



Radiation-Induced Copolymerization of Bis(β -Chloroethyl) Vinylphosphonate

Author(s): Shigetada Fujii

Source: *Radiation Research*, Vol. 33, No. 2 (Feb., 1968), pp. 249-262

Published by: [Radiation Research Society](#)

Stable URL: <http://www.jstor.org/stable/3572476>

Accessed: 22/06/2014 18:14

Your use of the JSTOR archive indicates your acceptance of the Terms & Conditions of Use, available at
<http://www.jstor.org/page/info/about/policies/terms.jsp>

JSTOR is a not-for-profit service that helps scholars, researchers, and students discover, use, and build upon a wide range of content in a trusted digital archive. We use information technology and tools to increase productivity and facilitate new forms of scholarship. For more information about JSTOR, please contact support@jstor.org.



Radiation Research Society is collaborating with JSTOR to digitize, preserve and extend access to *Radiation Research*.

<http://www.jstor.org>

Radiation-Induced Copolymerization of Bis(β -chloroethyl) Vinylphosphonate

SHIGETADA FUJII

Government Industrial Research Institute, Nagoya, Hirate-machi, Kita-ku, Nagoya, Japan

FUJII, SHIGETADA. Radiation-Induced Copolymerization of Bis(β -chloroethyl) Vinylphosphonate. *Radiation Res.* **33**, 241-254 (1968).

The γ -ray-induced copolymerization of bis(β -chloroethyl) vinylphosphonate (CEVP) with styrene (St) and methyl methacrylate (MMA) was studied. The copolymerization reactions proceeded by a free radical mechanism, and the reactivity of CEVP with other monomers is not so high. The reactivity ratios for the copolymerization of CEVP with St and MMA have been measured at 30°C.

$$\text{CEVP-St:} \quad r_1 = 0.16, \quad r_2 = 2.3$$

$$\text{CEVP-MMA:} \quad r_1 = 0.26, \quad r_2 = 29.9$$

The molecular weight of the resulting copolymer decreases as the content of CEVP increases. The apparent activation energies were established to be 4.2 kcal/mole for the copolymerization of CEVP with St, and 1.6 kcal/mole with MMA. The copolymerization mechanisms for CEVP with other monomers were also studied kinetically.

INTRODUCTION

Recently, several investigations have been made on the esters of vinylphosphonic acid. It has been reported that bis(β -chloroethyl) vinylphosphonate (CEVP) grafts on the cellulose fibers to form graft copolymers of low flammability (1), and on the polypropylene films to form graft copolymers of high adhesive ability on the surface of metals (2). Orlov and Tarakanov (3) studied the copolymerization of CEVP with methacrylic acid (MAA) and styrene (St), using benzoyl peroxide as an initiator. Their work reports on the reactivity ratios of monomer, the apparent activation energies of copolymerization, and the relations between the rate of copolymerization and the concentration of the initiator. They did not undertake,

however, a kinetic experiment for copolymerization with St. Another experiment for the radiation-induced copolymerization of CEVP has not been reported.

The present authors have reported the γ -ray-induced bulk polymerization (4) and solution polymerization (5) of CEVP in previous papers. In bulk polymerization, both the G value of free radical production (G_r) of monomer and the rate of polymerization were observed to be considerably large, and remarkable chain transfer reactions to the monomer occurred. On the other hand, strong protection effects by the solvents were observed in solution polymerization of CEVP, owing to the energy transfer reactions from the monomer to the solvents.

In connection with these results, the γ -ray-induced copolymerization of CEVP with St and methyl methacrylate (MMA) was studied. Thus, the reactivity ratios of the monomer were established, and the copolymerization mechanisms were further examined.

EXPERIMENTAL PROCEDURE

Preparation of Monomers

CEVP was prepared as described in previous papers (4, 5). Monomers of St and MMA were obtained by distillation after drying by the ordinary method.

Copolymerization and Treatment of Copolymers

CEVP monomer was weighed in a glass tube for irradiation, degassed at 10^{-4} mm Hg by three alternate freeze-thaw cycles, and then St or MMA monomer degassed in the same way was distilled into the tube from another glass tube and sealed. The total quantity of the monomers was nearly 5 ml. The glass tube was then irradiated by γ -rays from a ^{60}Co source at various temperatures.

For the measurement of polymer composition, molecular weight, and infrared spectrum, the copolymer was purified by reprecipitation. Only in the copolymerization with St, the copolymer cannot be easily precipitated by methanol, as the content of CEVP increases in the copolymer, so that, for the polymer obtained from an initial CEVP-to-St molar ratio of 90/10, ethyl ether was used as a precipitant instead of methanol. As the homopolymer of CEVP dissolves in methanol, the possibility was taken into account that the CEVP-rich copolymer was lost in the filtrate in the separation of the resulting polymer from the monomer. No precipitate was formed from the ether which was poured with the concentrated filtrate containing benzoquinone. Thus, it was ensured that no copolymers dissolved in the methanol.

