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Radical Group-Transfer Polymerization of 2-Thiocyanatoethyl Vinyl Ether

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ABSTRACT: 2-Thiocyanatoethyl vinyl ether (TCEVE), a vinyl ether, was observed to be polymerized in moderate yields with radical initiators such as dimethyl 2,2′-azobisisobutyrate (MAIB) and 2,2′-azobisisobutyronitrile. The rate (R_p) of polymerization of TCEVE with MAIB in benzene at 60 °C was given by $R_p = k[\mathrm{MAIB}]^{0.8}[\mathrm{TCEVE}]^{1.0}$. The overall activation energy of the polymerization was 105 kJ/mol. The number-average molecular weight ($\bar{M}_n$) of the resulting poly(TCEVE) was in the range of 1700−3600, corresponding to polymerization degrees of 13−27. $\bar{M}_n$ tended to decrease with increasing TCEVE concentration, suggesting chain transfer to the monomer. The IR, ^{1}H-, and ^{13}C-NMR spectra and the thermal degradation behavior of the radically formed poly(TCEVE) distinguishably differed from those of a cationically formed polymer and indicated that the radical polymerization of TCEVE propagates with transfer of the cyano group. Radical copolymerizations of TCEVE with some vinyl monomers were examined on the monomer reactivity ratios and structures of copolymers.

Introduction

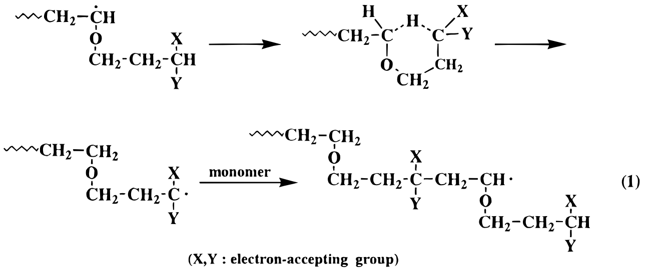
On one hand, with radical polymerization of vinyl ethers, it is difficult to yield high polymers because highly reactive propagating polymer radicals from vinyl ethers readily undergo chain transfer to monomer.[1] On the other hand, vinyl ethers, typical electron-donating monomers, are reported to be alternatively copolymerized with electron-accepting monomers such as maleic anhydride and ethyl α-cyanoacrylate.[2,3] So, vinyl ethers carrying a labile hydrogen and electron-accepting groups at a suitable position are predicted to be polymerized via a propagation mechanism involving intramolecular hydrogen-abstraction (addition-abstraction mechanism) as shown in Scheme 1.

In fact, the radical polymerizations of 3-cyano-3-ethoxycarbonylpropyl vinyl ether, 3,3-bis(ethoxycarbonyl)propyl vinyl ether, and 3,3-dicyanopropyl vinyl ether were observed to proceed via the addition-abstraction mechanism to yield polymers containing ether linkages in the main chain.[4−6]

The polymerization according to Scheme 1 is formally similar to the hydrogen-transfer polymerization of acrylamide and related monomers with base catalysts to yield polyamides.[7−9] Thus, the above radical polymerization via the addition-abstraction mechanism may be termed a radical hydrogen-transfer polymerization. The extension of the transfer of hydrogen to the transfer of other atoms or groups in radical polymerization can provide a new method to produce polymers with novel main chains.

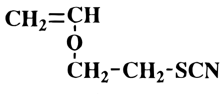
In the present paper, we have prepared 2-thiocyanatoethyl vinyl ether (TCEVE) as a suitable monomer for radical group-transfer polymerization and studied its radical polymerization behaviors. The present polymerization clearly differs in the propagation mode from the anionic group-transfer polymerization of acrylates and methacrylate with a silyl ketene acetal.[10]

Scheme 1



(X,Y : electron-accepting group)

Scheme 2



$CH_2{=}CH{-}O{-}CH_2{-}CH_2{-}SCN$

(TCEVE)

Experimental Section

Materials. TCEVE was prepared by the reaction of 2-chloroethyl vinyl ether (l.0 mol) with potassium thiocyanate (l.2 mol) in water for 12 h at 100 °C in the presence of tetra-*n*-butylammonium bromide as the phase-transfer catalyst. The crude TCEVE was purified by distillation as a colorless oil: 28% yield bp 91 °C. TCEVE thus obtained was miscible with the usual organic solvents except for alkanes such as cyclohexane and *n*-hexane. IR (neat): 2155 (ν_{CN}), 1620 ($\nu_{C=C}$) cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$, TMS): δ 3.22 (t, 2.0H, CH$_2$C**H**$_2$S), 4.00 (t, 2.0H, OC**H**$_2$CH$_2$), 4.11 (q, 1.0H, C**H**$_2$=CH), 4.23 (q, 1.0H, C**H**$_2$=CH), 6.46 (q, 1.0H, CH$_2$=C**H**). ^{13}C NMR (100 MHz, CDCl$_3$, TMS): δ 32.40 (CH$_2$CH$_2$S), 64.95 (O**C**H$_2$CH$_2$), 87.37 (**C**H$_2$=CH), 111.38 (CH$_2$S**C**N), 150.24 (CH$_2$=**C**H). Elemental Anal. Calcd for C_5H_7NOS: C, 46.51; H, 5.42; N, 10.85. Found: C, 46.38; H, 5.41; N, 10.86.

