Radiation-Induced Copolymerization of Vinylphosphonic Dichloride with Methyl Methacrylate and Styrene

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Synopsis

The γ-ray-induced copolymerization of vinylphosphonic dichloride (VPDC) with methyl methacrylate (MMA) and styrene (St) was studied at 25°C (liquid phase) and -78°C (solid phase). The reaction mechanisms are discussed. The reactivity ratios for the copolymerization of the VPDC–MMA system were determined as follows:

$$25°C: \quad r_1 = 0.084, \quad r_2 = 6.6$$

$$-78°C: \quad r_1 = 0.081, \quad r_2 = 2.1$$

The difference between the reactivity between the liquid-phase (25°C) and solid-phase (-78°C) copolymerization is mainly attributable to the r_2 value. The behavior of the liquid-phase copolymerization of the VPDC–St system was anomalous, the r_1 value being negative in the range from 0 to 80 mole-% of VPDC monomer. In the solid-phase (-78°C) copolymerization for the VPDC–St system, the reactivity ratios r_1 and r_2 were 0.097 and 1.6, respectively. The rate of copolymerization (R_p) at 25°C, for both the VPDC–MMA and VPDC–St systems, passes a maximum point at a certain monomer concentration, suggesting that the composition of copolymer is considerably affected by R_p. This phenomenon was interpreted by the assumption that an energy transfer reaction from VPDC monomer to the other vinyl compound can easily occur.

INTRODUCTION

The authors have recently studied a series of radiation-induced polymerizations of bis β-chloroethyl vinylphosphonate (CEVP),[1-3] and the reaction mechanisms were elucidated. From these experiments, the rate of solution polymerization of CEVP is much lower than that of the bulk polymerization. This fact has been explained by an energy transfer reaction from monomer to solvent. On the other hand, the rate of copolymerization (R_p) of CEVP with styrene (St) and methyl methacrylate (MMA) is strongly affected by the G value of the radical production, and these radicals were presumed to be formed by the energy transfer reactions from CEVP monomer to the other vinyl monomers. To elucidate these reaction mechanisms more clearly, the radiation-induced bulk polymerization of vinylphosphonic dichloride (VPDC) was studied.[4]

In connection with these experiments, the γ-ray-induced copolymerization of VPDC with MMA and St was studied, and the reaction mechanism was discussed.

EXPERIMENTAL

Preparation of Monomers

VPDC monomer was prepared by the same method as described previously.[4]   Monomers of MMA and St were purified by the ordinary methods and dried with calcium hydride overnight, followed by distillation under reduced pressure in a nitrogen atmosphere.   Calcium hydride was then added in the purified MMA or St monomer before introduction to the vacuum line of 10^{-5} mm Hg, where the monomer was degassed and stored prior to distillation into the reaction tube.   The purified VPDC monomer, which was distilled four or five times under reduced pressure in a nitrogen atmosphere, was degassed in the vacuum line, distilled into the reaction tube, and then mixed with the MMA or St monomer by distillation, and the tube was sealed.

Copolymerization and Treatment of Copolymers

After γ-irradiation from a ^{60}Co source at a prescribed temperature, the contents of the ampoule were poured into a large excess of dry petroleum ether or ethanol.   The copolymers thus obtained were collected by filtration, washed with dry petroleum ether, dried under reduced pressure, and then weighed.   These operations after irradiation were undertaken within a dry box; as a precipitant, the petroleum ether or ethanol was used after drying by calcium chloride.   The irradiation was stopped before the yield of the copolymer was expected to reach to about 5 wt-%.   The analysis of phosphorous content of the copolymer was carried out by the method of Arcus and Matthews.[5]   In addition, the IR spectra of the copolymer were obtained by using the potassium bromide pellet technique.

RESULTS AND DISCUSSION

Copolymerization of VPDC with MMA

The copolymer produced by γ-irradiation can be obtained as a white powder, soluble in dimethylformamide (DMF), insoluble in dry petroleum ether.   It was ensured that the composition of the copolymer obtained by precipitation from dry ethanol (poly-VPDC is soluble) was equal to that of the copolymer obtained from dry benzene (good solvent for poly-MMA). The IR spectrum of the copolymer exhibits a strong absorption band of C=O stretching vibration of MMA at 1720 cm^{-1}, and that of the P=O structure of VPDC at 1230 cm^{-1}.