Measurement of Molecular Weight

The copolymer was dissolved in chloroform to prepare a solution of 1.5 to 2.5 gm per 100 ml of concentration. The number average molecular weight of polymer was determined by osmometric measurement in the chloroform solution referred to above, by the use of the Hitachi-Perkin Elmer vapor pressure osmometer, model 115. A standard reagent of benzil was used for the calibration.

Determination of Copolymer Compositions

The composition of the copolymer was determined mainly by an infrared method. The standard samples for the calibration curves were obtained from γ -ray-induced homopolymerization of each monomer. The homopolymers thus obtained were mixed in each ratio, and dissolved in chloroform for the measurement. For the copolymer of CEVP with St, the St content was determined by making use of a characteristic absorption band of poly-St at 1600 cm^{-1} , and for the copolymer with MMA, the MMA content was determined by the characteristic absorption band of poly-MMA at 1720 cm^{-1} . In addition, the analysis of phosphorus content of the copolymer was carried out by the method of Arcus and Matthews (6). These two methods were comparatively in good agreement within the error of $\pm 2.7\%$.

G Value of Radical Production

The experimental procedure for measuring the G value of radical production (G_r) was the same as that reported in previous papers (4, 5).

RESULTS AND DISCUSSION

I. COPOLYMERIZATION OF CEVP WITH ST

Properties of Copolymer

The homopolymer obtained in the early stage of γ -ray-induced polymerization of CEVP appears colorless and viscous, whereas the copolymer with St can be obtained as a white powder, except for a portion of the copolymers containing more than about 50% (mole) of CEVP. The copolymer which was obtained from the initial CEVP-to-St molar ratio of 50/50, for example, dissolves in chloroform,

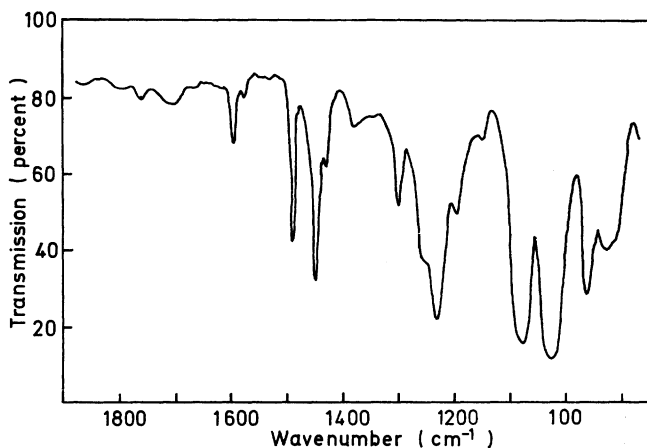


FIG. 1. Infrared spectrum of CEVP-St copolymer. The copolymer contains 50.5% (mole) CEVP. Irradiation temperature = 30°C ; dose rate = 5.0×10^4 R/hr.

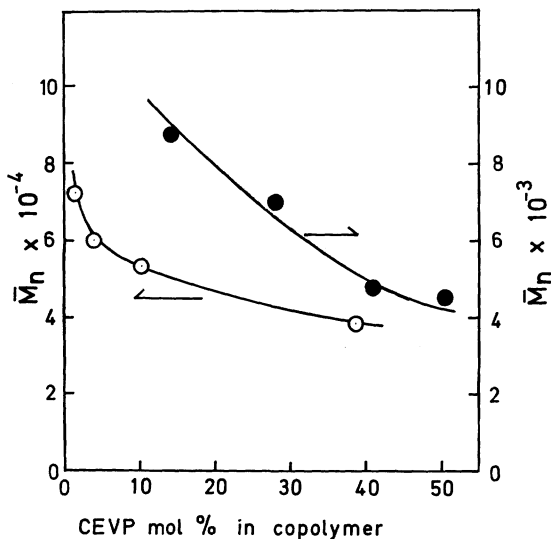


FIG. 2. Relationship between molecular weight and CEVP content. Irradiation temperature = 30°C, dose rate = 5.0×10^4 R/hr: (●) CEVP-St; (○) CEVP-MMA.

methylene chloride, and benzene, but is insoluble with methanol, ether, and tetrahydrofuran at room temperature.

The infrared spectrum of copolymer, the CEVP-to-St molar ratio of which is 50/50, is shown in Fig. 1. There is no evidence for a double bond, and strong absorption characteristics of P—O—, P=O, and benzene ring were observed at 1025 cm^{-1} , 1230 cm^{-1} , and 1600 cm^{-1} , respectively.