Dimethyl 2,2′-azobisisobutyrate (MAIB), 2,2′-azobisisobutyronitrile (AIBN), and benzoyl peroxide (BPO) were recrystallized from methanol. Di-*t*-butyl peroxide (DBPO) was purified by distillation. 2,2′-Azobis(2,4-dimethylvaleronitrile) (AVN) and SnCl$_4$ (Wako Pure Chemicals) were used as received. Benzene was treated with sulfuric acid and distilled. Chlorobenzene and ethyl acetate were used after distillations. Methyl methacrylate (MMA) and vinyl acetate (VAc) were treated with 5% NaOH aqueous solution, dried over CaCl$_2$, and distilled. Acrylonitrile (AN) was used after distillation.

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Table 1. Polymerization of TCEVE with Various Initiators

run	[TCEVE] (mol/L)	initiator (I)	[I] × 10^2 (mol/L)	solvent	temp. (°C)	time (h)	conv. (%)	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$	$\bar{M}_w/\bar{M}_n$
1	2.07	MAIB	5.00	benzene	60	20	49.5	3.4	5.2	1.5
2	2.75	MAIB	5.00	benzene	60	5	18.0	3.1	4.5	1.5
3	2.07	MAIB	5.00	benzene	60	5	18.2	3.2	4.7	1.5
4	1.38	MAIB	5.00	benzene	60	5	20.2	3.4	5.0	1.5
5	1.03	MAIB	5.00	benzene	60	5	20.7	3.3	4.8	1.5
6	2.07	AIBN	5.00	benzene	60	20	45.0	3.6	5.5	1.5
7	2.07	DBPO	5.00	chlorobenzene	120	20	25.9	1.8	2.2	1.2
8	2.07	BPO	5.00	benzene	60	20	5.5	1.8	3.3	1.8
9	2.07	AVN	5.00	benzene	30	20	7.5	3.4	5.2	1.5
10	0.52	MAIB	5.00	benzene	60	20	30.7	4.3	6.3	1.5
11	2.07	MAIB	5.00	benzene	hν^a	20	59.9	4.0	6.3	1.6
12	2.07	DBPO	5.00	benzene	hν^a	20	21.8	3.8	6.2	1.6
13	2.07	none		benzene	hν^a	20	1.8	3.1	4.9	1.6
14	2.07	$SnCl_4$	12.00	toluene	−55	24	35.2	10.1	26.3	2.6

[a] Photopolymerization at 19 °C.

Polymerization. The polymerization and copolymerization of TCEVE were carried out in a degassed and sealed tube. The resulting polymer was isolated by pouring the polymerization mixture into a large excess of cyclohexane containing a small amount of acetone, dried in a vacuum, and weighed.

Measurements. Gel permeation chromatograms (GPC) were recorded at 38 °C by a TOSO-HLC 802A instrument with tetrahydrofuran (THF) as the eluent. From the GPC results, the number-average ($\bar{M}_n$) and weight-average ($\bar{M}_w$) molecular weights of the resulting poly(TCEVE)s were estimated after calibration with polystyrene standards. ^{1}H- and ^{13}C-NMR spectra of the TCEVE monomer and the resulting polymers were obtained in $CDCl_3$ at 25 °C using a JEOL-400 (400 MHz) spectrometer with tetramethylsilane as the internal standard. IR spectra of TCEVE and the polymers were observed with a Perkin-Elmer 1600 FT-IR spectrometer. Dynamic thermogravimetry (TG) of the polymers was studied in N_2 (flow rate of 20 mL/min) with a Shimadzu TGA-50 thermogravimeter at a heating rate of 10 °C/min. Each run was terminated at 500 °C.

Results and Discussion

Polymerizations of TCEVE with Radical and Cationic Initiators. To check the polymerizability of TCEVE, its polymerization was examined with MAIB, AIBN, AVN, BPO, and DBPO as radical initiators and $SnCl_4$ as the cationic initiator. Table 1 summarizes the results observed. Although the radical initiators used could induce the polymerization of TCEVE, AIBN and MAIB as the azo-initiators were found to be more effective than BPO as the peroxide initiator (runs 1, 6, and 8). BPO may be consumed by nonradical reactions with the thiocyano group of TCEVE.

On one hand, photopolymerization of TCEVE with MAIB at room temperature showed a high polymer yield (59.9%, run 11). On the other hand, the photopolymerization without any initiator gave little yield (run 13), though thiocyanates such as phenyl, benzyl, and cyclohexyl thiocyanates are reported to be photosensitive.[11,12] $\bar{M}_n$ of radically formed poly(TCEVE)s was in the range of 1800−4300, corresponding to the degrees of polymerization of 14−33. TCEVE was also polymerized in a good yield using $SnCl_4$ as the cationic initiator (run 14).

Kinetic Study on the Polymerization of TCEVE with MAIB. The polymerization of TCEVE with MAIB was kinetically studied in benzene.

Figure 1 shows the time−conversion plots observed in the temperature range of 50−70 °C, keeping the concentrations of TCEVE and MAIB constant at 2.07 M and 50 mM, respectively. Thus, the polymer yield in the initial polymerization stage was found to linearly increase with time without any induction period. From the Arrhenius plot of the polymerization rate (R_p) estimated from the plots in Figure 1, the overall activation energy of the polymerization was calculated to be 105 kJ/mol. This value is fairly higher than those (ca. 84 kJ/mol) reported for the polymerizations of MMA and styrene (St) with AIBN,[13] although the activation energy of the decomposition of MAIB (117 kJ/mol) is reported to be rather lower than that of AIBN (126 kJ/mol).[14,15]

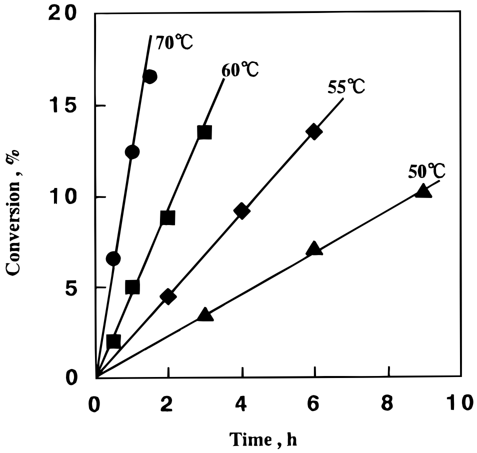


Figure 1. Time−conversion curves in the polymerization of TCEVE with MAIB at various temperatures in benzene. [TCEVE] = 2.07 M; [MAIB] = 5.00 × 10^{-2} M.

