

Radical Polymerization Behavior of Dimethyl Vinylphosphonate: Homopolymerization and Copolymerization with Trimethoxyvinylsilane

Tsuneyuki Sato, Makoto Hasegawa, Makiko Seno, Tomohiro Hirano

Department of Chemical Science and Technology, Institute of Technology and Science, Tokushima University, Minamijosanjima 2-1, Tokushima 770-8506, Japan

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ABSTRACT: Dialkyl vinylphosphonates such as dimethyl vinylphosphonate (DMVP) and diethyl vinylphosphonate were quantitatively polymerized with dicumyl peroxide (DCPO) at 130°C in bulk. The polymerization of DMVP with DCPO was kinetically studied in bulk by fourier transform near-infrared spectroscopy (FTNIR) and electron spin resonance (ESR) spectroscopy. The initial polymerization rate (R_p) was given by $R_p = k[\text{DCPO}]^{0.5}[\text{DMVP}]^{1.0}$ at 110°C, being the same as that of the conventional radical polymerization involving bimolecular termination. The overall activation energy of the polymerization was estimated to be 26.2 kcal/mol. The polymerization system involved ESR-observable propagating polymer radicals under the practical polymerization conditions. ESR-determined rate constants of propagation (k_p)

and termination (k_t) were $k_p = 19 \text{ L/mol s}$ and $k_t = 5.8 \times 10^3 \text{ L/mol s}$ at 110°C, respectively. The molecular weight of the resultant poly(DMVP)s was low ($M_n = 3.4 - 3.5 \times 10^3$), because of the high chain transfer constant ($C_m = 3.9 \times 10^{-2}$ at 110°C) to the monomer. DMVP (M_1) showed a considerably high reactivity in the radical copolymerization with trimethoxyvinylsilane (TMVS) (M_2) at 110°C in bulk, giving an inorganic component-containing functional copolymer with potential flame-retardant properties; $r_1 = 1.6$ and $r_2 = 0$. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 3746–3752, 2008

Key words: radical polymerization; kinetics; ESR; copolymerization; dialkyl vinylphosphonate; trimethoxyvinylsilane

INTRODUCTION

Considerable attention has been paid to phosphorus-containing polymers because of their flame-retarding effects, excellent adhesion to metals, metal ion binding characteristics, and so on.^{1–7} Radical homo- and copolymerizations of various P-vinyl monomers have been studied by some workers from the standpoints of not only the synthesis of phosphorus-containing polymers but also the substituent effects of the phosphorus on the vinyl polymerization.^{8–15} Dialkyl vinylphosphonates show a relatively high polymerizability but give only oligomers in the radical homopolymerization, whereas their anionic polymerizations afford high molecular weighted polymers.^{10,11,13} In the radical copolymerization they can be well copolymerized with vinyl acetate, as nonconjugative monomer, but not with conjugative monomers such as styrene, acrylonitrile, and methyl methacrylate.^{8,10–12,14} Thus, dialkyl vinylphosphonates have been established to be an electron-accepting nonconjugative monomer in the radical copolymer-

ization. However, radical polymerization kinetics of dialkyl vinylphosphonates has not been reported.

Here we have studied kinetically the radical homopolymerizations of dimethyl vinylphosphonate (DMVP) and diethyl vinylphosphonate (DEVP), and also the copolymerization of DMVP with trimethoxyvinylsilane (TMVS) as a nonconjugative monomer giving an inorganic component-containing functional copolymer with potential flame-retardant properties.⁷ Dicumyl peroxide (DCPO) was used as an initiator.

This article describes the kinetic behaviors of DMVP and DEVP in the polymerization with DCPO and the results of the copolymerization of DMVP and TMVS.



EXPERIMENTAL

Materials

DMVP (98%) (Lancaster, UK) and DEVP (97%) (Aldrich, USA) were used as received. TMVS and dioxane were used as solvent after distillations. DCPO was recrystallized from methanol, containing a small amount of water.

Polymerization

Homo- and copolymerizations of dialkyl vinylphosphonates were carried out in a degassed sealed

Correspondence to: T. Hirano (hirano@chem.tokushima-u.ac.jp).

