Macromolecules 1991, *24*, 2963-2967 **2963**

Radical Polymerization of 3,3-Bis(ethoxycarbonyl)propyl Vinyl Ether via an Addition-Abstraction Mechanism

Tsuneyuki Sato,* Daisuke Ito, Manabu Kuki, Hitoshi Tanaka, and Tadatoshi Ota

Department of Chemical Science and Technology, Faculty of Engineering, Tokushima University, Minamijosanjima 2-1, Tokushima 770, Japan

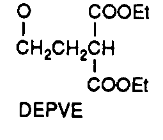
Received September 26, 1990; Revised Manuscript Received December 4, 1990

ABSTRACT: 3,3-Bis(ethoxycarbonyl)propyl vinyl ether (DEPVE) was polymerized in a good yield by radical initiators. The polymerization of DEPVE with di-*tert*-butyl peroxide (DBPO) was kinetically investigated near 110 °C in chlorobenzene. The polymerization rate (R_p) was expressed as follows: $R_p = k[\text{DBPO}]^{0.5}[\text{DEPVE}]^{1.5}$. The overall activation energy of the polymerization was calculated to be 115 kJ mol^{-1}. The number-average molecular weight ($\bar{M}_n$) of the resulting poly(DEPVE) was in the range 6700-10 700. $\bar{M}_n$ decreased with rising temperature, increasing initiator concentration, and decreasing monomer concentration. The IR spectrum, ^{1}H and ^{13}C NMR spectra, and thermal degradation behavior of the radically formed poly(DEPVE) were distinguishably different from those of the cationically formed one. From these results, radical poly(DEPVE) was found to involve two structures in the polymer chain, one (15-40%) through normal addition polymerization and the other (60-85%) through addition-abstraction polymerization. The latter mechanism involving intramolecular hydrogen abstraction prevails progressively with decreasing monomer concentration and rising temperature. The addition-abstraction mechanisms was, however, observed to have little participation in the copolymerizations of DEPVE with acrylonitrile and benzyl methacrylate at 60 °C.

Introduction

Radical polymerization of vinyl ethers is well-known to yield no high polymers, because the high reactivity of the unconjugated propagating radicals causes easy chain-transfer reaction to the monomers.[1] On the other hand, vinyl ethers, typical electron-donating monomers, undergo readily alternating copolymerization with electron-accepting monomers such as maleic anhydride[2] and α-cyanoacrylate esters.[3] So vinyl ethers carrying a labile hydrogen and electron-accepting groups at a suitable position are expected to polymerize through a propagation mechanism involving intramolecular hydrogen abstraction (addition-abstraction mechanism). In fact, in our previous paper, the radical polymerization of 3-cyano-3-(ethoxycarbonyl)propyl vinyl ether was found to proceed quantitatively via the addition-abstraction mechanism.[4]

In the present paper, we have studied the radical polymerization behavior of 3,3-bis(ethoxycarbonyl)propyl vinyl ether (DEPVE) as another suitable monomer for the addition-abstraction mechanism.



DEPVE

Experimental Section

DEPVE was prepared by the reaction[5] of the sodium salt of diethyl malonate with 2-chloroethyl vinyl ether, which was obtained by dehydrochlorination of bis(2-chloroethyl) ether,[6] bp 106 °C/5 mmHg. Radical initiators, monomers, and chlorobenzene as solvent were used after the usual purifications. Commercial boron trifluoride diethyl etherate was used as the cationic initiator without purification.

The polymerization and copolymerization of DEPVE were carried out in a degassed and sealed tube. The resulting polymer was isolated by pouring the polymerization mixture into a large excess of petroleum ether.

Table I
Polymerization of DEPVE with Radical and Cationic Initiators (I)

[DEPVE], mol L^{-1}	I	10^2[I], mol L^{-1}	solvent	temp, °C	time, h	yield, %
3.00	DBPO	5.00	C_6H_5Cl	130	6	85
1.50	DBPO	5.00	C_6H_5Cl	130	6	83
0.75	DBPO	5.00	C_6H_5Cl	130	6	74
1.50	DBPO	5.00	C_6H_5Cl	110	1	14
1.69	AIBN	2.00	C_6H_6	60	45	56
1.09	BF_3OEt_2	2.41	$C_6H_5CH_3$	-60	27	65

