

## Studies on Polymers from Cyclic Dienes. XIII. Cationic Polymerization of Spiro[4,4]nona-1,3-diene\*

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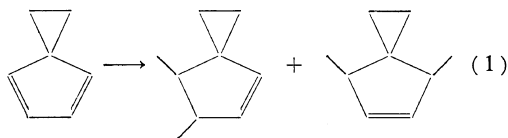
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**ABSTRACT:** Polymerization and copolymerization of spiro[4,4]nona-1,3-diene were conducted with several cationic initiators. The homopolymer was formed slowly only in polar  $\text{CH}_2\text{Cl}_2$  and/or at  $0^\circ\text{C}$ . The polymer was white, amorphous powders of relatively low molecular weight (1500–1700). No polymer was obtained with anionic initiators. Spectroscopic data indicated that the monomer unit contained trisubstituted double bonds instead of disubstituted counterparts. This result was explained by assuming isomerization to occur during propagation. Apparently, the severe steric crowding suppressed the usual 1,2- and 1,4-additions. The following reactivity ratios were obtained for spiroonadiene ( $M_1$ ) and  $\alpha$ -methylstyrene ( $M_2$ ) ( $\text{BF}_3\text{OEt}_2$ , toluene,  $-78^\circ\text{C}$ ):  $r_1=0.0$ ,  $r_2=25\pm 15$ . This result was again indicative of the steric hindrance of the spiro cyclopentyl group lowering the reactivity of the cyclopentadiene ring when compared with cyclopentadiene.

**KEY WORDS** Cationic Polymerization / Spiro[4,4]nona-1,3-diene / Cyclopentadiene /  $\alpha$ -Methylstyrene / Isomerization Polymerization /

In a previous paper,<sup>1</sup> we showed that spiro[2,4]hepta-4,6-diene underwent cationic polymerizations very readily without opening of the cyclopropyl ring as in eq 1.

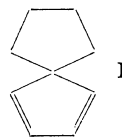


The enhanced cationic reactivity of this monomer was attributed to the conjugation effect of the cyclopropyl ring. In order to investigate further the influence of the spiro structure on the cationic reactivity of the cyclopentadiene unit, we studied cationic polymerization and copolymerization of spiro[4,4]nona-1,3-diene (I). This monomer may not be particularly reactive, since the influence of the cyclopentane group should be limited to the conventional inductive and steric effects.

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The radical copolymerization of this monomer has been reported previously.<sup>2</sup>



**EXPERIMENTAL**

### Materials

Cyclopentadiene was obtained by thermal decomposition of dicyclopentadiene and distilled before use. Spiro[4,4]nona-1,3-diene was prepared from cyclopentadiene and 1,4-dibromobutane in the presence of 50-% aqueous NaOH and triethylbenzylammonium chloride, and then purified by repeated distillation<sup>2</sup>: bp  $44-45^\circ\text{C}$  (20 mm). Commercial  $\alpha$ -methylstyrene was fractionally distilled: bp  $72-73^\circ\text{C}$  (30 mm). The preparation and purification of Friedel–Crafts catalysts and triphenylmethyl salts have been described before.<sup>3</sup>  $\text{AlEt}_3$ ,  $\text{AlEt}_2\text{Cl}$ , and  $\text{AlEtCl}_2$  (Ethyl Corporation) were used without further purification. Solvents were purified by the conventional method.

*Polymerization*

The procedure of the cationic polymerization is the same as described before.<sup>1</sup> In the polymerization with Ziegler-type catalysts, solvent and catalyst were placed under nitrogen in a glass-stoppered test tube with a side-arm for a nitrogen inlet, stirred for 20 min at 20°C, and the monomer added. The polymerization was terminated by adding methanol containing hydrochloric acid. The polymers obtained were reprecipitated from benzene and methanol, and dried *in vacuo*.

*Instruments*

The molecular weight was determined in benzene at 37°C by a vapor-pressure osmometer (Mechrolab Model 301A). IR and NMR spectra were obtained by using JASCO DS 301 and Varian A60 instruments, respectively.

## RESULTS

*Polymerization*

The polymerization of spirononadiene was carried out with cationic and Ziegler-type catalysts. The results are summarized in Table I.