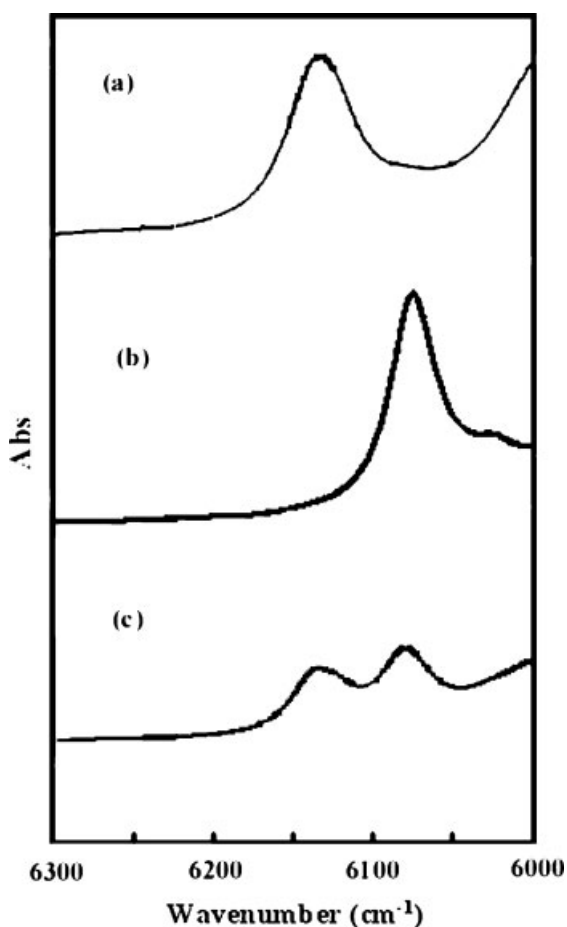


Figure 1 FTNIR spectra of (a) DMVP in bulk, (b) TMVS in bulk, and (c) an equimolar mixture of DMVP and TMVS in bulk.

Pyrex tube (5 mm in diameter) in the custom-made aluminum furnace in which Fourier transform near-infrared (FTNIR) spectroscopic measurements were performed.¹⁶ The polymerization mixtures were degassed by the freezing and thawing method before sealing in a vacuum. The conversions of dialkyl vinylphosphonates and TMVS were monitored by absorbances at 6140 and 6080 cm^{-1} , respectively. These bands are ascribable to the overtone absorptions due to the stretching vibration of $=\text{C}-\text{H}$ bonds in the vinyl groups of the monomer. Figure 1 shows the FTNIR spectra of DMVP, TMVS, and an equimolar mixture of DMVP and TMVS. Each monomer conversion in the copolymerization system was estimated by computer integration of the nonoverlapped peak area of each monomer band, in which Spectra Manager (Jasco, Japan) was used as software.

Measurements

FTNIR spectra were recorded with a Jasco INT-400 spectrometer equipped with a mercury-cadmium-

telluride detector. The ^1H NMR spectra were measured with an EX-400 spectrometer (Jeol, Japan) (400 MHz). Gel-permeation chromatography (GPC) was conducted at 40°C using a Tosoh (Japan) HLC-8220 GPC chromatograph (columns; TSK-Gels SuperHM-M and SuperHM-H, [polymer] = 1 mg/mL, flow rate = 0.35 mL/min) with tetrahydrofuran as eluent. From the GPC results, the number-average (M_n) and weight-average (M_w) molecular weights of the resulting poly(DMVP)s were estimated with polystyrene standards calibration. Electron spin resonance (ESR) spectrum of the polymerization mixture in a degassed and sealed ESR quartz tube was recorded on a Jeol-JES-FE 2XG spectrometer operating in the X band (9.5 GHz) with a transverse electric wave-mode cavity. The radical concentration of the polymerization mixture was determined by computer double integration of the first derivative ESR spectrum, in which 2,2,6,6-tetramethylpiperidin-1-oxyl radical in chlorobenzene was used as a standard. A MgO marker was used for the calibration of the radical concentration in different media. Dynamic thermogravimetry (TG) of the polymer was performed under a nitrogen atmosphere (flow rate = 20 mL/min) with a Shimadzu (Japan) TGA-50 thermogravimeter at a heating rate of 10°C/min. A differential scanning calorimetric (DSC) curve was obtained with a Shimadzu DSC 50 under a nitrogen atmosphere (heating rate = 10°C/min).

