NOTE

2-Vinyl-3-(β-phenyl)-Vinyloxirane의 라디칼 중합

박 영 철 · 김 병 구 · 공 명 선 · 김 창 배
단국대학교 화학과
(1989년 12월 8일 접수)

Radical Polymerization of 2-Vinyl-3-(β-phenyl)-Vinyloxirane

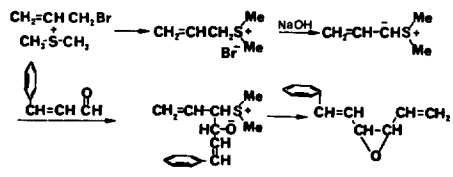
Young-Cheol Park, Byung-Ku Kim, Myoung Seon Gong, and Chang Bae Kim
Department of Chemistry, Dankook University, Cheonan 330-180, Chung-Nam, Korea
(Received December 8, 1989)

INTRODUCTION

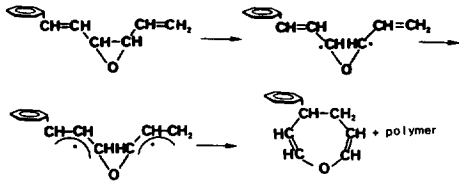
It has been reported that 4-methylene-1,3-dioxolane derivatives undergo free radical polymerization to give the polymers via three polymerization modes such as addition, ring-opening, and elimination.[1~4] Recently Bailey and his coworkers also reported that 2-methylene-4-vinyl-1,3-dioxolane was polymerized by regiospecific free radical ring-opening and subsequent isomerization to allyl radical.[5] As an other examples, polymerization of 4,7-dihydro-2-methylene-1,3-dioxepine was formed via quantitative radical ring-opening and isomerization of the allyl radical is followed to allyl radical in a concerted process.[6] The major driving force involved in the free radical process of vinyl oxirane is considered to be the release of ring strain and subsequent formation of more stable radical. This paper reports on the synthesis and polymerization of 2-vinyl-3-(β-phenyl)-vinyloxirane.

RESULTS AND DISCUSSION

2-Vinyl-3-(β-phenyl)-vinyloxirane(VPVO) was prepared in a 60% yield by the phase transfer reaction of allyldimethylsulfonium salt with cinnamaldehyde, according to the modified procedure[7] as follows.



When the freshly distilled VPVO was treated at 130℃ for 72hrs, 4-phenyloxepine(4-POX) was obtained as major product with the yield ratio 9 : 1 to polymer. The thermal rearrangement to 4-POX is considered to proceed via the formation of biradical by ring opening and subsequent isomerization to more stable allylic radical and cyclization, which can be visualized as follows.



No isomerization product was detectable at lower temperature than 100℃ during vacuum distillation of VPVO.

At higher temperature than 100℃, the rate of this intramolecular processes to give 4-phenyloxepine was found to be fast enough to compete with the polymerization and relatively low yield of the polymerization product was observed. Polymerization of the VPVO was carried out in the presence of common free radical initiators, such as azobisisobutyronitrile(AIBN), benzoylperoxide(BPO), di-tert-butyl peroxide(DTBP) at various temperatures. The results on polymerization were summarized in Table 1.

In the case of polymerization with 5 mol % of BPO at 80℃ for 40 hrs, the conversion of polymer was 17%, but isomerization product was negligible in unreacted portion. The VPVO was also polymerized with 20 mol % of DTBP at 120℃ for 48 hrs to give the white powdery polymer in 63% yield.

The chemical structure of polymer was analyzed by IR and NMR spectroscopies. IR spectrum of polymer in Fig. 2-b) showed a strong absorption bands at 1680 cm^{-1}, assigned to the C=C stretching and at 1000~1200 cm^{-1}, assigned to C−O−C of vinyl ether in Fig. 2-b).

By comparison with IR spectrum of the polymer with that of VPVO in Fig. 2-a), it appears that the characteristic bands of oxirane ring at around 950 cm^{-1} has been disappeared. These facts demonstrate that the oxirane ring opens to form the divinyl ether by the ring-opening and subsequent isomeri-

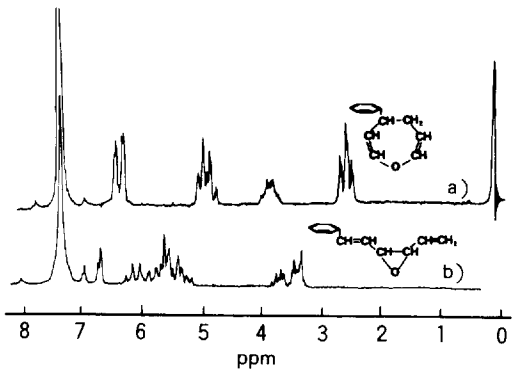


Fig. 1. ^{1}H-NMR spectra of a) 4-phenyloxepine and b) monomer (VPVO).

