

Synthesis of 5-Vinyl-*m*-Phenylene-*m'*-Phenylene-32-Crown-10 and Its Radical Polymerization Behavior

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ABSTRACT: Synthesis of a vinyl monomer, containing a 32-membered crown ether unit (VCE) as a pendant group, was achieved by using tetra(ethylene glycol) dichloride, resorcinol, and 3,5-dihydroxyacetophenone as starting materials. The product was identified by means of FTIR and ¹H-NMR. It was found that this monomer readily polymerizes by the conventional radical initiator 2,2'-azobisisobutyronitrile (AIBN) to afford a polymer whose number-average molecular weight is 36 kg/mol; however, the final conversion of the polymer was < 80%. The results of the copolymerization of VCE with styrene (ST) or acrylonitrile (AN) are also discussed. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 84: 2372–2379, 2002

Key words: vinyl crown ether; radical polymerization; copolymerization; styrene; acrylonitrile

INTRODUCTION

Tremendous efforts have been made to synthesize polymeric crown ethers,^{1–10} because of their peculiar property of complex formation with diversified metal cations. As functional polymeric materials, polymeric crown ethers have many advantages over their corresponding monomeric analogs.^{11–17} Polymeric crown ethers are easily recoverable after use but also show excellent selectivity for cation binding, which is not observed in monomeric analogs because of the potential to form 2 : 1-type complexes (two crown ether rings to one cation) with particular metal ions whose radii are a little larger than the cavity radius of the crown ether ring.^{18,19}

In this study, we report the results of 5-vinyl-*m*-phenylene-*m'*-phenylene-32-crown-10 (VCE) synthesis and its radical polymerization behavior.

EXPERIMENTAL

Materials

Tetra(ethylene glycol), 3,5-dihydroxyacetophenone, resorcinol, tetrabutylammonium iodide (TBAI), and *p*-toluenesulfonic acid monohydrate (Aldrich) were used as received. 2,2'-Azobisisobutyronitrile (AIBN) was recrystallized from acetone. Styrene (ST) and acrylonitrile (AN) were successively washed with aqueous sodium hydroxide solution and water and then dried with anhydrous magnesium sulfate and purified by distillation under reduced pressure, in the presence of calcium hydride. Tetra(ethylene glycol) dichloride was prepared according to the literature.²⁰

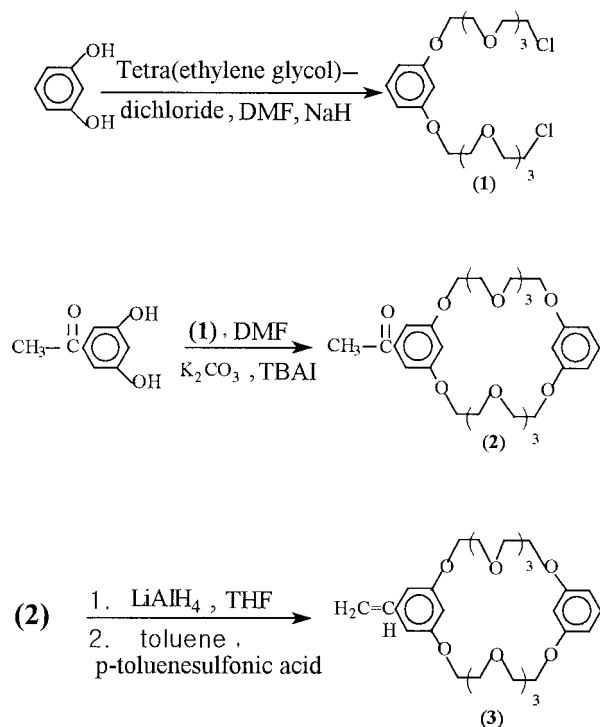
Measurements

A Nicolet model 520 infrared spectrometer was used for infrared spectroscopy. ¹H-NMR spectra of the polymers were recorded by a Bruker 250 MHz NMR spectrometer by using CDCl₃ as solvent. Tetramethylsilane was used as the internal standard. The number-average molecular weights of polymers

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Scheme 1 Synthetic route of VCE monomer.

were determined by GPC (Spectra Physics SP 8430 RI detector) using THF as an eluant (flow rate: 1 mL/min; column: 10^3 , 10^4 , 10^5 in series). Polystyrene was used as the calibration standard. The DSC measurements were done with a Shimadzu DSC-50 at a scan rate of $10^\circ\text{C}/\text{min}$. Thermogravimetric analyses were performed on a Shimadzu TGA-50 at a scan rate of $10^\circ\text{C}/\text{min}$ in N_2 atmosphere. Mass spectra were obtained with a Shimadzu QP5050A GC/MS. Elemental analyses were performed by Organometallic Chemistry Laboratory, Inha University.