Table I. Polymerization of spirononadiene

Run No.	Catalyst		Monomer, <i>M</i>	Solvent	Temp, °C	Time, hr	Conv, %	MW	A/B <sup>a</sup>
	Nature	<i>M</i> × 10 <sup>3</sup>							
1	Ph <sub>3</sub> C <sup>+</sup> BF <sub>4</sub> <sup>-</sup>	5.0	0.50	Toluene	-78	120	0		
2	Ph <sub>3</sub> C <sup>+</sup> SnCl <sub>5</sub> <sup>-</sup>	2.5	0.50	CH <sub>2</sub> Cl <sub>2</sub>	-78	48	0		
3	Ph <sub>3</sub> C <sup>+</sup> SnCl <sub>5</sub> <sup>-</sup>	50	0.50	CH <sub>2</sub> Cl <sub>2</sub>	0	72	21.1		
4	BF <sub>3</sub> OEt <sub>2</sub>	50	0.50	Toluene	-78	240	0		
5	BF <sub>3</sub> OEt <sub>2</sub>	20	1.0	Toluene	0	6.5	8.7		10.4
6	SnCl <sub>4</sub>	5.0	0.50	CH <sub>2</sub> Cl <sub>2</sub>	-78	240	6.1		10.3
7	AlEtCl <sub>2</sub>	30	1.0	Toluene	-78	38	4.3 <sup>b</sup>	1500	11.4
8	AlEtCl <sub>2</sub>	24	0.73	CH <sub>2</sub> Cl <sub>2</sub>	-78	5	13.7 <sup>c</sup>	1520	11.3
9	AlEtCl <sub>2</sub>	50	1.0	CH <sub>2</sub> Cl <sub>2</sub>	-78	24	24.0		
10	AlEt <sub>3</sub> /TiCl <sub>4</sub> (1:1)	50	1.0	Toluene	0	48	<1.4		
11	AlEtCl <sub>2</sub> /TiCl <sub>4</sub> (1:1)	50	1.0	Toluene	0	48	24.2 <sup>d</sup>	1720	

<sup>a</sup> NMR peak area ratio of aliphatic and olefinic protons.

<sup>b</sup> Softening point, above 200°C.

<sup>c</sup> Softening point, 190–220°C. *Anal.* Calcd for (C<sub>9</sub>H<sub>12</sub>)<sub>n</sub>: C, 89.93; H, 10.07.

Found: C, 89.53; H, 10.23.

<sup>d</sup> 50% of the product is yellowish and insoluble in common organic solvents. Molecular weight was determined for the soluble product.

This monomer was reluctant to polymerize: for instance, no polymer was formed with BF<sub>3</sub>OEt<sub>2</sub> at -78°C. The polymer yield increased in polar methylene chloride and with AlEtCl<sub>2</sub>. The efficiency of Ziegler-type catalysts was also limited, and the AlEt<sub>3</sub>-TiCl<sub>4</sub>(1:1) catalyst gave little polymer. On the other hand, the AlEtCl<sub>2</sub>-TiCl<sub>4</sub> system gave polymer in a fair yield, although the cationic species might be the true catalyst. About 50% of the product was insoluble in this system probably due to cross-linking. Anionic catalysts (*e.g.*, Na-naphthalene) did not give polymer. The polymers were white powders

Table II. Cationic copolymerization of spirononadiene (M<sub>1</sub>) and α-methylstyrene (M<sub>2</sub>)<sup>a</sup>

No.	M <sub>1</sub> in monomer, mol%	Time, min	Conversion, %	M <sub>1</sub> unit in copolymer, mol%
1	25.0	15	4.8	2.5
2	50.0	15	6.7	8.8
3	70.9	25	5.5	10.1
4	83.3	40	5.2	13.3
5	95.2	180	1.8	20.6

<sup>a</sup> Total monomer concentration, 1.0 *M*; catalyst, BF<sub>3</sub>OEt<sub>2</sub>, 0.01 *M*; solvent, toluene; temp., -78°C.

## Cationic Polymerization of Spiroonadiene

which were soluble in benzene and  $\text{CCl}_4$ . The softening points of the polymer were high (190—220°C), in spite of their low molecular weight (1500—1700).

### Cationic Copolymerization

The cationic copolymerization of spiroonadiene with  $\alpha$ -methylstyrene was performed with  $\text{BF}_3\text{OEt}_2$  at  $-78^\circ\text{C}$ , as shown in Table II. The rate of polymerization decreased with the increase of spiroonadiene in the monomer feed. The copolymer composition was determined in chloroform by the use of an IR peak ( $\nu_{\text{C}=\text{C}}$ ) of the

$\alpha$ -methylstyrene unit at  $1600\text{ cm}^{-1}$  (molecular extinction coefficient:  $44.6\text{ l/mol cm}$ ). The composition determined by NMR spectroscopy was in fair agreement with the IR result. The monomer reactivity ratios were obtained by curve fitting:  $r_1(\text{spiroonadiene})=0.0$ ,  $r_2(\alpha\text{-methylstyrene})=25\pm 15$ .