Figure 2 presents the relationship between R_p and the initiator concentration observed at 60 °C at a fixed monomer concentration (2.07 M). Thus, R_p increases in proportion to the 0.8 power of the initiator concentration. The 0.8 power observed here is considerably higher than the 0.5 one for the usual radical polymerization involving bimolecular termination. This may come from the complicated polymerization mechanism of the present system. The reason for the 0.8 power dependence is obscure at present.

Figure 3 illustrates the effect of the TCEVE concentration on R_p at 60 °C for a fixed MAIB concentration (50 mM). R_p is proportional to the 1.0 power of monomer concentration, similar to the usual radical polymerization.

From the above findings, R_p is given as follows: $R_p = k[\text{MAIB}]^{0.8}[\text{TCEVE}]^{1.0}$.

Characterization of the Resulting Poly(TCEVE). As mentioned above, TCEVE was found to be polymer-

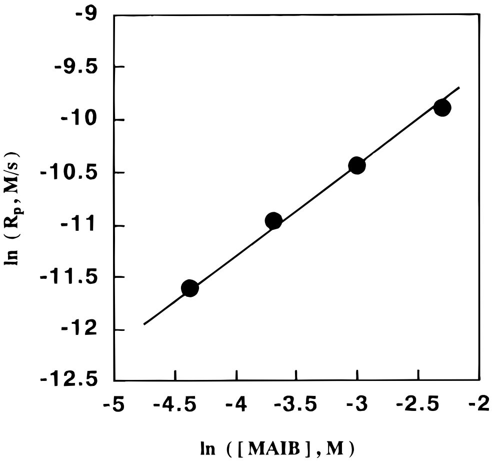


Figure 2. Dependence of the polymerization rate (R_p) on the MAIB concentration at 60 °C in benzene. [MAIB] = 5.00×10^{-2} M.

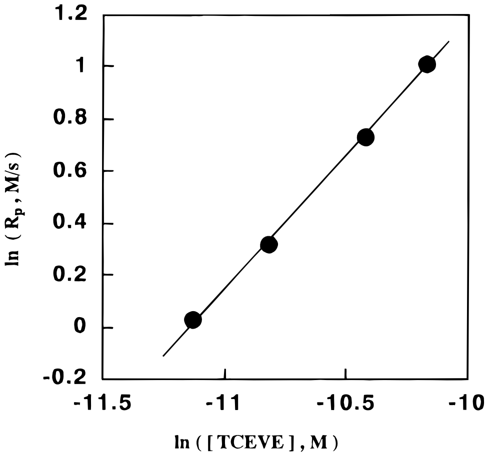


Figure 3. Dependence of the polymerization rate (R_p) on the TCEVE concentration at 60 °C in benzene. [TCEVE] = 2.07 M.

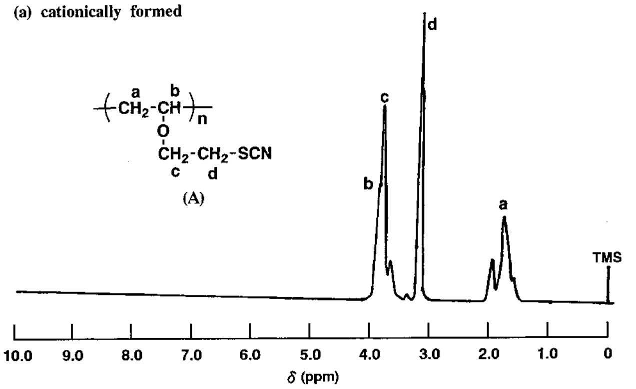
Table 2. Solubility of Poly(TCEVE)s at Room Temperature[a]

solvent	radical poly(TCEVE)	cation poly(TCEVE)
cyclohexane	×	×
n-hexane	×	×
toluene	×	×
benzene	△	×
dichloromethane	○	○
chloroform	○	○
ethyl acetate	○	×
acetone	○	○
methanol	×	×
THF	○	○
DMF	○	○
DMSO	○	○
MEK	○	○
acetonitrile	○	○
water	×	×

[a] ○, soluble; △, partiary soluble; ×, insoluble.

ized by both radical and cationic initiators. Table 2 compares the solubilities of radical and cationic poly(TCEVE)s. Radical poly(TCEVE) was soluble in chloroform, ethyl acetate, acetone, THF, methyl ethyl ketone (MEK), dimethyl formamide (DMF), dimethylsulfoxide (DMSO), and acetonitrile and was insoluble in water, methanol, and hydrocarbons such as hexane, cyclohexane, and toluene. It is noteworthy that the cationic polymer was insoluble in ethyl acetate which is a good solvent for the radical one.

