

Copolymerization of 4'-vinylbenzo-15-crown-5 with Di(ethylene glycol) Ethyl Ether Acrylate

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Abstract: Radical copolymerization behavior of 4'-vinylbenzo-15-crown-5, a vinyl monomer having a pendant 15-membered crown ether unit (VCE) with di(ethylene glycol) ethyl ether acrylate (DEGEEA) was carried out in toluene solution using 2,2-azobisisobutyronitrile (AIBN) as an initiator. The copolymers were characterized by means of FT-IR, ¹H-NMR, and ¹³C-NMR. The reactivity ratio of VCE and DEGEEA, determined by Fineman-Ross and Kelen-Tudos method, gave values 0.55 for VCE, and 0.11 for DEGEEA respectively.

Keywords: Radical polymerization, Vinyl crown ether, Di(ethylene glycol) ethyl ether acrylate, Complex, Reactivity ratio

Introduction

Numerous efforts has been made in order to obtain various polymers containing crown ether unit via the polymerization for the separation purposes of aqueous metal ions[1-4]. Since it is expected that the polymeric membrane is advantageous when compared to their monomeric analogues, not only in the promotion of the efficiency in the continuous separation process due to the prevention of the loss of crown ether unit from the membrane but also improvement in the selectivity of the metal ions by the formation of 2(host)/1(guest) type complex[5-13], it is suitable as carriers for selective transport particular metal ions. However, few literature has been reported about radical polymerization behavior of vinyl crown ether monomer and corresponding comonomers[5].

In this study, we report the results of synthesis of 4'-vinylbenzo-15-crown-5 (VCE) and its copolymerization behavior with di(ethylene glycol) ethyl ether acrylate (DEGEEA) in order to develop a Carrier-Facilitated Transport Membrane (CFM) having the function of selective transport of aqueous metal ion.

Experimental

Materials

Tetra(ethylene glycol), catechol, methanesulfonic acid, sodium borohydride, and p-toluenesulfonic acid monohydrate were purchased from Sigma-Aldrich Korea Ltd., and used as received. Tetra(ethylene glycol) dichloride was prepared according to the procedures given in the literature[14]. AIBN was purified by recrystallization from acetone. Di(ethylene glycol) ethyl ether acrylate(Aldrich) was purified by distillation under reduced pressure (95 °C/ 5 mmHg), just before use. Other chemical reagents were

used as received (DC. Chemical Co., Ltd.(Korea)).

Measurements

Infrared analysis was performed by infrared spectrometer (Nicolet model 520). NMR spectra of the copolymers were recorded by a Varian Unity Inova 400 MHz NMR spectrometer, using CDCl₃ as a solvent. Tetramethylsilane was used as the internal standard. The thermal properties of the polymer was measured by Shimadzu DSC-50 at a scan rate of 5 °C/min.

Synthesis of 4'-vinylbenzo-15-crown-5 (VCE)

VCE was synthesized by dehydration of 4'-(1-hydroxyethyl) benzo-15-crown-5 using p-toluenesulfonic acid in accordance with the procedures reported by Kondo *et al.*[15] via the synthetic route shown in Scheme 1.

Benzo-15-crown-5

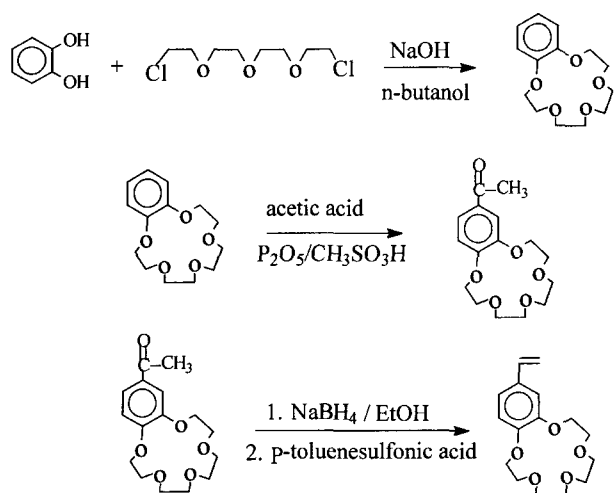
Benzo-15-crown-5 was prepared in accordance with procedures reported by Pedersen[14]. i.e., 85.5 g (0.37 mol) of tetra(ethylene glycol) dichloride was slowly added dropwise for 2 h to a mixture of aqueous solution of sodium hydroxide (31.5 g, 0.79 mol in 40 ml water) was added to 550 ml butanol solution of catechol (40.7 g, 0.37 mol) under nitrogen atmosphere and the mixture was refluxed for 30 h. And after the mixture was neutralized with diluted hydrochloric acid, cooled to room temperature, followed by filtration. After thorough washing of the solid mixture with 200 ml methanol, the residue was separated from the mixture by evaporation and followed by repeated recrystallization from n-heptane gave 55 g product (yield 52 %).

