Solid State Polymerization of Binary Component System

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During the past few years it has been reported that various vinyl[1-3] and cyclic compounds[4-6] can be polymerized in a solid state by high-energy ionizing radiation. However, there have been few reports on the solid state polymerization of a binary component system. In the solid of a binary component system, there are various states of aggregation, such as a solid solution or mixed crystals, and these states are expected to affect the polymerization and the polymer structure. The present study was undertaken to elucidate the correlation of the polymerization with those aggregation states. Various oxetane derivatives polymerize in a solid state, and the mixture of these may be expected to give solid solution because of the similarity of the molecular structures. Therefore, in this investigation, mixtures of 3-chloromethyl-3-ethyloxetane (CMEO), with 3-fluoromethyl-3-ethyloxetane (FMEO) and with 3,3-bis(chloromethyl)-oxetane (BCMO) were chosen as the binary component system of a solid solution. As the mixed crystals, mixtures of CMEO with diketene and with trioxane were chosen. All of these cyclic compounds have been reported to polymerize in the solid state,[4-6] and the crystal states of these monomers play important roles in the solid state polymerization. Recently Okamura and his co-workers have independently from our study reported[7]

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[1] A. Chapiro and V. Stannett, *J. chim. phys.*, **56**, 830 (1959).

[2] N. Sobue and Y. Tabata, *J. Polymer Sci.*, **43**, 459 (1960).

[3] T. A. Fadner and H. Morawetz, ibid., **45**, 475 (1960).

[4] S. Okamura, K. Hayashi and Y. Kitanishi, ibid., **58**, 925 (1962).

[5] S. Nakashio, M. Kondo and H. Tsuchita, *Makromol. Chem.*, **52**, 79 (1962).

[6] M. Miura, T. Aoyagi and T. Hirai, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **67**, 485 (1964).

[7] K. Hayashi, H. Watanabe and S. Okamura, *J. Polymer Sci.*, B1, 3971 (1963).

the radiation-induced polymerization of the solid solution of oxetane derivatives. However, no detailed studies of the polymerization behavior of the solid solution have yet been published.

Experimental

Monomer.—CMEO and FMEO were prepared by the method reported previously,[6] while commercially available BCMO (Kōei Chemicals) and diketene (Tokyo Chem. Ind.) were used. All the oxetanes were purified by dehydration with CaH_2 and redistillation under reduced pressure in a nitrogen anhydrous stream before use. Diketene was purified, in the same manner as has been described above, using anhydrous sodium sulfate as a drying agent. Trioxan (Tokyo Chem. Ind.) was recrystallized two times from methylene chloride.

The phase diagram of the monomer mixture was made from the freezing or melting curves of the mixtures of various compositions. The rate of cooling or heating was about 0.3°C/min.

Polymerization. — *γ-Ray-induced Polymerization.* — The monomer mixture in a glass ampoule was degassed by three successive freezing-by-melting procedures and then sealed. The mixture of CMEO and trioxane was not degassed because of the sublimation tendency of trioxane. The ampoule was set in a Dewar vessel containing a suitable cooling agent and irradiated at an appropriate distance from a source of ^{60}Co. The cooling agents were as follows: Dry ice-methanol (−80°C). Dry ice-acetone (−86°C), such freezing materials as benzene (5°C), ethyleneglycol (−15.6°C) and 1,2-dichloroethane (−35°C), and cryohydrates of $BaCl_2$ (−8°C), KCl (−11°C), NaCl (−21°C), $CuNO_3$ (−24°C) and $CaCl_2$ (−55°C). The sample irradiated was extracted with methanol and dried in vacuo. To determine the polymer yield, the extraction was performed below the irradiation temperature so as to prevent post-polymerization.

BF_3-catalyzed Copolymerization. — In a reaction vessel containing 25 g. of the CMEO-BCMO mixture and 75 g. of chloroform, 15 g. of a 1.4 wt. % solution of BF_3-etherate was added at room temperature under a gentle stream of nitrogen. The reaction was stopped with less than 10% conversion by the addition of methanol. The polymer obtained was purified by the manner described above. The copolymerization of CMEO and FMEO was carried out by the same procedure with 10 g. of a monomer mixture, 90 g. of chloroform, and 9 g. of a BF_3-solution.

