

Radiation-Induced Solid-State Polymerization in Binary Systems. V. Polymerization in Binary Systems Containing Long Chain Compounds

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Synopsis

Radiation-induced solid-state polymerization in binary systems containing long-chain compounds has been investigated. Butyl stearate-methyl methacrylate and stearyl alcohol-methyl methacrylate systems have been studied in detail. In these systems in-source polymerization does not occur but a remarkable post-polymerization takes place on warming after irradiation at low temperature. The limiting conversion characteristics of this post-polymerization depend greatly on the nature and the concentration of the long-chain compounds. The post-polymerization is observed to be more marked in the butyl stearate-methyl methacrylate system than in the stearyl alcohol-methyl methacrylate system, and it increases with increasing concentration of the long-chain component. An optimum warming rate and warming temperature exists for the maximum saturated conversion. Irradiation in air causes some decrease of conversion compared to irradiation *in vacuo*. The possible mechanism is that monomer diffuses into the crystals of the long-chain compound after melting at the eutectic temperature. The polymerization may be initiated by trapped radicals of the long-chain compound and carried out in the crystal of the long-chain compound with a smaller possibility of termination. In binary systems containing long-chain compounds, lowering of the melting point is slight, and the eutectic composition exists at the richer composition of monomer, so almost all the long-chain substance remains as excess crystals, which are suitable for holding trapped radicals. The crystal lattices of long-chain compounds may be softer than those of compounds of small molecular size. This fact is favorable for monomer diffusion. This explains why such a post-polymerization takes place only in systems containing long-chain molecules.

INTRODUCTION

We have previously investigated^{1,2} the mechanism of phase formation and the characteristics of radiation-induced polymerization in binary systems. This report deals with the characteristics of radiation-induced polymerization in binary systems including long-chain compounds. In this field of study, we have found that methyl methacrylate polymerizes well in a mixture with glycerol at a low temperature, and Chapiro^{4,5} reported that methyl methacrylate and methyl acrylate can be easily polymerized in a mixture with mineral oil or castor oil at a low temperature (below the melting point of the pure monomer). Also, Chapiro showed from

the result of electron microscopic observations that methyl methacrylate is in a supercooled liquid state in the mixture and possibly polymerizes by irradiation even at such low temperatures. However, the fact that mineral oil and castor oil are multicomponent mixtures of several long-chain compounds renders these substances unsuitable for accurate analysis of phase equilibria. For this reason, we have investigated binary systems containing simple long-chain compounds as part of a systematic study of radiation-induced polymerization in binary systems consisting of several phases.

EXPERIMENTAL

The monomer used in this study was generally methyl methacrylate. Butyl stearate and stearyl alcohol were chosen as representative long-chain substances. All materials were purified by distillation or recrystallization and mixed homogeneously, by heating if necessary. Samples were irradiated at constant temperature ($-78^{\circ}\text{C}.$) by 60 γ -rays from a ^{60}Co source. Post-polymerization was carried out by warming the sample after irradiation. Polymerized samples were quickly treated with cooled acetone or methanol containing inhibitor to precipitate the polymer.

The conversions were determined gravimetrically. The phase diagrams of binary systems were determined by the method of differential thermal analysis. The viscosity of the monomeric system and of the polymer in benzene solution were measured with an Ostwald viscometer at definite temperatures. The molecular weights of the polymers were calculated by using the viscosity data for $20^{\circ}\text{C}.$ in benzene according to the equation:⁶

$$[\eta] = 0.84 \times 10^{-4} M^{0.73}$$

RESULTS

Phase Equilibrium Diagram of Binary Systems Containing Long-Chain Substances

Phase diagrams of the butyl stearate–methyl methacrylate system and the stearyl alcohol–methyl methacrylate system are shown in Figures 1 and 2.

These diagrams are different from the usual phase diagrams obtained for eutectic mixtures consisting of components of similar molecular sizes. The characteristics of the phase diagrams for binary systems containing a long-chain compound can be summarized as follows: (1) the eutectic point exists at very high concentration of monomer and no spread in the melting point (i.e., coexisting liquid and solid region) is noted on the monomer-rich side of the eutectic point; (2) the liquidus curve for the composition richer in long-chain substance rises sharply from the eutectic point to a plateau close to the melting point of pure long-chain component; (3) the solidus curve is slightly lower than the melting point of pure monomer in the MMA–stearyl alcohol system, whereas it is a little higher in the case of the butyl stearate–methyl methacrylate system.

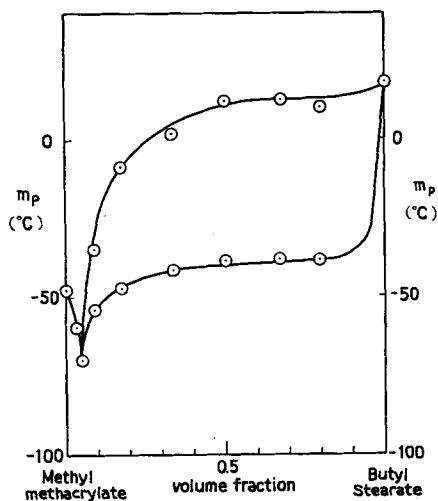


Fig. 1. Phase equilibrium diagram of butyl stearate-methyl methacrylate system.

