4'-vinylbenzo-15-crown-5의 합성과 Di(ethylene glycol) ethyl ether acrylate와의 라디칼 공중합

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Synthesis of 4'-vinylbenzo-15-crown-5 and its copolymerization behavior with Di(ethylene glycol) ethyl ether acrylate

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1. Introduction

Poly(crown ether)s as a functional polymer materials have powerful and selective complexation properties with a large number of metal cations and have advantage of facility of their recovery and modification of their complexation properties in contrast to their monomeric analogues. Poly(crown ether)s having pendant macrocyclic groups can easily form 2:1-type crown ether ring-to-cation complexes with particular metal ions which are a little larger than the cavity of the crown ether ring. Therefore the poly(crown ether)s often exhibit excellent cationbinding selectivities, which are very different from those of the corresponding monomeric analogs. Because of its advantage of processing for nonporous density Carrier-Facilitated Transport Membrane (CFM), it is widely used as carriers for selective transport particular metal ions. However, there is few literature has been reported radical polymerization behaviour of vinyl crown ether monomer and corresponding comonomers. [1~5]

In this study, synthesis of 4'-vinylbenzo-15-crown-5 (VCE) and its copolymerization behavior with di(ethylene glycol) ethyl ether acrylate(DEGEEA) have been investigated.

2. Experimental

Materials.

4'-vinylbenzo-15-crown-5 has been prepared in accordance with the literature(3,

6), using tetra(ethylene glycol), catechol, MeSO₃H, sodium borohydride, p-toluenesulfonic acid monohydrate (all chemical reagents received from Sigma-Aldrich Korea Ltd.) via tetra(ethylene glycol) dichloride, Benzo-15-crown-5, 4-acetylbenzo-15-crown-5, 4-(1'-hydroxyethyl)benzo-15-crown-5 as shown in scheme 1 and was identified by ¹H-NMR spectroscopy.

Copolymerization of VCE with DEGEEA

Copolymerization samples were prepared by degassing of toluene solution containing various molar ratios of DEGEEA and VCE (9/1, 7/3, 5/5, 3/7 1/9) on a vacuum line and sealing off. Copolymerization was carried out at 60°C using AIBN as an radical initiator. After certain period of reaction, polymer was precipitated in n-hexane and dried overnight under reduced pressure at room temperature. the concentration of the initiator was 2.5 x 10⁻³M and the total concentration of monomer was kept at 0.5M.

Scheme 1. Synthetic Route of the VCE

3. Results and discussion

Vinyl crown ether monomer, i.e, 4'-vinylbenzo-15-crown-5, prepared in accordance with the modified Smid procedures(3) was duly identified using ¹H-NMR spectroscopy as shown in Figure 1.

¹H-NMR: 4.0(m, 16H), 5.15(d,1H), 5.62(d,1H), 6.6(m, 1H) and 6.95(m, 3H)

Figure 2 shows ¹H-NMR spectrum of copolymers. It is observed that with increasing monomer feed ratios for DEGEEA, the intensity of peaks at 6.02 ppm is rapidly shifted downfield. It is explained that the proximate crown ether rings proportion is decreased when copolymerization is progressed in increasing of DEGEEA.

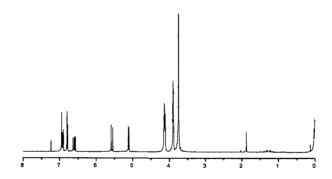


Figure 1. Monomer's ¹H-NMR spectrum (Solvent CDCl₃).

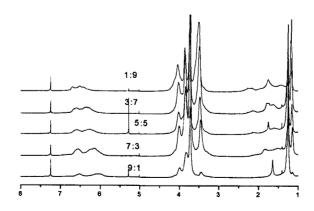


Figure 2. ¹H-NMR spectrum of poly(DEGEEA-co-VCE) (Solvent CDCl₃).

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Figure 3 shows monomer-copolymer composition curves of copolymerization of VCE with DEGEEA. its result shows that with increases VCE mole fraction in comonomer it content in copolymer is increased, however when DEGEEA / VCE = 3 /7, monomer-copolymer composition value is equal. Monomer reactivity ratios r_1 and r_2 calculated by the Fineman-Ross method were , 0.55 for VCE, and 0.04 for DEGEEA respectively.

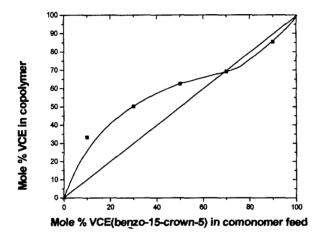


Figure 3. Copolymer composition as a function of monomer feed ratio in the copolymerization of VCE with DEGEEA.

4.Conclusion

Copolymers of 15-membered ring benzovinyl crown ether monomers with DEGEEA was synthesized via free radical polymerization. The reactivity ratios were 0.04 for DEGEEA, 0.55 for VCE respectively.

References

- 1. Herweh JE, J polym Sci: polym Chem Ed 21, 3101(1983)
- 2. Blasius E, Janzen KP, Keller M, Talanta 27, 107(1980)
- 3. Kopolow S, Smid J, Macromolecules 6, 133(1973)
- 4. Hogen-Esch T E, Smid J, Macromolecules 4, 359(1971)
- Thunhorst K. L., Boman C. N., J. Membrane Sci., 156, 293-303 (1999).
- 6. Parish W, Stott P, J. Org. Chem., 43, 4577 (1978)