Figure 2 represents the relationship between molecular weight and composition of copolymers. It is apparent from the figure that the molecular weight of copolymer decreases as the CEVP content increases. This result can be explained by the fact that remarkable chain transfer reactions occur in the homopolymerization of CEVP, and accordingly, a low molecular weight of polymers is easily obtained.

Relationship between Monomer and Polymer Compositions

The results of the copolymerization of CEVP and St which was carried out at 30°C and 5.0×10^4 R/hr are shown in Table I. Figure 3 shows the relationship between the composition of copolymer and the initial monomer mixture. The copolymers contain a larger proportion of St than do the initial monomer mixtures. The data for the benzoyl peroxide catalytic copolymerization of CEVP with St which were obtained by Orlov and Tarakanov (3) are indicated in the same figure, normalized to the same unit as that in Table I. These two results are in good agreement within the error, suggesting that these two reactions proceed with the same mechanism.

TABLE I
COPOLYMERIZATION OF CEVP WITH St
(Irradiation temperature = 30°C; dose rate = 5.0×10^4 R/hr)

<i>CEVP/St</i> (molar ratio)	<i>Irradiation time</i> (hr)	<i>Yield (weight %)</i>	<i>Copolymer</i>		
			<i>CEVP</i> (mole %)	<i>St (mole %)</i>	<i>CEVP/St</i> (molar ratio)
0.429	6.0	4.80	14.2	85.8	0.166
1.000	8.0	4.96	28.1	71.9	0.391
2.333	8.0	5.58	41.0	59.0	0.695
4.000	8.0	4.07	50.5	49.5	1.020
9.000	5.0	6.40	66.5	33.5	1.985

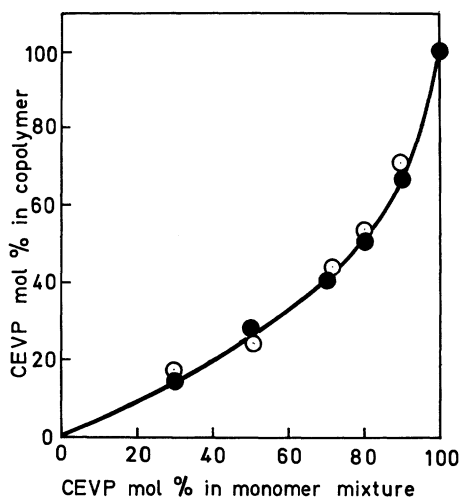


FIG. 3. Monomer-polymer composition curve in the copolymerization of CEVP with St. Irradiation temperature = 30°C; dose rate = 5.0×10^4 R/hr: (●) observed; (○) data of Orlov and Tarakanov.

The reactivity ratios were calculated by the method of Fineman and Ross (7) (equation 1):

$$F(f - 1)/f = r_1 F^2/f - r_2 \quad (1)$$

where

$$F = [M_1]/[M_2], \quad f = d[M_1]/d[M_2]$$

$$r_1 = k_{p11}/k_{p12}, \quad r_2 = k_{p22}/k_{p21}$$

In the above relations, $[M_1]$ and $[M_2]$ represent the concentrations of CEVP and

St, respectively. The best fit found for the Fineman and Ross plot is shown in Fig. 4. The values of r_1 and r_2 were calculated to be 0.16 and 2.30, respectively. These values are comparable with those of $r_1 = 0.2$ and $r_2 = 2.2$, obtained by Orlov and Tarakanov (3). The values of Q and e for CEVP were calculated to be 0.195 and 0.20, respectively, from the equation of Alfrey and Price (8) (equation 2):

$$k_{12} = P_1 Q_2 \exp(-e_1 e_2) \quad (2)$$

where P_1 is characteristic of radical 1; Q_2 is the mean reactivity of monomer 2; e_1 is proportional to the charge on the end group of radical 1; and e_2 is proportional to the charge on the double bond of monomer 2.

These values for CEVP monomer indicate that the resonance stability of the monomer is not so high, and the polarity is positive.

Effect of Irradiation Temperature on Rate of Copolymerization

Figure 5 shows the relationship between the initial rate of copolymerization (R_p) and the reciprocal of absolute temperature (T) in the copolymerization of CEVP with St. The rate linearly decreased with falling temperature, and the apparent activation energy (E_a) established was 4.2 kcal/mole. The value lies between the E_a of CEVP (4) (2.4 kcal/mole) and that of St (9-12) (5 to 7 kcal/mole).

Effect of Dose Rate on Rate of Copolymerization

The dose rate (I) dependence of the R_p with samples having various monomer concentration ratios at 30°C was studied, and the following relations were established.

