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Radiation-Induced Solid-State Polymerization in Some Methacrylates

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SUMMARY

This paper presents a comparison of some of our results on the polymerization of methacrylic acid, octadecyl methacrylate, zinc methacrylate, and barium methacrylate monohydrate in the solid state. Polymerization was initiated by cobalt-60 γ rays, both in-source and post-irradiation polymerization techniques being used. Electron spin resonance studies showed that the polymerization proceeded by a free radical mechanism in all cases. The initial radicals formed by irradiation at low temperatures added a first monomer unit about 100° below the temperature of long-chain polymerization. Some radical decay occurred in the early stages of polymerization. The rate of polymerization increased rapidly, approaching the melting point or other phase change in the monomer.

INTRODUCTION

There has been increasing interest in solid-state polymerization with the aim of either producing new or improved polymers, or of elucidating details of the mechanism of this type of solid-state reaction. A large number of

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monomers have now been shown to polymerize in the solid state, but there is little fundamental understanding of the process or even of the relative importance of static (or structural) and dynamic (or mobility) factors. This can only come about by the detailed investigation of suitable systems using as many techniques as possible.

The methacrylates provide such a system since the acid, $\text{CH}_2=\text{C}(\text{CH}_3)\text{COOH}$, the salts, $\text{CH}_2=\text{C}(\text{CH}_3)\text{COO}^-\text{M}^+$, and the esters, $\text{CH}_2=\text{C}(\text{CH}_3)\text{COOR}$, can be used, covering a wide range of physical properties and side-chain effects. They are also particularly suitable for electron spin resonance studies because 1) high radical concentrations can be obtained; 2) the spectra are well resolved for polycrystalline, organic solids; 3) only a few radical species are present; and 4) considerable work has been published on methacrylate spectra, so they can be interpreted.

The radiation-induced solid-state polymerization of methacrylate salts was discovered and investigated by Morawetz and co-workers [1-4]. They were concerned exclusively with post-irradiation polymerization and found that the polymerizability varied markedly with the nature of the metal salt and with the degree of hydration. However, there was no direct correlation and the differences were attributed to the spatial arrangements of the molecules in the crystalline lattice, although these were, in general, not known, i.e., a structural effect. Parrish and Kochanny [5] have also reported the polymerization of zinc methacrylate and Fydeler and Charlesby [6] the effect of high pressures on the polymerization of barium methacrylate.

Bamford and co-workers [7, 8] have studied the photopolymerization of methacrylic acid in the solid state. In particular they have demonstrated the reversible, inhibiting effect of pressure on the polymerization [5], which they have interpreted as being due to a change in the mobility of defects in the solid. The relative importance of spatial arrangement and mobility and the nature of the mobility are probably the most important unresolved problems in solid-state polymerization. They both reflect the physical influence of the lattice on chemical reaction, known as topochemical control.

Hardy and co-workers [9] have investigated the solid-state polymerization of cetyl (C_{16}) methacrylate and Chapiro and co-workers [10, 11] have reported the polymerization of lauryl (C_{12}) methacrylate and of methyl methacrylate in solid mixtures with paraffin oil.

EXPERIMENTAL

Methacrylic acid (Rohm and Haas) was distilled under a reduced nitrogen

atmosphere, bp $50^{\circ}\text{C}/10$ mm Hg, and stored at 0°C . Care must be taken to avoid absorption of oxygen or water. Barium methacrylate was prepared by neutralization of methacrylic acid with barium hydroxide and the monohydrate crystallized from aqueous solution. Zinc methacrylate was prepared similarly and the anhydrate crystallized from methanol. Octadecyl methacrylate (Borden Chemical Co.) was purified from inhibitor with aqueous NaOH and dried; the absolute purity of this monomer was uncertain.

The purified monomers were sealed under vacuum, after freeze-thaw degassing for the liquids, or in air, in glass tubes, or Spectrosil ESR tubes. Cobalt-60 γ irradiations were carried out in the pond facility of the Australian Atomic Energy Commission. Polymer yields were calculated by gravimetric separation using a suitable solvent for monomer/nonsolvent for polymer, and residual monomer by double bond titration with bromine. ESR measurements were made with a Varian V-4502 instrument using a variable temperature cavity.