¹H-NMR (CDCl₃) δ (ppm): 3.75(m, 8H), 3.89(m, 4H), 4.12(m, 4H), 6.93(m, 4H).

4'-acetylbenzo-15-crown-5

4'-acetylbenzo-15-crown-5 was prepared according to the procedures given in elsewhere[16]. To a 27 g of condensing agent, which composes of 83 g of phosphorus pentoxide and

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Scheme 1. Synthetic route of VCE monomer.

695 ml of methanesulfonic acid, added 5.4 g (0.02 mol) of benzo-15-crown-5 and 1.3 g (0.02 mol) of acetic acid. And the mixture was stirred at room temperature for 6 h. The reaction mixture was poured into 100 ml water, followed by neutralization with sodium bicarbonate. The product was extracted with methylene chloride three times and dried on sodium sulfate anhydride. The final yield was 3.0 g (50 %) after purification by recrystallization from n-hexane.

$^1\text{H-NMR}$ (CDCl_3) δ (ppm): 2.55(s, 3H), 3.73(m, 8H), 3.86(m, 4H), 4.12(m, 4H), 6.96(d, 1H), 7.5(m, 2H).

4'-(1-hydroxyethyl)benzo-15-crown-5

4'-(1-hydroxyethyl)benzo-15-crown-5 was prepared by reduction of 4'-acetylbenzo-15-crown-5 by sodium borohydride in ethanol solution in accordance with the procedures given in the literature[5]. Yield: 75 %.

$^1\text{H-NMR}$ (CDCl_3) δ (ppm): 1.5(d, 3H), 2.7(s, 1H), 3.75(m, 8H), 3.89(m, 4H), 4.12(m, 4H), 4.8(q, 3H), 6.93(m, 3H).

4'-vinylbenzo-15-crown-5 (VCE)

VCE was prepared by dehydration of 4'-(1-hydroxyethyl)benzo-15-crown-5 using p-toluenesulfonic acid according to the Kondo's modified method[15]. To a 300 ml benzene solution of 4'-(1-hydroxyethyl)benzo-15-crown-5 (5.0 g, 18 mmol) p-toluenesulfonic acid monohydrate (0.16 g, 0.9 mmol) was added. The mixture was refluxed for 3 h with keeping agitation and poured into ice water and dried on sodium sulfate anhydride after successive washing with diluted aqueous sodium bicarbonate, water. After removal of the organic solvent under reduced pressure and the product was isolated using flash liquid silica gel column chromatography. Mixed solvent of ethyl acetate/n-hexane (v/v:1/4) was used as eluent. Recrystallization from n-hexane gave pure white VCE (1.5 g, 32 %).

$^1\text{H-NMR}$ (CDCl_3) δ (ppm): 3.75(m, 8H), 3.89(m, 4H), 4.12(m, 4H), 5.11(d, d, 1H), 5.57(d, d, 1H), 6.61(m, 1H), 6.9(m, 4H).

Copolymerization of VCE with DEGEEA

Toluene solutions containing various molar ratios of DEGEEA and VCE (9/1, 7/3, 5/5, 3/7, 1/9) were thoroughly degassed on a vacuum line and sealed off for the copolymerization of VCE with DEGEEA and initiated in the presence of 2.5×10^{-3} M AIBN at 60°C . After certain period of reaction, polymer was precipitated in n-hexane and dried overnight under reduced pressure at room temperature. The total concentration of monomer was kept at 0.5 M. Yields of copolymers and their compositions were determined by gravimetry and $^1\text{H-NMR}$ spectroscopy, respectively.

IR (NaCl): 2873 and 2968(C-H), 1743(C=O), 1125(C-O-C) cm^{-1} .