RESULTS AND DISCUSSION

Kinetic study of polymerization of dialkyl vinylphosphonates with DCPO

To elucidate the radical homopolymerizability of dialkyl vinylphosphonates, the polymerizations of DMVP (8.3 mol/L) and DEVP (6.5 mol/L) in bulk were performed at 130°C. DCPO (5.0×10^{-2} mol/L) was used as an initiator because DCPO was reported to be effective for the polymerizations of dialkyl vinylphosphonates.⁹ The conversions of DMVP and DEVP were estimated *in situ* by FTNIR. Figure 2 shows time-conversion curves observed in the polymerizations of DMVP and DEVP. Thus, the polymerization of DMVP proceeded faster than that of DEVP. This might come from the difference in the steric hindrance because of methyl and ethyl groups, although the true reason is obscure at present. DMVP was completely polymerized in about 3 h and DEVP in about 4 h. As a conclusion, dialkyl vinylphosphonates show a high polymerizability in the radical polymerization at a temperature as high as 130°C. The resulting poly(DMVP) was observed to exhibit no absorptions (6.0 ~ 6.4 ppm) due to the vinyl protons of DMVP monomer and instead show the absorptions (1.2 ~ 2.8 ppm) because of the newly

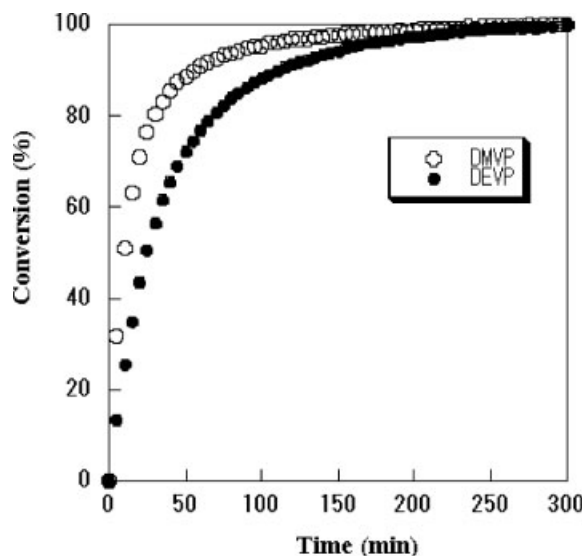


Figure 2 Time-conversion curves in the bulk polymerizations of DMVP (○) and DEVP (●) with DCPO at 130°C ([DCPO] = 5.0×10^{-2} mol/L).

formed main-chain protons in its ^1H NMR spectrum, suggesting that the usual vinyl polymerization proceeds with consumption of the double bond.

Figure 3(a) presents the first-order plots for the monomer concentration in the bulk polymerization of DMVP with DCPO at different temperatures (90 ~ 120°C), where the DCPO concentration was 5.0×10^{-2} mol/L. The half-life time of DCPO at 120°C, as the highest temperature used was estimated to be 4 h [k_d (decomposition rate constant) = $9.24 \times 10^{15} \exp(-152.67/RT)$],¹⁷ indicating that there is no significant decrease in the DCPO concentration during observation for 60 min. Thus, the linear plot was observed at each temperature, revealing that the propagating polymer radical concentration is constant (as confirmed below by ESR), and also that the initial polymerization rate (R_p) depends on the first order of the monomer concentration. Figure 3(b) illustrates the Arrhenius plot of R_p estimated from the time-conversion curves at different temperatures. From the slope of the plot, the overall activation energy (E_a) of the polymerization was calculated to be 26.2 kcal/mol.

Similarly, the first-order dependence of R_p on the monomer concentration was observed and E_a was estimated to be 27.6 kcal/mol for the bulk polymerization of DEVP with DCPO.

Figure 4 shows the effect of DCPO concentration on R_p observed in the polymerization of DMVP in bulk at 110°C, where the DCPO concentration was changed. Thus, R_p is proportional to the square root (0.5 th) of the initiator concentration, indicating that the polymerization involves bimolecular termination between the propagating polymer radicals.

