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비시클로[2,2,1^{8,11}] 헵트-7,9-일-2-메틸렌-1,4,6-트리옥사피로[4,4] 노난의 합성 및 중합

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Synthesis and Polymerization of Bicyclo[2,2,1^{8,11}]Hept-7,9-yl-2-Methylene-1,4,6-Trioxaspiro [4,4] Nonane

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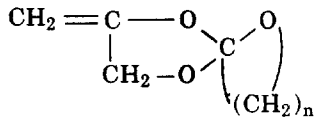
요 약 : 비시클로[2,2,1^{8,11}]헵트-7,9-일-2-메틸렌-1,4,6-트리옥사스피로 [4,4] 노난(BIMTN) 은 6-옥사트리시클로[3,2,1,1^{3,8}]노난-7-온을 에피크로로히드린과 반응시킨 후 탈염화수소 반응에 의해 합성되었다. BIMTN은 DTBP를 개시제로 한 라디칼 중합에서는 좋은 열 안정성을 갖는 용매에 녹기 쉬운 중합체를 얻었다. IR과 NMR 스펙트럼으로부터 DTBP에 의해 합성된 중합체의 구조는 중합체의 골격내에 라디칼 개환 진행 때문에 나타나는 에스터와 케톤그룹이 존재함을 알 수 있었고 또한, 모노머가 희석된 조건에서는 개환율이 높은 것으로 나타났다.

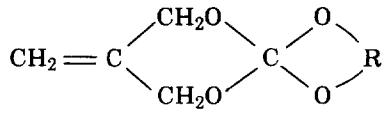
Abstract : Bicyclo[2,2,1^{8,11}]hept-7,9-yl-2-methylene-1,4,6-trioxaspiro[4,4]nonane (BIMTN) was synthesized by the reaction of 6-oxatricyclo[3,2,1,1^{3,8}] nonan-7-one with epichlorohydrin followed by dehydrochlorination. BIMTN was polymerized with di-tert-butyl peroxide(DTBP) in benzene to give a soluble polymer which has a high thermal stability. The infrared(IR) and nuclear magnetic resonance(NMR) spectra indicated that the structure of the polymer obtained by DTBP contains ester and ketone linkages in the polymer backbone, which were generated by the radical double ring-opening processes. In the radical ring-opening polymerization, it was observed that high dilution promotes the radical ring-opening process.

INTRODUCTION

Errede[1] established that spiro-di-o-xylene is polymerized via ring-opening process to form a high molecular weight polymer. Unsaturated spiro-o-esters[Ⅰ][2,3] and unsaturated spiro-o-carbonates [Ⅱ][4,5], were shown by Endo and Bailey to undergo facile radical ring-opening polymerization and copolymerization with vinyl monomers.



n=3,4,5 [I]



R=$(CH_2)_2$ [II]
$(CH_2)_3$
$(CH_2)_4$
$(CH_2)_2C=CH_2$

The cationic ring-opening polymerization of spiro-o-carboxylates, such as 1,4,6-trioxaspiro[4,4] nonane[6] and spiro-o-carbonates, such as 1,5,7,11-tetraoxaspiro iro[5,5] undecane[7], and 3-methylene-1,5,7,11-tetraoxaspiro[5,5] undecane[8] have also been reported.

In this paper we describe the synthesis and poly-merization of bicyclo[2,2,1^{8,11}]hept-7,9 yl-2-methylene-1,4,6-trioxaspiro[4,4]nonane(BIMTN).

EXPERIMENTAL

Materials

Monomer, solvents, and epichlorohydrin were purified in the usual manner. Potassium t-butoxide was prepared by the method reported elsewhere[9]. Radical initiators and Lewis acids were purified by the conventional methods. The other materials were commercial products and adequately purified according to the literature methods.

Preparation of 6-oxatricyclo[3,2,1,1^{3,8}]nonan-7-one

The synthesis of 6-oxatricyclo[3,2,1,1^{3,8}]nonan-7-one was carried out by the method described by Buchholz.[10] The product was purified by recrystallization from n-pentane followed by sublimation.