RESULTS AND DISCUSSION

In-Source Polymerization

All the monomers polymerized readily during irradiation at suitably high temperatures. Typical polymerization (conversion vs time) curves are shown in Fig. 1. They were usually sigmoidal-shaped, consisting of an initial

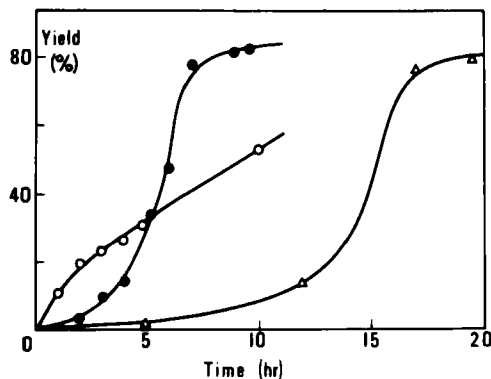


Fig. 1. In-source polymerization. (●) MAA, 36,000 rad/hr at 0°C . (○) ODMA, 109,000 rad/hr at -20°C . (△) BaMA, 327,000 rad/hr at 35°C .

"induction" period of low rate followed by a rapid acceleration leading to high polymer yields. At high dose rates or temperatures the "induction" period could be eliminated. The high polymerization rates in the accelerating period provide a serious problem in maintaining the monomer at a constant temperature, due to the exothermic heat of reaction. In large samples serious temperature rises may occur, invalidating rate data and sometimes leading to thermal explosions.

The in-source polymerization rates of methacrylic acid (MAA) and octadecyl methacrylate (ODMA) were very high. Barium methacrylate monohydrate (BaMA) had a much longer "induction" period, but then polymerized rapidly. The polymerization rates increased and "induction" periods decreased with increasing dose rate and temperature.

Post-Irradiation Polymerization

Typical polymerization curves (conversion vs time) for MAA, ODMA, BaMA, and ZnMA are shown in Fig. 2. ODMA polymerized very rapidly after small radiation doses, the rate being particularly fast initially. However, the rate diminished markedly after about 40% conversion, even after quite high doses. The high polymerizability of ODMA may be due in part to impurity effects, but in MAA, which is known to be of high purity, the polymerization rate was also quite high.

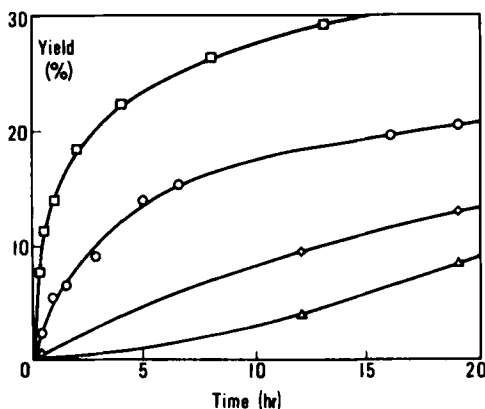


Fig. 2. Post-irradiation polymerization. (\square) ODMA at -10°C (0.1 Mrad at -196°C). (\circ) MAA at 0°C (0.5 Mrad at -196°C). (\diamond) ZnMA at 100°C (1.0 Mrad at -196°C). (\triangle) BaMA at 50°C (1.0 Mrad at -80°C).

Polymerization rates were slower in the metal salts ZnMA and BaMA. In particular, the initial rate was low and in BaMA there was actually an "induction" period under most conditions.

Polymer yields after separation from samples taken directly from the irradiation temperature of -196°C were negligible, except for ODMA. This was shown to be due, predominantly, to polymerization during dissolution.