(a) cationically formed



(b) radically formed

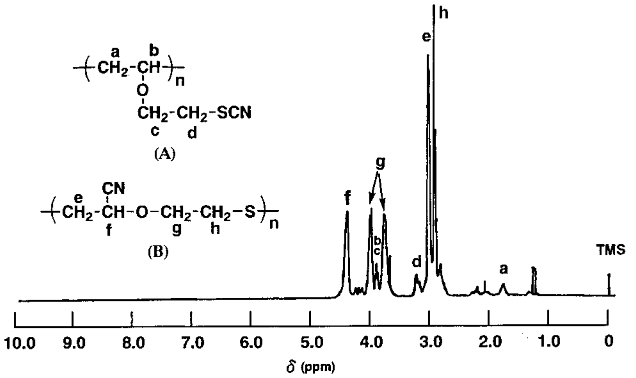


Figure 4. ^{1}H-NMR spectra of poly(TCEVE)s obtained in the (a) cationic and (b) radical polymerizations. Solvent: $CDCl_3$.

Table 3. Molecular Weights and Molecular Weight Distributions of Poly(TCEVE)

temp. (°C)	[MAIB] × 10^2 (mol/L)	[TCEVE] (mol/L)	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
50	5.00	2.07	3570	5290	1.48
55	5.00	2.07	3530	5160	1.46
60	5.00	2.07	3240	4860	1.50
70	5.00	2.07	1730	4220	2.44
60	1.25	2.07	3240	4790	1.48
60	2.50	2.07	3240	4780	1.47
60	10.00	2.07	3270	4860	1.49
60	5.00	1.03	3360	5130	1.53
60	5.00	1.38	3430	5180	1.51
60	5.00	2.75	2990	4480	1.50

Table 3 summarizes the molecular weights of poly(TCEVE)s formed under various conditions in the polymerization with MAIB in benzene. The molecular weight decreases with rising temperature. It tends to decrease with increasing monomer concentration, while it is almost independent of the initiator concentration. These findings suggest that the chain transfer to the monomer plays a significant role in the present polymerization. The $\bar{M}_n$ values are not so high and in the range of 1730–3570 (degree of polymerization = 13–27). The $\bar{M}_w/\bar{M}_n$ showed rather narrow values of about 1.5.

Figure 4 compares ^{1}H-NMR spectra of cationically (a) (run 14 in Table 1) and radically (b) (run 2 in Table 1) formed poly(TCEVE)s. The absorptions at 6–7 ppm due to vinyl protons in the monomer completely vanished, indicating that both the radical and cationic polymerizations of TCEVE proceed through opening of the double bond. The cationic polymerization of TCEVE is

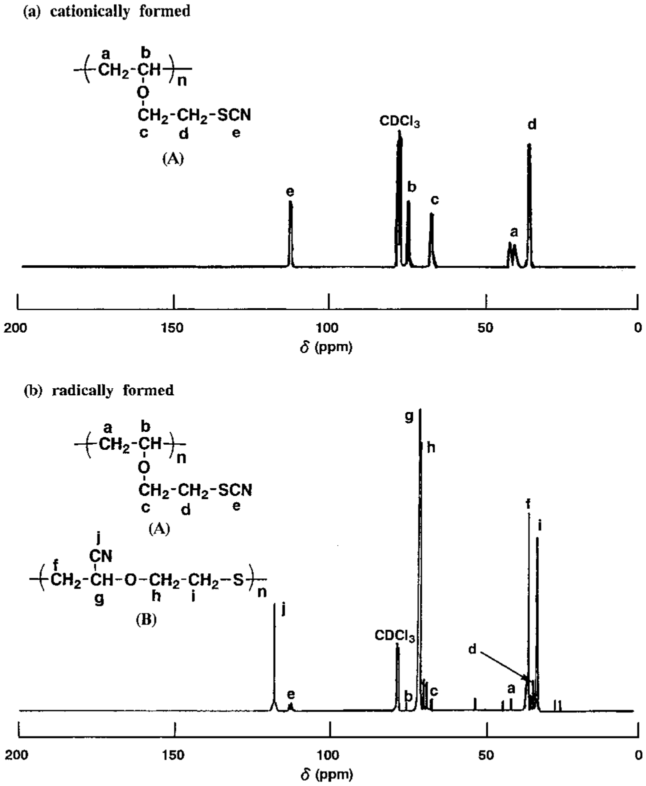
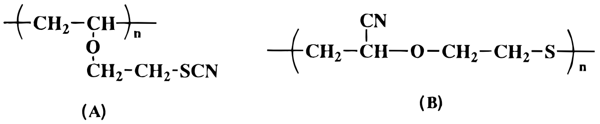


Figure 5. ^{13}C-NMR spectra of poly(TCEVE)s obtained in the (a) cationic and (b) radical polymerizations. Solvent: CDCl$_3$.

Scheme 3


$$\left(\mathrm{CH_2{-}CH}\right)_n,\ \mathrm{CH{-}O{-}CH_2{-}CH_2{-}SCN}\qquad \left(\mathrm{CH_2{-}\overset{CN}{CH}{-}O{-}CH_2{-}CH_2{-}S}\right)_n$$

considered to proceed via the usual vinyl polymerization to yield poly(TCEVE) of structure A. The spectrum (b) of the radical polymer is quite different from that (a) of the cationic polymer, revealing that the radical and cationic polymerizations of TCEVE proceed in different modes to give different polymer structures. The absorptions at 1.5−2.2 ppm due to the methylene protons in the polymer main chain of structure A almost disappeared in the spectrum of radical poly(TCEVE), although not completely. These observations imply that the radical polymerization of TCEVE propagates mainly with the transfer of the cyano group (eq 2), yielding a polymer of structure B. Thus, the radically formed poly(TCEVE) contains ether and thioether linkages in the main chain. The assignment of each peak in the spectra is notated by letters in the figure. The hydrogens of the oxymethylene group (−O−CH$_2$−) in structure B were observed to be magnetically unequivalent (Scheme 3).