$^1\text{H-NMR}$ (CDCl_3) δ (ppm): 1-2.2(m, main chain CH_2 , CH, and pendant CH_3), 3.5-4.1(m, OCH_2), 5.8-6.77(m, aromatic H).

$^{13}\text{C-NMR}$ (CDCl_3) δ (ppm): 15.07(CH_3), 41.1(main chain carbon), 63.25-70.9(OCH_2), 114.1, 121.3, 129.5, 133.6, 149.1, 165.3(aromatic carbon), 174.1(carbonyl group).

Results and Discussion

Synthesis of VCE

4'-vinylbenzo-15-crown-5 has been synthesized in accordance with the procedures given in the literatures[5,16], using tetra(ethylene glycol), catechol, methanesulfonic acid, sodium borohydride, p-toluenesulfonic acid monohydrate, and tetra(ethylene glycol) dichloride as starting materials via benzo-

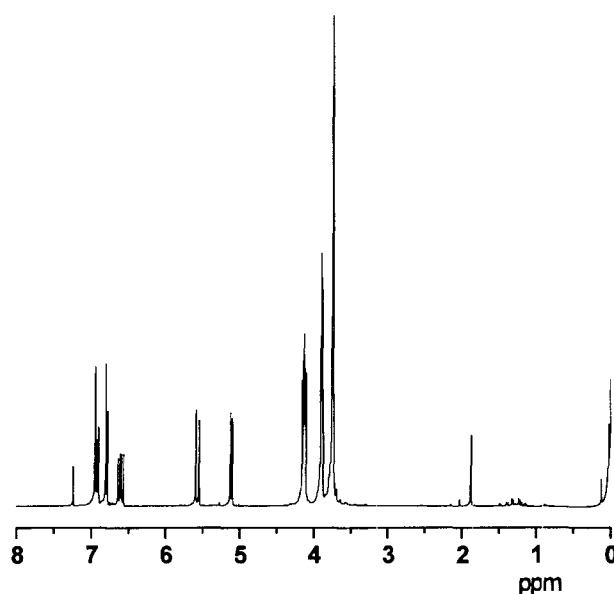


Figure 1. $^1\text{H-NMR}$ spectrum of VCE monomer. Solvent: CDCl_3 .

15-crown-5, 4'-acetylbenzo-15-crown-5, 4'-(1-hydroxyethyl)benzo-15-crown-5. The intermediates were identified by $^1\text{H-NMR}$ spectroscopy. The presence of the signals of vinyl protons ($=\text{CH}_2$) at 5.15 and 5.63 ppm, of α , $-\text{OCH}_2$, β , $-\text{OCH}_2$, and γ , δ , $-\text{OCH}_2$ protons at 3.75, 3.89, 4.12 ppm, of vinyl ($=\text{CH}$) protons at 6.50 ppm and of aromatic protons at 6.95 ppm, respectively, reveals that VCE monomer was duly synthesized via the route shown in Scheme 1 (see Figure 1). In this synthesis, a route of acetylation of benzo-15-crown-5 to 4'-acetylbenzo-15-crown-5 using a condensing agent which consists of phosphorus pentoxide and methanesulfonic acid was adapted without using 3,4-dihydroxyacetophenone as starting material which was used by Smid *et al.*[5] in his early to synthesize 4'-acetylbenzo-15-crown-5. Yield of the product was 50%. However, an attempt to use aluminum chloride, a Friedel-Crafts catalyst, was not successful for the acetylation, probably due to the lack of reactivity of benzo-15-crown-5 and also difficulty was encountered in the isolation of the product from the reaction mixture. Since there is no difficulty in the processes of subsequent reduction and dehydration of 4'-acetylbenzo-15-crown-5 to vinylbenzo-15-crown-5, it is believed that this is one of the efficient and powerful method for the synthesis of vinylbenzo-15-crown-5.

