

Radiation-Induced Solid-State Polymerization in Binary Systems. VII. Polymerization in Solid-Liquid Equilibrium Phase Containing Long-Chain Compounds

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Synopsis

The radiation-induced polymerization of binary systems consisting of vinyl monomers (mainly methyl methacrylate) and various long-chain compounds in solid-liquid equilibrium state has been studied. Phase diagrams of these systems showed that all systems containing long-chain compounds form a complete crystalline phase at temperatures below the solidus line. It was found that remarkable acceleration of the polymerization occurred in the solid-liquid equilibrium state. The long-chain compounds are classified into three groups according to the acceleration effect. The group including paraffin, long-chain esters, and cetyl alcohol exerted the largest acceleration effect over wide temperature regions at which the solid-liquid equilibrium exists. Maximum polymerization rate was observed at temperatures below the melting point in the presence of long-chain compounds of the above-mentioned group. It was observed in this case that the long-chain compounds crystallized to form very fine colloidal particles and the system was soft and waxy in the solid-liquid equilibrium state. The acceleration of the polymerization in the binary system consisting of a vinyl monomer and a compound having no long-chain substituents or in the homogeneous solution consisting of monomer and viscous solvent were far less than that in the presence of long-chain compounds. It is suggested that the effect can be attributed to the effect of a special reaction matrix favorable to polymerization in the solid-liquid equilibrium.

INTRODUCTION

In a preceding paper,¹ the authors studied the radiation-induced polymerization in binary systems containing long-chain compounds and disclosed two findings as follows: These binary systems formed a crystalline phase but not a glassy phase below their melting points. No in-source polymerization occurred in the crystalline state, but the evident post-polymerization occurred by heating the system beyond the melting point after irradiation below it.

Chapiro et al.² studied the radiation-induced polymerization in binary systems consisting of a vinyl monomer and a mixture of long-chain compounds. They reported that the glassy phase of monomer formed in these

systems and the in-source polymerization occurred in the supercooled phase of monomer.

The difference in the results in these two studies by Chapiro and by us is presumably due to the difference in the type of long-chain compounds; Chapiro used oily or fatty multicomponent mixtures consisting mainly of glyceride as long-chain components, while we used pure straight-chain compounds. It was found that long straight-chain compounds with simple structure are easily crystallized and difficult to be glassified, but long-chain compounds with branched structures such as glyceride can be glassified readily. Therefore, it is not unreasonable to consider that the two types of polymerization are possible in binary systems if they contain long-chain compounds of different types; that is, one is the in-source polymerization in the supercooled phase and the other is the postpolymerization in crystalline binary systems by heating beyond their melting points after irradiation.

In the preceding report,¹ the authors explained the mechanism of postpolymerization in binary systems containing long-chain compounds as follows: The initiation takes place as the monomer diffuses to the trapped radical in the crystals of long-chain compounds, and the propagation reaction proceeds also inside the crystal as if it acted as a special reaction matrix with much reduced termination probability.

Considering that the postpolymerization occurred in the solid-liquid equilibrium state in the binary systems containing long-chain compounds, a marked acceleration of the in-source polymerization can also be expected in the solid-liquid equilibrium owing to the special reaction matrix effect of the long-chain compounds. In this report, the radiation-induced in-source polymerization in binary systems consisting of vinyl monomers and various long-chain compounds in solid-liquid equilibrium was studied to ascertain the polymerization mechanism in connection with the preceding study.

EXPERIMENTAL

All reagents used in this work were purified by distillation or recrystallization according to conventional methods. The mixtures of monomer and long-chain compounds were charged into glass ampoules, dissolved homogeneously by heating, and then partly crystallized by standing at room temperature. The ampoules were degassed and sealed off under reduced pressure of 10^{-4} – 10^{-5} mm Hg. γ -Ray irradiation was carried out with the use of a 100,000-Ci ^{60}Co source at various temperatures which were maintained by immersing the ampoules in Dewar vessels filled with cryostats or a thermostatic bath. After irradiation, the samples were dissolved in acetone containing hydroquinone, and the polymer was then precipitated with methanol. The long-chain compound and residual monomer were removed carefully by washing with methanol above the melting point of the long-chain compounds. The isolated polymer was dried and weighed to determine the conversion. The conversions were often more than 100% based on the amount of original monomer, presumably owing to occlusion

of the long-chain compound in the polymer. Thus, the real conversion was obtained by subtracting the content of long-chain compounds determined by elemental analysis from the apparent quality of polymer.