Figure 5 presents ^{13}C-NMR spectra of cationic (a) and radical (b) polymers from TCEVE. Reflecting the different structures of cationic and radical poly(TCEVE)s, the two spectra are distinguishably different from each other. None of the absortions due to vinyl carbons were detected in both the spectra. Thus, neither the radical nor cationic poly(TCEVE)s were again shown to contain any vinyl group. Spectrum a is assignable to structure A, that is, a normal vinyl polymer of TCEVE. The thiocyanato carbon in the cationic poly(TCEVE) resonates at 112.5 ppm, similar to that of the TCEVE monomer. Compared with the SCN group, the absorption due to the cyano carbon of the radical polymer is shifted to rather a lower magnetic field (117 ppm) as shown in spectrum b, being assignable to structure B. The peak assignments are again shown by letters in the figure. A small peak due to the carbon of the intact thiocyanato group was still observed in spectrum b.

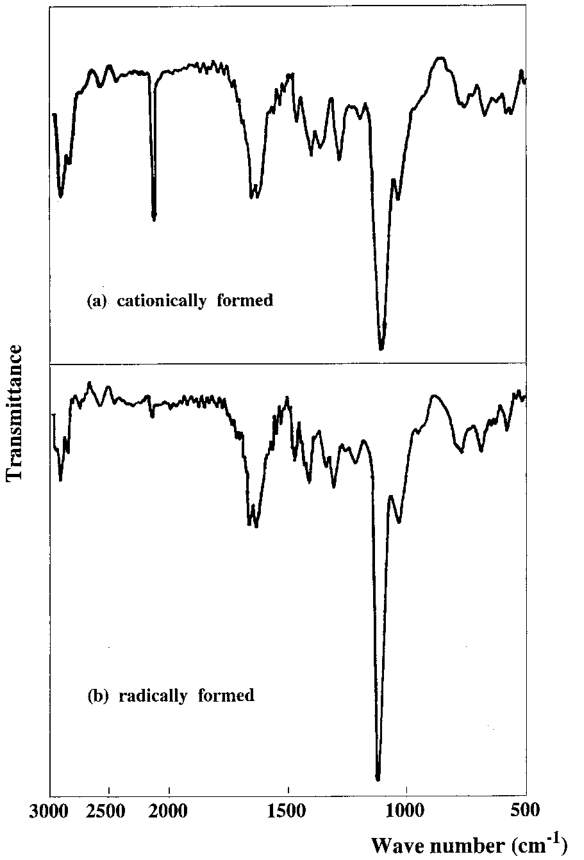


Figure 6. IR spectra of poly(TCEVE)s obtained in the (a) cationic and (b) radical polymerizations.

As expected from the above results, different IR spectra were observed for the cationic and radical poly(TCEVE)s as shown in Figure 6a,b. It is worth noting that the CN absorption of the radical polymer is much weaker compared to that of the cationic polymer. The CN absorption is known to be weakened by an α-alkoxy substituent group.[16] This is in conformity with the fact that structure A contains such a structure (−CH(CN)−O−CH$_2$−).

Thermal degradations of the cationic and radical poly(TCEVE)s were examined by thermogravimetry. TG and differential themogravimetric (DTG) curves of the cationic and radical polymers are shown in Figure 7a,b. Thus, the cationic polymer, on one hand, degradates by two steps. The residue at 500 °C was 30% of the initial polymer weight. On the other hand, the radical polymer degradates by one step. The residue at 500 °C was 14% of the initial polymer weight. These results also support the fact that the radical and cationic polymers have different structures.

Polymerization Mechanism. From the above observations, the radical polymerization of TCEVE proceeds with the transfer of the cyano group as follows (Scheme 4).

Intramolecular cyano group transfer occurs in the propagating radical (I) to yield a polymer thiyl radical (II) (eq 2) through a six-membered transition state. Thiyl radicals are generally known to be highly electron-

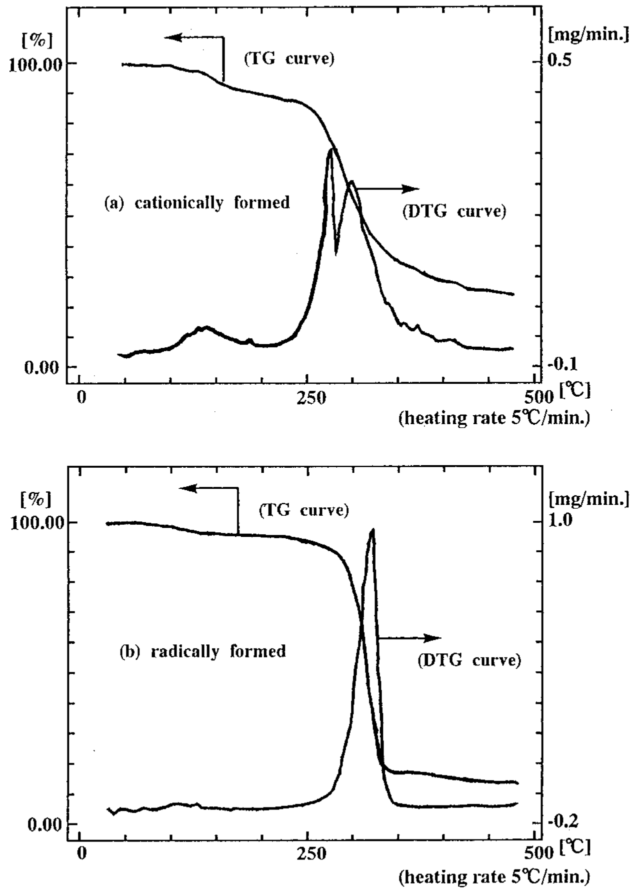


Figure 7. TG and DTG curves of poly(TCEVE)s obtained in the (a) cationic and (b) radical polymerizations.