Relation between Monomer and Polymer Compositions

Figure 1 shows the relation between the initial monomer mixture and the composition of the copolymer. The copolymers obtained by solid-state ($-78°C$) copolymerization contain a larger proportion of VPDC than the copolymers obtained by liquid-state ($25°C$) copolymerization at the same initial monomer mixture ratio. In Figure 2, the Fineman and Ross plot was done assuming VPDC as M_1 and MMA as M_2, and the following results were obtained:

$$25°C: r_1 = 0.084, r_2 = 6.6$$

$$-78°C: r_1 = 0.081, r_2 = 2.1$$

The values of r_1 for $25°C$ and $-78°C$ are almost equal, and r_2 for the liquid-phase copolymerization is about three times higher than that of the solid-phase copolymerization. This indicates that the different behavior between the liquid-phase ($25°C$) and solid-phase ($-78°C$) copolymerizations mainly comes from the value of r_2. The value of $r_1r_2 = 0.170$ is remarkably small, which suggests that the monomer molecules are uniformly distributed in this matrix, and the possibility of alternating copolymerization is high owing to the elimination of the mobility of molecules. The value of $r_1r_2 = 0.554$ for the liquid-phase copolymerization of VPDC is, though higher than that of the solid-phase copolymerization, much lower than that of CEVP the structure of which is similar to VPDC. In addition, the Q_1 and e_1 values for VPDC from the equation of Alfrey and Price[6] were calculated as follows, assuming the Q_2 and e_2 for St to be 1.0 and -0.8, respectively:

$$25°C: e_1 = 1.170, Q_1 = 0.153$$

$$-78°C: e_1 = 1.730, Q_1 = 0.599$$

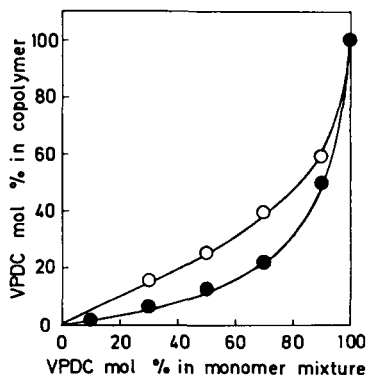Each e_1, both for the liquid and solid phase, takes a positive value.

Fig. 1. Monomer–polymer composition curve in the copolymerization of VPDC with MMA. Reaction temperature: (●) $25°C$; (○) $-78°C$. Dose rate 3.73×10^4 R/hr.
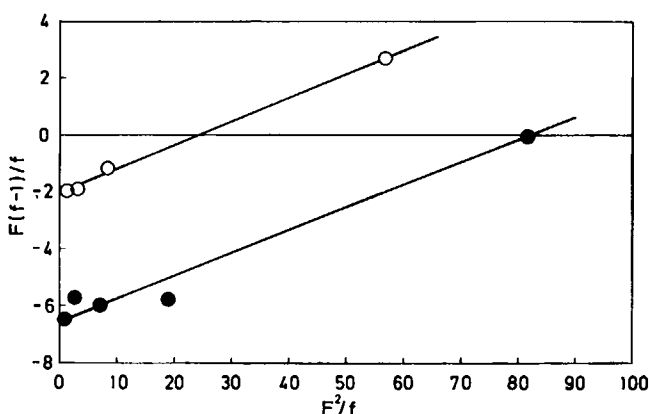
Fig. 2. Fineman and Ross plot for the copolymerization of VPDC with MMA at 25°C
(●) and −78°C (○).

Relation Between Monomer Composition and Rate of Copolymerization

The dependence of the rate of copolymerization (R_p) on the monomer composition for the VPDC–MMA system, both for liquid and solid phase, is illustrated in Figure 3. From this figure, the R_p for the solid phase increases continually with increase in the concentration of VPDC monomer, with a maximum value at 100% VPDC, whereas for the liquid phase it reaches a maximum at about 20 mole-% VPDC. A similar result was obtained for the VPDC–St system at 25°C (liquid phase), as will be described later. Such acceleration phenomena can be seen very seldom for the copolymerization of other vinyl monomer systems for which the rate of bulk polymerization for each monomer is not zero.

Ouchi et al.[7] observed such a phenomenon for the acrolein–St system. They presumed that the acceleration phenomenon for this system is due
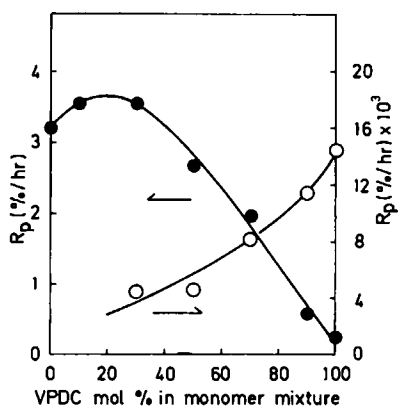

Fig. 3. Dependence of the rate of copolymerization (R_p) in the mixture of VPDC with MMA on monomer composition at 25°C (●) and −78°C (○). Dose rate 3.73 × 10⁴ R/hr.

to the large value of the propagation rate constant of the reaction, and that the termination reaction occurred by a coupling between the same kind of monomer radicals of the chain end. If such a reaction is also operative in our system, judging from the fact that the r_2 takes relatively large value, the block polymerization of MMA should be accelerated by the presence of a small amount of VPDC monomer in the system. This phenomenon is responsible for the acceleration of the apparent R_p of the system.