The phase diagrams were measured by differential thermal analysis (DTA).

RESULTS

Phase Diagrams of MMA-Long-Chain Compound Systems

Phase diagrams of various binary systems consisting of MMA (methyl methacrylate) and long-chain compounds are shown in Figure 1. It is

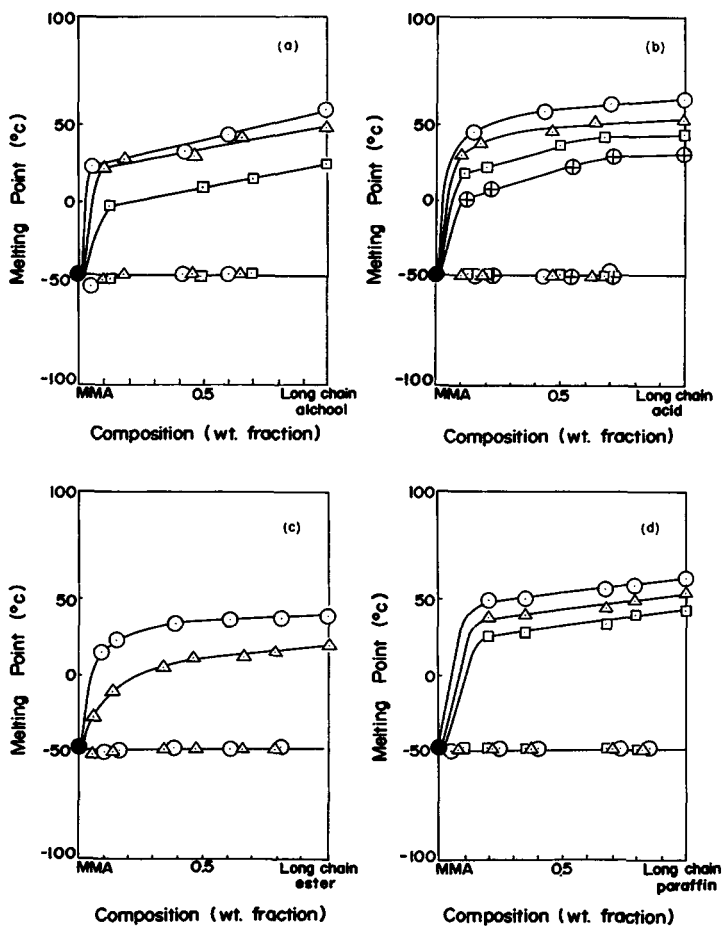


Fig. 1. Phase diagram of MMA-long-chain compound systems. (a) Phase diagram of MMA-long-chain alcohol systems, long chain alcohol: (○) steryl alcohol; (△) cetyl alcohol; (◻) lauryl alcohol. (b) Phase diagram of MMA-long-chain acid systems, long-chain acid: (○) stearic acid; (△) myristic acid; (◻) lauric acid; (⊕) capric acid. (c) Phase diagram of MMA-long-chain ester systems, long chain ester: (○) methyl stearate; (△) butyl stearate. (d) Phase diagram of MMA-paraffin systems, paraffin: (○) mp 62-64°C; (△) mp 52-54°C; (◻) mp 42-44°C.

obvious that all these binary systems form a complete crystalline phase at temperatures below the solidus line.

In the previous study,¹ the authors pointed out that the phase diagram of a binary system consisting of a long-chain compound and a compound of relatively small molecules has two general characteristics, as follows: The eutectic point exists at extremely high concentrations of monomer, and the lowering of melting point with change in composition is rather small except in the vicinity of the eutectic point. These facts suggest that the solid phase of the binary system consists of pure crystals of a long-chain compound and eutectic crystals extremely rich in the non-long-chain component, and therefore is close to the structure of binary systems which are immiscible in the liquid phase. It was explained that long-chain compounds with a straight-chain structure have high coagulative ability due to the larger van der Waals forces at the long straight chain, compared with intermolecular interaction of the component pair having relatively small molecular size. This is also the reason why binary systems containing long straight-chain compounds are hardly glassified.

Results in Fig. 1 agreed consistently with the general characteristics stated above.