The Characterization of the Polymer. — The infrared absorption spectra were obtained with an Hitachi EPI-2 Type spectrophotometer. The composition of the copolymer of CMEO and FMEO was determined by measuring the intensities of absorptions at 730 cm^{-1} (C-Cl stretching vibration) and 1010 cm^{-1} (C-F stretching vibration). The composition of the coploymer of CMEO and BCMO was calculated from the chlorine content of the elemental analysis. An X-ray diffraction diagram was obtained by means of the Rigaku D-3F Type diffractometer.

The viscosities of the polymer solution were measured at 42±0.02°C in a chloroform solution. The intrinsic viscosities were calculated by the single-point determination method at a concentration of 0.2 g./100 cc. The melting points of the polymers were determined by means of a hot-stage microscope. The fractionation of the copolymers was carried out using chloroform as a solvent and acetone as a nonsolvent. The polymer blend was fractionated by extracting it with dimethylformamide containing 1% β-naphthylamine as an antioxidant under a nitrogen stream at 50°C.

Results and Discussion

The CMEO-FMEO Binary Component System.—The phase diagram given in Fig. 1 indicates that the binary component system forms a solid solution over the whole range of the composition. γ-Ray-induced polymerization was carried out at −86°C with the solid solution crystallized at a temperature about 5°C below its melting point. Figure 2 shows the melting points of the polymers obtained with 311-hr. radiation at 1.5×10⁴ r./hr. The melting point is as sharp as that of the polymer obtained from each single component crystal.

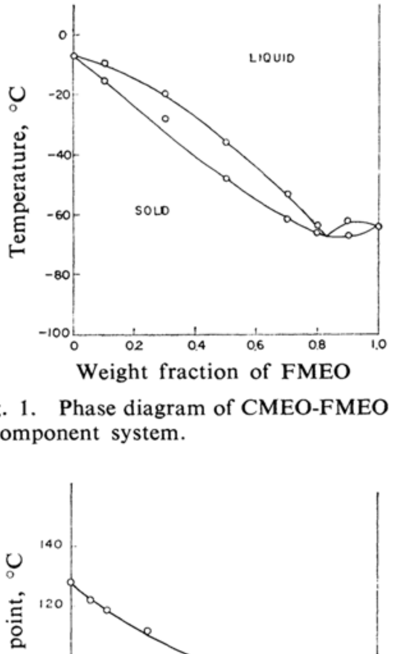

Fig. 1. Phase diagram of CMEO-FMEO binary component system.

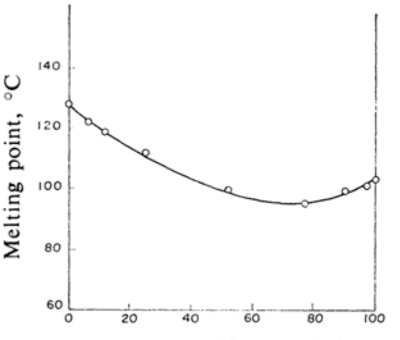

Fig. 2. Melting point of CMEO-FMEO copolymers.

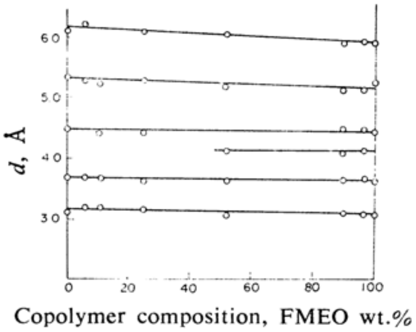

Fig. 3. X-Ray diffraction pattern of CMEO-FMEO copolymer.

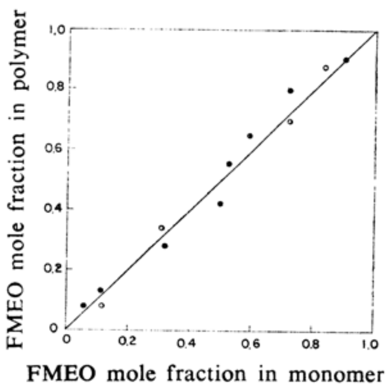

Fig. 4. Copolymer composition curve for CMEO-FMEO binary component system (●) γ-ray induced solid state polymerization, (○) BF_3-catalized liquid state polymerization.