An equimolar mixture of spiroonadiene and cyclopentadiene was copolymerized ( $\text{BF}_3\text{OEt}_2$ , toluene,  $-78^\circ\text{C}$ ) and the copolymer composition was determined from the peak areas of olefinic and aliphatic protons in the NMR spectrum.

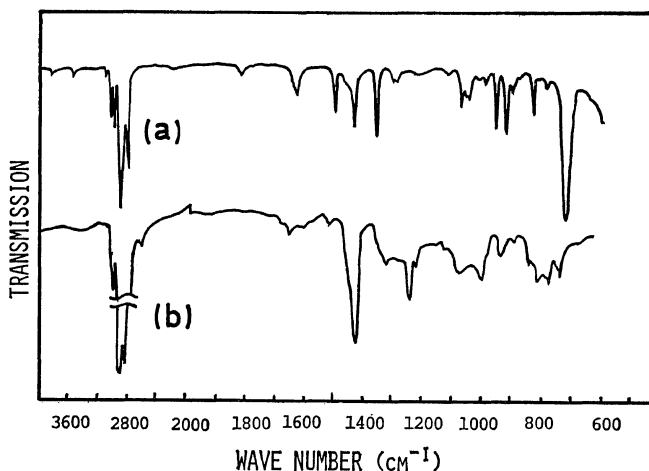


Figure 1. Infrared spectra of (a) spiroonadiene monomer (neat) and (b) polyspiroonadiene (KBr disc) ( $\text{BF}_3\text{OEt}_2$ , toluene,  $0^\circ\text{C}$ ).

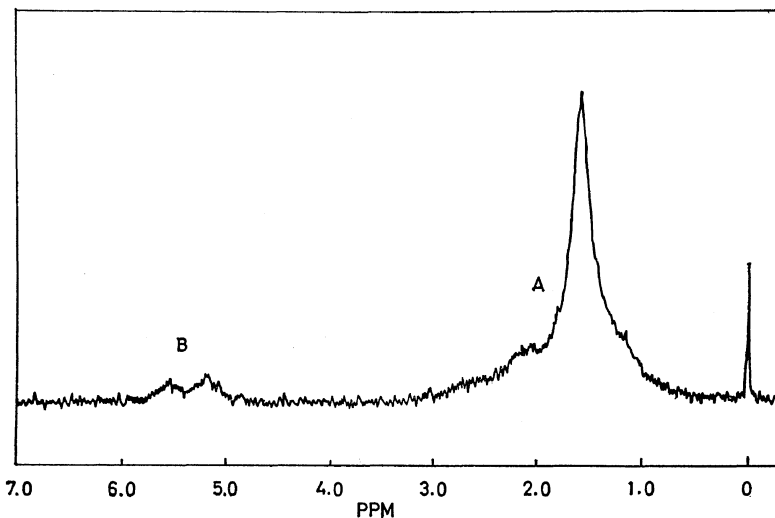


Figure 2. NMR spectra of polyspiroonadiene:  $\text{CDCl}_3$ , solvent; TMS, internal standard; sample, Table I, No. 8.

The content of the spirononadiene unit was 8% or 16% depending on whether or not the hydride shift as discussed below was assumed to occur. The experimental confirmation for the presence or absence of the isomerized unit was difficult.

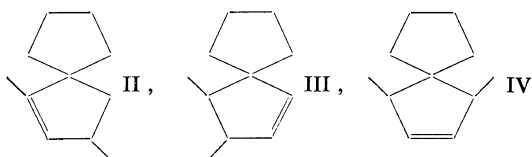
#### Polymer Structure

All the samples of polyspirononadiene showed similar IR spectra. An example is given in Figure 1, in comparison with a spectrum of the monomer.