From the above results, R_p of DMVP at 110°C is expressed by the same equation [eq. (1)] as that of the conventional radical polymerization.

$$R_p = k[\text{DCPO}]^{0.5}[\text{DMVP}]^{1.0} \quad (1)$$

ESR study of the polymerization of DMVP with DCPO in bulk

Figure 5 presents ESR spectrum observed in the bulk polymerization of DMVP (8.3 mol/L) with DCPO at 110°C, in which the DCPO concentration is 5.0×10^{-2} mol/L. The observed spectrum is assignable to the propagating poly(DMVP) radical (I). Its unpaired electron mainly interacts with an α -phosphorus and

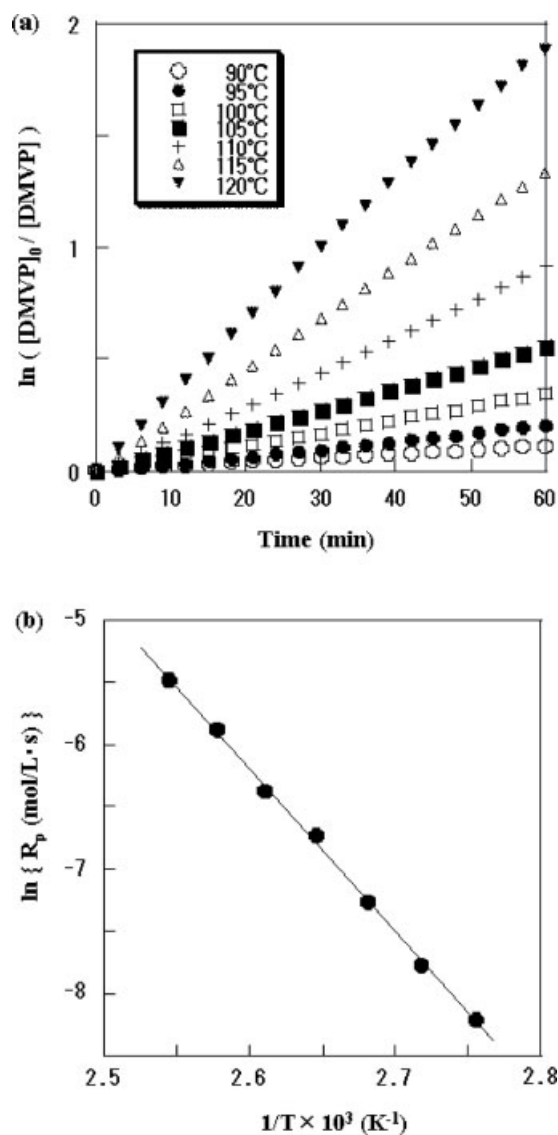


Figure 3 (a) First-order plots for the monomer concentration in the bulk polymerization of DMVP with DCPO at different temperatures and (b) temperature effect on the initial polymerization rate (R_p) ([DCPO] = 5.0×10^{-2} mol/L).

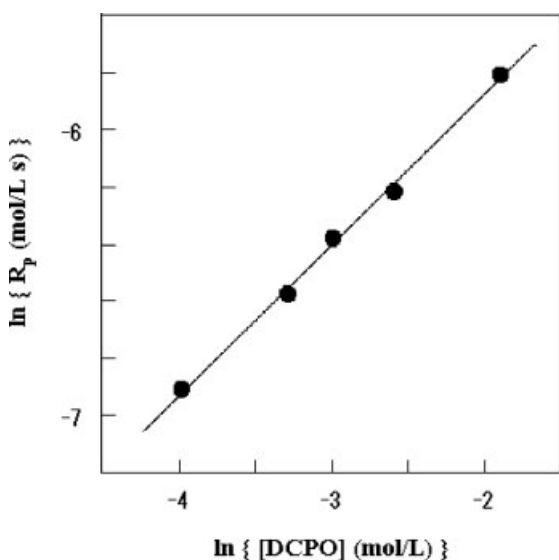


Figure 4 Dependence of the initial polymerization rate (R_p) on the DCPO concentration in the bulk polymerization of DMVP with DCPO at 110°C.

an α -hydrogen, and with only one of the two β -hydrogens, in which the coupling constants are $A_{\alpha-P} = 40$ G, $A_{\alpha-H} = 34$ G, and $A_{\beta-H} = 34$ G, respectively. It is of great interest that the DMVP polymerization system involved ESR-observable propagating polymer radical under the actual polymerization conditions at a temperature as high as 110°C. To our knowledge, the ESR spectrum of the propagating radical from the P-vinyl monomer has not been reported yet.