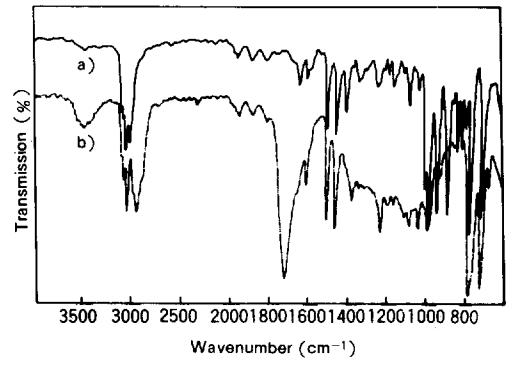


Fig. 2. IR spectra of a) monomer (VPVO) and b) poly (VPVO) initiated by 5-mole % DTBP at 120℃ for 48 hrs.

Table 1. Thermal and Radical Polymerization of 2-Vinyl-3-(β-phenyl)-Vinyloxirane

Exp. No.	Monomer (g)	Solvent (ml)	Initiator (mole%)	Temp. (℃)	Time (hr)	Yield(%)[a]		η inh[b]
						Polymer	4-POX	
1	30	toluene (30)	–	130	72	10	90	–
2	1	benzene(1)	AIBN, 5	65	48	5	0	–
3	1	benzene(2)	BPO, 5	80	48	17	0	–
4	1	benzene(2)	DTBP, 5	120	48	33	60	0.14
5	1	benzene(2)	DTBP, 10	120	48	50	50	0.09
6	1	benzene(2)	DTBP, 20	120	48	63	30	0.07

[a] Yields of powdery polymers were measured gravimetrically. 4-POX means the isomerization compound (4-phenyloxepine) produced during radical polymerization. The residual values except polymer and 4-POX yields were those of the unreacted VPVO.

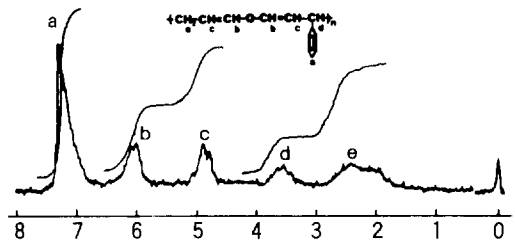
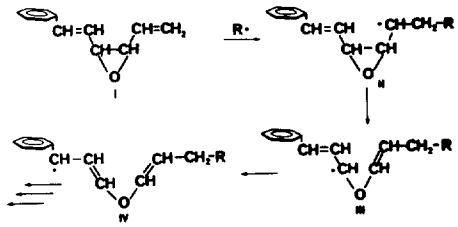


Fig. 3. ^{1}H-NMR spectrum of poly(VPVO) obtained by Exp. No. 4.



zation. This observation is consistent with the NMR data of polymer, shown in Fig. 3. The NMR spectrum of polymer shows signals at 4.9 and 6.1 ppm, which are attributable to symmetrical olefin protons(−CH=CH−O−CH=CH−). Also a broad signal at 3.6 ppm corresponding to benzyl proton (Fig. 3) and the absence of a signal 6.7~6.9 ppm, corresponding to a benzyl proton(Ph−CH=) of monomer (Fig. 1-b)), clearly indicated that the VPVO underwent the ring-opening and followed by isomerization of the more stable allyl radical (IV) in the presence of radical initiators.

In the radical polymerization in the presence of radical initiator, the initiator radical attacks the vinyl group of VPVO(I), to form the radical(II) which rearranges immediately to the more stable allyl radical(III) via C−C bond scission in the oxirane ring.

Furthermore it appears that the radical(III) isomerizes to the radical(IV) probably in a concerted mechanism, and the propagation started from radical(IV) which produces a polymer containing divinyl ether units in the polymer chain. Further studies of the copolymerization and other substituents on the investigated ring-opening and isomerization polymerization are now in progress.