Polymerization in Binary Systems Consisting of MMA-Long-Chain Compounds

In-source polymerization of binary systems consisting of MMA and a long-chain compound was investigated at various temperatures in the solid-liquid equilibrium phase. The effect of composition in the solid-liquid equilibrium phase on the polymerization of MMA-long-chain alcohol systems is shown in Fig. 2. According to these results, a large acceleration of the polymerization was observed in the higher concentrations of long-chain alcohols. It should be noted that the acceleration was evident even at temperatures below 25°C in the MMA-cetyl alcohol system, while the

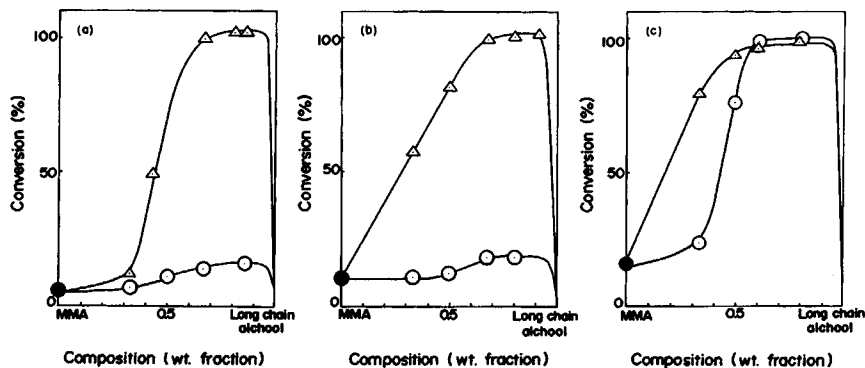


Fig. 2. Effect of the composition on the conversion for MMA-long-chain alcohol systems at various temperatures. Dose rate: 5×10^5 R/hr; dose 5×10^6 R in vacuo; long-chain alcohol: (○) steryl alcohol; (Δ) cetyl alcohol; temperature: (a) 0°C; (b) 25°C; (c) 45°C.

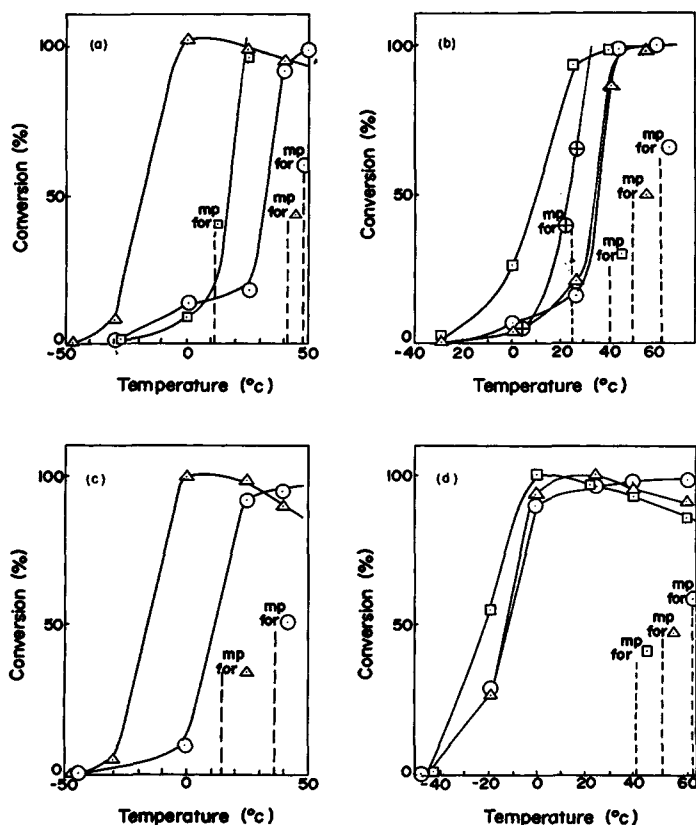


Fig. 3. Effect of temperature on the conversion for MMA-long-chain compound systems. Dose rate: 5×10^5 R/hr, dose: 5×10^5 R, in vacuo; monomer concentration: 67%, mp: temperature of liquidus curve of the phase diagram. (a) Polymerization of MMA-long-chain alcohol systems, long-chain alcohol: (○) stearic alcohol; (△) cetyl alcohol; (◻) lauryl alcohol. (b) Polymerization of MMA-long-chain acid systems, long-chain acid: (○) stearic acid; (△) myristic acid; (◻) lauric acid; (◊) capric acid. (c) Polymerization of MMA-long-chain ester systems, long-chain ester: (○) methyl stearate; (△) butyl stearate. (d) Polymerization of MMA-paraffin systems, paraffin: (○) mp 62–64°C; (△) mp 52–54°C; (◻) mp 42–44°C.

acceleration occurred above 45°C in the MMA-stearyl alcohol system. These results indicate the different mode of temperature effect on the acceleration.