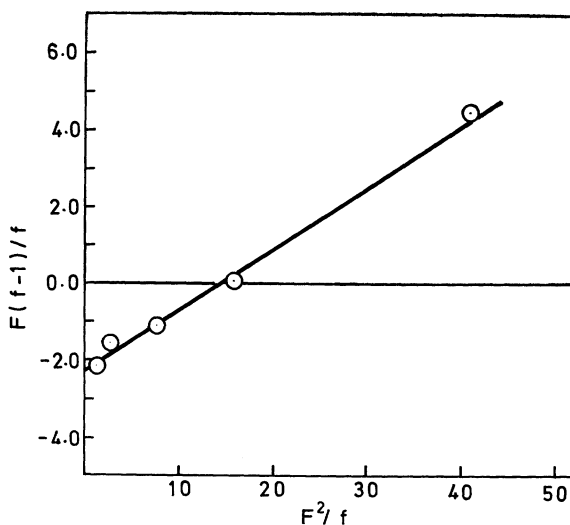


FIG. 4. Fineman-Ross plot for the copolymerization of CEVP with St.

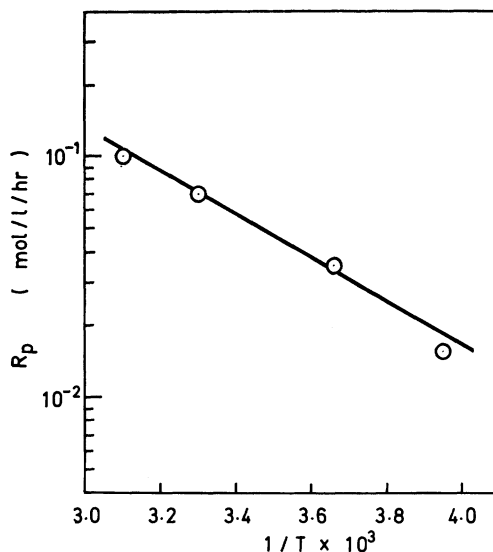


FIG. 5. Arrhenius plot of the rate of copolymerization of CEVP with St. CEVP/St = 50/50 (moles); dose rate = 5.0×10^4 R/hr.

$$\begin{array}{ll}
 [\text{CEVP}]/[\text{St}] = 50/50, & R_p \propto I^{0.56} \\
 [\text{CEVP}]/[\text{St}] = 70/30, & R_p \propto I^{0.62} \\
 [\text{CEVP}]/[\text{St}] = 90/10, & R_p \propto I^{0.60}
 \end{array}$$

The above relations indicate that the copolymerizations take a bimolecular termination mechanism.

On the other hand, these reactions were inhibited by radical scavengers such as DPPH or benzoquinone, which indicates that the copolymerization proceeds by a free radical mechanism.

Relationship between Rate of Copolymerization and Monomer Composition

The rates of copolymerization of CEVP with St, as shown in Fig. 6, exhibit remarkably low values compared with those of the bulk polymerization of CEVP, and, moreover, these values do not always change linearly with initial monomer composition.

To examine further the reaction mechanism, the G_r values obtained by the DPPH method were established under the same conditions with kinetic measurement. These results are illustrated in the same figure, in comparison with the kinetic data. The G_r value approaches 15 as the concentration of CEVP approaches 100%, as was seen in the solution polymerization of CEVP. Furthermore, the G_r value curve shows a tendency parallel with the corresponding kinetic curve, which indicates that the rate must be under the control of the G_r value. The energy transfer reactions from CEVP to St, as observed in the solution polymerization of CEVP, must

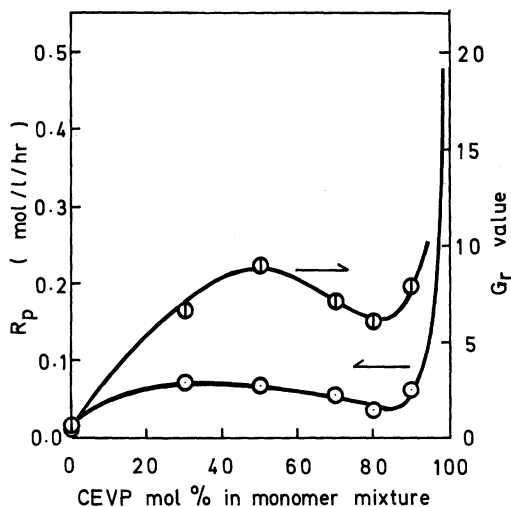


FIG. 6. Dependence of the rate of copolymerization (moles/liter/hr) and G_r value in the mixture of CEVP with St on monomer composition. Irradiation temperature = 30°C; dose rate = 5.0×10^4 R/hr.

occur in these systems, from the fact that values of both R_p and G_r are remarkably low compared with those in the bulk polymerization of CEVP. The fact that the G_r value approaches 15 as the concentration of CEVP approaches 100% suggests a mechanism for these reactions similar to that of solution polymerization of CEVP.