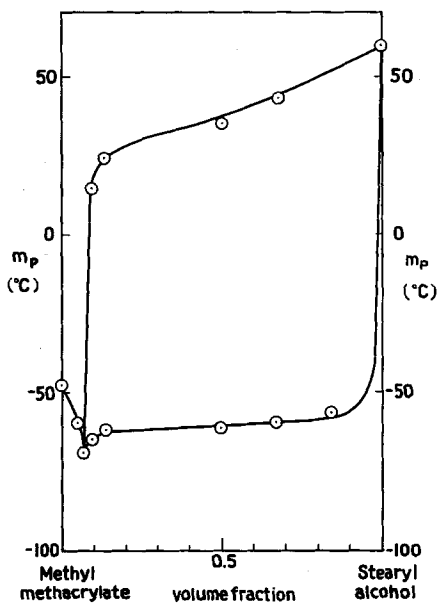


Fig. 2. Phase equilibrium diagram of stearyl alcohol-methyl methacrylate system.

Such characteristics might be explained as follows. Long-chain substances have a large molecular size and a high coagulative ability owing to the van der Waals forces at the long hydrocarbon chain. The molecular interactions between the two components are therefore very small, and long-chain substances can crystallize without a marked decrease in the melting point, while in the usual eutectic mixture of components of equivalent molec-

TABLE I
Results of the Post-Polymerization in Binary Systems^{a,b}

Additive	Monomer									
	Methyl acrylate	Ethyl acrylate	Butyl acrylate	Methyl methacrylate	Ethyl methacrylate	Butyl methacrylate	Acrylic acid	Methacrylic acid	Acrylamide	Methacrylamide
Methyl stearate	+	+	+	+	+	+	+	+	+	0
Butyl stearate	+	+	+	+	+	+	+	+	+	0
Vinyl stearate	+	+	+	+	+	+	+	+	+	0
Methyl palmitate	+	+	+	+	+	+	+	+	+	0
Ethyl palmitate	+	+	+	+	+	+	+	+	+	0
Stearyl alcohol	+	+	+	+	+	+	+	+	+	0
Stearic acid	+	+	+	+	+	+	+	+	+	0
Cetyl alcohol	+	+	+	+	+	+	+	+	+	0
Paraffin	+	+	+	+	+	+	+	+	+	0
Lauryl alcohol	-	-	-	-	-	-	+	+	+	+
Octyl alcohol	-	-	-	-	-	-	+	+	+	+
Butyl alcohol	-	-	-	-	-	-	+	+	+	+
Capric acid	-	-	-	-	-	-	+	+	+	+
Caprylic acid	-	-	-	-	-	-	+	+	+	+
Caproic acid	-	-	-	-	-	-	+	+	+	+
Butyric acid	-	-	-	-	-	-	+	+	+	+
Propionic acid	-	-	-	-	-	-	+	+	+	+
Acetic acid	-	-	-	-	-	-	+	+	+	+
Propionamide	-	-	-	-	-	-	+	+	+	+
Acetamide	-	-	-	-	-	-	+	+	+	+

^a Preirradiation at -78°C ., 1.40 Mrad; post-polymerization at 18 and 32°C . for 20 min.

^b (+) polymerization occurs; (-) no polymerization; (0) immiscible.

ular size, the crystallization proceeds by a compact mutual attraction of two component molecules, resulting in the decrease of melting point. So the change of liquidus and solidus curves from the melting point of the pure components is relatively small, and both curves correspond closely to those of binary systems which are immiscible in the liquid phase. The mole fraction of long-chain substances at the eutectic composition is small owing to their large molecular size and coagulative power, and long-chain molecules hardly crystallize at the eutectic composition and may be dispersed homogeneously in the monomer crystal. This may be the reason for the narrow of the melting range for monomer-rich compositions.

Polymerization of Binary Systems Containing Long-Chain Substances

Polymerization. In-source polymerization is not recognized to occur in any system containing long-chain compounds in the solid state. However, marked post-polymerization is found to occur in many binary systems containing long-chain substances. The results of post-polymerization experiments on some binary systems are listed in Table I.

