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Study of Radiation-Induced Copolymerization of Hexanediol Diacrylate and Various Comonomers Trained in Urea Canal Complexes

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ABSTRACT

Long chain monomers such as hexanediol diacrylate (HDDA) trained in canals various monomers of relatively large size to form urea canal complexes. The relationship between the monomer composition and copolymer composition after in-source copolymerization and post-copolymerization of irradiated HDDA and the second monomers (styrene and methacrylonitrile) in urea canal was investigated. With in-source copolymerization at 25°C, the content of the second components in the polymer was far larger than that in the monomer feed, while, in post-copolymerization at elevated temperatures, the ratio of the two components in the polymer nearly agreed with their ratio in the monomer mixture.

INTRODUCTION

Radiation-induced polymerization in urea canal complexes has been studied by various workers [1-9]. However, the monomers

studied previously were limited to those of relatively small molecular size, owing to the restricted space capacity of the urea canal to accept the monomer.

The authors have found [10] that certain kinds of long chain monomers such as hexanediol diacrylate (HDDA) and hexanediol monoacrylate have a trailing effect, and even monomers of relatively large molecular size can be entrapped with long chain monomer in the urea canal by this effect. In-source and post-polymerization of trailed monomers with long chain monomer in irradiated canals took place easily, though the canal was destroyed as polymerization proceeded. It may be a problem of increasing interest to clarify to what degree the obtained copolymer composition is affected by the comonomer composition in the canal. In this report, the relation between the composition of the trailed comonomer and of formed copolymer was studied in relation to the polymerization behavior.

EXPERIMENTAL

Materials

Urea was purified by recrystallization twice from methanol, then dried at 50°C under reduced pressure for 48 hr. The monomers were purified by passage through an ion-exchange resin (Amberlyst A-27, Rohn and Haas Co.) to remove inhibitor for HDDA and by distillation for styrene (St) and methacrylonitrile (MAN).

Formation of Canal Complexes and Copolymerization

HDDA and the comonomer were mixed with urea at room temperature; the ampoules were sealed under air at ambient pressure and stored at room temperature [10]. The formation of canal complexes was signaled by the change in appearance of the mixture to fluffy powder from a slurry with time. The γ irradiation was carried out by a 100,000 Ci ^{60}Co source at 25°C. After polymerization, the samples were poured into methanol containing hydroquinone at 25°C. The copolymer was washed with methanol to remove urea and residual monomers and then dried under reduced pressure for 24 hr at 25°C. The post-polymerization was carried out by heating the sample at a determined temperature after irradiation at 25°C. After post-polymerization, the samples were treated in the same way as those subjected to in-source polymerization.

Copolymer Composition and Homopolymer

The copolymer composition was determined by elemental analysis for nitrogen content in the HDDA-MAN system and estimated by infrared spectra analysis of the intensity ratio at 1495 cm^{-1} (absorption band of monosubstitute benzene nuclei) for St polymer and 2940 cm^{-1} (methylene groups) for HDDA polymer in HDDA-St system. The homopolymer of HDDA is insoluble in all solvents [10] but MAN polymer and St polymer can be extracted with dimethylformamide and benzene, respectively.

RESULTS AND DISCUSSION

Relationship between Composition of Monomer and of Polymer in In-Source Copolymerization

The change of polymer yields, insoluble fraction in formed polymer, and copolymer composition in insoluble fraction of the product of in-source copolymerization at 25°C are shown as a function of comonomer composition for HDDA-trailed monomer systems in Fig. 1. MAN constitutes less than 66.6 mole % and St less than 50 mole % in the urea canal [10]. It was ascertained from the results of differential thermal analysis and x-ray analysis that in these compositions, all both monomer components were completely entrapped in the canal in the same ratio as in the mix used [10]. According to Fig. 1 a, the overall polymer yields increased with increasing content of the second monomer component. The insoluble fraction began to decrease with second monomer compositions more than 50%, but it is still larger than 80% in this second monomer composition. The content of second component in the insoluble fraction began to increase at this second monomer composition range and reached more than 80%. These facts suggest that in mixtures rich in the second monomer, a considerable part of the insoluble copolymer consists of a very rich fraction of second monomer and small fraction of HDDA. Though the homopolymer of HDDA cannot be separated, it would be a very small fraction. The soluble fraction increased with increasing second monomer, infrared spectral analysis showed that this fraction contained little copolymer. According to those results, with in-source copolymerization at 25°C , the reactivity of the second component monomer in copolymerization was considerably higher than that of HDDA. It was observed in the previous study [10] that with in-source homopolymerization of HDDA alone, the polymerization rate of HDDA was far lower at relatively low temperature such