Figure 3 gives the interplanar distances of the polymers as determined by X-ray diffractometry. Figure 3 suggests that all polymers have the same crystal structures, regardless of their compositions, whereas the interplanar distance varies a little. From the facts shown in Figs. 2 and 3, it may be concluded that a copolymer is formed from the solid solution by irradiation of γ-rays. Figure 4 shows the composition curve of the copolymer obtained by the procedure described above. The composition of the polymer is the same as that of the corresponding initial monomer mixture. BF_3-catalyzed copolymerization also seems to give the same result, as is shown in the same figure. However, this agreement is only apparent. A detailed discussion of the polymerization of a solid solution will be given in the following section.

The CMEO-BCMO Binary Component System.—The phase diagram of the binary component system is shown in Fig. 5. The system also crystallizes to a solid solution. The solid solution with a 1 : 1 composition by weight was irradiated at 0°C. As is shown in Figs. 6 and 7, the polymerization rate, the saturation polymer yield and the molecular weight of the polymer are all higher in a large crystal grown by slow cooling than in a small crystal. Figure 8 shows that similar behavior is also observed with the solid solu-

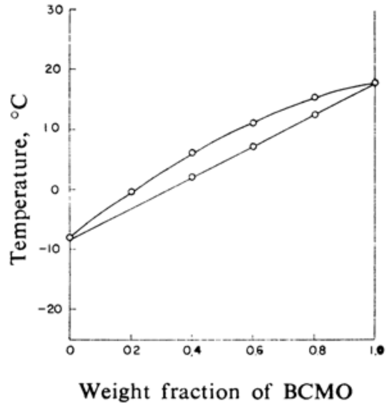

Fig. 5. Phase diagram of CMEO-BCMO binary component system.

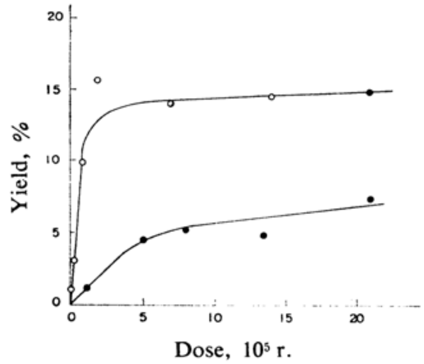

Fig. 6. Solid state polymerization of CMEO-BCMO binary component system at the composition 1 : 1 : crystallization temperature (○) 0°C, (●) −196°C, irradiation temperature 0°C, dose rate 4.3×10^4 r./hr.

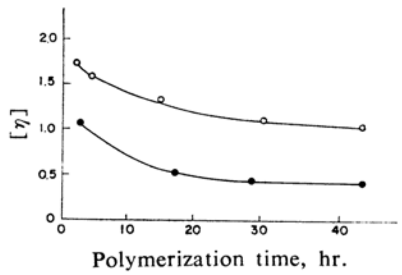

Fig. 7. Relationship between polymerization time and intrinsic viscosity of polymer in the solid state polymerization of CMEO-BCMO binary component system at the composition 1 : 1 : crystallization temperature (○) 0°C, (●) −196°C; irradiation temperature 0°C; dose rate 4.3×10^4 r./hr.

tion of a 9 : 1 composition, but that both the rate and the yield are less than those of a 1 : 1 composition. However, in order to compare the results of Figs. 8 and 6, the influence of the irradiation temperature on the polymer yield should be taken into consideration. Figure 9 represents the relation between the irradiation temperature and the polymer yield at various monomer compositions. Each monomer mixture was crystallized at a temperature about 5°C below its melting point. In any composition, the maximum yield was obtained at a temperature 10—20°C lower than the melting point of the corresponding solid solution. The polymerization behavior in Figs. 6 and 9 agrees with that of each single component crystal,[5,6] and its also comfirmed by the fact that crystal structure of the solid solution is almost the same as that of each single component. Figure 10 shows the

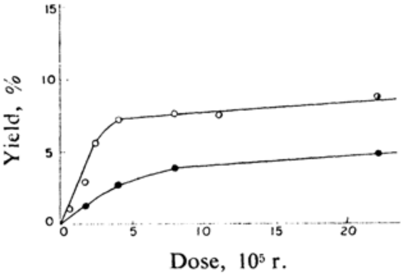

Fig. 8. Solid state polymerization of CMEO-BCMO binary component system at the composition 9 : 1 : crystallization temperature (○) −11°C, (●) −196°C; irradiation temperature −21°C; dose rate 1.3×10^5 r./hr.