The polymer yield is shown as functions of the polymerization temperature for various systems of MMA-long-chain compounds in Fig. 3, in which the classification of groups is the same as in Fig. 1. The acceleration of polymerization is more clearly illustrated in Fig. 3; the temperature dependence of the acceleration effect differed considerably depending on the long-chain component. That is, long-chain compounds can be classified into three different groups according to the temperature dependence of their acceleration effect. The first group includes paraffins, cetyl alcohol,

and lauric acid and esters having nearly 15 carbon atoms in a molecule and a melting point of 30–50°C. The acceleration effect by this group is the largest, and the effect was observed over most temperature ranges where liquid–solid equilibrium occurs. The maximum polymerization rate was attained at a certain temperature below the melting point, and this maximum rate was higher than the polymerization rate above the melting point. The postpolymerization of this group occurred quite evidently when the system was warmed to the solid–liquid equilibrium phase after irradiating it in the solid state.

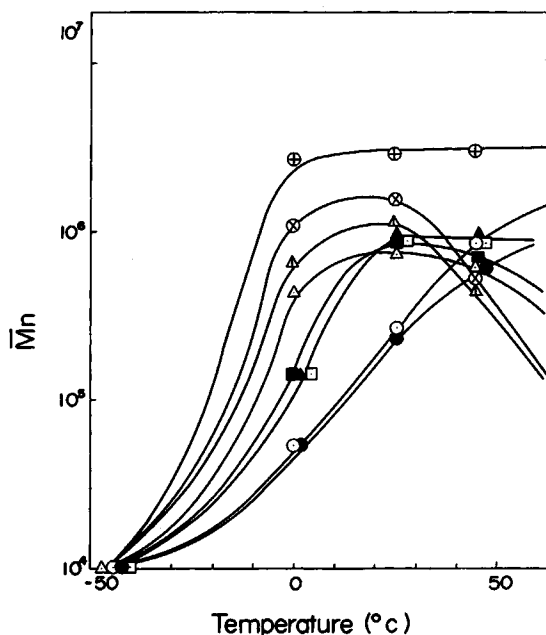


Fig. 4. Effect of temperature on molecular weight of polymers obtained by the polymerization of MMA–long-chain compound systems. Dose rate: 5×10^5 R/hr; dose: 5×10^6 R, in vacuo; monomer concentration: 67%; long-chain compounds: (⊕) paraffin (mp 62–64°C); (⊗) paraffin (mp 52–54°C); (Δ) paraffin (mp 42–44°C); (■) butyl stearate; (○) stearyl alcohol; (△) cetyl alcohol; (□) lauryl alcohol; (●) stearic acid; (▲) capric acid.

The second group includes long-chain compounds such as stearic acid and stearyl alcohol having more than 17 carbon atoms in a molecule and a melting point higher than 50°C. This group shows the acceleration effect in a relatively narrow temperature range just below the melting point, and no clear maximum of the polymerization rate could be observed. The polymerizability in the postpolymerization stage was not so large in this group.

The third group includes compounds such as lauryl alcohol and capric acid having less than 12 carbon atoms in a molecule and a melting point

lower than 30°C. This group showed no effective acceleration in the solid-liquid equilibrium phase, and the polymerization was accelerated evidently only in the liquid phase. The polymerization rate increased with the increase in temperature, and no maximum rate was observed. No post-polymerization occurred in this group by irradiation below the temperatures of solidus.