Table II
Molecular Weights of Radically Formed Poly(DEPVE)s

temp, °C	[DEPVE], mol L^{-1}	10^2[DBPO], mol L^{-1}	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
100	1.50	5.00	10 300	16 000	1.6
110	1.50	5.00	8 200	13 000	1.6
120	1.50	5.00	7 100	11 000	1.5
130	1.50	5.00	6 700	9 000	1.4
110	0.75	5.00	8 200	12 000	1.4
110	2.26	5.00	10 100	16 000	1.6
110	3.01	5.00	10 700	17 000	1.6
110	1.50	1.08	10 700	15 000	1.4
110	1.50	1.80	9 300	14 000	1.5

Gel permeation chromatograms were recorded at 38 °C by using a TOSO-HLC 802A instrument with tetrahydrofuran as carrier. From GPC results, the number-average ($\bar{M}_n$) and weight-average ($\bar{M}_w$) molecular weights of the resulting poly(DEPVE)s were determined using polystyrene standards. NMR spectra of the resulting polymers were obtained at 50 °C in deuteriochloroform by using a JEOL GX-400 (100-MHz ^{13}C) spectrometer. Dynamic thermogravimetry (TG) of the polymers was studied in a nitrogen atomosphere (flow rate 20 mL/min) with a Shimadzu TGA-50 thermogravimeter at a heating rate of 10 °C/min. All runs were terminated at 500 °C.

Results and Discussion

Polymerization of DEPVE with Radical and Cationic Initiators. Table I shows the results obtained in the polymerization of DEPVE initiated with radical initiators (azobis(isobutyronitrile) (AIBN) and di-*tert*-butyl peroxide (DBPO)) and a cationic initiator (boron trifluoride diethyl etherate, BF_3OEt_2). Thus, such conventional radical initiators were found to easily induce

0024-9297/91/2224-2963$02.50/0 © 1991 American Chemical Society

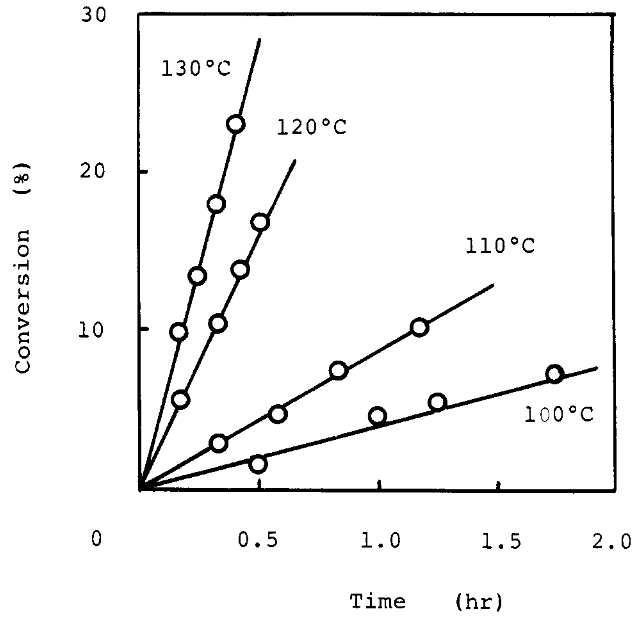


Figure 1. Time–conversion curves in the polymerization of DEPVE with DBPO in chlorobenzene: [DEPVE] = 1.50 mol L^{-1}, [DBPO] = 5.00×10^{-2} mol L^{-1}.

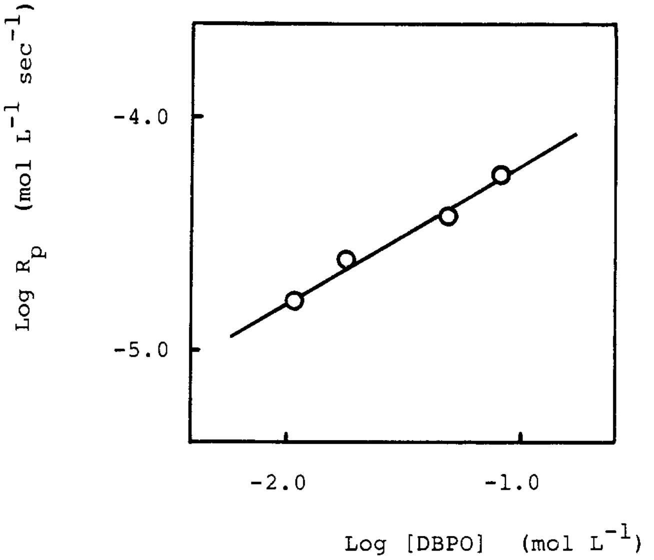


Figure 2. Dependence of the polymerization rate (R_p) on the DBPO concentration at 110 °C in chlorobenzene: [DEPVE] = 1.50 mol L^{-1}.

the polymerization of DEPVE. It is noteworthy that DEPVE, a vinyl ether, is polymerized in a high yield of more than 80% in the usual radical polymerization.