accepting and to undergo exclusively double-bond addition without any hydrogen abstraction.[17-19] The resulting electron-attractive polymer thiyl radical readily adds the electron-rich double bond of another TCEVE monomer (eq 3).

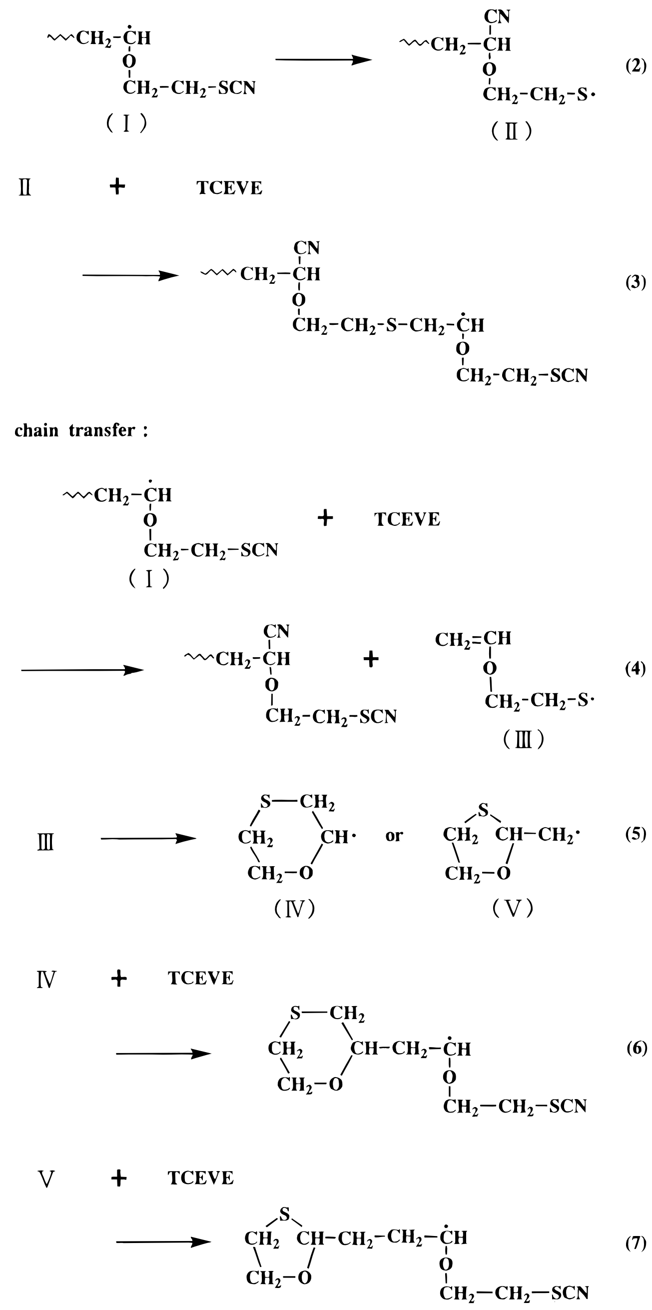
As stated above, the present polymerization involves chain transfer to the monomer. The chain transfer occurs through intermolecular attack of polymer radical I on the cyano group of the TCEVE monomer (eq 4). However, the resulting radical (III) is not considered to reinitiate the polymerization as such because ^{1}H- and ^{13}C-NMR spectra of the radical polymer showed no evidence for the existence of a C=C double bond in the polymer. Radical III may cyclize to a six- or five-membered ring, radical IV or V, which can reinitiate the polymerization (eqs 5 or 6).

As a conclusion, the radical polymerization of TCEVE propagates with intramolecular transfer of the cyano group to yield the following polymer ((VI) or (VII)), containing ether and thioether linkages in the main chain (Scheme 5): The present polymerization is a novel type of radical polymerization which can be termed a radical group-transfer polymerization.

Radical Copolymerization of TCEVE with Some Vinyl Monomers. To see whether intramolecular cyano group transfer can also participate in the radical copolymerization, the copolymerization of TCEVE was examined with VAc, AN, and MMA in benzene at 60 °C. The copolymer yields in all runs were controlled to be less than 10%. The copolymer compositions were determined from nitrogen contents by elemental analysis.

propagation :

Scheme 4



Scheme 5

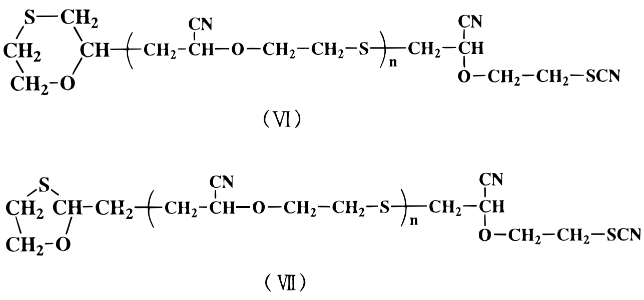


Figure 8 illustrates the copolymer composition curve observed for the copolymerization of TCEVE (M_1) and VAc (M_2) in benzene at 60 °C, where $[M_1] + [M_2] = 1.00$ M and [MAIB] = 50 mM. The monomer reactivity ratios were estimated to be $r_1 = 2.63$ and $r_2 = 0.92$ according to the curve-fitting method based on a nonlinear least-squares analysis.[20] The dashed line in Figure 8 shows the copolymer composition curve from the reported values ($r_1 = 0$ and $r_2 = 3.7$) for the copolymerization of