On the other hand, both the R_p and G_r values pass each one of the maximum and minimum values with the change in monomer concentration. This indicates that a monomer can take two energy levels in the excited state. Magat and his collaborators (13) observed a similar phenomenon which was explained as due to two stages of excited energy levels of halides in the systems of $\text{CHCl}_3\text{-C}_6\text{H}_6$ and $\text{CCl}_4\text{-C}_6\text{H}_6$.

II. COPOLYMERIZATION OF CEVP WITH MMA

Properties of Copolymer

The copolymer obtained by precipitation from methanol appears to be a white powder, which is soluble in chloroform and benzene but is insoluble in ether. Figure 2 shows the relationship between molecular weight and CEVP content of the copolymer. The molecular weight of the copolymer decreases remarkably as the CEVP content increases.

An infrared spectrum of the copolymer having an initial CEVP-to-MMA molar ratio of 90/10 is shown in Fig. 7. The copolymer exhibited a strong absorption band at 1720 cm^{-1} due to the $\text{C}=\text{O}$ stretching vibration of MMA, and at 1025 cm^{-1} due to the $\text{P}-\text{O}-$ structure of CEVP.

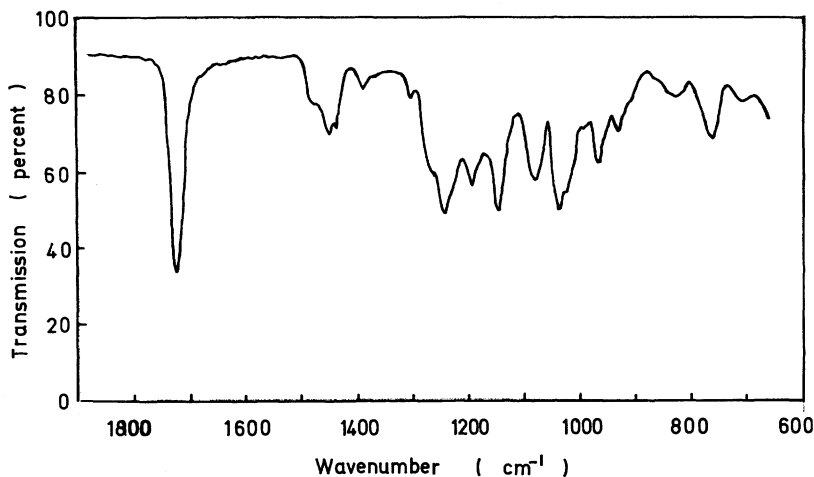


FIG. 7. Infrared spectrum of CEVP-MMA copolymer. The copolymer contains 38.6% (mole) CEVP. Irradiation temperature = 30°C; dose rate = 6.4×10^4 R/hr.

TABLE II
COPOLYMERIZATION OF CEVP WITH MMA
(Irradiation temperature = 30°C; dose rate = 6.4×10^4 R/hr)

CEVP/MMA (molar ratio)	Irradiation time (hr)	Yield (weight %)	Copolymer		
			CEVP (mole %)	MMA (mole %)	CEVP/MMA (molar ratio)
0.111	1.5	5.97	0.4	99.6	0.004
0.429	1.0	4.48	1.5	98.5	0.015
1.000	1.0	4.61	4.0	96.0	0.042
2.333	1.0	4.56	10.2	89.8	0.114

Relationship between Monomer and Polymer Compositions

Table II shows the results of the copolymerization of CEVP with MMA at 30°C of irradiation temperature and a dose rate of 6.4×10^4 R/hr. CEVP is not so active for copolymerization with MMA, and the resulting copolymers contain a larger proportion of MMA than the monomer mixtures.

The Fineman and Ross plot was carried out as shown in Fig. 8 on the basis of Table II, by denoting CEVP as M_1 and MMA as M_2 . The reactivity ratios established were $r_1 = 0.26$ and $r_2 = 29.9$. As the value of r_2 is considerably large, equation 2 is not applicable to these results.