Kinetic Study on the Polymerization of DEPVE with DBPO. The polymerization of DEPVE initiated with DBPO was studied kinetically in chlorobenzene. Figure 1 shows the time–conversion curves observed in the temperature range 100–130 °C, fixing the concentrations of monomer and initiator constant. No induction period was observed in the polymerization. The polymerization rate (R_p) at each temperature was determined from the corresponding time–conversion curve. The Arrhenius plot of R_p gave an overall activation of polymerization of 115 kJ mol^{-1}.

Figure 2 shows the dependence of R_p on the DBPO concentration at 110 °C, keeping the monomer concentration constant. R_p increases in proportion to the square root of the initiator concentration, indicating that the usual bimolecular termination between the polymer radicals takes place in this polymerization.

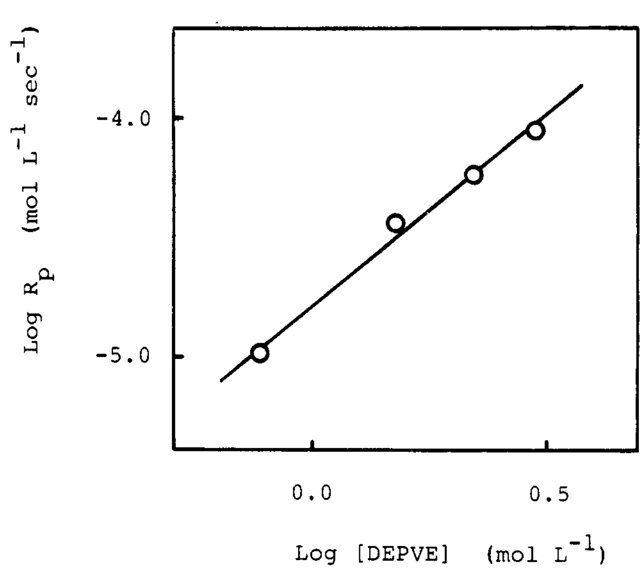


Figure 3. Dependence of the polymerization rate (R_p) on the DEPVE concentration at 110 °C in chlorobenzene: [DBPO] = 5.00×10^{-2} mol L^{-1}.

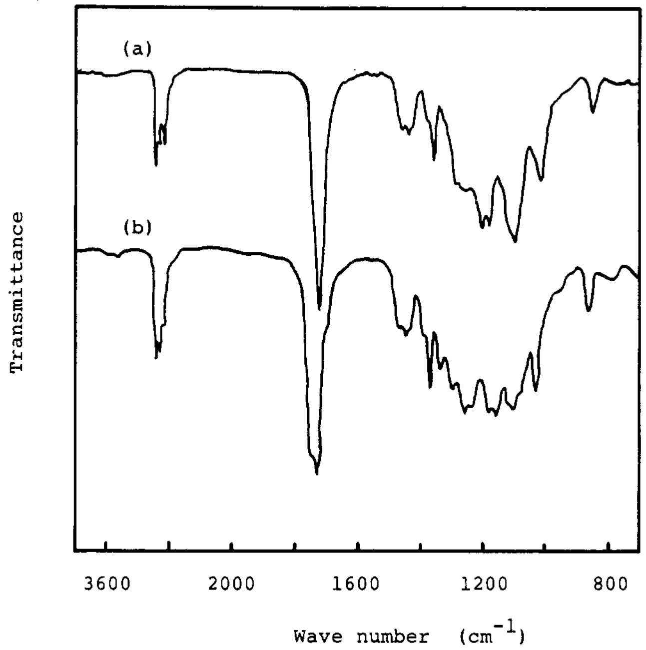


Figure 4. IR spectra of radically (a) and cationically (b) formed poly(DEPVE)s: (a) [DEPVE] = 0.75 mol L^{-1}, [DBPO] = 5.00×10^{-2} mol L^{-1}, 130 °C; (b) [DEPVE] = 1.09 mol L^{-1}, [BF_3OEt_2] = 2.41×10^{-2} mol L^{-1}, -60 °C.