Preparation of Bicyclo[2,2,1^{8,11}]hept-7,9-yl-2-chloromethyl-1,4,6-trioxaspiro[4,4]nonane(BICMTN)

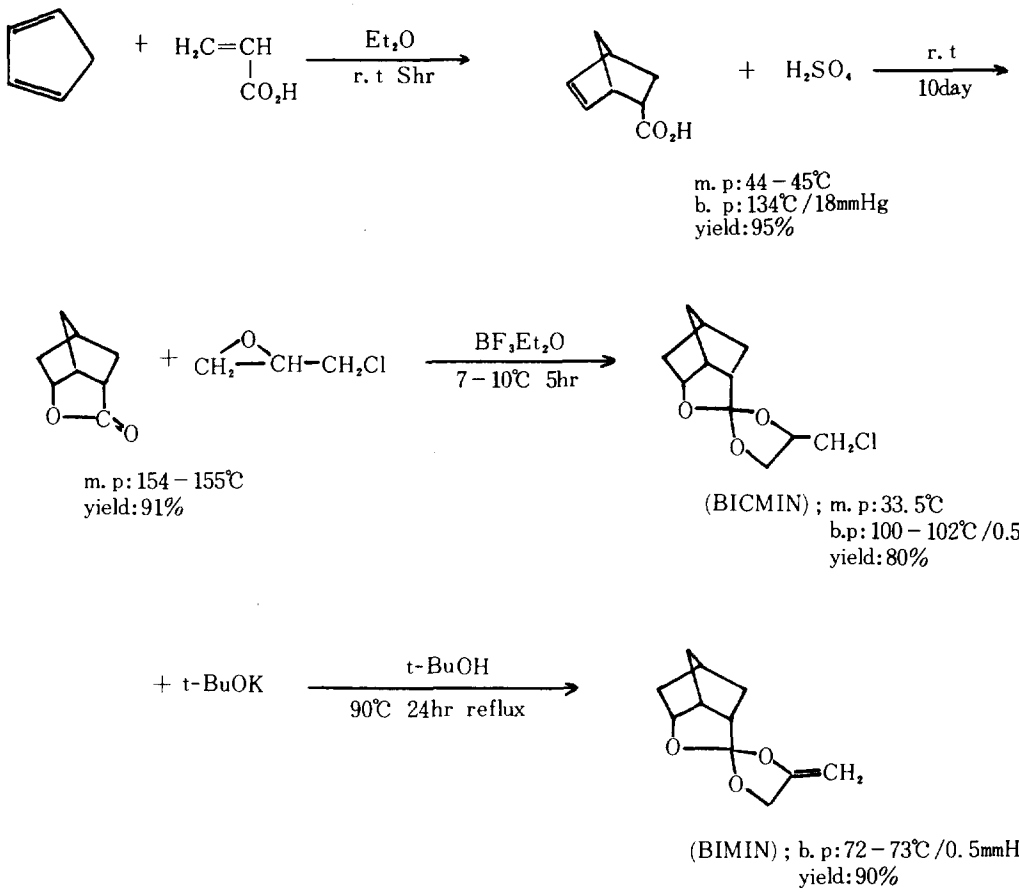
To a solution of 13.8 g(0.1 mol) of 6-oxatricyclo[3,2,1,1^{3,8}]nonan-7-one and 0.61 ml of boron trifluoride etherate as a catalyst in 100 ml of anhydrous 1,2-dichloroethane, 15 g (0.61 ml) of epichlorohydrin was added dropwise over a period of 1 hr at 7~10℃. The solution was then stirred for 5 hr at the same temperature and the catalyst was destroyed by the addition of 2 g of triethylamine. The reaction mixture was washed twice with water and dried over anhydrous magnesium sulfate. After the solvent was removed under reduced pressure, the residue was fractionally distilled to yield 18.4 g (80 %) of BICMTN, bp : 100~102℃/0.5 mmHg. The product was purified by recrystallization from ethanol. mp : 33~34℃.