VCE Monomer Synthesis

VCE monomer was synthesized by using tetra(ethylene glycol) dichloride, resorcinol, and 3,5-dihydroxyacetophenone as starting materials via 5-acetyl-*m*-phenylene-*m'*-phenylene-32-crown-10 (2), as shown in Scheme 1.

Synthesis of 5-Acetyl-*m*-Phenylene-*m'*-Phenylene-32-Crown-10 (2)

A mixture of compound (1) (8.13 g, 16.3 mmol), which was prepared according to the literature,²¹ and 3,5-dihydroxyacetophenone (2.48 g, 16.3 mmol) in DMF (total volume, 90 mL) was slowly added to 800 mL DMF where K_2CO_3 (22.5 g) and TBAI (30 mg) were suspended. The reaction mix-

ture was then allowed to stand for 5 days at 110°C , while keeping agitation. After the solvent was evaporated, the residue was extracted with chloroform and the product was separated by silica gel column chromatography by using ethyl acetate/*n*-hexane (v/v: 3/1) as eluant, which gave 2.5 g (26.5%) of oily product, 5-acetyl-*m*-phenylene-*m'*-phenylene-32-crown-10 (2).

IR (NaCl): 2868 and 2930 (C—H) 1684 (C=O), 1127 (C—O—C) cm^{-1} . $^1\text{H-NMR}$ (CDCl_3) δ (ppm): 2.50 (s, 3H), 3.65 (m, 16H), 3.82 (m, 8H), 4.05 (m, 8H), 6.45–6.65 (m, 4H), 7.06 (m, 3H). MS (EI) m/z (rel. int.): 578 [M]⁺ (43%), 563 [$\text{M}-\text{CH}_3$]⁺ (3.4%), 429 [$\text{M}-\text{C}_{17}\text{H}_{17}\text{O}_3$]⁺ (2.5%), 179 [$\text{M}-\text{C}_{20}\text{H}_{31}\text{O}_8$]⁺ (14.6%), 137 [$\text{M}-\text{C}_{22}\text{H}_{33}\text{O}_9$]⁺ (26.1%), 43 [$\text{C}_2\text{H}_3\text{O}$]⁺ (100%). ANAL. calcd for $\text{C}_{30}\text{H}_{42}\text{O}_{11}$: C, 62.27; H, 7.32. Found: C, 62.16; H, 7.27.

Synthesis of 5-(1'-Hydroxyethyl)-*m*-Phenylene-*m'*-Phenylene-32-Crown-10

Compound (2) was converted to 5-(1'-hydroxyethyl)-*m*-phenylene-*m'*-phenylene-32-crown-10 by reduction with lithium aluminum hydride as follows. Lithium aluminum hydride (0.50 g, 13 mmol) was slowly added to a stirred solution of (2) (2.0 g, 3.5 mmol) in 30 mL THF and stirred for 3 h at 0°C . The solution was poured into a mixture of ice and water and neutralized with dilute hydrochloric acid. The mixture was then extracted with chloroform, followed by drying over anhydrous sodium sulfate. The oily residue was then allowed to stand for crystallization and was followed by washing with ethyl ether, which gave 1.8 g (89.5%) of 5-(1'-hydroxyethyl)-*m*-phenylene-*m'*-phenylene-32-crown-10. mp: $76.5\text{--}77.7^\circ\text{C}$.