Polymerization in Binary Systems Consisting of Other Monomer-Long Chain Compound Systems

The γ -ray-induced polymerization of binary systems consisting of long-chain alcohols and various vinyl monomers other than MMA was investigated to clarify the acceleration effect due to long-chain components. The temperature dependence of polymer yield of various monomers is shown in Figures 5-7. Both stearyl alcohol and cetyl alcohol belonging

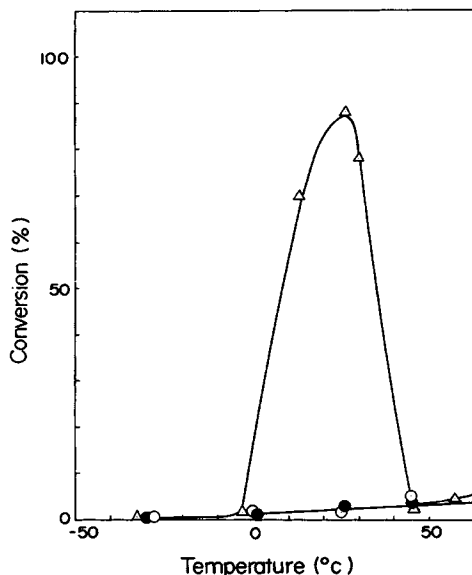


Fig. 5. Effect of temperature on the conversion for styrene-long-chain alcohol systems. Dose rate: 5×10^5 R/hr; dose: 5×10^5 R, in vacuo; monomer concentration: 67%; long-chain alcohol: (○) stearyl alcohol; (△) cetyl alcohol; (●) styrene only.

to the first and second groups showed the evident acceleration in the polymerization of glycidyl methacrylate. In the polymerization of acrylonitrile and styrene, only cetyl alcohol was effective. In glycidyl methacrylate-long-chain alcohol systems, monomer was supercooled at low temperatures, and two maximum polymerization rates due to the acceleration effect of long-chain binary systems at relatively higher temperature and the acceleration effect of glass-forming system⁴ at relatively lower temperatures appeared to be exist.

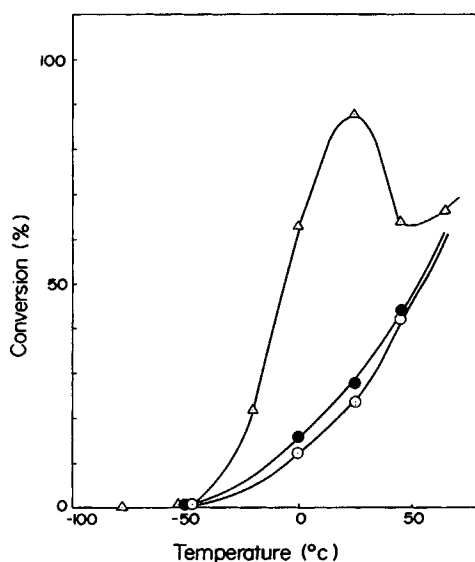


Fig. 6. Effect of temperature on the conversion for acrylonitrile-long-chain alcohol systems. Dose rate: 1×10^6 R/hr; dose: 1×10^8 R, in vacuo; monomer concentration: 67%; long-chain alcohol; (○) stearyl alcohol; (△) cetyl alcohol; (●) acrylonitrile only.

DISCUSSION

Results of the γ -rays-induced polymerization in binary systems consisting of MMA and various compounds having no long-chain substituents are shown in Table I. These compounds were chosen because their melting points are similar to long-chain compounds investigated in this study. These binary systems were found to form eutectic mixtures by DTA measurements. Evidently, the acceleration effect is far smaller than that in the polymerization in binary systems containing long-chain compounds.

In Table II, results of the γ -ray-induced polymerization in homogeneous MMA-triacetin systems characterized by high viscosity are plotted for

TABLE I
Polymerization of Methyl Methacrylate in the Presence of Organic Small Molecules*

Compound	Conversion, % monomer
Propionamide	14.9
Acetamide	19.8
Trioxane	18.6
Crotonic acid	15.1
Phenol	29.0
Methyl oxalate	21.4
None	12.6

* Composition: MMA:added compound = 1:2 in weight; dose rate: 5×10^6 R/hr; dose: 5×10^8 R; temperature: 25°C, in vacuo.

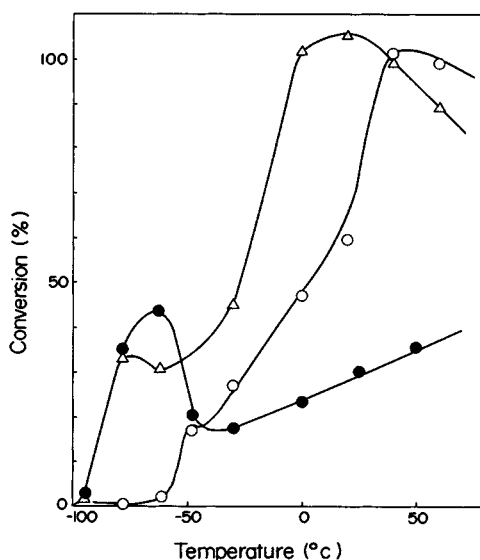


Fig. 7. Effect of temperature on the conversion for glycidyl methacrylate-long-chain alcohol systems. Dose rate: 2×10^5 R/hr; dose: 2×10^5 R, in vacuo; monomer concentration: 67%; long-chain alcohol: (○) stearyl alcohol; (△) cetyl alcohol; (●) glycidyl methacrylate only.