As shown in Figure 3, R_p is proportional to 1.5th order of the DEPVE concentration. The higher order than unity with respect to the monomer concentration comes probably from the high viscosity of CEPVE, which retards diffusion-controlled termination to increase R_p and from the dependence of the propagation mechanism on temperature described below.

From the above results, R_p is expressed by

$$R_p = k[\mathrm{DBPO}]^{0.5}[\mathrm{DEPVE}]^{1.5} \qquad (1)$$

Characterization of the Resulting Poly(DEPVE). Table II summarizes the molecular weights of polymers formed in the polymerization of DEPVE with DBPO in chlorobenzene. The molecular weights obtained here by GPC are based on polystyrene standards without any consideration of differences in hydrodynamic volumes. $\bar{M}_n$ is in the range 6700–10 700, which is much higher than that of radically formed poly(n-butyl vinyl ether).[1] The

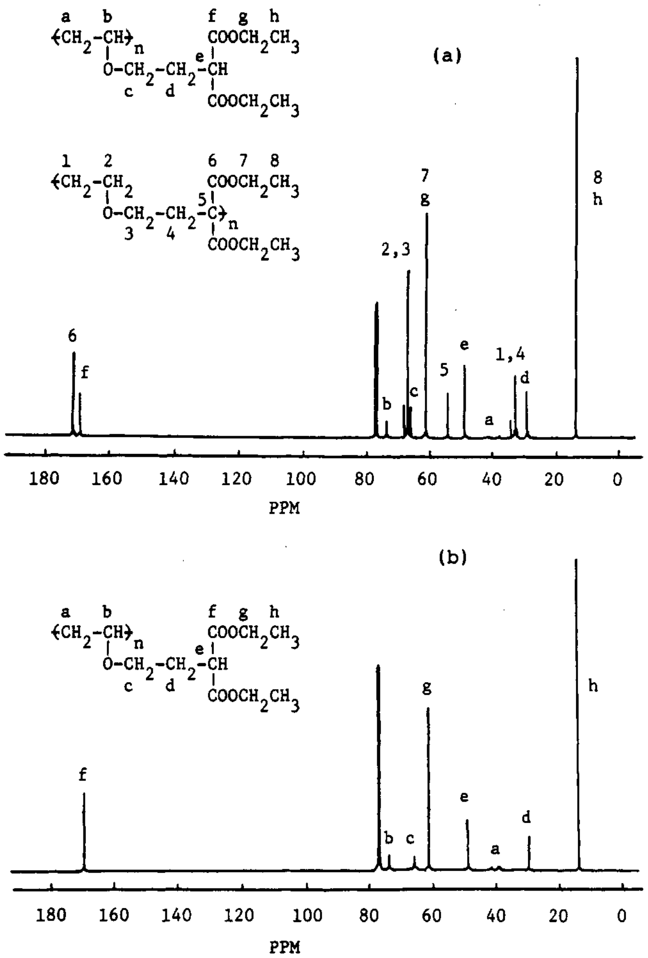
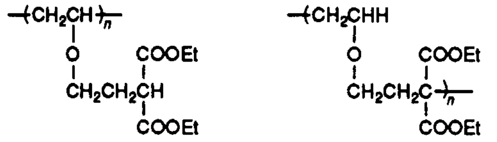


Figure 5. ^{13}C NMR spectra of radically (a) and cationically (b) formed poly(DEPVE)s: (a) [DEPVE] = 3.00 mol L^{-1}, [DBPO] = 5.00×10^{-2} mol L^{-1}, 130 °C; (b) [DEPVE] = 1.09 mol L^{-1}, [BF_3OEt_2] = 2.41×10^{-2} mol L^{-1}, −60 °C.

molecular weight distribution ($\bar{M}_w/\bar{M}_n$ = 1.4–1.6) is similar to those of the usual radical vinyl polymers. $\bar{M}_n$ decreases with rising temperature and increasing initiator concentration, but it increases with increasing monomer concentration. These behaviors are also observed in the usual radical polymerization.

Figure 4a shows an IR spectrum of poly(DEPVE) formed at 130 °C. The large absorption at 1600–1650 cm^{-1} due to the double bond of the DEPVE monomer vanished completely, indicating that the radical polymerization of DEPVE proceeds through opening of the double bond. However, the spectrum is not in agreement with that (b) of cationic poly(DEPVE) separately obtained in the polymerization at −60 °C with BF_3OEt_2, which proceeds via the usual cationic vinyl polymerization mechanism.[5] This reveals that radical and cationic poly(DEPVE)s differ from each other in their structures.