IR (NaCl): 3454 (O—H), 2868 and 2928 (C—H), 1127 (C—O—C) cm^{-1} . $^1\text{H-NMR}$ (CDCl_3) δ (ppm): 1.3 (d, 3H, $J = 6.4$ Hz), 2.68 (s, 1H), 3.63 (m, 16H), 3.74 (m, 8H), 4.03 (m, 8H), 4.65 (q, 1H, $J = 6.4$ Hz), 6.42 (m, 6H), 7.06 (t, 1H). MS (EI) m/z (rel. int.): 580 [M]⁺ (60.2%), 562 [$\text{M}-\text{H}_2\text{O}$]⁺ (8.0%), 181 [$\text{M}-\text{C}_{20}\text{H}_{31}\text{O}_8$]⁺ (11.5%), 163 [$\text{M}-\text{C}_{20}\text{H}_{29}\text{O}_7$]⁺ (34.5%), 45 [$\text{C}_2\text{H}_5\text{O}$]⁺ (100%). ANAL. calcd for $\text{C}_{30}\text{H}_{44}\text{O}_{11}$: C, 62.05; H, 7.64. Found: C, 61.98; H, 7.60.

Synthesis of 5-Vinyl-*m*-Phenylene-*m'*-Phenylene-32-Crown-10 (3)

5-(1'-Hydroxyethyl)-*m*-phenylene-*m'*-phenylene-32-crown-10 was converted to VCE monomer (3) in the presence of *p*-toluenesulfonic acid as follows. To a solution of 5-(1'-hydroxyethyl)-*m*-phenylene-*m'*-phenylene-32-crown-10 (2.5 g, 4.3

mmol) in 250 mL toluene was added a trace of *p*-toluenesulfonic acid. The mixture was refluxed with removal of water for 8 h and then cooled. After toluene was evaporated, the components of the mixture were separated by silica gel column chromatography. The yield of the final stage in VCE monomer synthesis was 61.8% (1.5 g). mp: 47.1–48.3°C.

IR (NaCl): 2880 and 2918 (C—H) 1596 (C=C), 1127 (C—O—C) cm^{-1} . $^1\text{H-NMR}$ (CDCl_3) δ (ppm): 3.66 (m, 16H), 3.76 (m, 8H), 4.01 (m, 8H), 5.15 (*trans*, d, 1H), 5.63 (*cis*, d, 1H), 6.35–6.55 (m, 7H), 7.06 (t, 1H). MS (EI) m/z (rel. int.): 562 $[\text{M}]^+$ (29.4%), 429 $[\text{M}-\text{C}_6\text{H}_{13}\text{O}_3]^+$ (3.4%), 207 $[\text{M}-\text{C}_{18}\text{H}_{27}\text{O}_7]^+$ (16.3%), 163 $[\text{M}-\text{C}_{20}\text{H}_{31}\text{O}_8]^+$ (40.2%), 137 $[\text{M}-\text{C}_{22}\text{H}_{33}\text{O}_8]^+$ (59.8%), 45 $[\text{C}_2\text{H}_5\text{O}]^+$ (100%). ANAL. calcd for $\text{C}_{30}\text{H}_{42}\text{O}_{10}$: C, 64.04; H, 7.52. Found: C, 63.93; H, 7.60.

Polymerization of VCE

A toluene (0.26 mL) solution containing 50 mg VCE and 0.89 mg AIBN was sealed off after repeated degassing on a vacuum line. Then, the ampoule was allowed to stand for 24 h at 60°C, followed by termination by addition of methanol. The precipitated polymer was purified by reprecipitation in methanol. The yield of the polymer was 23 mg (46% conversion) after drying overnight under reduced pressure at room temperature. Glass transition temperature (T_g) was 3°C. TGA was 10% weight loss at 396°C in N_2 atmosphere.

Copolymerization of VCE with ST or AN

Copolymerizations of VCE with ST or AN were performed under various monomer feed ratios in toluene at 60°C. Yields of copolymers and their compositions were determined by gravimetry and $^1\text{H-NMR}$ spectroscopy, respectively.