As is well known, acrylamide acrylic acid, methacrylamide, and methacrylic acid can be polymerized easily in the solid state by warming after irradiation. However, acrylic esters and methacrylic esters, which were observed to undergo only little post-polymerization in bulk,^{3,7} showed a remarkable post-polymerization in the systems containing long-chain sub-

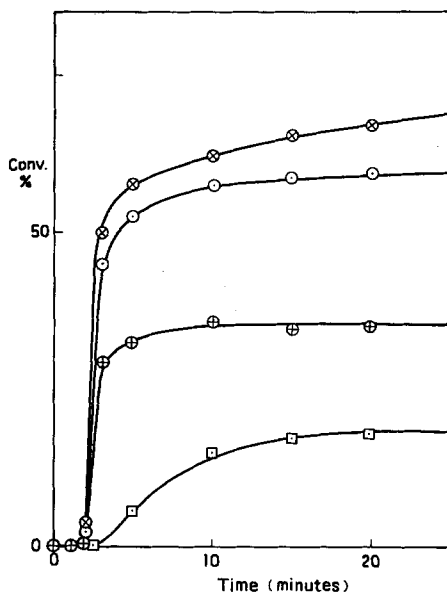


Fig. 3. Relationship between time and conversion at various polymerization temperatures for the butyl stearate-methyl methacrylate system. Composition: MMA = 67 vol.-%; dose = 1.40 Mrad. Temperature: (⊕) 32°C.; (⊙) 18°C.; (⊗) 0°C.; (⊠) -30°C.

stances. Long-chain fatty acid esters are found to be especially suitable for the post-polymerization of acrylic or methacrylic ester monomers.

Polymerization Rate. Time-conversion curves in post-polymerization of butyl stearate-methyl methacrylate and stearyl alcohol-methyl meth-

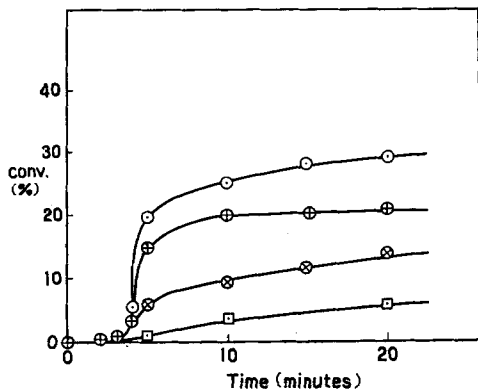


Fig. 4. Relationship between time and conversion at various polymerization temperatures for the stearyl alcohol-methyl methacrylate system. Composition: MMA = 67 vol.-%; dose = 1.40 Mrad. Temperature: (⊕) 50°C.; (⊙) 40°C.; (⊗) 18°C.; (⊠) 0°C.

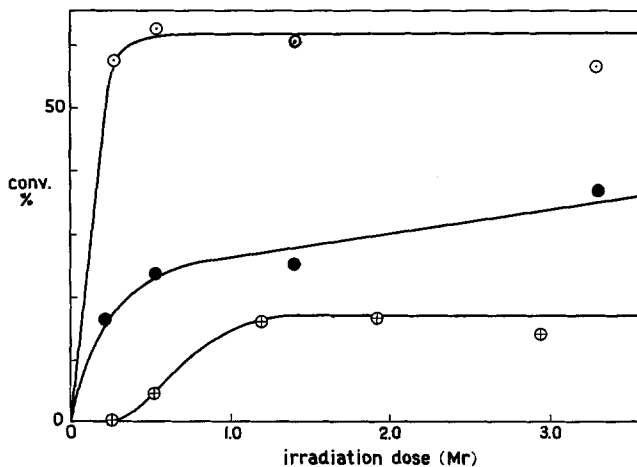


Fig. 5. Relationship between irradiation dose and conversion in the post-polymerization of binary systems containing long-chain compounds. Composition: MMA = 67 vol.-%; post-polymerization: BS-MMA, 18°C., 20 min.; SA-MMA, 40°C., 10 min. (⊙) BS-MMA (*in vacuo*); (⊕) BS-MMA (*in air*); (●) SA-MMA (*in vacuo*).

acrylate systems at various polymerization temperatures are shown in Figures 3 and 4.

The relationship between the irradiation dose and polymer yield for post-polymerization are shown in Figure 5.

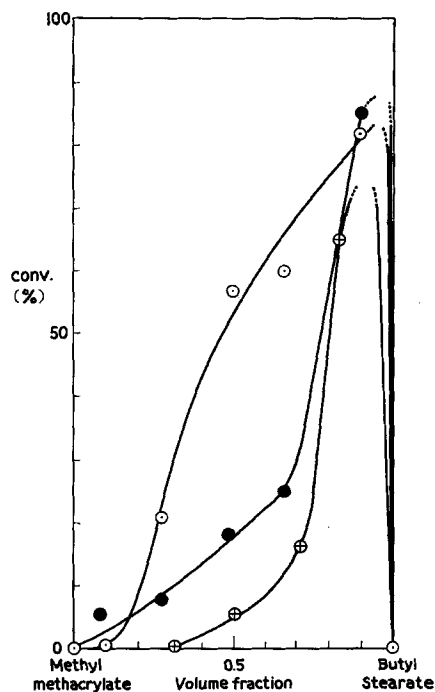


Fig. 6. Relationship between monomer composition and conversion in the post-polymerization of binary systems containing long-chain compounds. Dose = 1.40 Mrad; post-polymerization: BS-MMA, 18°C., 20 min.; SA-MMA, 40°C., 10 min. (○) BS-MMA (*in vacuo*); (⊕) BS-MMA (in air); (●) SA-MMA (*in vacuo*).