Synthesis of Poly(VCE-co-DEGEEA)

Radical copolymerization of VCE with DEGEEA was carried out in toluene solution using AIBN as an initiator. Figure 2 shows the $^1\text{H-NMR}$ spectrum of poly(VCE-co-

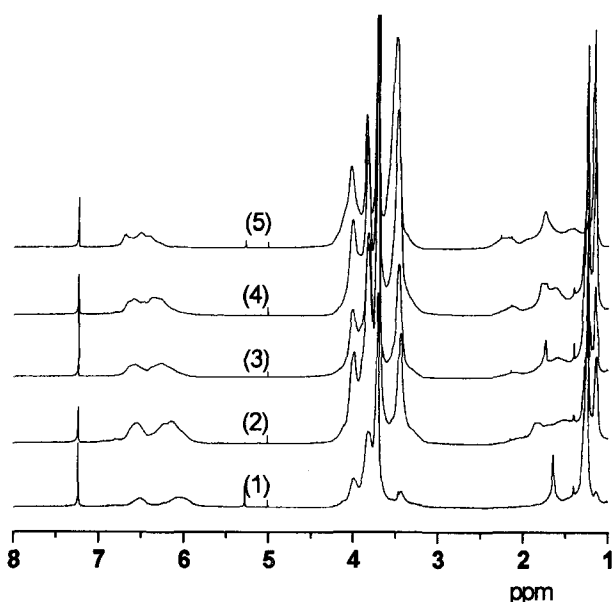


Figure 2. $^1\text{H-NMR}$ spectra of poly(VCE-co-DEGEEA). Solvent: CDCl_3 . Monomer feed in molar ratio of VCE/DEGEEA: (1) 9/1, (2) 7/3, (3) 5/5, (4) 3/7, (5) 1/9. Total monomer concentration: 0.5 M, $[\text{AIBN}] = 5 \times 10^{-3}$ M.

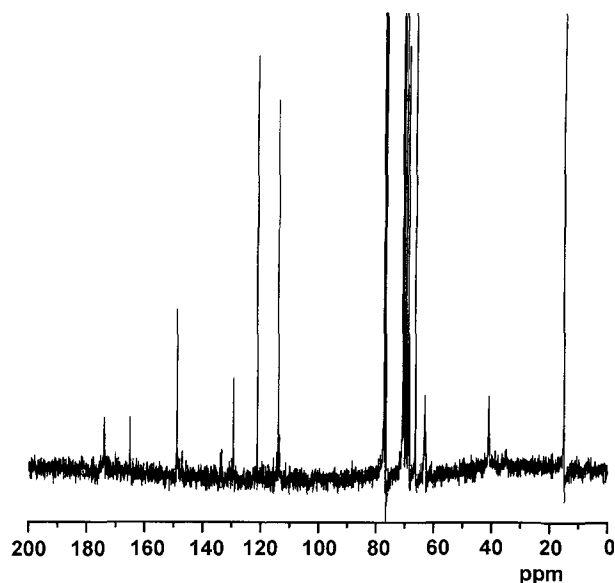


Figure 3. $^{13}\text{C-NMR}$ spectrum of poly(VCE-co-DEGEEA). Solvent: CDCl_3 . Monomer feed in molar ratio of VCE/DEGEEA value is 7/3. Total monomer concentration: 0.5 M, $[\text{AIBN}] = 5 \times 10^{-3}$ M.

DEGEEA). This reveals that the signals at 5.9-6.5 ppm due to aromatic protons of the crown ether unit are shifted downfield as the mole fraction of DEGEEA in the monomer feed increases, probably due to the shielding effect of proximate crown ether rings. The copolymer composition was determined by means of $^1\text{H-NMR}$ spectroscopy based on following equation.

$$\frac{m_{\text{DEGEEA}}}{n_{\text{VCE}}} = \frac{3y - 16x}{10x} \quad (1)$$

In the equation, m and n denote the number of DEGEEA 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 benzene ring unit of the crown ether (signals 5.8-6.7 ppm) and y is the area of the signals which are proportional to the number of methylene protons associated with the crown ether unit of VCE and DEGEEA (3.5-4.2 ppm), respectively.

Figure 3 shows $^{13}\text{C-NMR}$ spectrum of poly(VCE-co-DEGEEA) in CDCl_3 solution. The presence of 174.1 ppm signal of carbonyl group, signals at 114.1, 121.3, 129.5, 133.6, 149.1, and 165.3 ppm of aromatic group and signal at 63-71 ppm of $-\text{OCH}_2$, signal at 41.2 ppm of main chain carbon and signal at 15.1 ppm of methyl group carbon also revealed poly(VCE-co-DEGEEA) is duly obtained.