RESULTS AND DISCUSSION

VCE Monomer Synthesis

5-Acetyl-*m*-phenylene-*m'*-phenylene-32-crown-10 (Scheme 1) was prepared via reaction of 3,5-dihydroxyacetophenone with *m*-bis(11-chloro-3,6,9-trioxaundecyloxy)benzene (1) under highly diluted conditions with K_2CO_3 in DMF using TBAI as a phase transfer catalyst. Reduction of compound (2) with the LiAlH_4 in THF, followed by dehydration in the presence of a trace of *p*-toluenesulfonic acid, afforded vinyl monomer containing

crown ether unit as a pendant group, 5-vinyl-*m*-phenylene-*m'*-phenylene-32-crown-10 (3). The molecular structure of VCE monomer was identified by $^1\text{H-NMR}$ spectroscopy (Fig. 1). The presence of the signals of vinyl protons ($=\text{CH}_2$) at 5.15 and 5.63 ppm, signals of α,α' - OCH_2 , β,β' - OCH_2 , and γ,γ' , δ,δ' - OCH_2 protons at 4.01, 3.76, and 3.66 ppm, signals of the aromatic and vinyl ($=\text{CH}$) protons at 7.06, 6.51, and 6.40 ppm, reveals that VCE monomer was duly obtained from this synthesis. The VCE monomer is soluble in methanol and toluene but insoluble in *n*-hexane.

Polymerization of VCE

The polymerization of VCE in toluene was carried out at 60°C for 24 h by using AIBN as an initiator. The final value of percentage conversion in this system is always < 50%, implying that the radical initiator is exhausted before the monomer is fully consumed. The number-average molecular weight, obtained at 46% conversion, has a value of 36 kg/mol. Comparison of the $^1\text{H-NMR}$ spectrum of poly(VCE) with that of monomeric VCE clearly shows that the signals due to vinyl protons at 5.15 ppm disappeared and the appearance of new signals at 1.0–2.0 ppm due to methylene and methine protons of the polymer main chain appeared with a shift of the aromatic signals because of the protons of crown ether unit from 6.51 to 5.72 (2H) and 6.07 (1H) ppm during the course of the polymerization reaction, as shown in Figure 2. It is thought that the shift is probably caused by the shielding effect of proximate crown ether rings. Meanwhile, the signal due to aromatic proton at 7.06 ppm is unaffected by the polymerization. It was found that the polymer is soluble in toluene and THF but insoluble in methanol and *n*-hexane.

Copolymerization of VCE with ST or AN

Figure 3 shows time–conversion curves of the copolymerization of VCE (M_2) with ST (M_1) carried out in the presence of various initiator concentrations. A dead-end polymerization is also observed in the copolymerization of VCE with ST. The highest value of final conversion was < 85%. It is evident that the rate of copolymerization increases as initiator concentration increases and as the mole fraction of VCE in the monomer feed increases, as shown in Figure 4.

Figure 5 shows the $^1\text{H-NMR}$ spectrum of poly(ST-*co*-VCE). This reveals that the signals at