Preparation of Bicyclo[2,2,1^{8,11}]hept-7,9-yl-2-methylene-1,4,6-trioxaspiro[4,4]nonane (BIMTN)

To a solution of 11g (0.1mol) of potassium t-butoxide in 100 ml of t-butanol and 23 g (0.1 mol) of BICMTN in 50 ml of t-butanol was added dropwise in a period of 1 hr at room temperature. After the addition was completed, the temperature was raised to 90℃ to maintain a reflux for 24 hr. The resulting solution was filtered and poured into water . The solution was extracted three times with ethyl ether. After the organic layer was dried over magnesium sulfate, the solvent was evaporated. The residue was fractionally distilled under reduced pressure to give 19.3 g (90 %) of BIMTN, bp : 72~73℃/0.5 mmHg.

Homopolymerization

The freshly distilled BIMTN was charged into polymerization ampules containing catalyst, and sealed immediately. And then, the polymerization were allowed to proceed under given conditions. After a given period of polymerization, the polymer was precipitated by pouring the reaction mixture into excess petroleum ether. The crude polymer was reprecipitated from methylene chloride solution into excess petroleum ether and dried in vacuo at



Scheme 1

60℃ for 24 hr. The conversion was calculated by gravimetry.

RESULTS AND DISCUSSION

Preparation of BIMTN

The synthesis of BIMTN was conducted by the reaction scheme 1 :

The structure of BICMTN and BIMTN were assigned on the basis of their IR, NMR spectra. the IR spectrum of BICMTN (Fig. 1) showed no absorption band at 1790 cm^{-1} (ester of tricyclic lactone), and ^{1}H-NMR ($CDCl_3$) showed peaks at δ values 3.0-1.0(m, 9H, norbornyl group), 3.65(d, 2H, -CH_2Cl), and 3.7-4.5 ppm (m, 4H, dioxolane ring and norbornyl proton of α-position to oxygen), as shown in Figure 2. The IR spectrum of BIMTN monomer showed the characteristic C=C absorption band at 1700 cm^{-1} and absorption at 1130cm^{-1} and 1000cm^{-1} which was attributable to ether linkage (Fig 3). The ^{1}H-NMR ($CDCl_3$)

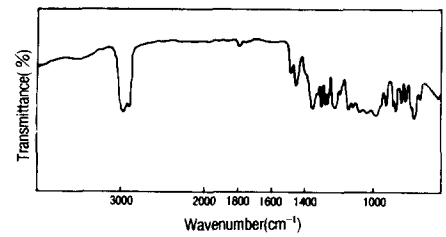


Fig. 1. IR spectrum of BICMTN.

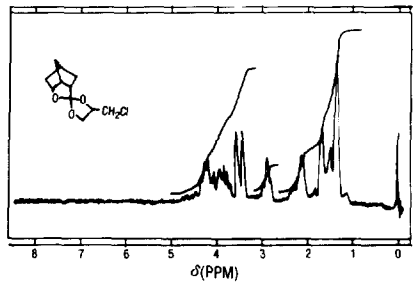


Fig. 2. ^{1}H-NMR spectrum of BICMTN.

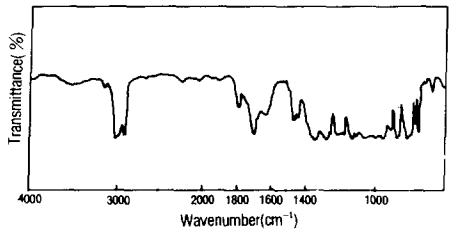


Fig. 3. 'R spectrum of BIMTN.