Esr Spectra

Elucidation of the mechanism of solid-state polymerization is difficult because most methods used in the liquid state are of dubious validity. Therefore, the identification of free radicals and quantitative measurements of their reactions by electron spin resonance spectroscopy is particularly valuable. The methacrylates have proved to be very suitable for ESR studies. We have obtained similar spectra from MAA, ODMA, ZnMA, and BaMA, differences occurring mainly in radical yields (G values), line widths, and reaction temperatures. Some typical spectra are shown in Fig. 3.

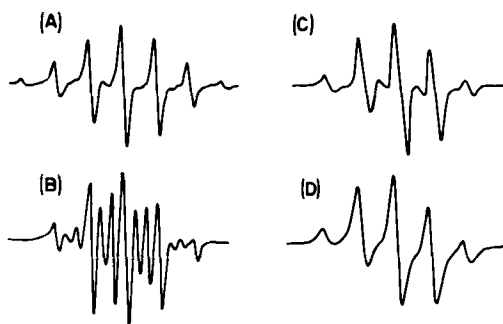
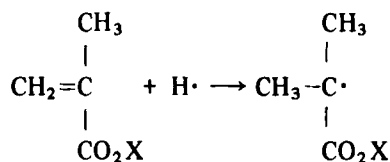


Fig. 3. ESR spectra. (A) BaMA at -196°C (0.2 Mrad at -196°C). (B) MAA on warming to -30°C (0.5 Mrad at -196°C). (C) ODMA during polymerization at -30°C (0.5 Mrad at -196°C). (D) BaMA after extended polymerization at 50°C (1 Mrad at -196°C).

Initial Radical

After irradiation at -196°C , the spectrum is predominantly 7 lines with a binomial intensity distribution and hfs of 23 G (Fig. 3A). This is attributed to radical I formed directly or indirectly by addition of a hydrogen atom to the double bond of the monomer.

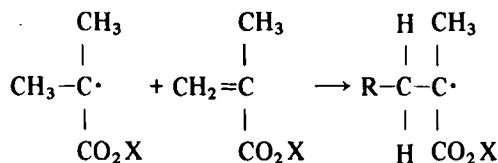


I

Intermediate peaks in the spectra were due to other radicals produced during irradiation, e.g., by C-H scission, or to propagating radicals.

Propagating Radical

The initial spectrum changed on warming to 9-lines with hfs of 11.5 G typical of the propagating radical II formed by addition of monomer.



I

II

The conversion I \rightarrow II followed reproducible kinetics which could be analyzed into simultaneous fast and slow first-order reactions [12]. Addition of the first monomer molecule occurred about 100°C below the region of long-chain polymerization.

The intermediate peaks in the spectra of the propagating radical showed a great variation with the monomer, temperature, and extent of polymerization. These variations can be explained by differences in the twist of the sp^2 plane of the radical with respect to the two β -methylene C-H bonds and in the line widths. The shape of the spectrum is very sensitive to these two parameters and the appropriate values are best derived by comparison with theoretical spectra. In BaMA the asymmetry increases steadily during polymerization from 58-62° to 55-65° accompanied by an increase in line width from 6 to 8 G. However, in MAA the radical apparently twists rapidly to 54.5-65.5° with a narrow line width of 4.5-5 G, which results in clearly split intermediate peaks. As polymerization proceeds the line width increases steadily (to 8 G) and the asymmetry actually decreases

slightly. An alternative explanation for MAA, based on a barrier between two conformation, has also been advanced [13].

CONCLUSIONS

The most interesting aspect of the radiation-induced solid-state polymerization of MAA, ODMA, ZnMA, and BaMA is that they all show similar polymerization behavior. The polymerization curves (polymer yield vs time) and the effects of radiation dose and temperature are similar for both in-source and post-irradiation polymerization.

ESR studies have been particularly useful, showing that the polymerization proceeds by a free radical mechanism, that initiation is by addition of a hydrogen atom to the double bond of the monomer, that addition of the first monomer molecule occurs much more rapidly than long-chain polymerization, and that there is some loss of radicals during polymerization, but that the long-chain radicals are effectively trapped. Also, interesting information has been obtained on the effect of the environment on the conformation of the radical end of the growing chain.

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