Figure 5 compares the ^{13}C NMR spectra of the radical (a) and cationic (b) poly(DEPVE)s. Thus, the radical polymer shows several absorption peaks other than those observed for the cationic one (usual vinyl polymer of structure A). Such peaks are considered to be due to



$$-(CH_2CH)_n- \quad O-CH_2CH_2CH(COOEt)_2$$

A

$$-(CH_2CHH \quad O-CH_2CH_2C(COOEt)_2)_n-$$

B

structure B formed through the addition–abstraction mechanism. The assignment of each peak in the spectra is donated by numbers and letters in the figure.

As a result, the radically formed poly(DEPVE) was found to contain two structures, A and B, in the polymer chain. The relative content of structure B was estimated from comparison of peaks 6 and f due to ester carbonyl groups in the figure. Table III summarizes the results obtained for poly(DEPVE)s formed under different polymerization conditions.

Figure 6 shows ^1H NMR spectra of the radical (a) and cationic (b) poly(DEPVE)s. The peak assignments are again shown by numbers and letters in the figure. Comparison of the areas of peaks x and y also results in estimation of the content of structure B. The obtained values are presented in Table III.

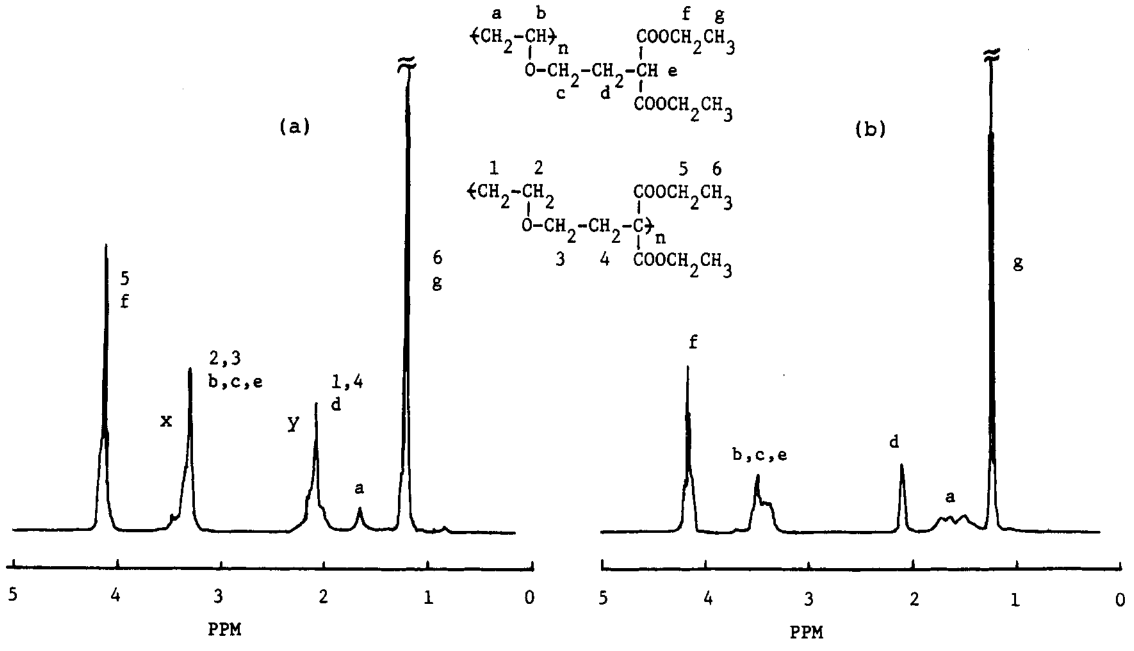


Figure 6. ^1H NMR spectra of radically (a) and cationically (b) formed poly(DEPVE)s: (a) [DEPVE] = 1.50 mol L^{-1}, [DBPO] = 5.00 $\times 10^{-2}$ mol L^{-1}, 130 °C; (b) [DEPVE] = 1.09 mol L^{-1}, [BF_3OEt_2] = 2.41×10^{-2} mol L^{-1}, −60 °C.