The characteristic peaks of the cyclopentadiene group appear at 1630 ( $\nu_{C=C}$ ), 1510, 1370 ( $\delta_{C-H}$  in-plane) and 730  $\text{cm}^{-1}$  ( $\delta_{C-H}$  out-of-plane) in the monomer spectrum. These absorptions disappear in the polymer spectrum. Instead, new peaks ascribable to the cyclopentene ring are found at 1660 ( $\nu_{C=C}$ ) and 835  $\text{cm}^{-1}$  ( $\delta_{C-H}$  out-of-plane). The corresponding peaks of polycyclopentadiene<sup>4</sup> exist at 1620 and 755  $\text{cm}^{-1}$ . Similar peaks appear at 1615 and 745  $\text{cm}^{-1}$  for polyspiroheptadiene.<sup>1</sup> These IR characteristics suggest that the double bond in polyspirononadiene is trisubstituted<sup>5</sup> in contrast with the presence of the disubstituted double bond in polycyclopentadiene and polyspiroheptadiene.

An NMR spectrum of polyspirononadiene is shown in Figure 2. Peaks at 0.8–3.0 ppm (peak A) and at 4.9–5.7 ppm (peak B) are due to the aliphatic and olefinic protons, respectively. The area ratios of peak A and B were approximately eleven (Table I). The usual 1,2- and 1,4-addition structures should give an area ratio of five.

Thus, it was concluded that polyspirononadiene consisted of an isomerized structural unit II rather than the normal 1,2-structure (III) or 1,4-structure (IV). Other isomerized structures appear improbable (see below).



The structure of the spirononadiene unit in the copolymer was not very certain from the spectroscopic data, because of its low content. However, since the IR spectra of the copolymer did not show the absorption of a trisubstituted double bond at 835  $\text{cm}^{-1}$ , the spirononadiene unit in the copolymer may possess the usual 1,2- and

1,4-addition units.

## DISCUSSION

### Monomer Reactivity

As reported in our previous paper, spiro[2,4]-hepta-4,6-diene is extremely reactive in the presence of cationic initiators. In fact, violent polymerization occurred under commonly employed polymerization conditions. This is probably attributable to the increased electron density of the cyclopentadiene ring due to the conjugative electron donation of the cyclopropyl group and/or to the release of ring strain upon polymerization. These factors would not be found in the spirononadiene monomer, since the spirocyclopentyl group is distorted neither electronically nor geometrically. This presumption was correct as can be seen from the data of Table I. The polymerization tendency of this monomer was quite small, and no polymer was formed under moderate polymerization conditions. Polymers were obtainable by the use of high temperature (0°C), polar solvent ( $\text{CH}_2\text{Cl}_2$ ), or strong initiator ( $\text{AlEtCl}_2$ ). Furthermore, the molecular weight of polyspirononadiene was only 1500–1700 (*i.e.*, DP 13–14), in contrast with that of polyspiroheptadiene. In the latter, the degree of polymerization easily reached several hundreds and still higher values were obtainable.

The diminished reactivity of spirononadiene is also reflected in the copolymerization data. As shown in Table III, cyclopentadiene monomer has a cationic reactivity comparable to that of  $\alpha$ -methylstyrene. On the other hand, the reactivity of spirononadiene toward the  $\alpha$ -methylstyryl cation is only 4% of that of  $\alpha$ -methylstyrene.

The alkyl substituent usually increases the

**Table III.** Monomer reactivity ratios of cyclopentadiene derivatives ( $M_1$ ) and  $\alpha$ -methylstyrene<sup>a</sup>

Monomer ( $M_1$ )	$r_1$	$r_2$	$1/r_2$	Remarks
Spirononadiene	0.0	$25 \pm 15$	0.04	This study
Cyclopentadiene	1.62	0.66	1.51	Imanishi, <i>et al.</i> <sup>b</sup>

<sup>a</sup> Polymerization condition;  $\text{BF}_3\text{OEt}_2$ , toluene,  $-76 \sim -78^\circ\text{C}$ .

<sup>b</sup> Y. Imanishi, K. Hara, S. Kohjiya, and S. Okamura, *J. Macromol. Sci.—Chem.*, **A2**, 1423 (1968).

cationic reactivity of the cyclopentadiene ring. Thus,  $1/r_2$  values in the cationic copolymerization of cyclopentadiene ( $M_1$ ) and substituted cyclopentadienes ( $M_2$ ) increase in the following order<sup>6</sup>: cyclopentadiene  $\cong$  methylisopropylcyclopentadiene < methylcyclopentadiene < dimethylcyclopentadiene < methylethylcyclopentadiene. The alkyl substituents in these derivatives are on the olefinic carbon and directly increase the electron density of the diene, although the steric effect apparently counteracts the rate-enhancing inductive effect in methylisopropylcyclopentadiene.