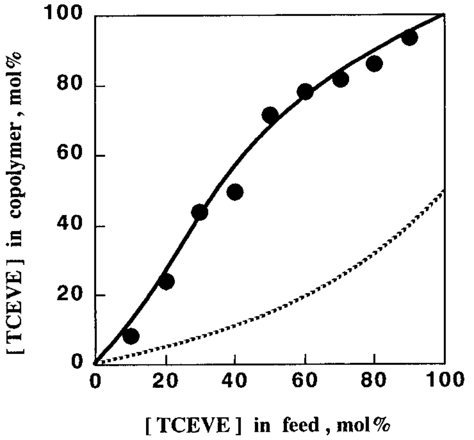


Figure 8. Copolymer composition curves for the copolymerization of TCEVE (M_1) and VAc (M_2) in benzene at 60 °C (●) and for that of *n*-BVE (M_1) and VAc (M_2) at 50 °C (- - -).

n-butyl vinyl ether (*n*-BVE) (M_1) and VAc (M_2) at 50 °C.[21] Such a higher reactivity of TCEVE compared to *n*-BVE reflects a significant contribution of group-transfer propagation of TCEVE in the copolymerization with VAc. Further, the product (r_1r_2) of r_1 and r_2 for the copolymerization of TCEVE and VAc is over unity. The r_1r_2 value is rarely observed in usual radical copolymerizations of vinyl monomers in which the propagating radicals are generally derived from the vinyl groups to be attacked. As described above, however, the electron-donating vinyl group of TCEVE is first attacked and then the electron-accepting thiyl radical (II) formed by cyano group transfer acts as the M_1 radical. This is responsible for the above results that the r_1r_2 value is larger than unity and TCEVE shows much higher reactivity than *n*-BVE in the copolymerization with VAc.

The copolymer formed at the equimolar feed composition of TCEVE and VAc was analyzed by ^{13}C-NMR spectroscopy. Figure 9a shows an expanded ^{13}C-NMR spectrum of the region of the nitrile carbon resonance. On one hand, peak b is assignable to the nitrile carbon in structure B formed via the cyano group transfer. On the other hand, peak a, due to the nitrile carbon in structure A, almost disappeared. Thus, TCEVE was found to be incorporated as structure B in the copolymer, indicating that TCEVE propagates via the group-transfer mechanism in the copolymerization with VAc. The propagating radical of TCEVE is an electron-accepting thiyl radical (II) in the polymerization via the group-transfer mechanism. The relative reactivity of the *p*-chlorophenylthiyl radical toward isobutyl vinyl ether (IBVE) and VAc is reported to be 3.89 at room temperature.[17] This value is comparable to $r_1 = 2.63$ obtained in the above copolymerization.

Figure 10 presents the copolymer composition curve obtained for the copolymerization of TCEVE (M_1) and AN (M_2) ($[M_1] + [M_2] = 1.00$ M) with MAIB (50 mM) at 60 °C in benzene. The application of the curve-fitting method to the results gave monomer reactivity ratios of $r_1 = 0.14$ and $r_2 = 0.50$. For comparison, the copolymer composition curve ($r_1 = 0$ and $r_2 = 1.05$) reported for the copolymerization of isobutyl vinyl ether (IBVE) (M_1) and AN (M_2) at 50 °C is shown together by the dashed line in the figure.[21] TCEVE was observed again to be more incorporated in the copolymer than IBVE in the copolymerization with AN.

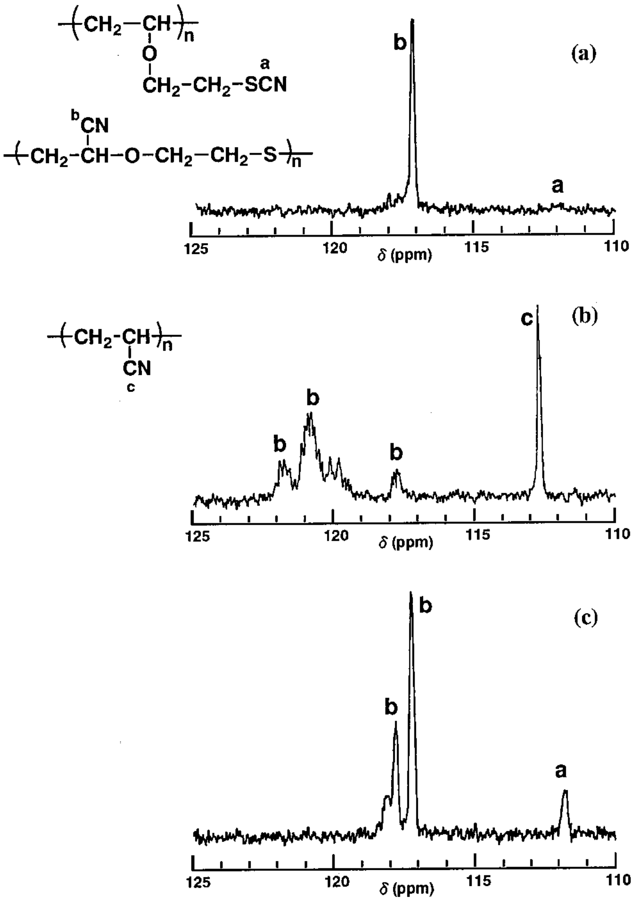


Figure 9. Expanded ^{13}C-NMR spectra of the nitrile carbon resonance region of (a) copoly(TCEVE−VAc) formed in a 0.5 feed composition of TCEVE at 60 °C, (b) copoly(TCEVE−AN) formed in a 0.5 feed composition of TCEVE at 60 °C, and (c) copoly(TCEVE−MMA) formed in a 0.8 feed composition of TCEVE at 60 °C.