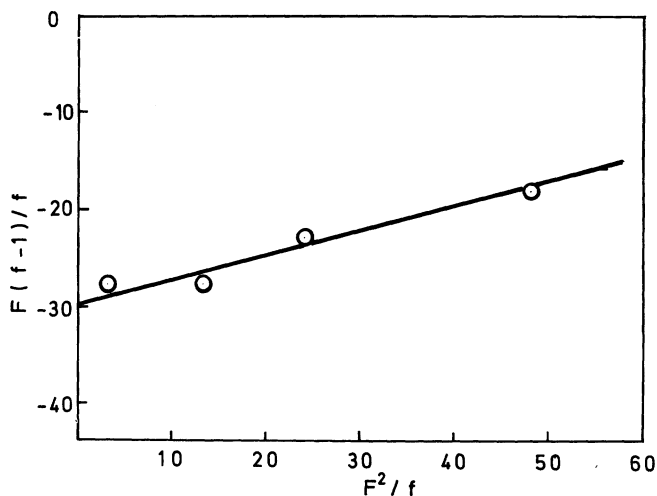


FIG. 8. Fineman-Ross plot for the copolymerization of CEVP with MMA

Effect of Irradiation Temperature on Rate of Copolymerization

The irradiation was carried out at various temperatures with samples having an initial CEVP-to-MMA molar ratio of 50/50; the results are shown in Fig. 9. From the relationship between R_p and $1/T$, as shown in Fig. 9, the activation energy, E_a , in this copolymerization was established to be 1.6 kcal/mole. This value is lower than that of 4 to 5 kcal/mole of MMA (12, 14) or 2.4 kcal/mole of CEVP (4) and is rather comparable with the value of 1.3 kcal/mole for the solution polymerization of CEVP in methylene chloride (5).

Effect of Dose Rate on Rate of Copolymerization

The initial copolymerization rate is proportional to the 0.57 power of dose rate in the region of 5.0×10^2 to 1.0×10^4 R/hr at 30°C. This fact indicates a bimolecular termination mechanism for the copolymerization of CEVP with MMA, as was seen in the copolymerization with St.

Relationship between Rate of Copolymerization and Monomer Composition

The initial rate of copolymerization gradually increases with the increasing monomer concentration of CEVP, as can be seen in Fig. 10. The G_r values obtained by the DPPH method are shown in the same figure. As was observed in the other polymerization systems of CEVP, the G_r value approaches 15 as the concentration of CEVP approaches 100%. Moreover, the G_r value of the system is considerably lower than that of 100% CEVP and is nearly equivalent to that of MMA. This suggests that the energy transfer reactions occur from CEVP to MMA.

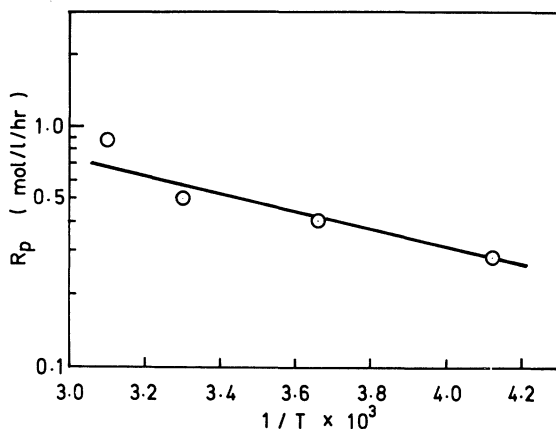


FIG. 9. Arrhenius plot of the rate of copolymerization of CEVP with MMA: CEVP/MMA = 50/50 (moles); dose rate = 5.0×10^4 R/hr.

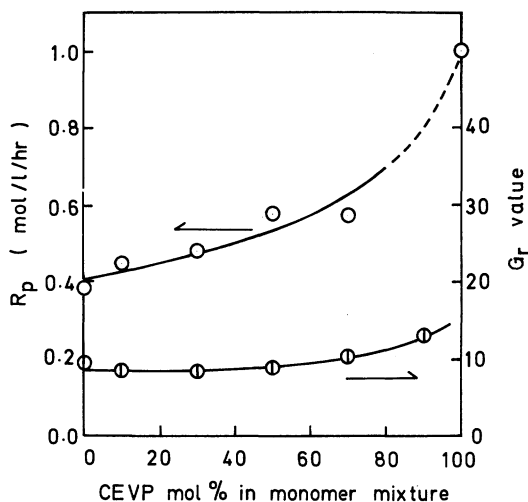


FIG. 10. Dependence of the rate of copolymerization (moles/liter/hour) and G_r value in the mixture of CEVP with MMA on monomer composition. Irradiation temperature = 30°C ; dose rate = 5.0×10^4 R/hr.

From the fact that the values of both R_p and G_r change as the monomer composition changes, each monomer will have a single energy level of excited state. Moreover, as the rate shows the same tendency with the G_r value, it must be under the control of the G_r value.

MECHANISM OF COPOLYMERIZATION

From the results mentioned above, a general reaction mechanism between those monomers must be considered for the γ -ray-induced copolymerization of CEVP.