Table III
Fraction of Addition–Abstraction Structure (Structure B) from ^{13}C and ^1H NMR Spectra

[DEPVE], mol L^{-1}	temp, °C	I	10^2[I], mol L^{-1}	solvent	fraction of structure B, % ^{13}C NMR	fraction of structure B, % ^1H NMR
3.00	130	DBPO	5.00	C_6H_5Cl	65	74
1.50	130	DBPO	5.00	C_6H_5Cl	72	77
0.75	130	DBPO	5.00	C_6H_5Cl	77	86
1.69	60	AIBN	2.00	C_6H_6	54	63
1.09	−60	BF_3OEt_2	2.41	$C_6H_5CH_3$	0	0

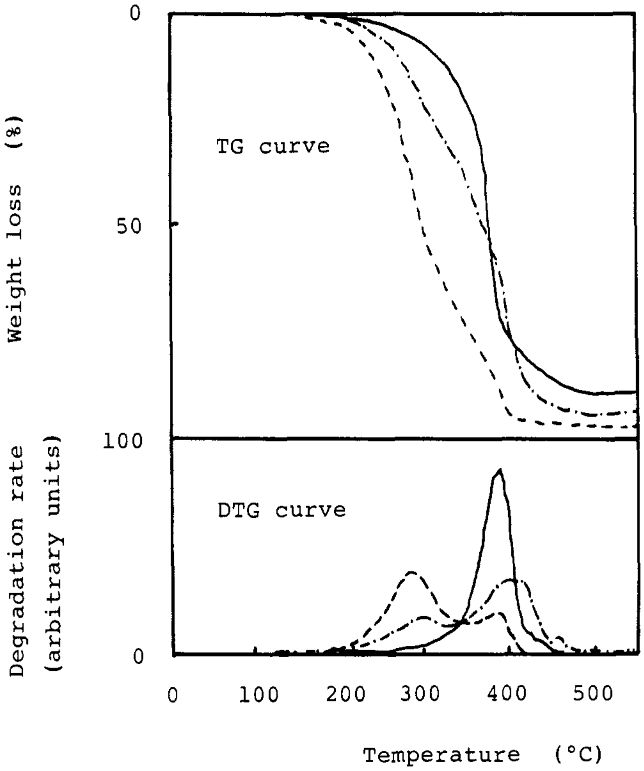
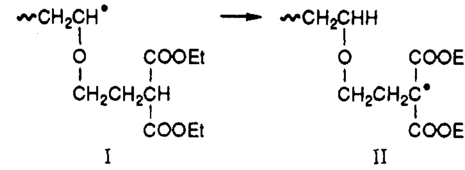


Figure 7. TG and DTG curves of radically and cationically formed poly(DEPVE)s: (- - -) [DEPVE] = 1.50 mol L^{-1}, [DBPO] = 5.00 × 10^{-2} mol L^{-1}, 130 °C; (- · -) [DEPVE] = 1.69 mol L^{-1}, [AIBN] = 2.00 × 10^{-2} mol L^{-1}, 60 °C; (—) [DEPVE] = 1.09 mol L^{-1}, [BF_3OEt_2] = 2.41 × 10^{-2} mol L^{-1}, −60 °C.

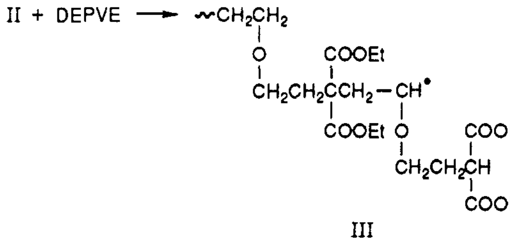
As can be seen from the above findings, in contrast to cationic poly(DEPVE), the radically formed polymer contains structure A via the usual addition polymerization and structure B via the addition–abstraction polymerization. The latter one constitutes 60–85% radical poly(DEPVE)s. The content of structure B increases with rising temperature and decreasing DEPVE monomer concentration.

Thermal degradation behaviors of the radical and cationic poly(DEPVE)s were studied by thermogravimetry. TG and differential thermogravimetric (DTG) curves of some poly(DEPVE)s are shown in Figure 7. Thus, the radical polymers show two maxima near 300 and 400 °C in the DTG curves, while the cationic one has only a peak near 400 °C. The peak near 300 °C is larger for the radical polymer formed at 130 °C than for that formed at 60 °C. The higher temperature peak has the opposite tendency. These results suggest that the peak at low temperature corresponds to structure B and the one near 400 °C to structure A.