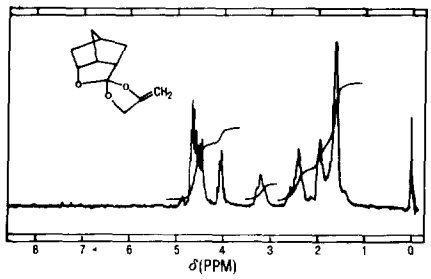


Fig. 4. ^{1}H-NMR spectrum of BIMTN.

spectrum had peaks at δ values of 3.0-1.0 (m, 9H, norbornyl group), 4.1 and 4.5 (d, 2H, respectively, $C=C<^{H_a}_{H_b}$ and 5.0-4.6 ppm (m, 3H, dioxolane ring and norbornyl proton of α-position to oxygen), as indicated in Figure 4.

Homopolymerization

Polymerization of BIMTN was carried out with DTBP as a radical initiator in bulk or solution system at 120℃. However, no polymerization was observed at 90℃. The effect of the ratio of monomr to solvent in the polymerization was shown in Table 1. These results indicates that high dilution was found to favor the ring-opening process. The IR spectra of the polymers initiated by DTBP are shown in Figure 5. The intensities of carbornyl stretching bands of 1735 cm^{-1} and of ketone at 1720 cm^{-1} increased with decrease in monomer concentration due to the ring-opening process.

Therefore, it is considered that the structure

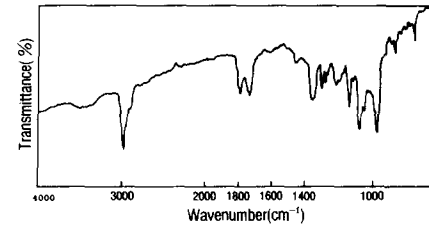


Fig. 5. IR spectrum of homopolymer initiated by DTBP.

Table 1. Radical Polymerization of BIMTN[a]

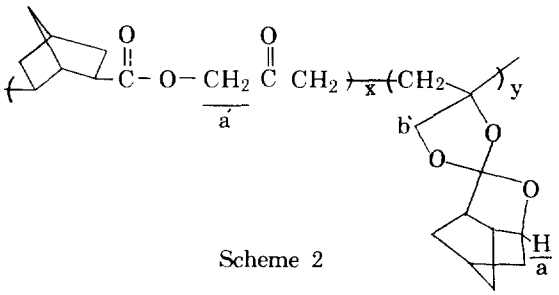
Exp. No.	Initiator (mole %)	Monomer/Solvent (g/ml)	Temp (℃)	Time (hr)	Ring-Opening content(%)	Coversion (%)	η_{inh}[b]
1	BPO (1.0)	0.5	90	24	—	—	—
2	DTBP (1.0)	0.25	120	24	—	oligomer	—
3	DTBP (1.0)	bulk	120	24	—	10	0.14
4	DTBP (2.0)	bulk	120	48	small	32	0.25
5	DTBP (2.0)	0.5	120	24	50	16	0.21
6	DTBP (2.0)	1.0	120	48	45	30	0.23
7	—[c]	—	120	48	—	7	—

a : Solvent : benzene

b ; Concentration of 0.5 g/dl in acetone at 30℃

c ; Thermal polymerization

of the polymers obtained by DTBP contains x with opening of BIMTN and y with unopening as a following structure (Scheme 2).



Scheme 2

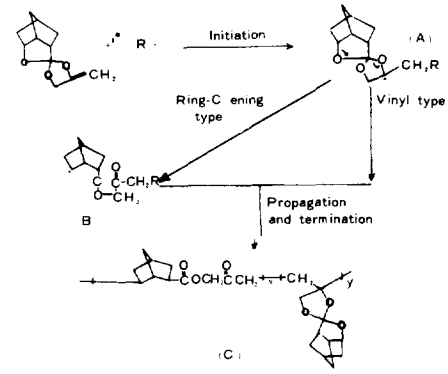
The ratio of x to y in scheme 2 could be calculated by NMR analysis. The NMR spectra of homopolymer initiated by DTBP exhibit resonance peaks at δ values of 5.2-4.8 (3H, $-\overset{O}{\overset{\|}{C}}OCH_2\overset{O}{\overset{\|}{C}}-$ and norbornyl proton of α-position to oxygen), 4.5-4.3(2H, dioxolane ring), 4.0-3.5 (4H, $-\overset{O}{\overset{\|}{C}}CH_2-$and terminal methylene group), and 3.0-1.0 ppm (18H, norbornyl group).