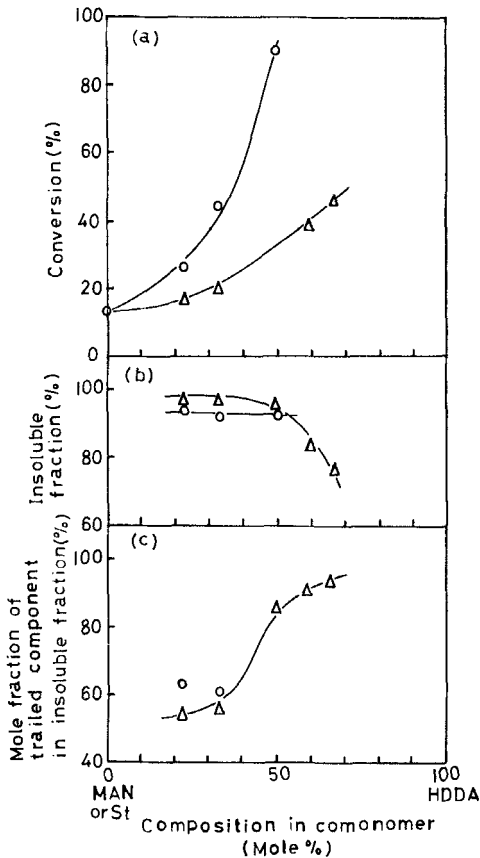


FIG. 1. Change of the (a) copolymer yield, (b) insoluble fraction obtained by solvent extraction of copolymer and (c) composition in copolymer of insoluble fraction in in-source polymerization of HDDA and trailed monomers: (Δ) HDDA-MAN copolymer; (\circ) HDDA-St copolymer. Solvent extraction: HDDA-MAN copolymer, dimethylformamide; HDDA-St copolymer, benzene. Dose rate, 8×10^5 rad/hr; irradiation time, 44 hr; irradiation temperature, 25°C .

as 25°C than those values observed for the second comonomers in this copolymerization study. It was also ascertained that in-source polymerization took place out of the canal, accompanied by canal decomposition during irradiation, regardless of whether homopolymerization or copolymerization was involved [10].

Consequently, it is probable that polymerization of the second monomer in the present case occurs out of the canal in the completely released state of second monomer. The very rich composition of second component in copolymer or apparent very high reactivity of second monomer might be explained by assuming that in those canals formed by trailing, the distribution of HDDA and trailed monomer molecules is not homogeneous, being similar to the monomer unit distribution of block copolymers; part of canal containing the portions rich in comonomer are less stable, being ready to decompose and release the second monomer in response to conditions such as irradiation.

Relationship between Composition of Monomer and of Polymer in Post-Polymerization

Post-polymerization of irradiated canals including HDDA and the second monomers was investigated by heating the canals after irradiation. It has previously been found [10] that post-polymerization of long chain monomers occurred at elevated temperatures near the decomposition temperature of the canal complexes and proceeded mainly outside the canal with the decomposition of the canal structure. Figure 2 shows the change of overall conversion, insoluble fraction in formed copolymer, and the composition of insoluble fraction of polymer as a function of post-polymerization temperature at various comonomer compositions added to form canal. The decomposition of canal complex occurred at lower temperature with increasing second monomer component, and the decomposition started at about 75°C for the canal complex including 66.6 mole % MAN [10]. As seen in Fig. 2, overall conversion increased rapidly with elevating temperature near the decomposition temperature of canal, but it decreased suddenly at the decomposition temperature and then gradually increased again with further increase in temperature. This sudden discontinuity may be related to a change in polymerization phase from semisolid state to completely liquid state. However, it was ascertained that post-polymerization at temperatures below the decomposition temperature is also caused by degradation of the canal and proceeds outside the canal in the semisolid state consisting of released monomer and remaining canal. It is probable, then, that post-polymerization in the semisolid state proceeds very quickly at such high temperatures with release of the monomer caused by canal decomposition. The polymerizability in this state is considerably higher than that in the completely liquid-phase polymerization, and the polymerization mechanism might be also different to some degree from that in the liquid phase owing to after-effects of phase structure of canal or molecular orientation of monomer in the canal before