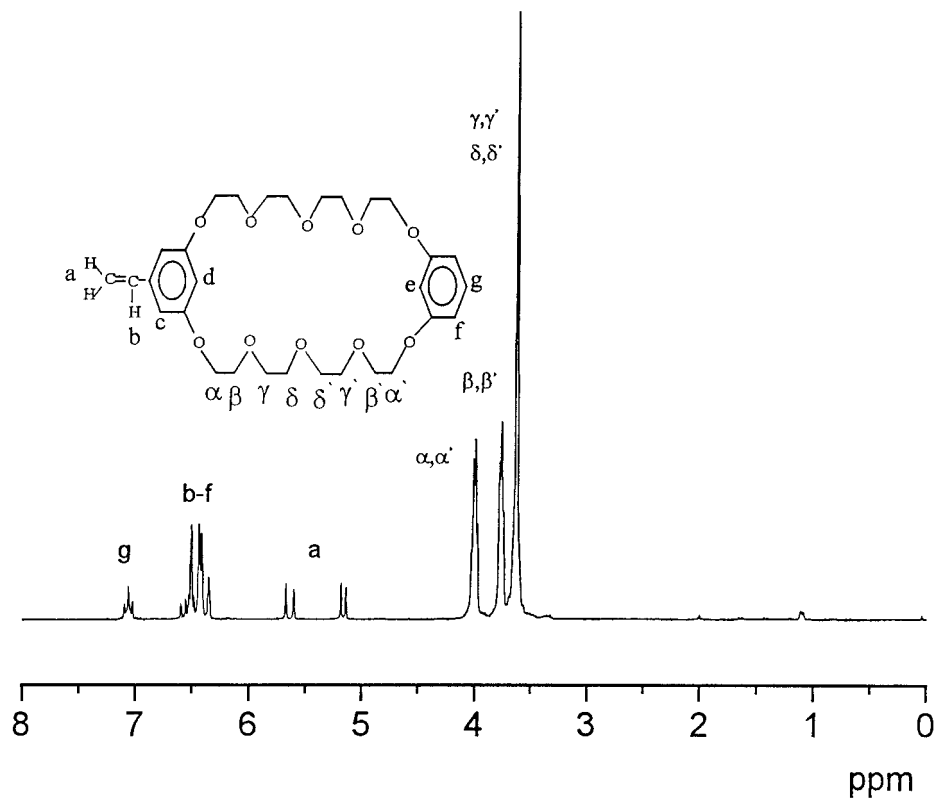


Figure 1 $^1\text{H-NMR}$ spectrum of VCE monomer (solvent CDCl_3).

5.72 and 6.07 ppm due to aromatic protons of the crown ether unit are rapidly reduced as the mole fraction of ST in the monomer feed increases.

Thus, the copolymer composition was determined by means of $^1\text{H-NMR}$ spectroscopy on the basis of the following equation. Polymer samples

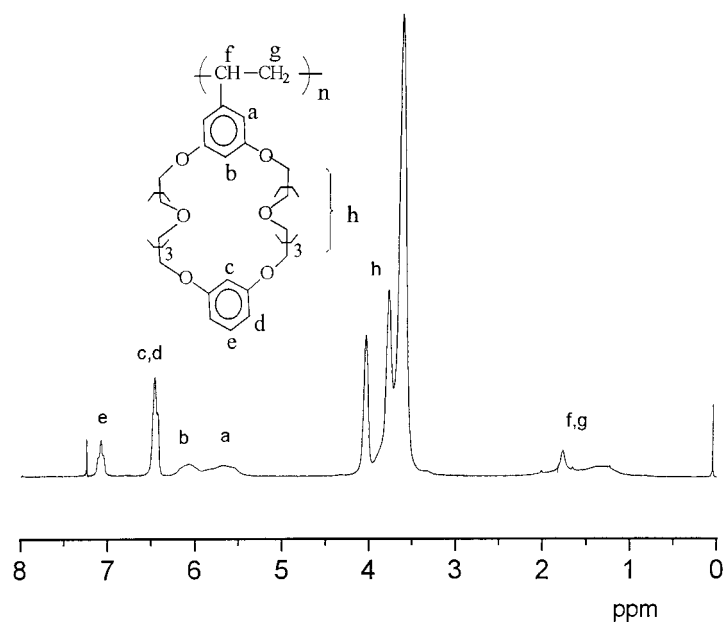


Figure 2 $^1\text{H-NMR}$ spectrum of poly(VCE) (solvent CDCl_3).

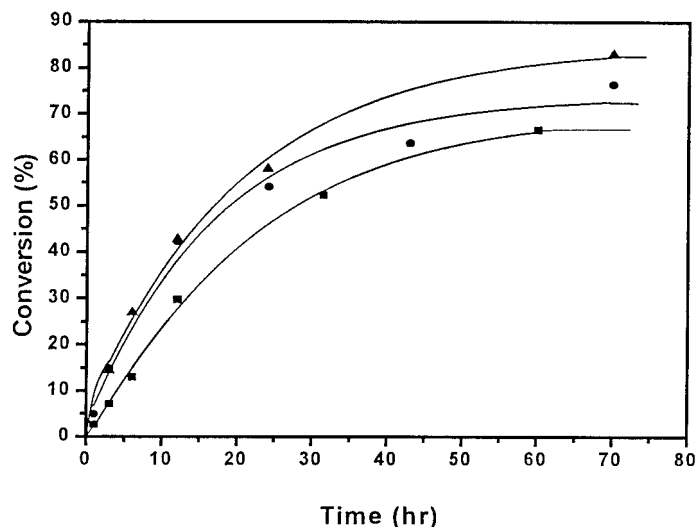


Figure 3 Time-conversion curves of copolymerization of VCE (M_2) with styrene (M_1) in the presence of various initiator concentrations. $[M_1] + [M_2] = 0.5252M$, monomer feed in molar ratio: $M_1/M_2 = 7/3$, $[I]$: $\blacktriangle 3.14 \times 10^{-2}M$, $\bullet 1.57 \times 10^{-2}M$, $\blacksquare 7.8 \times 10^{-3}M$.