As r_1 has a small value, the ability of block copolymerization of CEVP is small, and the reactivity between the CEVP radical and other monomer is relatively large. From the fact that the copolymerizations take a bimolecular termination mechanism, and that the molecular weight of the resulting copolymer decreases as the CEVP content of copolymer increases, and, moreover, that a bimolecular termination mechanism between growing chain and solvent radical was considered in the solution polymerization of CEVP, the following termination mechanism must be conceivable for the copolymerization of CEVP. A termination will occur by combining those two chains whose terminal of growing chain is different monomer unit from each other.

It is generally known that the rate of copolymerization is illustrated in the following equation by means of the same assumptions as in the case of homopolymerization.

$$-\frac{d([M_1] + [M_2])}{dt} = \frac{R_i^{1/2}(r_1[M_1]^2 + 2[M_1][M_2] + r_2[M_2]^2)}{(r_1^2\delta_1^2[M_1]^2 + 2\phi r_1 r_2 \delta_1 \delta_2[M_1][M_2] + r_2^2\delta_2^2[M_2]^2)^{1/2}} \quad (3)$$

where

$$\delta_1 = k_{t11}^{1/2}/k_{p11}$$

$$\delta_2 = k_{t22}^{1/2}/k_{p22}$$

$$\phi = k_{t12}/(k_{t11} \cdot k_{t22})^{1/2}$$

In the copolymerization of the CEVP-St system, for example, the application of equation 3 to the experimental data enabled us to obtain the ϕ values shown in Table III. Here, it provided that the rate of the production of radicals from the DPPH method is equal to that of the initiation of copolymerization.

Where two kinds of monomer have chemically similar reactivities, the value of ϕ is nearly equal to unity in the copolymerization. On the contrary, the high value of ϕ indicates the preference for cross-termination in the copolymerization. Bamford and his collaborators (17) pointed out that ϕ is significantly greater than unity for the copolymerization of two monomers with substituents inducing dissimilar polarity. Melville and his co-workers (18, 19) observed that the value of ϕ changes as the monomer composition changes in the copolymerization of St with other monomers such as butyl acrylate, which was attributed by Burnett and Gersmann (20) to the degradative chain transfer reaction of St monomer. The ϕ value obtained from equation 3 by substituting the δ_2 from Melville and Valentine (15) is significantly larger than that obtained by Matheson and his co-workers (16). Moreover, the ϕ value obtained by Matheson and his co-workers increases as $[M_1]$ increases.

TABLE III

THE VALUE OF ϕ FOR THE COPOLYMERIZATION OF CEVP WITH St(Irradiation temperature = 30°C; dose rate = 5.0×10^4 R/hr. $[M_1]$ and $[M_2]$ are denoted to be the concentration of CEVP and St, respectively.)

$[M_1]$ (moles/liter)	$[M_2]$ (moles/liter)	$-\frac{d([M_1] + [M_2])}{dt}$ (moles/liter/sec)	$R_i \times 10^7$ (moles/liter/sec)	ϕ^a	ϕ^b
2.241	5.227	2.016	0.961	183	—
3.414	3.414	1.894	1.40	157	4.61
4.411	1.872	1.568	1.18	86	15.2
4.839	1.209	0.996	1.03	166	87.5
5.245	0.583	1.785	1.37	424	223

^a $\delta_2 = 87.8$: from the data of Melville and Valentine (15).^b $\delta_2 = 129.1$: from the data of Matheson and his co-workers (16).

In the present research, the copolymerization has no degradative chain transfer reactions for the termination mechanism, and consequently the ϕ values obtained by Melville and Valentine must be more reasonable. In either way, the values of ϕ are considerably large for the copolymerization of CEVP with St, showing that the cross-termination reactions easily occur. This result directly endorses the termination mechanism mentioned above. Furthermore, this result indicates that each of these CEVP and St monomers shows an opposite polarity with each other, in accordance with the result that each of these two monomers takes an opposite sign of e value as mentioned above.

CONCLUSIONS

The copolymerization reactions proceed by a free radical mechanism, and the reactivity of CEVP with other monomers is not so high, especially with MMA. The reactivity ratios for the copolymerization were established as follows:

$$\begin{aligned} \text{CEVP-St: } r_1 &= 0.16, & r_2 &= 2.3 \\ \text{CEVP-MMA: } r_1 &= 0.26, & r_2 &= 29.9 \end{aligned}$$

The apparent activation energies of copolymerization were established to be 4.2 kcal/mole for CEVP with St, and 1.6 kcal/mole with MMA. The values of both R_p and G_r in these copolymerizations are close to that of the opposite monomer, owing to the energy transfer reactions from CEVP to the other monomer. Moreover, a cross-termination reaction can easily occur.