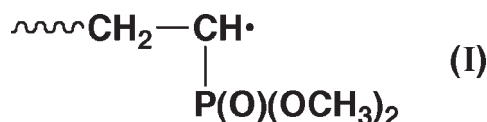


Figure 6 shows the relationship between the polymer radical concentration and time. Thus, $[\text{P}\cdot]$ was kept almost constant at 1.1×10^{-5} mol/L in the early stage of the polymerization although it tended to increase in the later stage. Such a small increase in the later stage might result from the decrease in the polarity of the polymerization system with increasing monomer conversion, leading to the enhanced ESR sensitivity. Thus, a steady state was found to be reached for the propagating polymer radical at least in the early stage of the polymerization. Using R_p and $[\text{P}\cdot]$ in the early stage, the rate constant (k_p) of propagation at 110°C was estimated to be 19 L/mol s according to eq. (2):

$$R_p = k_p[\text{P}\cdot][\text{DMVP}] \quad (2)$$

The significantly low k_p value comes probably from the polar and steric effects because of the bulky and strongly electron-accepting dimethyl phospho-



Figure 5 ESR spectrum observed in the bulk polymerization of DMVP with DCPO at 110°C ($[\text{DCPO}] = 5.0 \times 10^{-2}$ mol/L).

nate groups on the monomer and propagating polymer radical.¹⁴

Further, assuming the initiator efficiency (f) of DCPO = 0.5, the rate constant (k_t) of termination was calculated according to eq. (3) as the present polymerization proceeds via bimolecular termination as stated earlier:

$$2fk_d[\text{DCPO}] = k_t[\text{P}\cdot]^2 \quad (3)$$

where $k_d = 9.24 \times 10^{15} \exp(-152.67/RT)$.¹⁷ The obtained k_t value was 5.8×10^3 L/mol s at 110°C. The low k_t value might result from the rigidity of the propagating polymer chain due to the bulkiness of the dimethyl phosphonate group as side group.

It is noteworthy that these k_p and k_t values of DMVP are comparable with those ($k_p = 13$ L/mol s and $k_t = 3.1 \times 10^4$ L/mol s at 120°C) of TMVS.¹⁸

Molecular weight of the resulting poly(DMVP)s and chain transfer reaction to the monomer

Table I lists the molecular weight of poly(DMVP)s obtained in the bulk polymerization of DMVP at

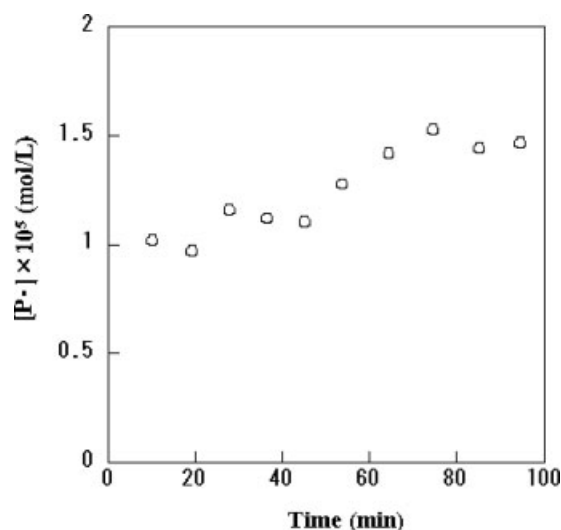


Figure 6 Time-profile of the polymer radical concentration ($[\text{P}\cdot]$) in the bulk polymerization of DMVP with DCPO at 110°C ($[\text{DCPO}] = 5.0 \times 10^{-2}$ mol/L).

TABLE I
Number–Average Molecular Weight (M_n)^a and Molecular Weight Distribution (M_w/M_n)^a of Poly(DMVP)s Formed in the Bulk Polymerization of DMVP^b with DCPO

Run	T (°C)	[DCPO] (10^{-2} mol/L)	$M_n \times 10^{-3}$	M_w/M_n
1	90	5.0	3.4	1.3
2	95	5.0	3.4	1.3
3	100	5.0	3.4	1.3
4	105	5.0	3.4	1.3
5	110	5.0	3.4	1.3
6	115	5.0	3.4	1.3
7	120	5.0	3.4	1.3
8	110	1.9	3.5	1.3
9	110	3.8	3.5	1.3
10	110	7.5	3.5	1.3
11	110	15.0	3.4	1.3

^a Calibrated with polystyrene standards.