EXPERIMENTAL

Preparation of 2-Vinyl-3-(β-phenyl)-Vinyloxirane (VPVO)

Solution containing allylbromide (14.6 g, 0.12 mole) and dimethylsulfide(8.5 g, 0.14 mole) in 7.5 ml of water was stirred at room temperature for 20 hrs. Unreacted dimethylsulfide was removed at reduced pressure. After cinnamaldehyde(10 g, 0.12 mole) in 22 ml of 2-propanol was added into the solution at room temperature, an aqueous solution (11.4 ml) of sodium hydroxide(4.8 g, 0.12 mole) was then added dropwise with vigorous stirring. After the solution was stirred for an additional 6 hrs. dimethylsulfide was removed. The organic layer was extracted with ethylether, and washed with water. The solvents was evaporated and the residue was vacuum distilled to obtain 6 g of monomer(VPVO). (60% yield, bp : 78℃/0.1 torr) ^{1}H−NMR($CDCl_3$, ppm) ; 7.2(s, 5H, phenyl), 5.2~6.2(m, 4H, =CH−C−O−C−CH=CH_2), 6.8~6.9(d, 1H, Ph−CH=), 3.3~3.8(m, 2H, −CH−CH−). IR(film, cm^{-1}) ; 3000(vinylic C−H), 1680(weak, C=C), 900~1000 (C−H of the oxirane ring).

Thermal Rearrangement of Monomer(VPVO)

A mixture of VPVO (30 g) and 30 ml of dry toluene was placed in a 100 ml flask equipped with a condenser. The mixture was bubbled with nitrogen for 5 min. After the flask was then equipped with nitrogen balloon, the temperature was raised to 130℃ to maintain a gentle reflux for 72 hrs. After the solvent was removed by distillation under reduced pressure, the residue was fractionally distilled to give 27 g of 4-phenyloxepine. (90% yield, bp : 61℃/0.1 torr) ^{1}H−NMR($CDCl_3$, ppm) : 7.2(s, 5H, phenyl), 6.4(d, 2H, =CH−O−CH=), 5(m, 2H, −CH=C−O−C=CH−), 3.8(m, 1H, Ph−CH), 2.5(t, 2H, $-CH_2-$); IR(neat, cm^{-1}) : 1680(strong, C=C), 1120(strong, C−O).

Representative Radical Polymerization of VPVO

In a 10ml sealed polymerization tube, 1 g of

VPVO in 2 ml of benzene was heated at 120℃ for 48 hrs with 3 mole % of DTBP as an initiator. After the tube was opened, the polymer was dissolved in 2 ml of chloroform. This solution was slowly added dropwise into a stirred n-hexane to precipitate the polymer. The collected solid was dried in vacuo at room temperature to give white powdery polymer. (0.33 g, 33% yield) ^{1}H−NMR ($CDCl_3$, ppm) : 7.2(s, 5H, phenyl), 6.1(broad, 2H, =CH−O−CH=), 4.9(broad, 2H, −CH=C−O−C=CH−), 3.5(m, 1H, ph−CH), 2.8~1.9(broad, 2H, $-CH_2-$); IR(film, cm^{-1}) : 3050(vinylic C−H), 1680(strong, C=C), 1000~1200(−C−O−C−).

* The present studies were supported by the Basic Science Research Institute Program, Ministry of Education, 1988.

REFERENCES

1. T. Endo and Y. Hiraguri, *J. Am. Chem. Soc.*, **109,** 3779 (1987).
2. C. Y. Pan, Z, Wu and W. J. Bailey, *J. Polym. Sci. Polym. Lett. Ed.*, **25,** 243 (1987).
3. I. Cho, M. S. Gong, and S. I. Chang, *Makromol. Chem., Rapid common.*, **10,** 201 (1989).
4. Y. C. Park, D. H. Yoon, J. K. Yang, C. B. Kim, and M. S. Gong, *Polymer (Korea)*, **14,** 82 (1990).
5. W. J. Bailey and L. L. Zhou, *J. Am. Chem. Soc. Div. Polym. Chem. Prepr.*, **30,** 195 (1989).
6. W. J. Bailey, IUPAC 32nd Inter. Sym., Macromolecules Prepr., 1 (1988).
7. T. Endo and N. Kanda, *J Polym. Sci. Polym. Chem. Ed.*, **23,** 1931 (1985).