various compositions. Again, the acceleration effect was not significant in comparison with that in the systems containing long-chain compounds. These facts suggest that the acceleration effect of long-chain compounds on polymerization can be attributed to the effect of a special reaction matrix favorable to polymerization in the solid-liquid equilibrium. The results of temperature dependence of the polymerization rate may provide a possible explanation for the acceleration effect.

As already described, long-chain compounds are classified into three groups depending on the acceleration effect. Upon cooling the most effectively accelerated systems (group 1), the long-chain compounds were precipitated as extremely fine colloidal particles and the whole system became soft and waxy. Most of paraffins and long-chain esters belong

TABLE II
Polymerization of Methyl Methacrylate in the Presence of Triacetin^a

Concentration of triacetin, mole fraction	Viscosity of system, centipoise	Conversion, % monomer
0	0.65	12.6
0.5	1.60	31.0
0.67	2.70	33.8
0.80	4.65	24.9
0.90	7.90	16.2

^a Dose rate: 5×10^5 R/hr; dose: 5×10^5 R; temperature: 25°C, in vacuo.

to this group. Some long-chain alcohols and acids having ca. 15 carbon atoms in the molecule and a melting point of 30–50°C also belong to this group. On the other hand, the system containing long-chain compounds of group 2 have narrow acceleration temperature ranges just below the melting point, and the long-chain compounds crystallize to form needles, plates, or other forms as observed in crystallization of the usual organic compounds. The solid–liquid equilibrium state formed in this case is not soft and waxy. Long-chain alcohols and acids with more than 17 carbon atoms and a melting point higher than 50°C belong to this group. Long-chain compounds of group 3 which exhibit no evident acceleration in the solid–liquid equilibrium state have a crystalline form not different from that of normal organic crystals. These compounds include long-chain alcohols and carboxylic acids with a number of carbon atoms less than 12 and a melting point lower than 30°C. They have no special functions for the acceleration of the polymerization due to the special reaction matrix in the long-chain compounds.

The special long-chain compounds having the remarkable acceleration effect over the solid–liquid equilibrium temperature are those belonging to group 1, which is characterized by crystals of colloidal form. The long-chain compounds of group 1 are effective for the polymerization of other vinyl monomers studied in the present report, while the other long-chain compounds have no acceleration effect for styrene and acrylonitrile. The long-chain compounds having no polar functional groups such as paraffins and esters are all effective in spite of different melting points. However, for the polymerization of ester monomers such as MMA and glycidyl methacrylate, long-chain compounds of group 2 are also effective.

These results suggest that the chemical structure of both long-chain and monomer components have an important effect on the crystallization favorable to polymerization. It is well known that the viscosity of colloidal systems is greater than that of the dispersion medium. Therefore, in the system containing a long-chain compound of group 1, the viscosity of the system appears to be markedly high due to the structural viscosity of concentrated colloidal systems. The termination reaction should be suppressed because of the high viscosity of the polymerization system containing long-chain compounds of group 1. At low temperature, phase separation of the monomer and the long-chain compound might occur as a result of destruction of this colloidal structure. At high temperature, viscosity should decrease because of melting of the long-chain compound. The high viscosity of the polymerization system might be realized at a certain temperature range in the solid–liquid equilibrium phase at which structural viscosity of concentrated colloidal structures is maintained. The acceleration effect of polymerization can, therefore, be attributed to the decrease in the termination rate owing to high viscosity. Thus, the remarkable acceleration effect at a certain temperature range and the negative apparent activation energy of the polymerization in the systems of group 1 can be explained.

In the systems of groups 2 and 3, the colloidal structure is not so stable that the long-chain compound crystallized to form a relatively rigid state.

Further study will be done concerning the structure of the system consisting of vinyl monomers and long-chain compounds and the mechanism of the acceleration effect.

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