Effects of monomer composition on conversion for post-polymerization are shown in Figure 6.

These results give the following information about the post-polymerization of systems containing long-chain compounds. Polymerization rates are very high and rapidly reach a conversion limit characteristic of the temperature. The polymerization is influenced strongly by temperature. Conversion at 0°C. is larger than that at 30°C. and 18°C. in the butyl stearate system; conversion at 40°C. is larger than that at 50°C. and 18°C. in stearyl alcohol system. Thus an optimum temperature for polymerization exists. However, as the polymerization is not considered to attain thermal equilibrium, it is more accurate to say there is an optimum warming rate for the maximum conversion. The saturated conversion limit does not strongly depend on the irradiation dose under the present experimental conditions. The presence of air during irradiation results in a decrease of conversion. Remarkable effects of monomer composition are observed.

Post-polymerization occurs effectively in compositions richer in long-chain substances, and conversion increases markedly with increase in concentration of the long-chain component. It reaches more than 80% conversion at high concentration of long-chain compound. It is concluded

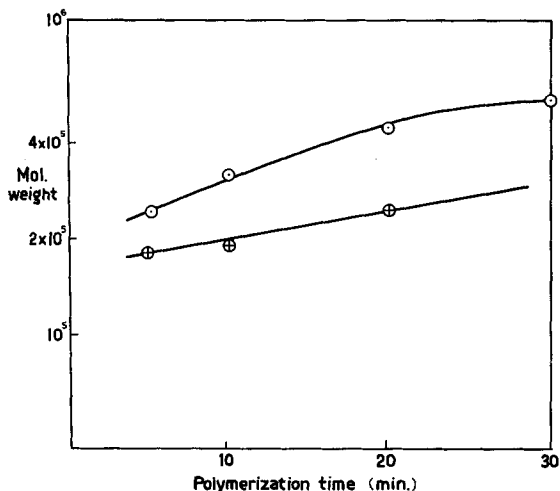


Fig. 7. Relationship between polymerization time and molecular weight of the polymer in the post-polymerization of binary systems containing long-chain compounds. Composition: MMA = 67 vol.-%; dose = 1.40 Mrad; polymerization temperature: BS-MMA, 18°C.; SA-MMA, 40°C. (\circ) BS-MMA (*in vacuo*); (\oplus) SA-MMA (*in vacuo*).

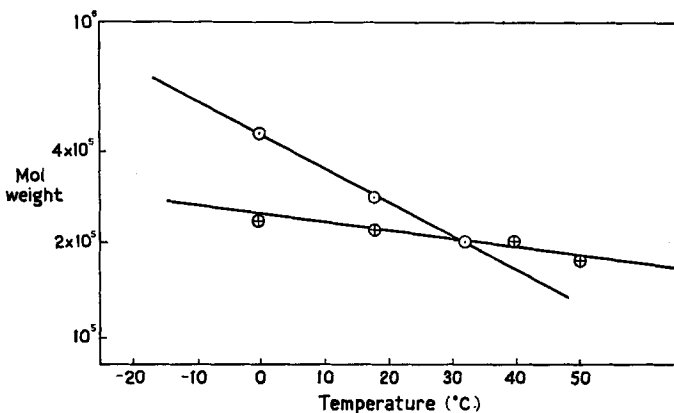


Fig. 8. Relationship between polymerization temperature and the molecular weight of polymer in the post-polymerization of binary systems containing long-chain compounds. Composition: MMA = 67 vol.-%; dose = 1.40 Mrad; post-polymerization time: BS-MMA, 20 min.; SA-MMA, 10 min. (\circ) BS-MMA (*in vacuo*); (\oplus) SA-MMA (*in vacuo*).

that effects arising from the nature and concentration of long-chain components on conversion under the various conditions are the most salient characteristics of this polymerization.

Degree of Polymerization. The degrees of polymerization of poly-(methyl methacrylate) produced under different conditions are shown in Figures 7-10. These results can be summarized as follows. The degree

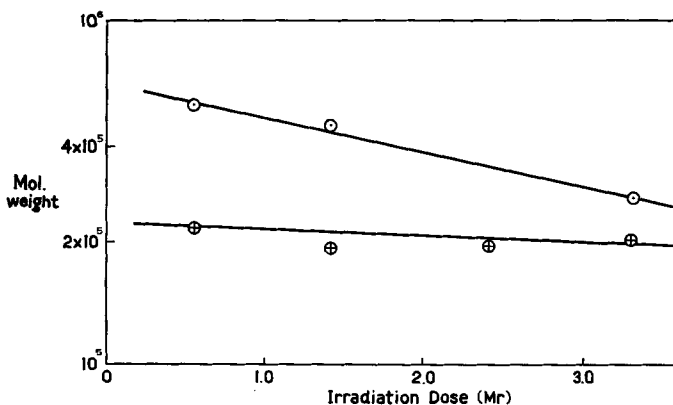


Fig. 9. Relationship between irradiation dose and the molecular weight of polymer in the post-polymerization of binary systems containing long-chain compounds. Composition: MMA = 67 vol.-%; post-polymerization: BS-MMA, 18°C., 20 min.; SA-MMA, 40°C., 10 min. (\circ) BS-MMA (*in vacuo*); (\oplus) SA-MMA (*in vacuo*).