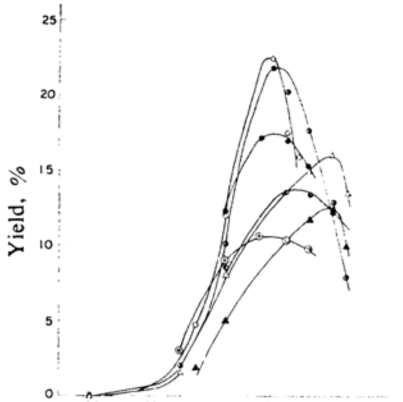

Fig. 9. Influence of irradiation temperature on polymer yield at various composition : irradiation dose, 9×10^5 r.; crystallization temperature, about 5°C below its melting point; composition of solid solution (CMEO-BCMO) (○) 10 : 0, (◎) 9 : 1, (●) 7 : 3, (◑) 5 : 5, (◐) 3 : 7, (▲) 1 : 9, (△) 0 : 10.

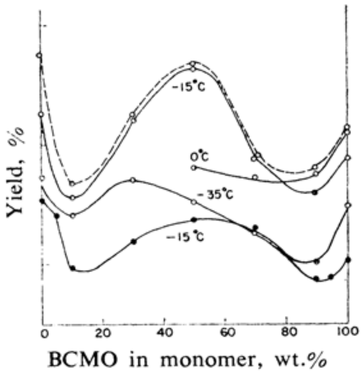

Fig. 10. Influence of monomer composition on polymer yield at various irradiation temperatures in CMEO-BCMO binary component system : irradiation dose 9.1×10^5 r.; crystallization temperature, (○) about 5°C below its melting point, (●) −196°C; -○- maximum yield at the each composition; irradiation temperatures are shown in the figure.

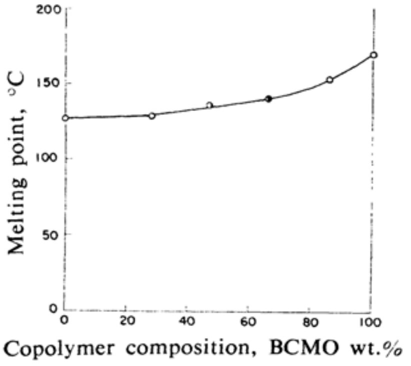

Fig. 11. Relationship between composition and melting point of CMEO-BCMO copolymer.

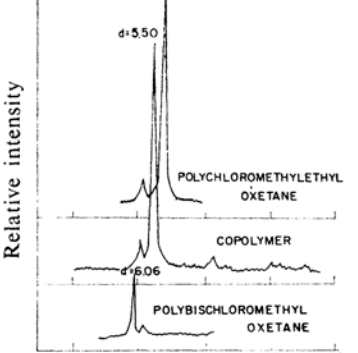

Fig. 12. X-Ray diffraction peaks of polymer. d: interplanar distance
Copolymer composition : (BCMO : CMEO 7 : 3)

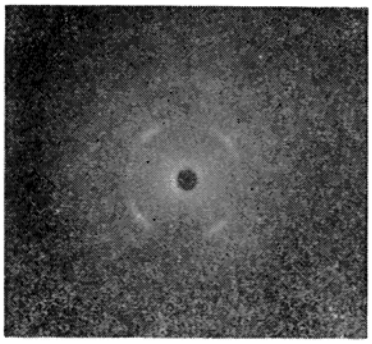

Fig. 13. X-Ray diffraction pattern of CMEO-BCMO copolymer.