Determination of Reactivity Ratio

The results of the copolymerization of VCE with DEGEEA are summarized in Table 1. The values of the monomer reactivity ratios of VCE and DEGEEA were

Table 1. Results of copolymerization of VCE with DEGEEA in toluene solution^{a)}

Monomer feed (m_1/m_2) ^{b)}	Copolymer composition ^{c)} (dm_1/dm_2)	G value	F value	η value	ξ value	Mean sequence length	
						μ_1	μ_2
9/1	5.85	13.85	7.46	0.517	0.9595	5.95	1.01
7/3	2.25	2.41	1.296	0.432	0.8057	2.28	1.04
5/5	1.35	0.598	0.4011	0.196	0.5594	1.55	1.11
3/7	1.008	0.182	0.0037	0.0049	0.2378	1.23	1.26
1/9	0.502	0.0246	-0.1101	-0.181	0.0404	1.61	1.99

^{a)} polymerization conditions: total monomer concentration: $[VCE] + [DEGEEA] = 0.5$ M, $[AIBN] = 5 \times 10^{-3}$ M, reaction temp: 60°C Polymerizations were terminated before % conversion reached at 10 % in all runs.

^{b)} $m_1/m_2 = \text{VCE/DEGEEA}$.

^{c)} was estimated by 400 MHz proton NMR spectrum.

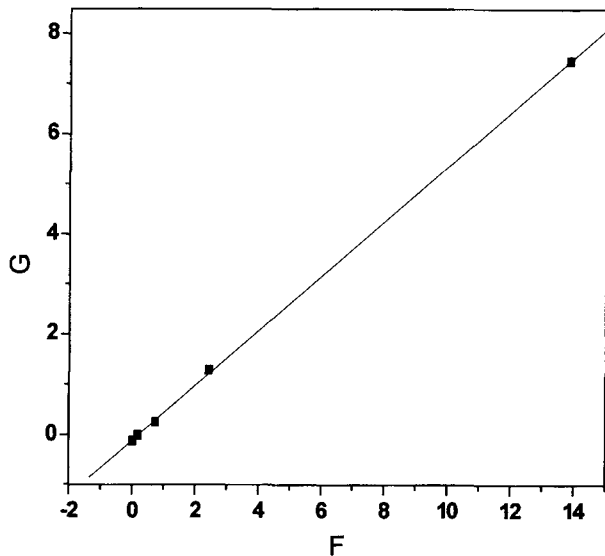


Figure 4. Plot of G versus F values of copolymerization of VCE with DEGEEA (Fineman-Ross method). $r_1 = 0.55$ (VCE), $r_2 = 0.10$ (DEGEEA).

determined from the data of copolymer compositions using following Fineman and Ross method[17,18].

$$G = r_1 F - r_2 \quad (2)$$

where $G = X(Y - 1)/Y$, $F = X^2/Y$, $X = m_1/m_2$, $Y = dm_1/dm_2$.

Graphical plot of equation (2) yield a straight line with a good coefficient as shown in Figure 4, whose slope and intercept give r_1 value 0.55 and r_2 value 0.10, respectively.

The determination of the value of the monomer reactivity ratios was also attempted by Kelen-Tudos method when the conversion is low using following equation[18].

$$\eta = \left(r_1 + \frac{r_2}{\alpha} \right) \xi - \frac{r_2}{\alpha} \quad (3)$$

In the equation, $\eta = G/(\alpha + F)$; $\xi = F/(\alpha + F)$; $G = X(Y -$

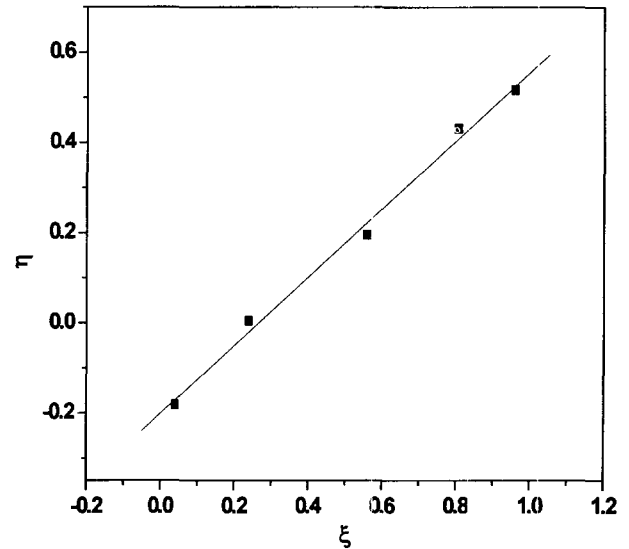


Figure 5. Plot of η versus ξ values of copolymerization of VCE with DEGEEA (Kelen-Tudos method). $r_1 = 0.55$ (VCE), $r_2 = 0.11$ (DEGEEA).