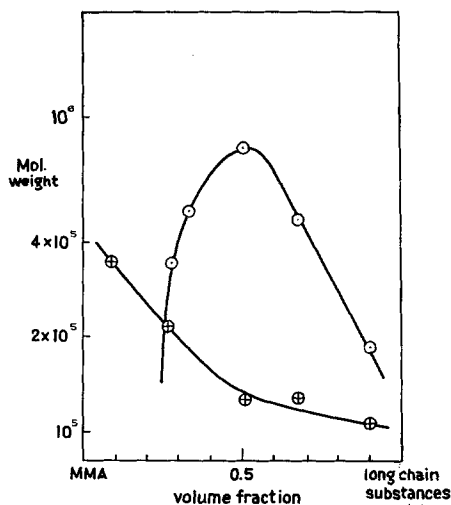


Fig. 10. Relationship between the monomer composition and molecular weight of the polymer in the post-polymerization of binary systems containing long-chain compounds. Dose = 1.40 Mrad; heating: BS-MMA, 18°C., 20 min.; SA-MMA, 40°C., 10 min. (\circ) BS-MMA (*in vacuo*); (\oplus) SA-MMA (*in vacuo*).

of polymerization decreases with irradiation dose. This decrease is sharper in the butyl stearate system than in the stearyl alcohol system. The degree of polymerization increases almost linearly with the polymerization time. The degree of polymerization decreases with increasing of polymerization temperature. The degree of polymerization in the butyl stearate system has a maximum value at a certain composition, but decreases at high concentration of long-chain substance, while in the stearyl alcohol system, the

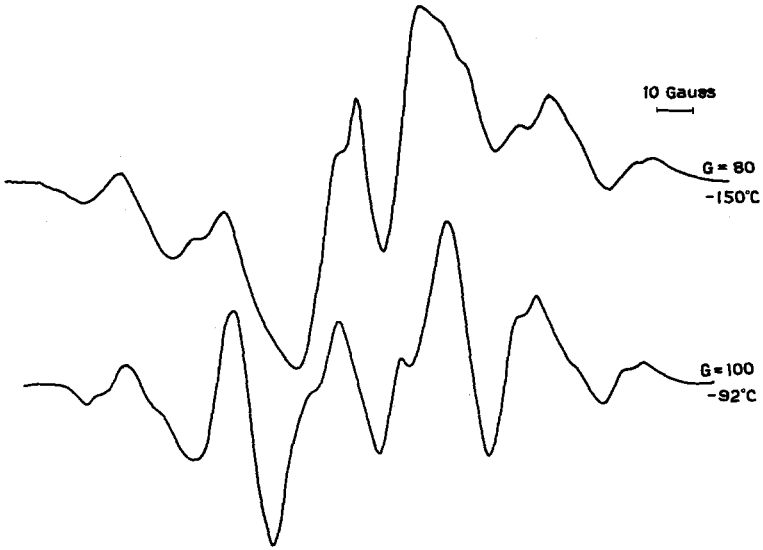


Fig. 11. Change with temperature of ESR spectrum of irradiated butyl stearate. Dose = 10^6 rad.

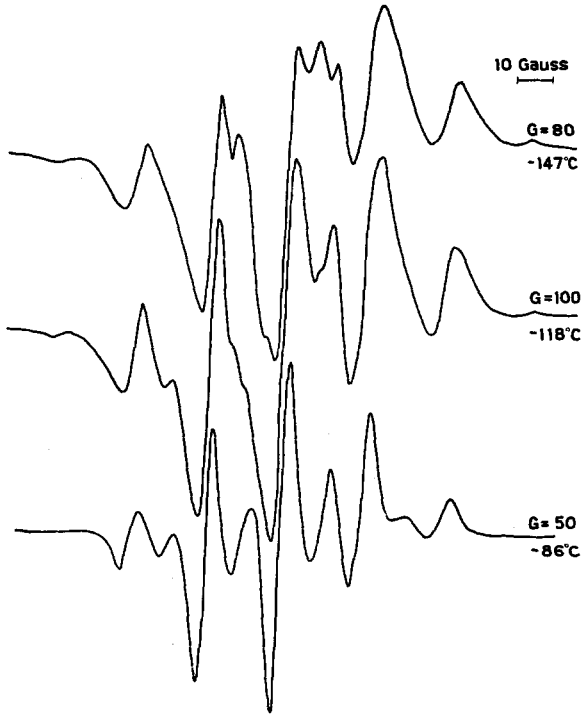


Fig. 12. Change with temperature of ESR spectrum of irradiated methyl methacrylate. Dose = 10^6 rad.

degree of polymerization decreases continuously with the concentration of long-chain component. The degree of polymerization of polymer formed in air shows the same tendency as that of polymer obtained *in vacuo*. However the former is much lower than the latter.