whose conversions were $< 10\%$ were used in the determination of the reactivity ratios:

$$\frac{m_{ST}}{n_{VCE}} = \frac{32x - 7y}{5y}$$

In the equation, m and n denote the number of ST and VCE units in the copolymer, respectively, and x is the area of the signals which are proportional to the number of aromatic protons associated with the benzene ring unit of ST (see

Fig. 5, signal f, 6.8–7.2 ppm) and the crown ether (signals a–e, 5.5–7.1 ppm) unit, and y is the area of the signals (h) which are proportional to the number of methylene protons associated with the crown ether unit of VCE (3.5–4.2 ppm), respectively.

The dependence of the polymer composition as a function of the monomer feed ratio is shown in Figure 6. The reactivity ratios of VCE (r_2) and ST (r_1), determined by Fineman–Ross method, gave values of $r_1 = 1.6$ and $r_2 = 0.6$, respectively. The

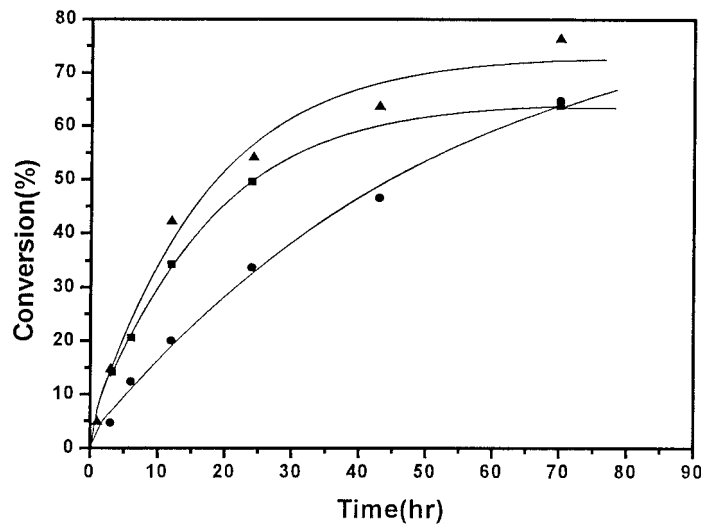


Figure 4 Time-conversion curves of copolymerization of styrene (M_1) with VCE (M_2). $[M_1] + [M_2] = 0.5252M$, $[I] = 1.57 \times 10^{-2}M$. Monomer feed in molar ratio: $\blacktriangle M_1/M_2 = 7/3$, $\blacksquare M_1/M_2 = 5/5$, $\bullet M_1/M_2 = 9/1$.