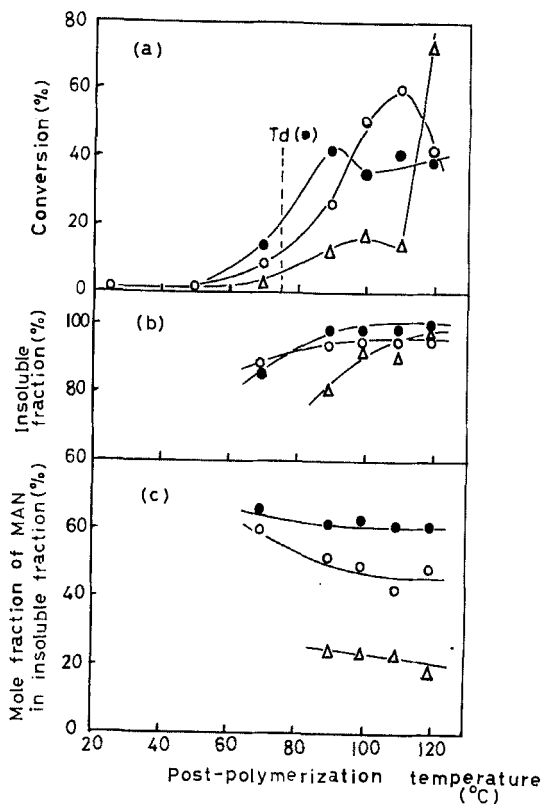


FIG. 2. Change of (a) copolymer yield, (b) insoluble fraction obtained by dimethylformamide extraction of formed copolymer and (c) composition in copolymer of insoluble fraction in post-polymerization at various compositions of HDDA and trailed MAN monomer: (Δ) 23.1% MAN; (\circ) 50% MAN; (\bullet) 66.6% MAN. Dose rate, 8×10^5 rad/hr; preirradiation dose, 4.8×10^6 rad; preirradiation temperature, 25°C ; post-polymerization time, 30 min, Td denotes decomposition temperature of canal complex including 66.6 MAN mole %.

degradation. It is interesting from this point of view that according to the results of Fig. 2c, the composition in the insoluble fraction of polymer is almost invariant with polymerization temperature and furthermore, nearly agrees with the composition in monomer added to form canal. This fact suggests that post-polymerization at elevated temperatures does not proceed by random mutual diffusion of all

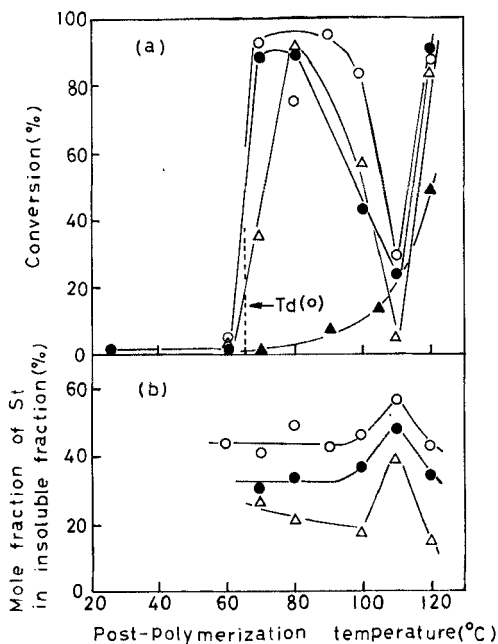


FIG. 3. Change of (a) copolymer yield and (b) composition in copolymer of insoluble part after extraction of copolymer formed by post-polymerization of various compositions of HDDA and trailed St comonomer: (Δ) 23.1% St; (\bullet) 33.3% St; (\circ) 50% St; (\blacktriangle) polymer formed in thermal polymerization of free comonomer without canal (St mole fraction, 50%). Dose rate, 8×10^5 rad/hr; pre-irradiation dose, 4.8×10^6 rad; preirradiation temperature, 25°C ; post-polymerization time, 30 min; Td denotes decomposition temperature of canal complex including 50 St mole %.

monomer components as in the liquid phase but is affected considerably by monomer orientation or distribution in the canal before decomposition. The reasons may be attributed to the fact that post-polymerization occurs and is completed very quickly with the decomposition of canal and that moreover, it proceeds in the semisolid state, not in the completely liquid phase. Then the diffusion step would not have a dominant effect on the propagation reaction. A similar phenomenon can be seen in post-polymerization of HDDA with St in the same state at temperatures below 100°C (Fig. 3b), though a deviation is observed in liquid phase polymerization. Those

results are quite different from those with in-source polymerization at 25°C. The reason perhaps lies in the difference in polymerization temperature. That is, at relatively low temperature, the canal portion, including HDDA-rich material, is stable, and then mainly the second monomer is released from the canal and polymerized. On the other hand, in post-polymerization, all canals decompose completely and HDDA is also released as well as the second monomer, owing to the elevated polymerization temperature.

In conclusion, the monomers are apt to copolymerize into copolymers having the same composition as the composition as monomers in the canal in rapid post-polymerization at elevated temperatures. A similar result was obtained by Kiss [11], who reported that acrylonitrile and acrolein in a urea canal complex copolymerized in the same composition as in monomeric system. However, in the present case, various comonomers can be used with long chain monomers. Further investigation would be expected from the view point of so-called topotactic copolymerization.

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