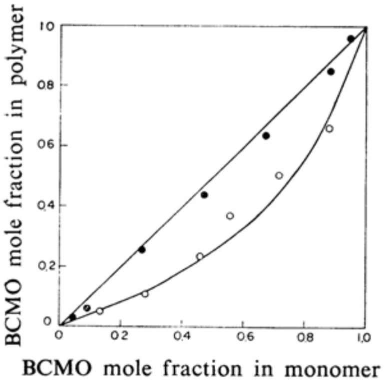

Fig. 14. Copolymer composition curve for CMEO-BCMO binary component system: (●) γ-ray induced solid state polymerization, (○) BF_3-catalyzed liquid state polymerization.

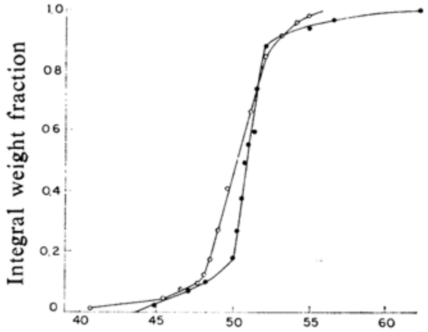

Fig. 15. Integral composition distribution curve of CMEO-BCMO copolymer; (○) copolymer from large crystal, (●) copolymer from small crystal.

polymer yield versus the monomer composition curves at various irradiation temperatures. In the same figure, the maximum yield is plotted against the composition. The polymer yield was at a minimum in the composition with a small quantity of the second component. This can be explained by the effect of the composition on the crystal state of the solid solution. The sizes and structures of the two component molecules are not exactly the same, so the introduction of the second component in a small quantity may cause a disorder of the crystal lattice to some extent and result in a decrease in the polymer yield. On the other hand, the existence of both the components in equal quantities may give preferable conditions for the crystallization, because the differences in the molecular size are compensated for each other in the lattice. Also, the temperature difference between the starting and the final points of the crystallization of the monomer mixture may help the crystallization into a preferable state; this difference is at a maximum in a 1 : 1 composition. However, the complete elucidation of those phenomena seems to be difficult at the present stage; the further experimental efforts are hoped for.

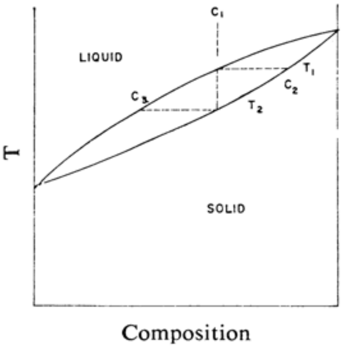

Fig. 16. Phase diagram of binary component system to form a solid solution.

Furthermore, the characteristics of the polymer obtained were examined. From the investigations of the melting point, X-ray diffraction and fractionation of the polymer, it has been concluded that a random copolymer is formed from the solid solution. As Fig. 11 shows, the melting point of the coploymer is as sharp as that of the homopolymer and decreases with an increase in the CMEO content. Figure 12 shows the X-ray diffraction diagrams of the copolymer and each component homopolymer. The crystallinity of the copolymer was proved to be as high as that of the homoploymer, and the interplanar distance corresponding to the highest peak in the copolymer is located between those in the two homopolymers. The X-ray diffraction pattern of the raw polymer obtained from the irradiated crystal by an extraction of the unreacted monomer is shown in Figure 13. It suggests the orientation of growing chains in the solid solution. This fact was also observed by means of the polarizing microscope. A similar result has been reported in the polymerization of a single-component crystal.4)

Figure 14 presents the composition curve of the copolymer obtained from the small crystal with an irradiation dose of 9.1×10^5 r. at -15°C. The composition of the copolymer obtained from the solid solution is the same over the whole range as that of the monomer mixture within experimental error. On the other hand, the copolymer obtained by BF_3 in the liquid state has a composition rich in CMEO, as is shown in the same figure. Those facts suggest that the propagating chain can grow only in a unique way controlled by the crystal lattice and that the difference in reactivities between monomers has little influence on the path of propagation in the solid solution. The above-mentioned mechanism is supported also by the oriention of the polymer chain in the irradiated solid solution.