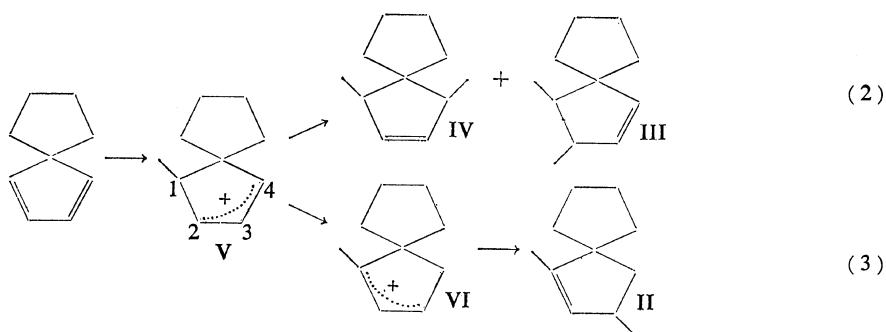
In the case of spiroonadiene, the cyclopentyl group is on the 5-position and the increase in the electron density of the diene portion would not be remarkable. Therefore its steric (negative)

influence must exceed its inductive (positive) influence, resulting in the decreased reactivity.

#### Polymer Structure

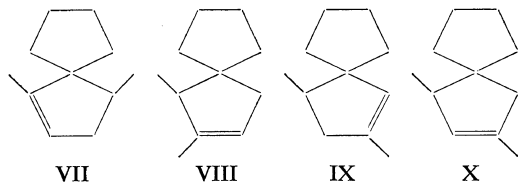
Spectroscopic data indicate that the monomer unit contains solely the trisubstituted double bond rather than the disubstituted counterpart. Thus, the polymerization process must include an isomerization step. Since the complete isomerization of the monomer unit after it has been incorporated into the polymer is difficult to conceive, propagation by a simple addition reaction is improbable.

It would be reasonable to assume that isomerization occurred during propagation, as shown in the following equation.



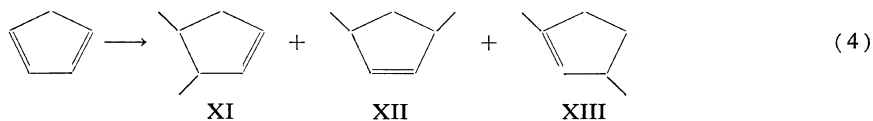
Monomer attack at the 2- and 4-positions of cation V to form III and IV must produce considerable steric crowding. Therefore, this process (eq 2) will be suppressed. When cation V isomerizes to the more stable cation VI, monomer attack can occur at the less crowded 3-position more readily (eq 3). The spectroscopic data for polyspiroonadiene are also compatible with other

structures are difficult to conceive as arising from isomerization during propagation. That the spiroonadiene unit in the copolymer seemed to consist of the 1,2- and 1,4-structure is not inconsistent with the supposition that the isomerization occurs during propagation due to steric crowding. Since the spiroonadiene unit does not continue in the copolymer as indicated by the reactivity ratio, steric crowding may not be severe enough to render isomerization preferable in the case of the copolymerization.



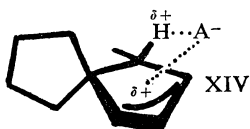
isomeric structures (VII—X) which possess the trisubstituted double bond. However, these

This type of isomerization has been observed also in the cationic polymerization of cyclopentadiene.<sup>7</sup> In polar solvents at relatively high temperatures, the isomerized unit XIII was formed in addition to the conventional 1,2- and 1,4-structures (XI and XII).



This isomerization is an example of the [1,4]-sigmatropic rearrangement, and is forbidden thermally according to the orbital symmetry rules of Woodward and Hoffmann.<sup>8</sup> Kennedy *et al.*, briefly discussed the relationship between isomerization propagation and the orbital symmetry rules.<sup>9</sup>

The Woodward—Hoffman rules apply only to concerted processes, and a different situation may arise when a counterion intervenes. For instance, Cram, *et al.*,<sup>10</sup> and Bergson and Weidler<sup>11</sup> observed that the base-catalysed 1,3-proton shift occurred stereospecifically in indene derivatives: the concerted-tour mechanism for proton transfer. The counteranion may also be involved in the isomerization of the propagating spirononadiene (XIV).



That the conversion depends very much on the initiator used and on the polymerization temperature is consistent with the scheme that the proton transfer assisted by the counteranion is the rate-limiting step of propagation.

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