^b [DMVP] = 8.3 mL/L.

different DCPO concentrations and temperatures, in which the molecular weights were estimated based on the polystyrene standards calibration although the absolute value will shift depending on the difference in hydrodynamic volume of the polymers. Thus, the M_n value of the polymers formed at 110°C was almost independent of the initiator concentration, although R_p increased in proportion to the square root of the initiator concentration, suggesting that the molecular weight of the poly(DMVP) was essentially limited by the chain transfer to the monomer. The importance of the chain transfer to the monomer was already pointed out in some articles concerning radical polymerizations of dialkyl vinylphosphonates including DMVP.^{9–11}

As the chain transfer to the initiator is negligible, the degree of polymerization (P_n) is related to R_p by eq. (4):

$$1/P_n = C_m + k_t R_p / (k_p [\text{DMVP}]^2) \quad (4)$$

where C_m is the chain transfer constant of the monomer. Figure 7 presents the relationship between the reciprocal of P_n and $(R_p / [\text{DMVP}]^2)$ for the poly(DMVP)s formed at 110°C in bulk. No slope was observed in the plot, revealing that the molecular weight of the resulting polymer was determined by the chain transfer to the monomer. From the intercept of the plot, C_m was estimated to be 3.9×10^{-2} , a very high value. This C_m value is similar to that (3.4×10^{-2} at 110°C) of TMVS.¹⁸ On the other hand, much smaller C_m values (at 60°C) are reported for common monomers such as vinyl acetate (2.0×10^{-4}), styrene (7.0×10^{-6}) and methyl methacrylate (1.0×10^{-5}).¹⁹ The rate constant (k_{tr}) of the chain transfer reaction to the DMVP monomer was estimated to be 7.4×10^{-1} L/mol s at 110°C using the $C_m (=k_{tr}/k_p)$ value and the above obtained k_p . The

M_w/M_n values (1.3) (Table I) were relatively low compared to M_w/M_n one close to 2, expected for the chain transfer controlled polymerization. The reason for this is not clear at present.

As described earlier, P_n is independent of R_p , leading to the fact that the $1/P_n$ values of poly(DMVP)s formed in bulk at different temperatures are equal to the C_m values at corresponding temperatures. As can be seen from Table I, the M_n values of the polymers formed at different temperatures were constant (3.4×10^3), indicating that the $C_m (=k_{tr}/k_p)$ value is independent of temperature. This leads to the fact that the activation energies of the propagation and the chain transfer reaction to the monomer are closely similar in the radical polymerization of DMVP in bulk at least in the temperature range of 90–120°C checked here.

As described above, the chain transfer to the DMVP monomer plays an important role in the present polymerization, resulting in the formation of the low molecular weighted polymers. However, no absorptions due to vinyl protons were observed in the ¹H NMR spectrum of poly(DMVP) formed in bulk. As depicted in Scheme 1, the monomer radical formed by the chain transfer to the monomer may cyclize to a five-membered radical and then the resulting cyclic radical reinitiates the polymerization to give the polymer carrying no end double bond.

Thermal behavior of the resulting poly(DMVP)

Figure 8(a) shows the DSC curve (second heating) of the poly(DMVP) formed in the bulk polymerization at 130°C for 5 h. An endothermic peak was observed

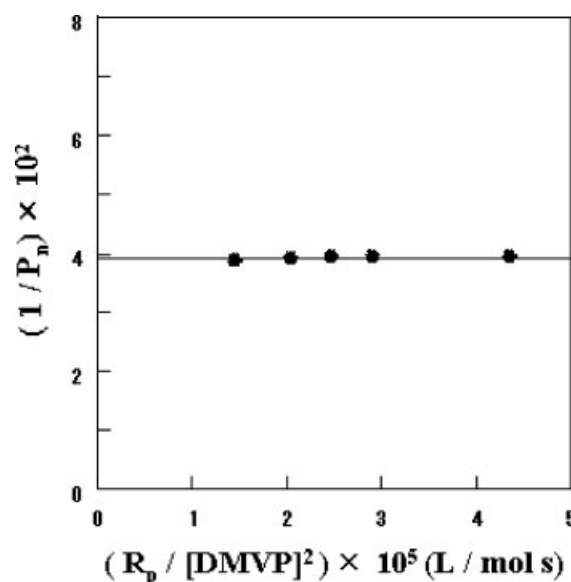
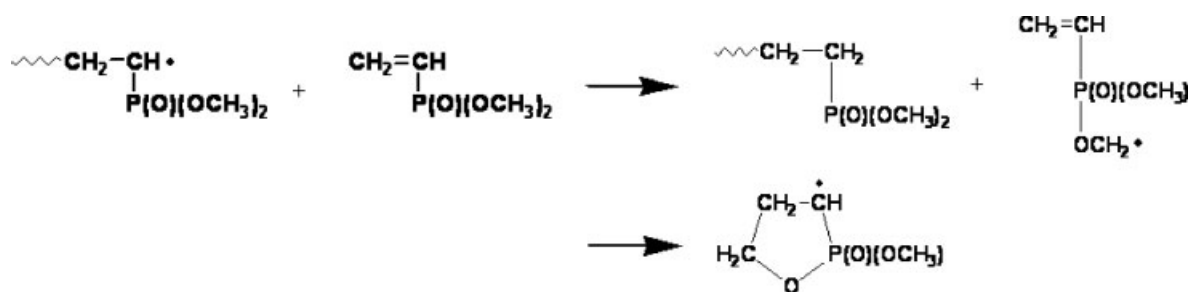