$1)/Y$; $F = X^2/Y$, $\alpha = \sqrt{F_m F_M}$. Where F_m and F_M indicate the lowest and the highest values respectively. Plotting η against ξ data also gives a straight line with a good coefficient (see Figure 5). Thus, when $\xi = 1$ and $\xi = 0$ gives r_1 and $-r_2/\alpha$ values, in this experiment reactant r_1 and r_2 value is 0.55 and 0.11 respectively, which is almost identical with the values determined by Fineman-Ross method. This implies that the copolymerization proceeds with preferential addition of VCE monomer. The mean of sequence length of the monomer unit in the copolymer are summarized in Table 1.

Figure 6 shows the polymer composition as a function of the monomer feed ratio, revealing that crossover point where the copolymer and monomer feed composition are same is appeared at the monomer feed ratio of VCE/DEGEEA=7/3.

Figure 7 shows the dependence of mean sequence length of each monomer on the content of VCE or DEGEEA of the

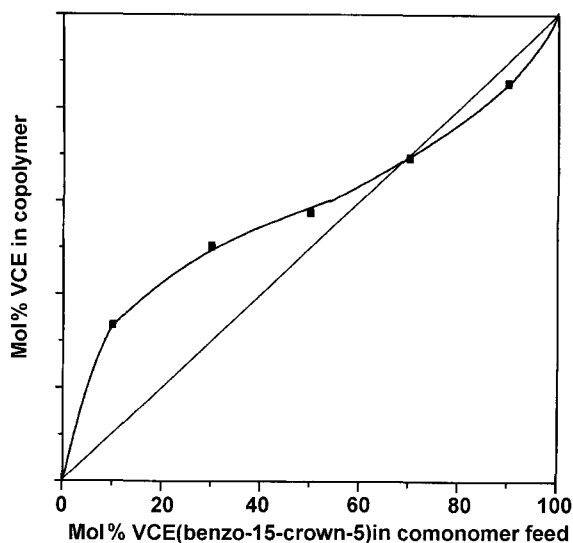


Figure 6. Copolymer composition as a function of monomer feed ratio in the copolymerization of VCE with DEGEEA.

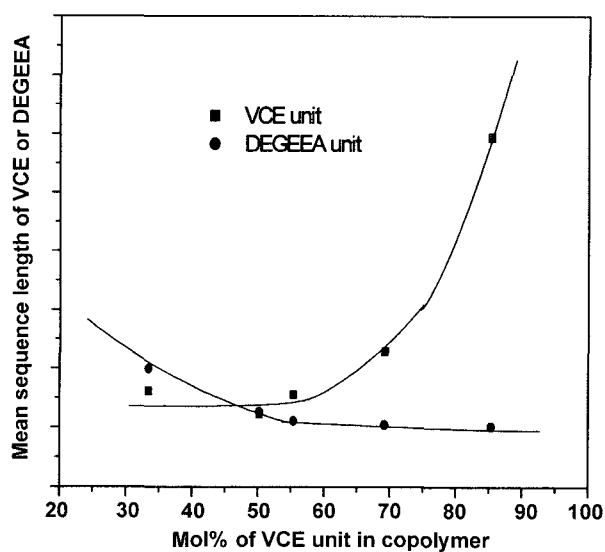


Figure 7. Dependence of mean sequence length of VCE or DEGEEA on mol% of VCE unit in the copolymer.

