR)
NO	190	0.71	70
NO	250	0.55	70
NO	500	0.54	70
SO <sub>2</sub>	100	0.67	50
SO <sub>2</sub>	310	0.50	50
SO <sub>2</sub>	570	0.38	50

### CONCLUSIONS

Methacrylamide polymerizes in the solid state in a manner similar to acrylamide, i.e., the polymer nucleates as a second phase early in the reaction. Defects such as dislocations are believed to be the favored reaction sites. Like acrylamide, it can polymerize both in the radiation field and by a postirradiation reaction. However, unlike acrylamide, it is sensitive to the presence of gases capable of reacting with the free radical. Sulfur dioxide and nitric oxide inhibit both the in-source and postirradiation reaction. Diffusion of the gas probably is facilitated along defects and at the monomer-polymer interface.

The behavior in the presence of oxygen is anomalous. A chain oxidation occurs. This is evidenced both by the amount of oxygen absorbed and by the amount of oxygenated compounds such as peroxides and carbonyl compounds formed. The ESR free-radical spectrum decays more rapidly in the presence of oxygen. Consistent with this, the postirradiation polymerization is inhibited by oxygen. However, the apparent rate of in-source polymerization is enhanced by oxygen. This enhancement seems to take the form of a considerably shortened induction period. The reason for this is at present obscure. However, it may be related to the formation of peroxy radicals by the addition of oxygen to the monomer or dimer radicals. These radicals could reorient more easily within the lattice and would not

have the bulky methyl and amide side groups at the reactive end to slow the reaction. As a result, it may be able to add the next monomer unit more rapidly than does the radical under a vacuum environment. Thus, the polymer would nucleate as a second phase more quickly and lead to the rapid polymerization stage earlier. This results in a shorter induction period. In the postpolymerization reaction the polymer phase has already nucleated and therefore only the effect of oxygen in quenching free-radical reactions is seen.

In the case of NO, no free radical results from the addition of a single gas molecule. When SO<sub>2</sub> adds, the result is a bulky sulfonyl group that will further hinder the freedom of the radical to reorient. The resultant radical is also probably less reactive. Therefore, these gases inhibit both the in-source and postirradiation reaction. This suggests that the use of oxygen as a radical inhibitor in a solid-state reaction should be viewed with caution even if it can be shown that it can reach the free radicals in a solid since it may, under some circumstances, have an accelerating effect as well.

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