Figure 7 Relationship between the degree of polymerization (P_n) and the initial polymerization rate (R_p) in the bulk polymerization of DMVP with DCPO at 110°C.



Scheme 1 Chain transfer reaction to the DMVP monomer.

at 42°C, corresponding to the glass transition temperature. Figure 8(b) presents TG and differential thermogravimetric (DTG) curves of the same polymer. The thermal degradation of the polymer began at 250°C and exhibited a maximal degradation rate at about 330°C. The residue at 500°C was 51% of the initial polymer weight.

Copolymerization of DMVP and TMVS with DCPO at 110°C

The flame-retardance of cured epoxy resins was reported to be improved by the incorporation of silicone and phosphorus moieties owing to synergistic effect of silicone and phosphorus.⁷ This led us to examine the copolymerization behavior of DMVP (M_1) and TMVS (M_2) as a nonconjugative monomer. The copolymerization was carried out at 110°C in bulk, in which the DCPO concentration was $5.0 \times$

10^{-2} mol/L. Figure 9 presents the time-conversion curves for DMVP and TMVS observed in the copolymerization of equimolar feed composition. Thus, the reactivity of DMVP is much higher than that of TMVS. Such a higher reactivity of DMVP than TMVS was also observed at all other different feed compositions used here.

The initial polymerization rates of DMVP and TMVS were estimated from the time-conversion curves of them. The ratio of them corresponds to the composition of the resulting copolymer. Thus, the copolymer compositions were estimated at different feed compositions. Figure 10 shows the comonomer-copolymer composition curve. According to the curve-fitting method based on nonlinear least-squares analysis,²⁰ the monomer reactivity ratios were estimated to be $r_1 = 1.6$ and $r_2 = 0$. The r_2 value indicates that the propagating TMVS radical adds exclusively to the DMVP monomer compared with the TMVS one. This is partly because the resonance effect of dimethyl phosphonate group

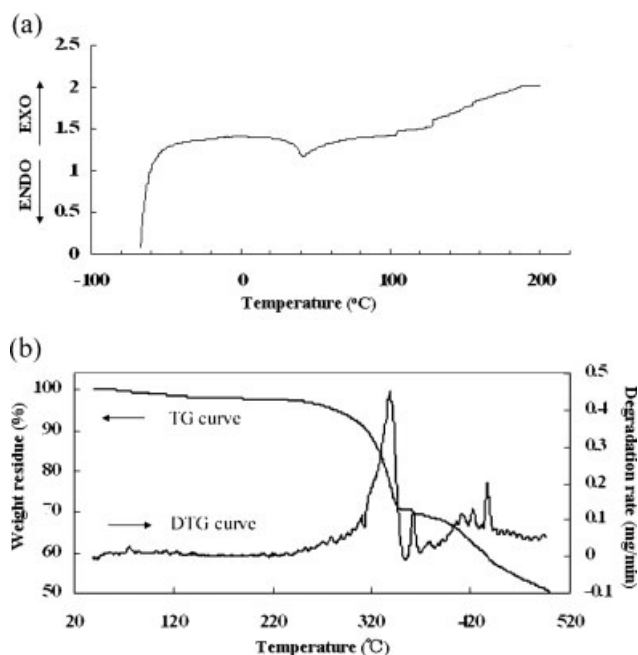


Figure 8 (a) DSC curve and (b) TG and DTG curves of the polymer formed in the bulk polymerization of DMVP with DCPO at 130°C for 5 h ($[DCPO] = 5.0 \times 10^{-2}$ mol/L).