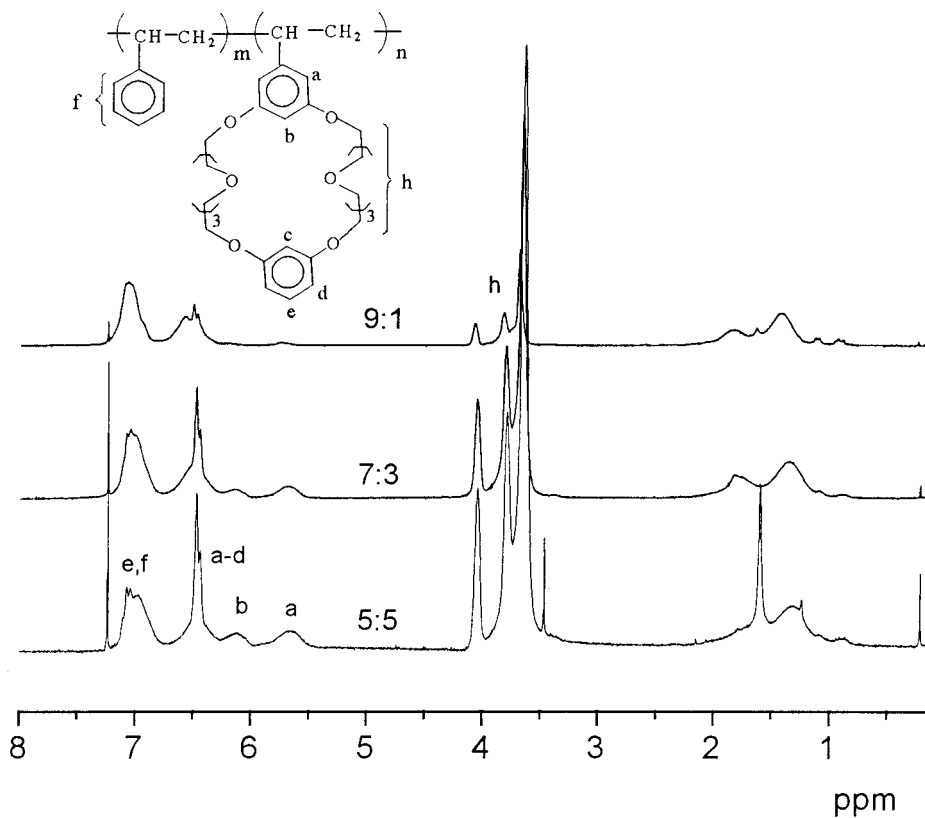


Figure 5 $^1\text{H-NMR}$ spectrum of poly(styrene-co-VCE) (solvent CDCl_3). Monomer feed in molar ratio of ST/VCE: 9/1, 7/3, 5/5.

copolymer is soluble in toluene and THF, but insoluble in methanol and *n*-hexane.

Copolymerization of VCE (M_2) with AN (M_1) was also carried under the same conditions as

that of the copolymerization of VCE with ST. A dead-end polymerization was also observed in this copolymerization system and the final conversion was always $< 55\%$. The rate of copolymer-

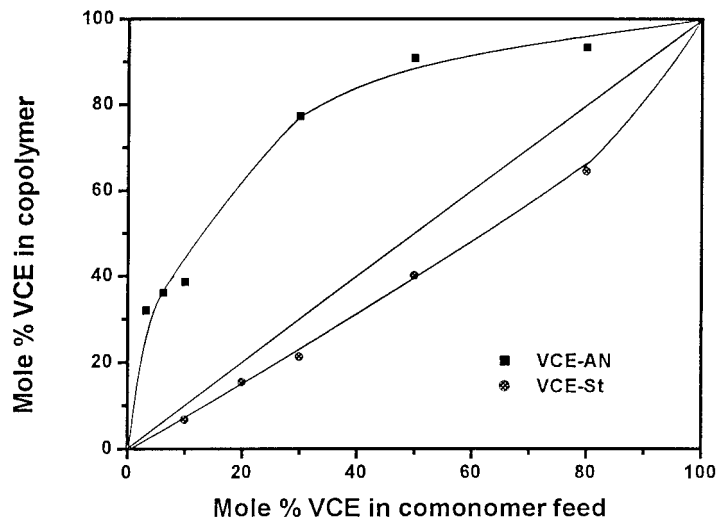


Figure 6 Copolymer composition as a function of monomer feed ratio in the copolymerization of VCE with ST or AN.

Table I Thermal Data of Poly(AN-co-VCE) and Poly(ST-co-VCE)^a

Copolymer	Composition ^b		\overline{M}_n^c	$\overline{M}_w/\overline{M}_n$	T_{d10}^d (°C)	T_g (°C)
	AN/VCE	ST/VCE				
1	1.3/10	—	14.3	1.40	395	7
2	2.9/10	—	9.9	1.63	372	20
3	15/10	—	— ^e	—	350	39
4	—	15/10	11.8	1.35	403	21
5	—	37/10	9.9	1.39	398	36
6	—	14/1	7.3	1.30	381	53

^a Copolymerization condition, solvent: toluene, [VCE] + [AN] or [ST] = 0.5252M, [AIBN] = 1.57 × 10⁻²M, reacted 24 h at 60°C.

^b From proton NMR.

^c From GPC, unit: kg/mol.

^d Temperature of 10% wt loss, determined by TGA under N₂.

^e Sample not soluble in THF.

ization decreased as the mole fraction of AN in the monomer feed increased. Thermal properties of the copolymers were investigated by using DSC and TGA. The results are summarized in Table I. It becomes evident that the temperature where 10% weight loss of the copolymers (T_{d10}) increased as the mole fraction of VCE in the monomer feed increased, whereas the glass transition

temperature (T_g) decreased as the mole fraction of VCE in the monomer feed increased.