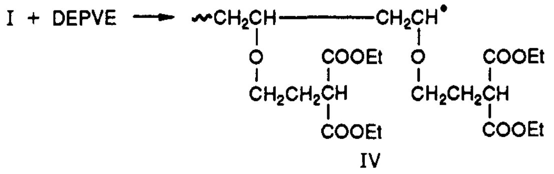
Polymerization Mechanism. From the above results, the radical polymerization of DEPVE is considered to propagate through two mechanisms, that is, the addition–abstraction mechanism and the normal addition one, as follows:



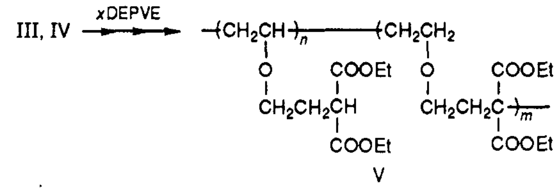
$$\underset{\text{I}}{\sim CH_2\dot{C}H\text{–}O\text{–}CH_2CH_2CH(COOEt)_2} \longrightarrow \underset{\text{II}}{\sim CH_2CHH\text{–}O\text{–}CH_2CH_2\dot{C}(COOEt)_2} \tag{2}$$



$$\text{II} + \text{DEPVE} \longrightarrow \underset{\text{III}}{\sim CH_2CH_2\text{–}O\text{–}CH_2CH_2C(COOEt)_2\text{–}CH_2\text{–}\dot{C}H\text{–}O\text{–}CH_2CH_2CH(COOEt)_2} \tag{3}$$



$$\text{I} + \text{DEPVE} \longrightarrow \underset{\text{IV}}{\sim CH_2CH(OCH_2CH_2CH(COOEt)_2)\text{–}CH_2\dot{C}H(OCH_2CH_2CH(COOEt)_2)} \tag{4}$$



$$\text{III, IV} \xrightarrow{x\text{DEPVE}} \underset{\text{V}}{\text{–}[CH_2CH(OCH_2CH_2CH(COOEt)_2)]_n\text{–}[CH_2CH_2\text{–}O\text{–}CH_2CH_2C(COOEt)_2]_m\text{–}} \tag{5}$$

An intramolecular hydrogen-abstraction reaction (eq 2) is reasonable to prevail progressively with decreasing monomer concentration, compared to a bimolecular addition reaction (eq 4). As mentioned above, the content of structure B increases with temperature, indicating that the activation energy of the abstraction reaction is greater than that of the addition reaction in the polymerization of DEPVE.

Radical Copolymerization of DEPVE with Acrylonitrile (AN) and Benzyl Methacrylate (BzMA). To see whether intramolecular hydrogen abstraction (eq 2) can participate in the copolymerization of DEPVE or not, we have examined copolymerizations with AN and BzMA. These electron-accepting comonomers were chosen because they are expected to show low reactivities toward strongly electron-deficient radical II. So if there is any participation of intramolecular hydrogen abstraction, such copolymerizations would give different composition curves from those observed in the copolymerizations of common alkyl vinyl ethers.

Figure 8 presents the copolymer composition curve obtained for the copolymerization of DEPVE (M_1) and AN (M_2) ([M_1] + [M_2] = 1.69 mol L^{-1}) with AIBN (2.00 × 10^{-2} mol L^{-1}) at 60 °C in benzene. Copolymer yields in all runs were controlled to be less than 10% by varying the polymerization time. The copolymer composition was determined from nitrogen content by elemental analysis. Application of the Kelen–Tüdos method[7] to the copolymerization results gave the monmomer reactivity ratios of r_1 = 0.06 and r_2 = 1.02. These values are close to r_1 = 0 and r_2 = 1.05 reported for the copolymerization of isobutyl vinyl ether (M_1) and AN (M_2).[8] Thus, the intramolecular hydrogen-abstraction reaction seems to make little contribution to the copolymerization of DEPVE with AN at 60 °C.