The integral composition distribution curves of the coploymer are shown in Fig. 15. It is found that the width of the distribution is narrower in the copolymer obtained from a small crystal grown by rapid cooling than in that obtained from a large crystal by slow cooling. The difference would seem responsible for the difference in the distribution of monomer components in the solid solution. As is shown in Fig. 16, a liquid mixture of the composition C_1 begins to crystallize at T_1 and the initial segregating crystal has the composition C_2. When the temperature gets to T_2, crystallization is complete; the composition of the portion crystallized at the final stage is C_3. The solid solution obtained in such a manner should have a composition distribution from C_2 to C_3. However, the rapid cooling hinders the fractional crystallization to give a more homogeneous solid solution than does the slow cooling. It is clear that the copolymer obtaned from a more homogeneous crystal has a narrower distribution.

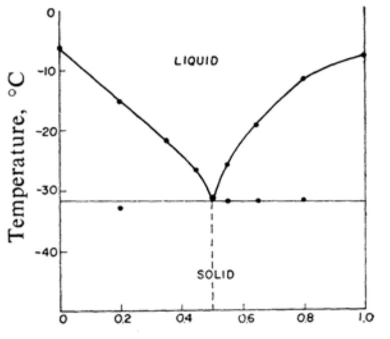

Fig. 17. Phase diagram of CMEO-diketene binary component system.

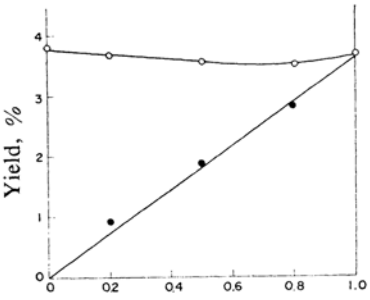

Fig. 18. Influence of monomer composition on polymer yield in the solid state polymerization of CMEO-diketene binary component system: crystallization temperature -35°C; irradiation temperature -35°C; irradiation dose 2.6×10^5 r.; (○) unfractionated polymer yield, (●) fractionated polyoxetane yield.

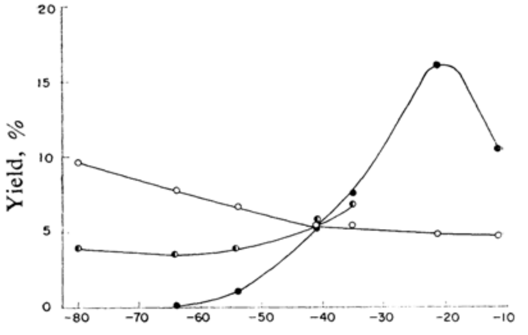

Fig. 19. Influence of irradiation temperature on polymer yield: crystallization temperature, single system -11°C, eutectic mixture -35°C; irradiation dose 5×10^5 r.; (●) 3-chloromethyl-3-ethyloxetane, (○) diketene, (◐) eutectic mixture (composition 1 : 1 mole fraction).

The CMEO-Diketene Binary Component System.—From the phase diagram in Fig. 17 it was found that this binary component system formed a mixed crystal. The binary component system polymerized at any composition when it was exposed to γ-ray at -35°C, which was below the eutectic point. The polymer obtained was determined by fractionation to be a blend of two component homopolymers. Infrared spectrum studies have proved that the dimethylformamide-soluble portion was polydiketene and the insoluble portion, polyoxetane. Figure 18 represents the yields of the unfractionated polymer and the fractionated polyoxetane respectively, plotted against the mole fraction of oxetane in the mixed crystal. The results show that yields of polyoxetane and polydiketene are proportional to the mole fraction of the corresponding monomer. Furthermore, the influence of the irradiation temperature on the polymer yield was examined; it is shown in Fig. 19. The relation between the yield and the temperature is a superposition of those two single component systems. These results suggest that in the mixed crystal the polymerization of each component takes place independently, even in the eutectic mixture.