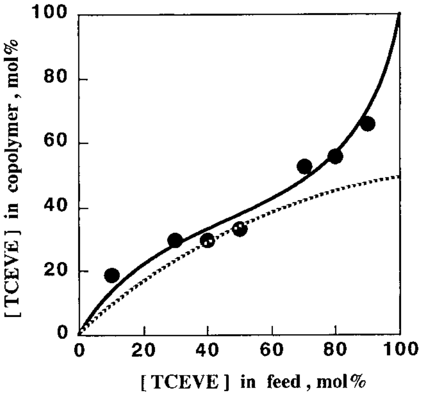


Figure 10. Copolymer composition curves for the copolymerization of TCEVE (M_1) and AN (M_2) in benzene at 60 °C (●) and for that of IBVE (M_1) and AN (M_2) at 50 °C (- - -).

Figure 9b presents an expanded ^{13}C-NMR spectrum of the region of nitrile carbon resonance of the copolymer formed at the equimolar feed composition of TCEVE and AN in benzene at 60 °C. The sharp peak (c) at 112.8 ppm is assignable to the nitrile group of AN in the copolymer. No peak due to the nitrile carbon in structure A was observed near 112 ppm. Thus, TCEVE was observed to be incorporated exclusively as structure B in the copolymer with AN, indicating that the thiyl radical (II) also acts as the propagating radical of TCEVE in the copolymerization with AN, a strongly electron-accepting conjugative monomer. The relative ratio of 0.39 is reported for the reactivity of the *p*-

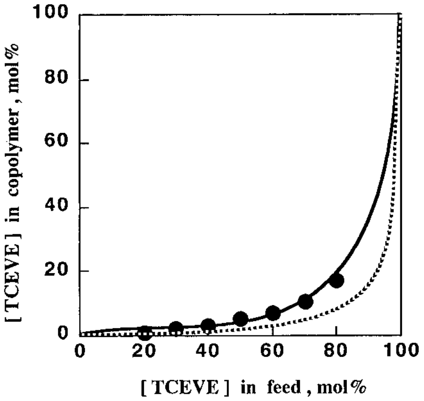


Figure 11. Copolymer composition curves for the copolymerization of TCEVE (M_1) and MMA (M_2) in benzene at 60 °C (●) and for that of EVE (M_1) and MMA (M_2) at 60 °C (- - -).

chlorophenylthiyl radical toward IBVE and AN.[17] Again, the value is comparable to r_1 of 0.14 in the TCEVE−AN system.

Figure 11 shows the copolymer composition curve observed in the copolymerization of TCEVE (M_1) and MMA (M_2) at 60 °C in benzene, together with that (dashed line) reported for the copolymerization of ethyl vinyl ether (EVE) (M_1) and MMA (M_2) at 60 °C ($r = 0.01$ and $r_2 = 37$).[21] According to the curve-fitting method, the monomer reactivity ratios were estimated to be $r_1 = 0.06$ and $r_2 = 20$. Thus, TCEVE was observed to be more incorporated in the copolymer compared to EVE in the EVE/MMA system, indicating some participation of the cyano group-transfer mechanism (eq 2) in the radical copolymerization of TCEVE with MMA.

Figure 9c shows an expanded ^{13}C-NMR spectrum of the nitrile carbon resonance region of the copolymer formed for a 0.80 mol fraction of TCEVE in the feed. A comparison of peak areas reveals that 92% of TCEVE monomer units are incorporated as structure B in the copolymer. It is noteworthy that TCEVE propagates also mainly with cyano group transfer in the copolymerization with MMA, a conjugative and reactive monomer. Compared with $r_1 = 0.06$ in the above TCEVE−MMA copolymerization, a similar value of 0.04 is reported as the relative reactivity ratio of the *p*-chlorophenylthiyl radical toward IBVE and MMA.[17]

Conclusions

TCEVE, a vinyl ether, is readily polymerized with radical azo-initiators such as MAIB and AIBN. The rate (R_p) of polymerization of TCEVE with MAIB in benzene at 60 °C is given by $R_p = k[\text{MAIB}]^{0.8}[\text{TCEVE}]^{1.0}$. The number-average molecular weight ($\bar{M}_n$) of the resulting poly(TCEVE) is in the range of 1700−3600, corresponding to polymerization degrees of 13−27. $\bar{M}_n$ tends to decrease with increasing TCEVE concentration, suggesting chain transfer to the monomer. The radical polymerization of TCEVE propagates with the transfer of the cyano group (via the group-transfer mechanism) to yield the polymer containing ether and thioether linkages in the main chain, which is quite different in the structure from poly(TCEVE) formed by vinyl cationic polymerization. TCEVE is also incorporated mainly through the group-transfer mechanism in the radical copolymerizations of TCEVE with VAc, AN, and MMA.

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