In scheme 2, the NMR spectrum showed peaks at 5.2-4.8 ppm [3H, one proton (a) and two proton(a')], 4.5-4.3 ppm [2H, b]. Then, the integration ratio on proton peaks of a+a' and b was 3/2. From the above results, the composition ratio of x to y in this polymer was one. From NMR and IR spectra of the polymer, the radical polymerization initiated by DTBP is believed to be proceeded by the following mechanism (Scheme 3).[2,3]

In this polymerization reaction a radical firstly attacks on the vinyl group of BIMTN to give the radical (A), and then the radical (A) which can be added to another monomer or undergoes double ring-opening to give the norbornyl radical (B). In fact the final polymer (C) has about 50% unopened units and about equal quantity of doubly opened units.

Viscosity measurements were carried out by an Ubbelohde-type viscometer. The inherent viscosities in acetone were in the range of 0.14~0.25. Most of the polymers obtained were completely soluble in chloroform, dichloromethane, THF, benzene, and acetone. However, these polymers were insoluble in n-hexane and ethyl ether (Table 3). It was found that these polymers were stable up to 290℃ by TGA analysis.

Mechanism of Polymerization



Scheme 3

Table. 2. Cationic Polymerization of BIMTN

Exp. No.	Initiator (mole%)[a]	Monomer/Solvent (g/ml)	Solvent	Temp (℃)	Time (hr)	Conversion (%)	η_{inh}[b]
1	BF_3Et_2O	0.5	CH_2Cl_2	-78	24	8	0.01
2	BF_3Et_2O	1.1	CH_2Cl_2	0	24	16	0.02
3	BF_3Et_2O	0.5	CH_2Cl_2	30	24	19	0.06
4	BF_3Et_2O	–	bulk	90	24	51	0.11
5	$AlCl_3$	0.5	CH_2Cl_2	30	24	trace	
6	$AlCl_3$	0.5	CH_2Cl_2	60	24	3	0.08
7	WCl_6	0.5	chlorobenzene	30	5	74	0.04

a : 1.0 mole%

b : Concentration of 0.5 g/dl in acetone at 30℃

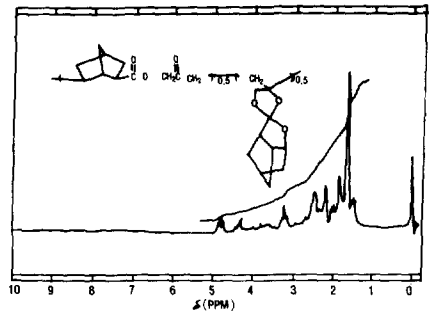


Fig. 6. ^{1}H-NMR spectrum of poly(BIMTN).

Table 3. Solubilities of Poly(BIMTN)

Solvent	solubility
methylene chloride	+
chloroform	+
acetone	+
benzene	+
THF	+
DMF	+
xylene	±
ethyl ether	−
methanol	−
n-hexane	−
pet-ether	−

+ = Soluble
± = Partially Soluble
− = Insoluble

Table 2 indicates that BIMTN was also polymerized by Lewis acids such as boron trifluoride etherate and aluminum chloride. Polymers of much lower molecular weight were obtained by the Lewis acids than by the radical initiators. This might be suggested that, in the cationic ring-opening polymerization the chain transfer from monomer and solvent to growing cationic species is more rapid than in the radical ring-opening polymerization.[11]

One more thing to be considered is that because many active sites in BIMTN, such as oxygens and double bond, are labile to cationic initiators and many side reactions occures during polymrization.[4,11] The polymer obtained from cationic initiator has no unique chemical structure.

The inherent viscosities in acetone were in the range of 0.01-0.11.

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