Table 2. Glass transition temperature ($^{\circ}\text{C}$) data of poly(DEGEEA-co-VCE)^{a)}

Monomer feed DEGEEA/VCE ^{b)}	9/1	7/3	5/5	3/7
Glass transition temperature(T_g) ^{c)}	-53	-48	-33	-22

^{a)} polymerization conditions: Temp: 60 $^{\circ}\text{C}$, reaction time: 24 h

Total monomer concentration: $[\text{VCE}] + [\text{DEGEEA}] = 0.5 \text{ M}$,

$[\text{AIBN}] = 5 \times 10^{-3} \text{ M}$

^{b)} in molar ratio

^{c)} T_g was measured by DSC (Shimadzu DSC-50) at a scan rate of 5 $^{\circ}\text{C}/\text{min}$.

copolymer, calculated from the following equations[19].

$$\mu_1 = 1 + r_1 m_1 / m_2 \quad (4)$$

$$\mu_2 = 1 + r_2 m_2 / m_1 \quad (5)$$

where m_1 and m_2 indicate monomer concentration, respectively and μ_1 , μ_2 denote mean sequence length of VCE or DEGEEA unit in the copolymer. It demonstrates that mean sequence length of VCE in the copolymer increases as mol% of VCE increases. It is worthwhile to mention that the mean sequence length of VCE becomes larger than 2 when the molar ratio of VCE/DEGEEA is higher than 7/3.

Results of DSC analysis is summarized in Table 2, revealing that glass transition temperature (T_g) of the copolymer increases as the VCE content of copolymer increases, however, T_g values of the copolymers of any compositions are lower than room temperature.

Conclusion

Vinylbenzo-15-crown-5 monomer (VCE) was successfully synthesized with a relatively good yield via 4'-acetylbenzo-15-crown-5 and copolymerized with DEGEEA. The reactivity ratios determined by Fineman-Ross and Kelen-Tudos methods gave values 0.11 for DEGEEA, 0.55 for VCE, respectively.

References

1. E. Blasius, K. P. Janzen, W. Klein, H. Klotz, V. B. Nguyen, T. Nguyen-Tien, R. Pfeiffer, G. Scholten, H. Simon, H. Stockemer, and A. Toussaint, *J. Chromatogr.*, **201**, 127 (1980).
2. E. Blasius and P. G. Maurer, *Makromol. Chem.*, **178**, 649 (1977).
3. E. Blasius, K. P. Janzen, M. Keller, H. Lander, T. Nguyen-Tien, and G. Scholten, *Talanta*, **27**, 107 (1980).
4. E. Blasius, K. P. Janzen, W. Adrian, W. Klein, H. Klotz, H. Luxenburger, E. Mernke, V. B. Nguyen, T. Nguyen-Tien, R. Rausch, J. Stockemer, and A. Toussaint, *Talanta*, **27**, 127 (1980).
5. S. Kopolow, T. E. Hogen Esch, and J. Smid, *Macromolecules*, **6**, 133 (1973).
6. G. Manecke and P. Reuter, *Makromol. Chem.*, **182**, 1973 (1981).
7. S. Kopolow, T. E. Hogen Esch, and J. Smid, *Macromolecules*, **4**, 359 (1971).
8. T. Maeda, K. Kimura, and T. Shono, *Bull. Chem. Soc. Jpn.*, **55**, 3506 (1982).
9. K. Kimura, H. Tamura, T. Maeda, and T. Shono, *Polym. Bull.*, **1**, 403 (1979).
10. Y. Delaviz and H. W. Gibson, *Macromolecules*, **25**, 18 (1992).
11. U. Tunca and Y. Yagci, *Prog. Polym. Sci.*, **19**, 233 (1994).

12. N. Yamaguchi and H. W. Gibson, *Macromol. Chem. Phys.*, **201**, 815 (2000).
13. K. L. Thunhorst, R. D. Noble, and C. N. Bowman, *J. Membrane. Sci.*, **156**, 293 (1999)
14. C. J. Pedersen, *J. Am. Chem. Soc.*, **89**, 7017 (1967).
15. T. Ando, T. S. Kwon, A. Kitagawa, T. Tanemura, S. Kondo, H. Kunisada, and Y. Yuki, *Macromol. Chem. Phys.*, **197**, 2803 (1996).
16. W. Parish and P. Stott, *J. Org. Chem.*, **43**, 4577 (1978).
17. M. Fineman and S. D. Ross, *J. Polym. Sci.*, **5**, 259 (1950).
18. G. Odian, "Principles of Polymerization", pp.467-470, Wiley & Sons Inc., New York, 1991.
19. C. W. Pyun, *J. Polym. Sci., Part A-2, Polym. Phys.*, **8**, 1111 (1970).