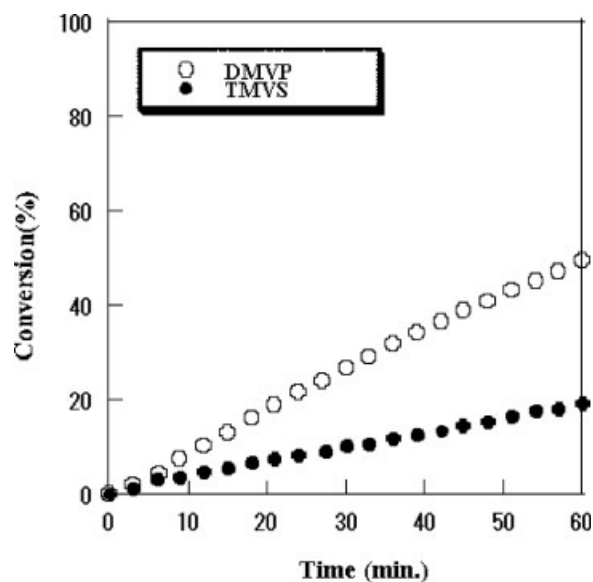


Figure 9 Time-conversion curves of the comonomers in the bulk copolymerization of DMVP and TMVS at 110°C ($[DCPO] = 5.0 \times 10^{-2}$ mol/L, $[DMVP]/[TMVS] = 1$).

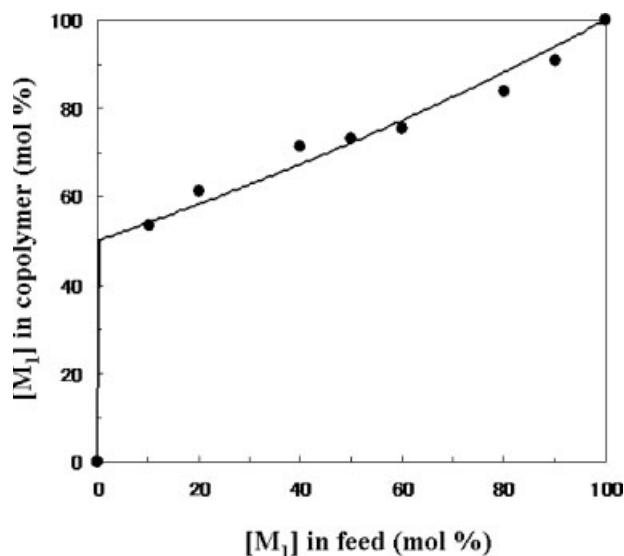


Figure 10 Copolymer-comonomer composition curve for the bulk copolymerization of DMVP (M_1) and TMVS (M_2) at 110°C.

($Q = 0.29$ for DMVP from the copolymerization with vinyl acetate)¹⁴ is considerably larger than that of trimethoxysilyl one ($Q = 0.08$ for TMVS from the copolymerization with vinyl acetate).¹⁸ On the other hand, the reactivity of DMVP monomer towards the propagating DMVP radical is only 1.6 times higher than that of the TMVS monomer. The strongly electron-accepting character of the dimethyl phosphonate group ($e = +1.51$ for DMVP from the copolymerization with vinyl acetate)¹⁴ seems to suppress the homopropagation of propagating DMVP radical.

CONCLUSIONS

DMVP and DEVP as dialkyl vinylphosphonate show a high homopolymerizability in the bulk polymerization with DCPO at 130°C. The polymerization of DMVP with DCPO in bulk exhibits a usual kinetic behavior at 110°C, $R_p = k[\text{DCPO}]^{0.5}[\text{DMVP}]^{1.0}$. The overall activation energy of the polymerization is 26.2 kcal/mol. The polymerization system involves ESR-observable propagating polymer radicals under

actual polymerization conditions. ESR-determined k_p and k_t values are 19 L/mol s and 3.8×10^3 L/mol s at 110°C, respectively. The molecular weight of resultant poly(DMVP) is limited by the chain transfer to the monomer ($C_m = 3.9 \times 10^{-2}$ at 110°C). DMVP (M_1) shows a high reactivity in the bulk copolymerization with TMVS (M_2); $r_1 = 1.6$ and $r_2 = 0$.

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