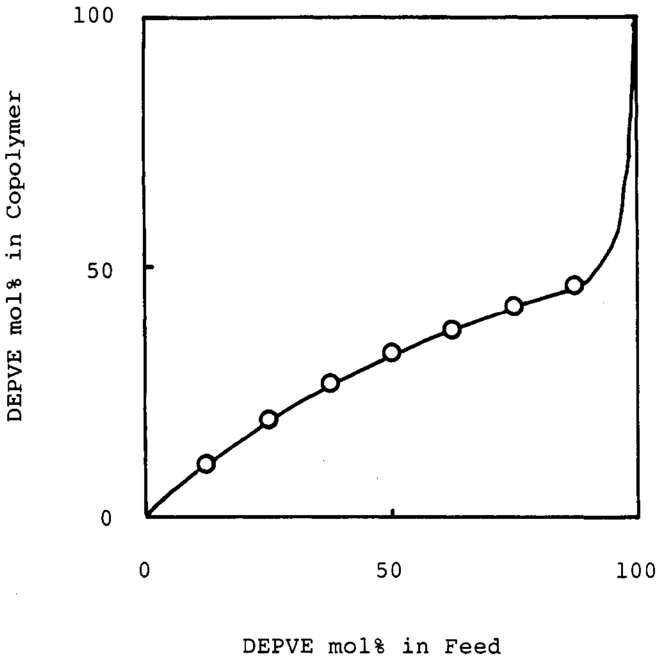


Figure 8. Copolymer composition curve for the copolymerization of DEPVE with AN at 60 °C in benzene.

Figure 9 shows the copolymer composition curve observed in the copolymerization of DEPVE (M_1) and BzMA (M_2) at 60 °C (with AIBN in benzene) and 130 °C (with DBPO in chlorobenzene). All copolymer yields were adjusted to be less than 10%. The composition of copolymers was calculated from the carbon content by elemental analysis. The composition curve at 60 °C is near to that for the copolymerization of a similar comonomer combination, ethyl vinyl ether and methyl methacrylate.[8] This indicates again little contribution of intramolecular hydrogen abstraction to this copolymerization at 60 °C. On the other hand, the copolymer formed at 130 °C was observed to contain considerably higher DEPVE monomer unit than that at 60 °C. Thus, the intramolecular hydrogen transfer in radical I can ultimately make some contribution at 130 °C.

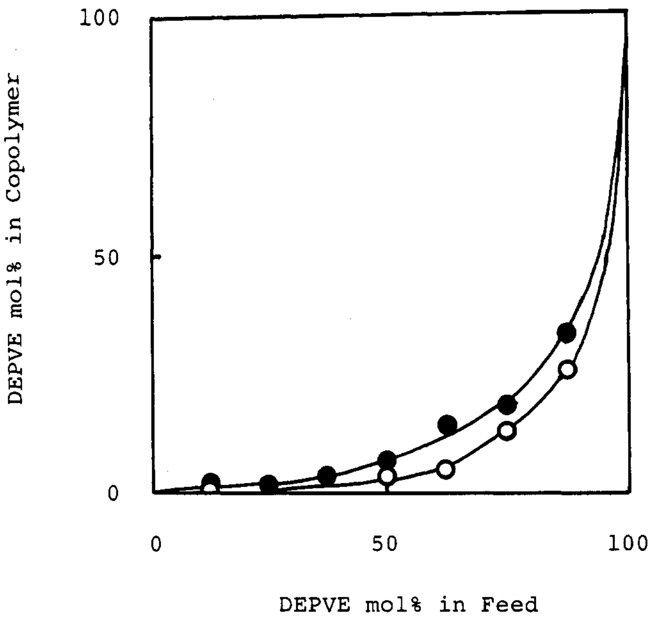


Figure 9. Copolymer composition curves for the copolymerization of DEPVE with BzMA at 60 °C in benzene (○) and at 130 °C in chlorobenzene (●).

Acknowledgment. We are grateful to Nitto Denco Co., Ltd., for NMR measurements.

References and Notes

(1) Matsumoto, A.; Oiwa, M. *Makromol. Chem., Rapid Commun.* **1983**, *4*, 277.
(2) Imoto, M.; Saotome, K. *J. Polym. Sci.* **1960**, *31*, 208.
(3) Cha, A.; Lee, J.-Y. *Macromolecules* **1983**, *16*, 150.
(4) Sato, T.; Takahashi, H.; Tanaka, H.; Ota, T. *J. Polym. Sci., Polym. Chem. Ed.* **1988**, *26*, 2839.
(5) Sawamoto, M.; Enoki, T.; Higashimura, T. *Macromolecules* **1987**, *20*, 1.
(6) Chalmers, W. M. *Can. J. Res.* **1986**, *7*, 464.
(7) Kelen, T.; Tüdos, F. J. *J. Macromol. Sci.-Chem.* **1981**, *A16*, 1283.
(8) *Polymer Handbook*, 2nd ed.; Bransrup, J., Immergut, E. H., Eds.; Wiley: New York, 1975; p II-188.