ACKNOWLEDGMENTS

I wish to express my sincere gratitude to Professor Hitoshi Yamamura of Hiroshima University for his helpful advise and to Dr. Tatsuo Matsuda, Dr. Kiyoshi Morita, and Dr. Machio Iwasaki for their interest in this work.

RECEIVED: March 31, 1967

REFERENCES

1. WU, MEI-YAN and Z. A. ROGOVIN, Synthesis of new derivatives of cellulose and other polysaccharides. XXVII. Synthesis of graft copolymers of cellulose and vinylphosphonic acid esters. *Vysokomolekul. Soedin.* **5**, (5), 706-711 (1963).
2. A. F. LEWIS and L. J. FORRESTAL, Chemical nature of polymer to metal adhesion. *Am. Soc. Testing Mater. Spec. Tech. Publ. No. 360*, 59-75; Discussion pp. 76-77 (1964).
3. V. A. ORLOV and O. G. TARAKANOV, The copolymerization of bis(β -chloroethyl) vinylphosphonate. *Plasticheskie Massy No. 6*, 6-9 (1964).
4. S. FUJII, H. YAMAKITA, and T. MATSUDA, Radiation induced polymerization of β -chloroethyl vinylphosphonate. *Chem. High Polymers (Tokyo)*, **23**, 369-373 (1966).
5. S. FUJII, H. YAMAKITA, and T. MATSUDA, Radiation-induced solution polymerization of bis(β -chloroethyl) vinylphosphonate. *Radiation Res.* **33**, 238-248 (1968).
6. C. L. ARCUS and R. J. S. MATTHEWS, Phosphonic polymers. I. The copolymerization of diethyl vinylphosphonate and styrene. *J. Chem. Soc.* 4607-4612 (1956).
7. M. FINEMAN and S. D. ROSS, Linear method for determining monomer reactivity ratios in copolymerization. *J. Polymer Sci.* **5**, 259-262 (1950).
8. T. ALFREY, JR., and C. C. PRICE, Relative reactivities in vinyl copolymerization. *J. Polymer Sci.* **2**, 101-106 (1947).
9. A. V. TOBOLSKY and J. OFFENBACH, Kinetic constants for styrene polymerization. *J. Polymer Sci.* **16**, 311-314 (1955).
10. M. S. MATHESON, E. E. AUER, E. B. BEVILACQUA, and E. J. HART, Rate constants in free radical polymerization. III. Styrene. *J. Am. Chem. Soc.* **73**, 1700-1706 (1951).
11. M. HAMASHIMA, Reaction of organic low-molecular weight compounds by cobalt-60 gamma radiation. I, II. Polymerization of styrene. *Nippon Kagaku Zasshi* **81**, 134-140, 1150-1154 (1960).
12. D. S. BALLANTINE, P. COLOMBO, A. GLINES, and B. MANOWITZ, The γ -ray-initiated polymerization of styrene and methyl methacrylate. *Chem. Eng. Progr. Symp. Ser.* **50**, 267-270 (1954).
13. M. MAGAT, L. BOUBY, A. CHAPIRO, and N. GISLON, The radiolysis of mixtures of organic solvents. *Z. Electrochem.* **62**, 307-311 (1958).
14. S. OKAMURA, Y. OISHI, and H. INAGAKI, Studies of polymerization reaction by γ -ray radiation. *Kyoto Daigaku Nihon-kagakuseni-kenkyusho Koenshu* **14**, 103-110 (1957).
15. H. W. MELVILLE and L. VALENTINE, Rate coefficients in the polymerization of styrene. *Trans. Faraday Soc.* **46**, 210-227 (1950).
16. M. S. MATHESON, E. B. BEVILACQUA, E. E. AUER, and E. J. HART, Rate constants in free radical polymerizations. I. Methyl methacrylate. *J. Am. Chem. Soc.* **71**, 497-504 (1949).
17. C. H. BAMFORD, W. G. BARB, A. D. JENKINS, and P. F. ONYON, *The Kinetics of Vinyl Polymerization by Radical Mechanisms* (Adlard and Son, eds.), 1st ed., pp. 178-179, Butterworths Publications Limited, London and Dorking, 1958.
18. J. H. BRADBURY and H. W. MELVILLE, The co-polymerization of styrene and butyl acrylate in benzene solution. *Proc. Roy. Soc.* **A222**, 456-470 (1954).
19. E. J. ARLMAN and H. W. MELVILLE, Studies in copolymerization. The evaluation of the kinetic coefficients for the system styrene-butyl acrylate. *Proc. Roy. Soc.* **A203**, 301-321 (1950).
20. G. M. BURNETT and H. R. GERSMANN, Interaction of radicals derived from methyl methacrylate and vinyl acetate. *J. Polymer Sci.* **28**, 655 (1958).