The CMEO-Trioxane Binary Component System.—The phase diagram in Fig. 20 shows that this system also forms a mixed crystal and that its eutectic point is in the side of oxetane. From the infrared spectrum and the elemental analysis, it was found that the mixed crystal gave only polyoxetane at any composition when it was irradiated at −21°C, which was below the eutectic point. As Fig. 21 shows, the polymer yield is proportional to the mole fraction of oxetane, except for a range close to pure oxetane, and the molecular weight of the polymer is not affected by the existence of trioxane. The data given in Fig. 21 indicate that the temperature dependence of the yield in the eutectic mixture is similar to that obtained in CMEO. When irradiation was done at room temperature, only trioxane was polymerized.

Okamura and his co-workers[8] have reported that trioxane polymerized only in the solid state above 0°C. The temperature range in which trioxane polymerizes is above the melting point of oxetane, whereas oxetane scarcely polymerizes at all in a liquid state.[6] If polymerization occurs independently in each component crystal, it should be impossible to polymerize two components at the same time.

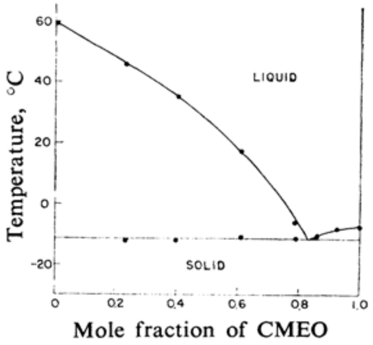

Fig. 20. Phase diagram of CMEO-trioxane binary component system.

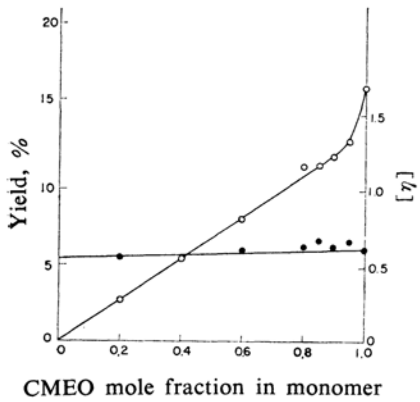

Fig. 21. Influnce of composition on polymer yield and molecular weight in CMEO-trioxane binary component system: crystallization temperature −16°C; irradiation temperature −21°C; irradiation dose 1.7×10^6 r.; (○) polymer yield, (●) intrinsic viscosity.

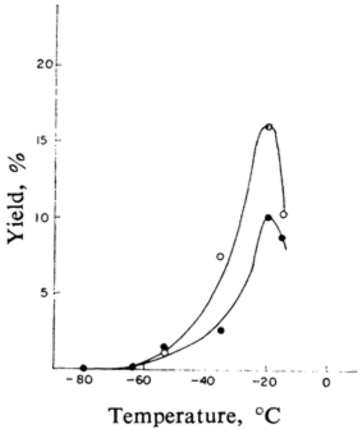

Fig. 22. Influence of irradiation temperature on polymer yield: (●), eutectic mixture of CMEO and trioxane, crystallization temperature −11°C, irradiation dose 9×10^5 r.; (○) CMEO crystallization temperature −11°C, irradiation dose 9×10^5 r.

Summary

The γ-ray irradiation of a solid solution of 3-chloromethyl-3-ethyloxetane and 3,3-bis(chloromethyl)oxetane has given a copolymer with the same composition as that of the initial monomer mixture, while a BF_3-catalyzed copolymerization has formed a copolymer with a different composition from that of the initial monomer mixture. In the polymerization, the solid solution has behaved like each single component crystal in respect to the relation of polymer yield to the irradiation temperature and to the crystal state of the monomers. The copolymer obtained from small crystals grown by rapid cooling has been found to have a narrower distribution of composition than that obtained from large crystals. With a solid solution of 3-chloromethyl-3-ethyloxetane

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8) S. Okamura, K. Hayashi and Y. Nakamura, *Isotopes and Radiation*, 3, 416 (1960).

and 3-fluoromethyl-3-ethyloxetance, the polymerization has been studied and similar results obtained.

The mixed crystal of 3-chloromethyl-3-ethyloxetane and diketene gives a polymer blend. The curve of the polymer yield versus the irradiation temperature is a superposition of those in the each component crystal. The mixed crystal of 3-chloromethyl-3-ethyloxetane and trioxane gives only a homopolymer of oxetane, and the temperature dependence of the yield is similar to that of oxetane, even in an eutectic composition.

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