As was observed in the copolymerization of VCE with ST, the area of the signal at 5.72 ppm due to the aromatic protons is rapidly reduced and shifted downfield with the increasing mole fraction of AN in the monomer feed, as shown in the ¹H-NMR spectrum (see Fig. 7). This implies

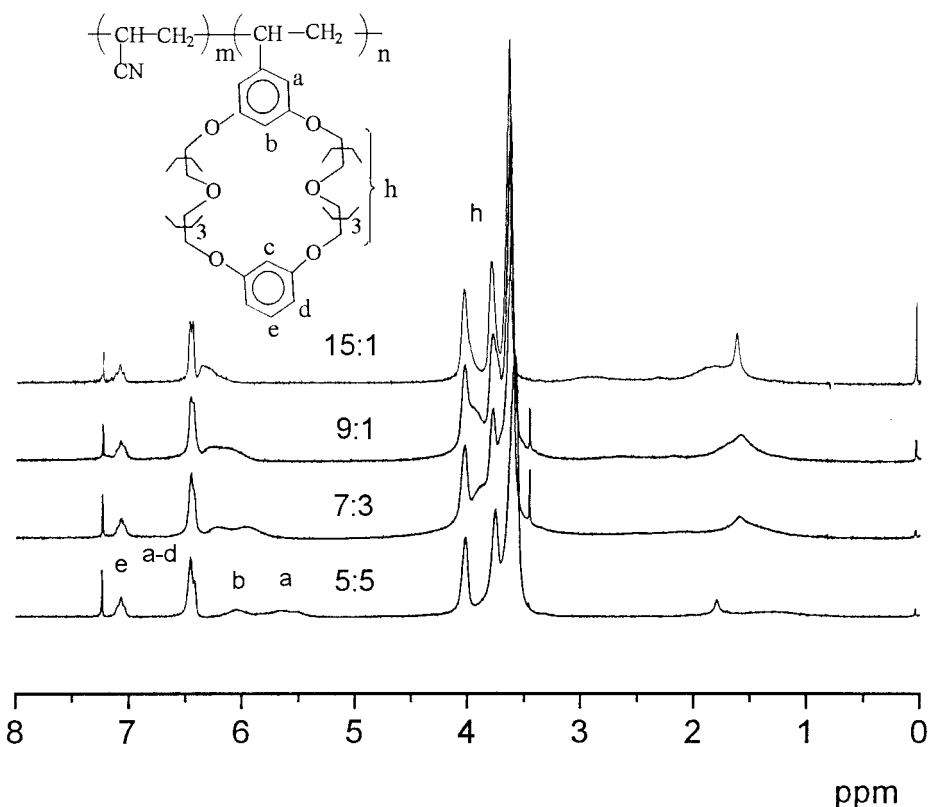


Figure 7 ¹H-NMR spectrum of poly(AN-co-VCE) (solvent CDCl₃). Monomer feed in molar ratio of AN/VCE: 15/1, 9/1, 7/3, 5/5.

that the sequence length of the VCE unit in the copolymer is sharply decreased as the mole fraction of VCE unit in the copolymer decreases.

Thus, the copolymer composition of VCE was determined by means of $^1\text{H-NMR}$ spectroscopy based on the following equation:

$$\frac{m_{\text{AN}}}{n_{\text{VCE}}} = \frac{32x - 3y}{3y}$$

In the equation, m and n denote the number of AN and VCE units in the copolymer, respectively, x is the area of the signals that are proportional to the number of protons associated with methylene and methine (see Fig. 7, 1–2 ppm), and y is the area of the signals which are proportional to the number of methylene protons of crown ether unit of VCE (3.5–4.2 ppm), respectively.

The dependence of the copolymer composition as a function of the monomer feed ratio is shown in Figure 6 together with that of ST-VCE copolymerization. The reactivity ratio of VCE (r_2) and AN (r_1), determined by Fineman–Ross method, gave values $r_1 = 0.05$ and $r_2 = 3.43$, respectively.

CONCLUSION

A VCE monomer having a 32-membered crown ether ring pendant unit was successfully synthesized by using tetra(ethylene glycol) dichloride, resorcinol, and 3,5-dihydroxyacetophenone as starting materials with a relatively good yield. The value of the reactivity ratios were determined from the copolymerization of VCE with ST or AN.

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