

5'-vinyl-m-phenylene-m-phenylene-32-crown-10 과 acrylonitrile 및 styrene의 라디칼 공중합

김용일, 마석일

인하대학교 섬유공학과

Copolymerization behaviors of 5'-vinyl-m-phenylene-m-phenylene-32-crown-10 with acrylonitrile or Styrene

LongYi Jin and Soukil Mah

Department of Textile Engineering, Inha University, Incheon, Korea

1. Introduction

Poly(crown ether)s as a functional polymer materials have powerful and selective complexation properties with a large number of organic and inorganic 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 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.[1~6]

In this study, copolymerization behaviors of 5'-vinyl-m-phenylene-m-phenylene-32-crown-10 (VCE) with acrylonitrile and styrene was investigated.

2. Experimental

Materials.

Acrylonitrile and Styrene were successively washed with aqueous sodium hydroxide solution and water, then dried on anhydrous magnesium sulfate and purified by distillation under reduced pressure, in the presence of calcium hydride. 5'-vinyl-m-phenylene-m-phenylene-32-crown-10(VCE) was synthesized according to the literature [7,8]

IR (NaCl): 2880 and 2918 (C-H), 1127 cm^{-1} (C-O-C)

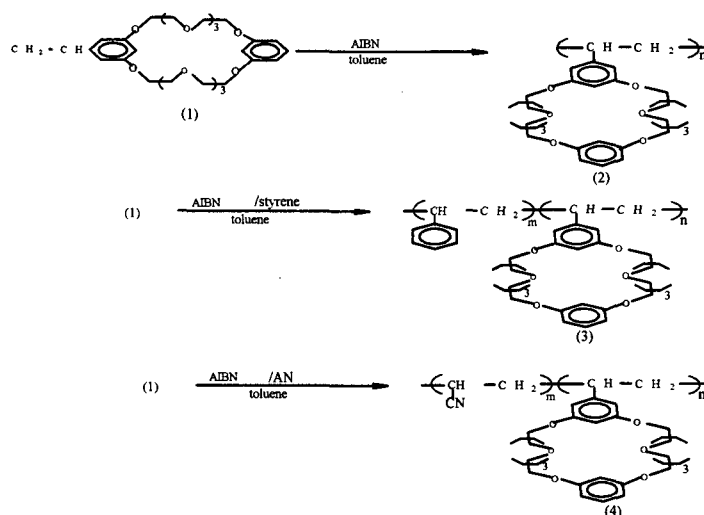
$^1\text{H-NMR}(\text{CDCl}_3)$: 3.66(m, 6H), 3.76(m, 8H), 4.01(m, 8H), 5.15(d,1H), 5.62(d,1H), 6.35-6.55(m, 6H), 7.06(t, 1H)

Copolymerization of VCE with Acrylonitrile

Copolymerization containing different ratios of VCE to acrylonitrile (1:30, 1:23, 1:15, 1:9, 3:7, 5:5, 8:2) were carried out in toluene at 60°C, using AIBN as initiator. General procedures:

A toluene solution containing of VCE, AN and AIBN was sealed off after repeated degassing on a vacuum line. Then, the ampoule was allowed to stand for at 60°C. The polymerization was terminated by addition of methanol. The precipitated polymer was purified by reprecipitation in methanol and then, dried overnight under reduced pressure at room temperature. (comonomer concentration: 1M, Initiator concentration: 0.01M)

Copolymerization of VCE with styrene (1:9,2:8,3:7,5:5,8:2) were also proceeded, according to above method.



scheme I

3. Results and discussion

The number average molecular weight of poly(VCE) is 36000 g/mol, and its intrinsic viscosity is 5.8 ml/g.

The copolymerization of VCE with acrylonitrile and styrene in toluene has been carried out under various monomer feed ratios.

In $^1\text{H-NMR}$ spectrum of copolymer (Figure 1.) it is observed with increasing monomer feed ratios for acrylonitrile or styrene, the intensity of peaks at 5.72 ppm is rapidly reduced. It is explained that the proximate crown ether rings proportion is decreased when copolymerization is progressed in increasing of acrylonitrile or styrene concentration.

Fig. 2 and 3 show the time-conversion curves of the copolymerization of

VCE(M_2) with acrylonitrile and styrene(M_1) carried out under various monomer feed ratios. In fig. 2 the rate of copolymerization increases as VCE concentration increases and the mole fraction of VCE increases in the copolymer composition. in fig. 3 its result is inversive.

Fig. 4 shows monomer-copolymer composition curve of copolymerization of VCE with acrylonitrile and styrene. monomer reactivity ratios r_1 and r_2 calculated by the Fineman-Ross method were 0.05 for AN, 3.43 for VCE and 1.6 for styrene, 0.6 for VCE respectively.