ESR Spectra of Binary Systems Containing Long-Chain Compounds

Butyl stearate was irradiated with the electron beam from a Van de Graaff accelerator at -196°C . to a dose of 10^6 rad. A six-line spectrum with a coupling constant of about 28 gauss was observed (Fig. 11) which is assigned to the free radical $-\text{H}_2\text{C}-\dot{\text{C}}\text{HCH}_2-$ formed by abstraction of a hydrogen atom from a main chain. This free radical decayed at about -40°C .

Methyl methacrylate (MMA) was irradiated at -196°C . to a dose of 10^6 rad. A seven-line spectrum with a coupling constant of about 21 gauss was observed till the temperature was raised to -147°C . This spectrum is assigned to the free radical $\text{R}-\text{CH}_2-\dot{\text{C}}\text{H}-\text{CH}_3$ formed by addition of hydrogen atom to the double bond. With increasing temperature, the spectrum changed into 5 + 4 line spectrum as shown in Figure 12 and decayed at -60°C . This is assigned to the propagating radical. Methyl methacrylate-butyl stearate (50:50) was irradiated to a dose of 10^6 rad with the electron beam from a Van de Graaff accelerator at -196°C . The change of ESR spectrum with temperature is shown in Figure 13.

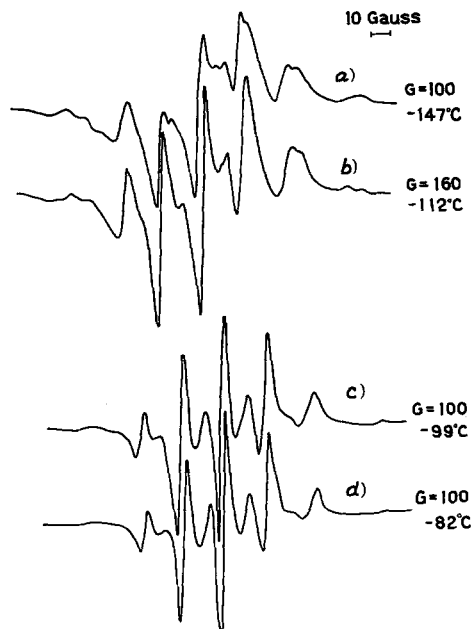


Fig. 13. Change with temperature of ESR spectrum of irradiated methyl methacrylate-butyl stearate (50:50) system. Dose = 10^6 rad. G represents an amplifier gain.

At the lower temperature, the spectra of methyl methacrylate and butyl stearate were superposed, but as the temperature of the sample was raised, the spectrum changed to the propagating radical of MMA. This spectrum decayed out at about -45°C . From these facts it is supposed that the free radical $\text{R}-\text{CH}_2-\dot{\text{C}}\text{H}-\text{CH}_3$ initiates the polymerization in the solid state. However the conversion is negligibly small owing to the inhibition of propagation.

DISCUSSION

Chapiro has reported that methyl methacrylate is a supercooled liquid in mixture with mineral oil and that in-source polymerization takes place in this state.^{4,5}

However, in binary systems consisting of simple long-chain compounds such as stearyl or palmitic derivatives and acrylic or methacrylic ester monomers, a liquid state is not maintained at very low temperatures. It may be that monomer is in the crystalline state in these systems at low temperature, based on the following experimental facts. Solidus curves appeared in the phase diagrams, and this suggests the crystallization of eutectic composition. These systems are prepared by conditions which hardly favor a supercooled state. That is, molecular interaction between the two components is small as already described, and the cooling rate is relatively low at -78°C . If monomer remains in a liquid-solid co-