Copolymerization of VPDC with St

The copolymer composition was determined both for the copolymers which were precipitated from dry ethanol (poly-VPDC is soluble) and for those precipitated from dry benzene (poly-St is soluble). These two values were essentially equal for the whole range of the monomer composition as far as we tested. No homopolymers of VPDC or St were found. The most suitable solvent for the copolymer is DMF, and precipitant is petroleum ether. In the IR spectrum of the copolymer, absorption bands at 1230 cm^{-1} and 1600 cm^{-1} were observed due to P=O of VPDC and the phenyl group of St, respectively.

Effects of Monomer Composition on Rate of Copolymerization and Copolymer Composition

In Figure 4, the relation between monomer composition and R_p is shown. From this figure, the R_p at 25°C copolymerization increases remarkably by adding a small amount of VPDC monomer in St, and reaches a maximum at about 62 mole-% VPDC monomer concentration. On the other hand, in the solid-state copolymerization at −78°C, the R_p increases slowly with increasing VPDC monomer concentration, and reaches a highest point at 100% VPDC.

The relation between the copolymer composition and the initial monomer mixture is shown in Figure 5. In the liquid phase, the content of VPDC in
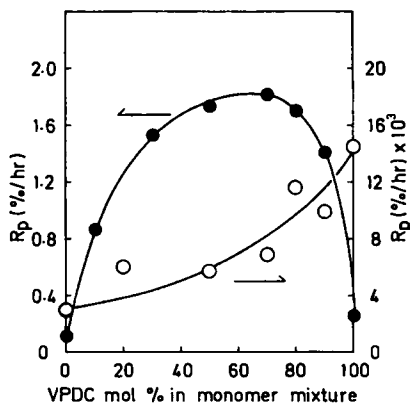

Fig. 4. Dependence of the rate of copolymerization (R_p) in the mixture of VPDC with St on monomer composition at 25°C (●) and −78°C (○). Dose rate 3.73 × 10^4 R/hr.
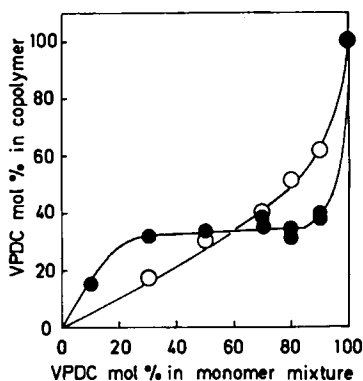
Fig. 5. Monomer–polymer composition curve in the copolymerization of VPDC with St. Reaction temperature: (●) 25°C; (○) −78°C. Dose rate 3.73 × 10⁴ R/hr.
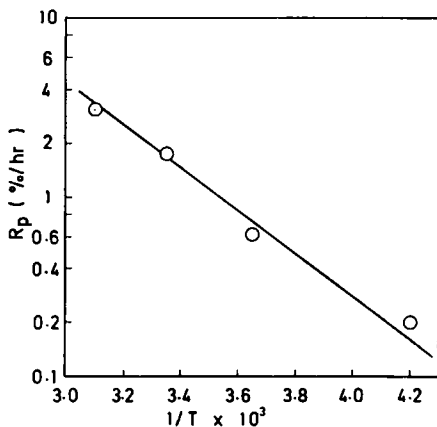

Fig. 6. Arrhenius plot of the rate of copolymerization of VPDC with St; [VPDC]/[St] = 50/50 (moles). Dose rate 3.73 × 10⁴ R/hr.

the copolymer is slightly higher than the corresponding monomer mixture in the region below 30 mole-% VPDC monomer concentration. However, in the region from 30 to 80 mole-% VPDC monomer concentration, the VPDC content in the copolymer is almost constant with increasing VPDC monomer concentration. Such a phenomenon can be observed in the system in which reaction proceeds by a partial ionic and a partial radical mechanism. However, as can be seen in Figure 6, the apparent activation energy for the copolymerization of the [VPDC]/[St] = 50/50 system in the region from −30° to 50°C is high enough (5.69 kcal/mole); and, moreover, these reactions are inhibited by benzoquinone or O_2. These facts suggest that the reaction, in the region from −30° to 50°C, proceeds only by a radical mechanism.