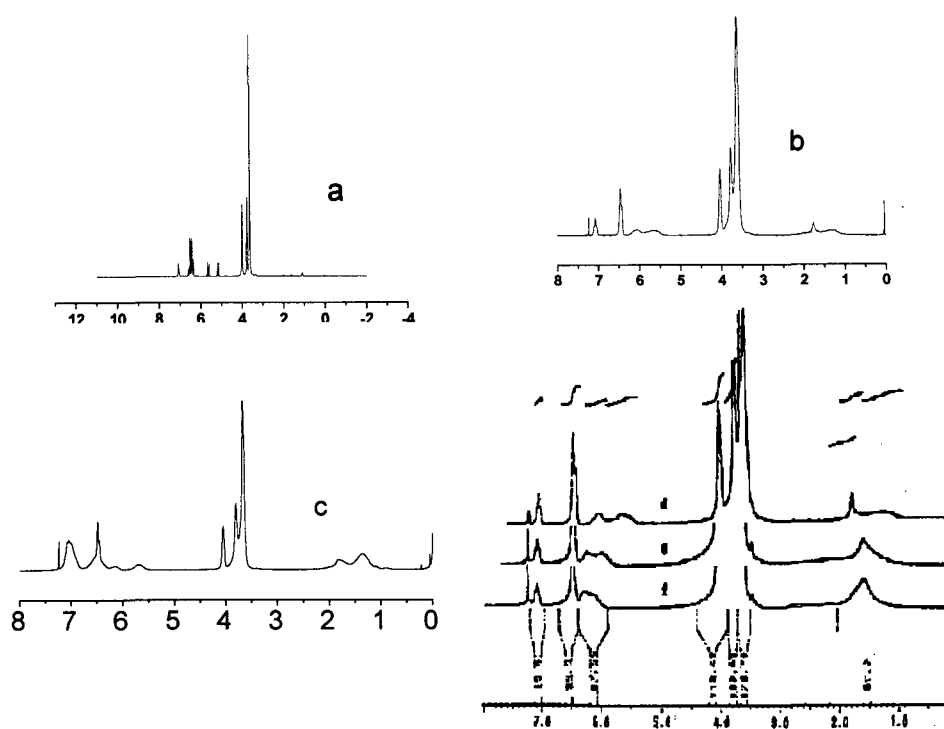


Figure 1. $^1\text{H-NMR}$ spectrum of monomer and its polymers (a) monomer (b) homopolymer (c) VCE-styrene copolymer (d)~(f) VCE-AN copolymer, VCE/AN molar ratios in copolymer: (d): 1:1 (e) 3:7 (f) 1:9

4. Conclusion

A new class of vinyl monomers having a macrocyclic unit and copolymers having pendant macrocyclic groups have been successfully synthesized via free radical polymerization. The reactivity ratios were 0.05 for AN, 3.43 for VCE and 1.6 for styrene, 0.6 for VCE respectively.

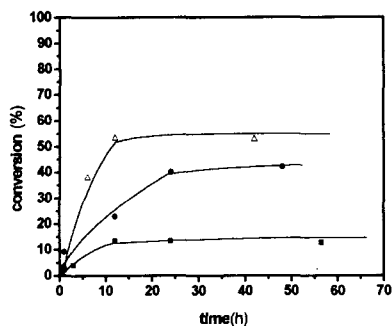


Figure 2. Time-conversion curve of copolymerization AN(M_1) with VCE(M_2), $[M]=1.0M$, $[I]=0.01M$, Monomer feed ratio(in mole ratio): \blacktriangle $M_1:M_2=1:1$, \blacksquare $M_1:M_2=9:1$ \bullet $M_1:M_2=7:3$

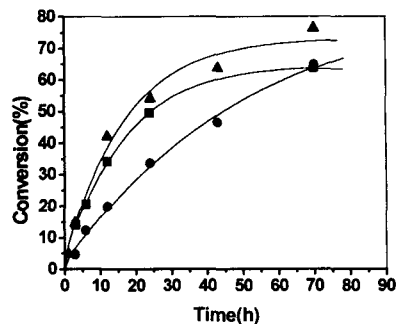


Figure 3. Time-conversion curve of copolymerization of styrene(M_1) with VCE(M_2) $[M]=1.0M$, $[I]=1.6 \times 10^{-2}M$. Monomer feed ratio (in mole ratio) \blacktriangle $M_1:M_2=7:3$, \blacksquare $M_1:M_2=5:5$ \bullet $M_1:M_2=9:1$

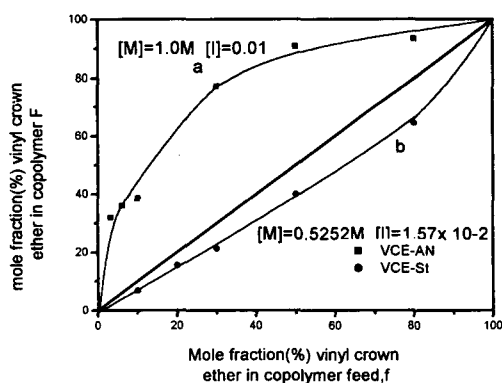


Figure 4. Monomer copolymer composition curve for AN and styrene with VCE conversion is controlled below 10% for determined reactivity ratios.

5. References

1. Hogen-Esch TE, Smid J, *macromolecules* **4**, 359(1971)
2. Kopolow S, Smid J, *macromolecules* **6**, 133(1973)
3. Herweh JE, *J polym Sci, polym Chem ed* **21**, 3101(1983)
4. Blasius E, Janzen KP, Keller M, *talanta* **27**, 107(1980)
5. Kakuchi T, Haba O, Yokota K, *makrom.Chem* **192**, 1601 (1991)
6. Delaviz, Y. Gibson, H. W. *macromolecules*, **25**, 18-20(1992)
7. Gibson HW, Nagvekar DS. *Can J Chem* **75**,1375(1997)
8. LongYi Jin, Soukil Mah 한국섬유공학회 추계학술발표회 논문집 **33**, 13(2000)