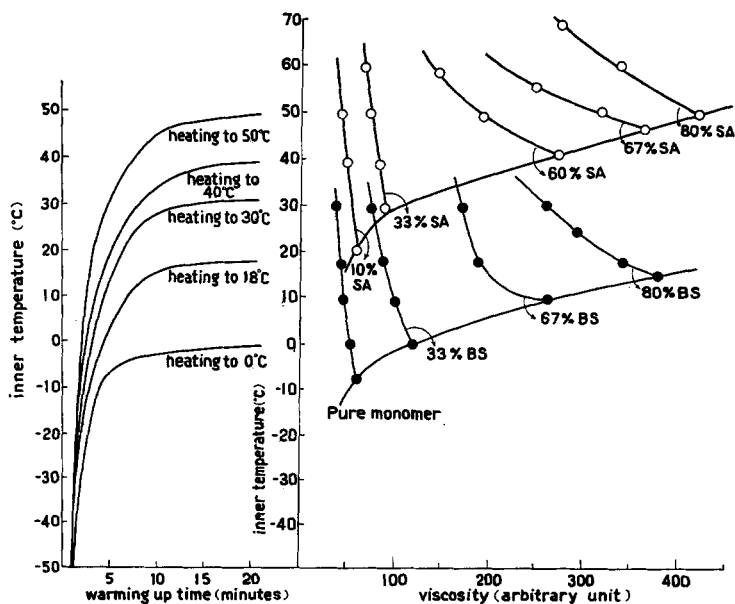


Fig. 14. Inner temperature and viscosity of the molten portion as a function of the warming up of binary systems containing long-chain compounds: (●) BS-MMA; (○) SA-MMA.

existent phase or in a supercooled phase at a temperature above the glass transition point, an in-source polymerization should take place. However, there occurred no in-source polymerization. If monomer is in a supercooled phase below the glass transition temperature, in-source polymerization does not occur, but a rapid post-polymerization does occur.² It is not likely that the glass transition temperature is higher than the melting point. The signal in the ESR spectrum for the monomer radical is recognized till the systems reach near the melting point. These facts suggest that the monomer is in a crystalline state at low temperature in these systems.

Figure 14 shows how the internal temperature of the sample rises as a function of treating time during warming to the various outer temperatures after irradiation at -78°C . It also shows the viscosity changes of the liquid part of the samples.

According to these results, it is obvious that the irradiated sample reaches the solidus line within a few minutes, and at the eutectic composition containing largely monomer, it melts at this temperature. This time coincides with the induction period in Figures 3 and 4, and so the polymerization probably takes place after melting of the monomer. A possible mechanism for the polymerization is proposed as follows. After melting, monomer molecules diffuse into crystalline long-chain compounds. In the crystal of long-chain compounds, the short polar group part forms a relatively soft crystalline structure (compared to the long hydrocarbon chain part) into which the monomer molecule easily diffuses.

It is possible to consider that the polymerization of diffused monomer is initiated by the trapped radicals of long-chain molecules, and a post-polymerization occurs rapidly.

In the range of composition of high monomer concentration, most of the system melts, the monomer radical easily disappears by mutual termination, and little polymer is obtained. However, for compositions with a high concentration of long-chain compounds, the monomer disperses into a large excess of crystals of the long-chain compound; hence the probability of termination between propagating radicals is relatively small, and so the polymerization proceeds effectively.

In binary systems consisting of smaller equivalent molecules, a eutectic composition exists relatively in the middle of the composition range. The eutectic mixture melts at the eutectic temperature and the radicals terminate rapidly. Moreover, crystals of compounds, of smaller molecular size have a relatively rigid structure compared with crystals of long-chain compounds, and monomer diffusion into the crystal is considerably reduced. These may be the reasons why the post-polymerization of monomer takes place only in binary systems containing long-chain compounds, and conversions are high at compositions with high concentrations of long-chain compounds.

The influence of the nature of long-chain substances on the polymerization rate shown in Figures 3-6 is explained by the differences in rigidity of crystal structure. Stearyl alcohol has a more rigid structure than stearyl

esters owing to the hydrogen bond of —OH group. The dependence of final conversion and polymerization rate on the polymerization time and temperature may vary according to the chemical structure and physical properties of the long-chain substance in the crystalline state.

At very low temperatures, monomer diffusion into the long-chain crystal is difficult. At high temperatures, the long-chain crystal melts at a very high rate, and radicals of long chain substances terminate easily. This is the reason for the existence of an optimum temperature for the maximum conversion. The effects of viscosity increase as a result of melting of the long-chain substance are next considered. As shown in Figure 12, the viscosity of the polymerizing system is not so high when the conversion reaches the limiting value, and after some time the viscosity increases owing to the melting of long chain substance. Thus, the viscosity of the system may not be the essential factor for the post-polymerization. A highly viscous system is obtained after sufficient polymerization time. This situation decreases the radical termination and increases the conversion and the degree of polymerization.

In the butyl stearate–methyl methacrylate system almost all crystals of the long-chain component melt within 20 min. at 18°C. The decrease of the degree of polymerization as a function of preirradiation dosage is explained by the increase of active species in this system.

In the stearyl alcohol–methacrylate system, a relatively small amount of crystal melts, but almost all the crystals of the long-chain substance remain on heating for 10 min. at 40°C., and some increase of conversion may be due to trapped radicals in the long-chain crystals. Thus the degree of polymerization does not decrease with the preirradiation dosage. The effect of monomer composition on the polymerization is also important. In the range of higher concentration of long-chain substances, the monomer molecules diffuse and disperse in a smaller unit into excess crystals of the long-chain compound, and the probability of termination becomes lower. The concentration of trapped radicals in long-chain crystals is higher, and the probability of initiation increases in this composition. These are the reasons for the increase of conversion with increasing concentration of the long-chain compound.