The Fineman and Ross plot was carried out as shown in Figure 7 on the basis of Figure 5 by denoting VPDC as M_1 and St as M_2. In this figure, r_1
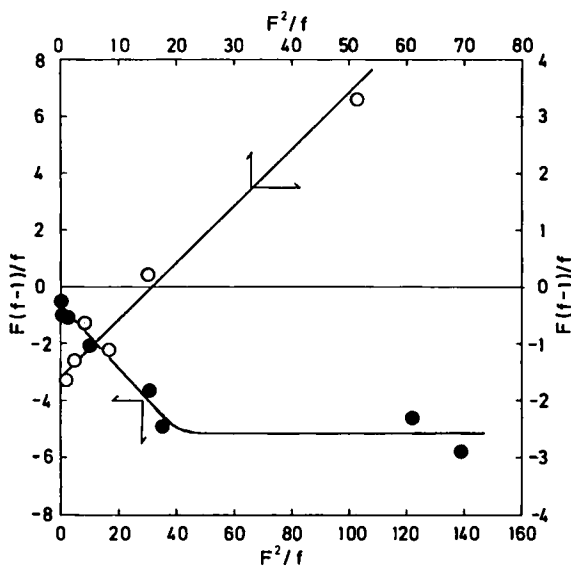
Fig. 7. Fineman and Ross plot for the copolymerization of VPDC with St at 25°C (●) and −78°C (○).

takes a negative value in the concentration range from 0 to 80 mole-% VPDC; and from 80 to 100 mole-%, the r_1 value is nearly equal to zero. Joshi[8] derived a kinetic equation introducing the rate constants k' for depropagation reactions. It can be pointed out from his equation that the value of r_1 or r_2 may be negative if $k_{11}'/[M_1]$ or $k_{22}'/[M_2]$ takes a very large value. O'Driscoll et al.[9] pointed out that a depropagation reaction by α-methylstyrene (α-MeSt) is operative from their copolymerization experiment for St with α-MeSt at 60°C. They further postulated that a rapid termination of copolymerization occurs because of the presence in the system of low molecular weight free radicals of poly-α-MeSt of chain length 3 or less. However, from the fact that an acceleration effect for R_p at 25°C is observed, as can be seen in Figure 4, such a rapid termination by the low molecular weight free radicals of poly-VPDC or poly-St should not be operative for the system in which the rate of formation of the initiation radical for the copolymerization is the rate-determining step. (For the copolymerization of the CEVP–St and CEVP–MMA systems, R_t is the rate-determining step.)

On the other hand, Novikov et al.[10] concluded that R_p is remarkably accelerated by the monomer complex because it seems to have a great affinity for the propagation radical. In solution polymerization[2] or copolymerization[3] of CEVP, the sturcture of which is similar to that of VPDC, the energy transfer reactions from CEVP to the other coexisting solvents or vinyl compounds were postulated to occur. Taking into account the above results for the copolymerization of VPDC, the energy transfer reaction presumably can occur from VPDC monomer to the other vinyl compounds

passing through a transient monomer complex or an activated complex at a suitable monomer ratio. Such an energy transfer reaction will lead to an increase in initiation radical concentration followed by an increase in R_p. As a result of the energy transfer reaction from VPDC to the other monomer, the VPDC content of the copolymer should decrease.

The VPDC content in the copolymer for the liquid-phase copolymerization in which a maximum for R_p can be observed is less than that for the corresponding solid-phase copolymerization in the whole range of the monomer mixture, as can be seen in Figure 1. The energy transfer reaction passing through the activation complex should be greatly eliminated for the solid phase due to the reduction of the mobility of the molecules. In such a system, as can be seen in Figures 4 and 5 for the copolymerization at $-78°C$, the R_p maximum cannot be observed, and the VPDC content in copolymer increases continually with increasing VPDC concentration in the monomer mixture. The values of 0.097 and 1.6 for r_1 and r_2, respectively, were established from the Fineman and Ross plot for the solid-phase copolymerization. These values are very close to the values for the copolymerization of the VPDC–MMA system at $-78°C$. This suggests that the reaction mechanism for the VPDC–St system at $-78°C$ is very close to that of the VPDC–MMA system. The R_p for these two solid-phase copolymerizations at $-78°C$ are almost equal for the corresponding monomer composition as far as was observed. This fact supports the presumption that the reaction mechanism is similar for these two systems; i.e., in the solid-phase copolymerization of VPDC with MMA or St, the concentration of VPDC in the monomer mixture seems to dominate the reaction mainly.

On the other hand, the values of Q_1 and e_1 for VPDC were calculated to be 0.210 and 0.565, respectively. This indicates that the Q_1 and e_1 value for VPDC in the solid-phase copolymerization changes with change in the other monomer.

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