This consideration is supported by the decrease of degree of polymerization with the increase of concentration of the long-chain substance. Some initial increase of the degree of polymerization with the concentration of long-chain substance in the butyl stearate–methyl methacrylate system may be caused by the effect of a viscosity increase in the system, because under the conditions of heating for 20 min. at 18°C. a highly viscous system is formed by melting.

A lower conversion is obtained for the polymerization in air than for that *in vacuo*, because the number of radicals formed by irradiation in air is generally smaller than that formed *in vacuo*.

Finally, it is concluded that post-polymerization occurs on warming after irradiation in the solid state in binary systems containing long-chain

substances. The characteristics of this polymerization result from the nature and the concentration of the long-chain compounds. All experimental results can be explained by the mechanism of polymerization caused by the diffusion of molten monomer molecules into the long-chain crystals and by initiation of the polymerization by trapped radicals of long-chain compounds.

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Résumé

On a étudié la polymérisation à l'état solide initiée par irradiation sur des systèmes binaires contenant des substances à longues chaînes. Des systèmes stéarate de butyle-méthacrylate de méthyle et alcool stéarylique-méthacrylate de méthyle ont été principalement étudiés en détails. Dans ces systèmes, la polymérisation immédiate ne se passe pas, mais une post-polymérisation remarquable a lieu par chauffage après irradiation à basse température. La caractéristique de cette post-polymérisation est la grande différence dans les effets de la nature et de la concentration des substances à longue chaîne sur la conversion à saturation. Cette post-polymérisation est observée être la plus remarquable dans le système stéarate de butyle-méthacrylate de méthyle plutôt que dans le système alcool stéarylique-méthacrylate de méthyle; elle augmente avec une augmentation de concentration de composants à longue chaîne. Une vitesse de chauffage optimum et une température de chauffage optimum existent pour une conversion maximum. L'irradiation à l'air occasionne une certaine diminution de degré de conversion comparée à l'irradiation sous vide. Une explication possible consiste en ce que le monomère diffuse au sein des cristaux de la substance à longue chaîne après fusion à la température eutectique, et la polymérisation est initiée par des radicaux piégés de la substance à longue chaîne formée dans le cristal de la substance à longue chaîne avec une faible possibilité de terminaison. Dans les systèmes binaires contenant des substances à longue chaîne, l'abaissement du point de fusion est faible et la composition eutectique existe dans un mélange plus riche en monomères de telle sorte que pratiquement toute la substance à longue chaîne reste dans les cristaux en excès capables de piéger les radicaux. Les réseaux cristallins des substances à longue chaîne peuvent être plus mous que ceux des substances de bas poids moléculaires. Ce fait est favorable à la diffusion des monomères.

Zusammenfassung

Die strahlungs-induzierte Polymerisation in fester Phase wurde an binären Gemischen mit langkettigen Substanzen untersucht. Eingehendere Versuche wurden hauptsächlich

lich an den Systemen Butylstearat-Methylmethacrylat und Stearylalkohol-Methylmethacrylat angestellt. Bei diesen Systemen tritt keine Polymerisation unter der Strahlungsquelle ein, es findet aber eine bemerkenswerte Nachpolymerisation bei der Erwärmung nach der Tieftemperaturbestrahlung auf. Charakteristisch für diese Nachpolymerisation ist ein grosser Unterschied im Einfluss von Natur und Konzentration der langkettigen Substanzen auf den erreichten Umsatz. Die Nachpolymerisation tritt im System Butylstearat-Methylmethacrylat stärker hervor als bei Stearylalkohol-Methylmethacrylat; sie nimmt mit steigender Konzentration der langkettigen Komponente zu. Für maximalen erreichbaren Umsatz besteht eine optimale Aufwärmgeschwindigkeit und Aufwärmtemperatur. Die Bestrahlung in Luft liefert einen niedrigeren Umsatz als die Bestrahlung im Vakuum. Als möglicher Mechanismus wird eine Diffusion des Monomeren in die Kristalle der langkettigen Substanz nach dem Schmelzen bei der eutektischen Temperatur angenommen sowie ein Polymerisationsstart durch die eingeschlossenen Radikale der langkettigen Substanz mit anschliessender Polymerisation des Monomeren im Kristall der langkettigen Substanz bei herabgesetzter Abbruchwahrscheinlichkeit. In den binären Systemen mit langkettigen Substanzen ist die Schmelzpunktniedrigung gering und es besteht eine monomer-reichere eutektische Zusammensetzung, so dass fast die gesamte langkettige Substanz als überschüssige, für Radikaleinschluss geeignete Kristalle zurückbleibt. Das Kristallgitter langkettiger Substanzen kann weicher sein als dasjenige von Substanzen mit geringerer Molekülgrösse. Dieser Umstand ist für die Monomerdiffusion günstig. Die angeführten Gründe erklären, warum eine merkliche Nachpolymerisation nur in Systemen mit einer langkettigen Substanz stattfindet.

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