

## Ring-Opening Polymerization of Bicyclo[2, 2, 1] Heptene Derivatives

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The Diels-Alder reaction of dimethyl fulvene and maleic anhydride gave 7-isopropylidenebicyclo[2, 2, 1]-hept-2-ene-5, 6-dicarboxylic acid anhydride which has been shown to undergo ring-opening polymerization. The catalytic system used being produced by reaction of either tungsten hexachloride or molybdenum pentachloride with tetramethyl tin in chlorobenzene at 70°C.

### INTRODUCTION

Various aspects of ring-opening polymerization of norbornene and its derivatives have been reported<sup>1-10</sup>; thus metathesis polymerization of norbornenes bearing ester<sup>2</sup>, nitrile<sup>3</sup>, chloride<sup>4</sup>, flouride<sup>5,6</sup>, imide<sup>7</sup>, pyridyl and anhydride<sup>8-10</sup> groups have been reported using different catalytic systems. A relatively small number of reports have been published concerning the ring-opening polymerization of bicyclo fulvene-derivatives<sup>11,12</sup>. It has been shown that metathesis ring-opening polymerization of bicyclo fulvenes substituted with polar and aryl groups could be effected with the appropriate catalyst system. It was shown that the catalyst system produced by the reaction of tungsten hexachloride with tetramethyl tin was not effective for the polymerization of these monomers<sup>12</sup>. This paper reports that monomer (I) is susceptible to polymerization by ring opening at the double bond using either of the two catalyst systems  $WCl_6/(CH_3)_4Sn$  or  $MoCl_5/(CH_3)_4Sn$ .

### RESULTS AND DISCUSSION

Monomer I was obtained from the Diels-Alder reaction between dimethyl fulvene and maleic anhydride in boiling benzene for 4 hrs<sup>13</sup>. The collected product was purified by crystallization from chlorobenzene. The compound showed a m.pt. of 135-136°, its IR, <sup>1</sup>Hnmr and <sup>13</sup>Cnmr (Figure 1) were consistent with its exo structure (Scheme I).

Calderon<sup>1</sup> reported that the exo-adduct of 5-norbornene-2, 3-dicarboxylic anhydride polymerized readily, but that the endo adduct polymerized only with some difficulty and in low yield<sup>8</sup>; this observation is in complete accord with the results obtained in this work. The exo adduct of the collected monomer (I) was polymerized using an activated catalyst of either  $WCl_6/(CH_3)_4Sn$  or  $MoCl_5/(CH_3)_4Sn$  in chlorobenzene at 70°C, the experimental procedure adopted was the same as that described

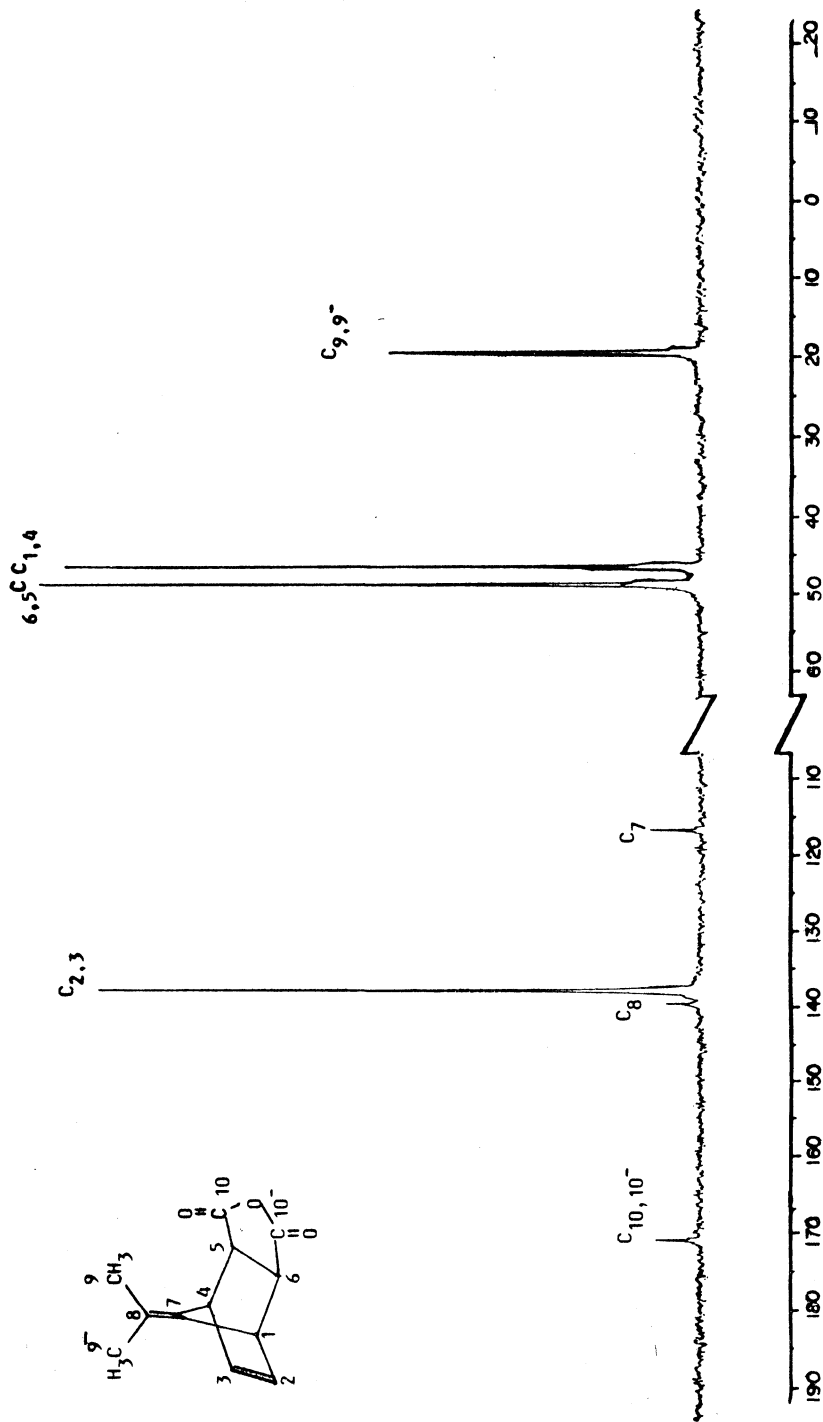
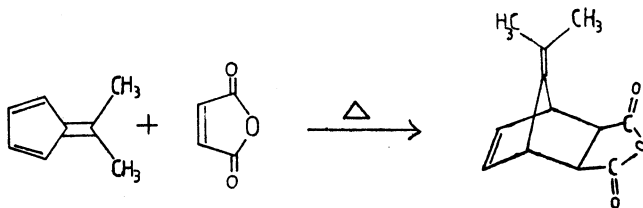
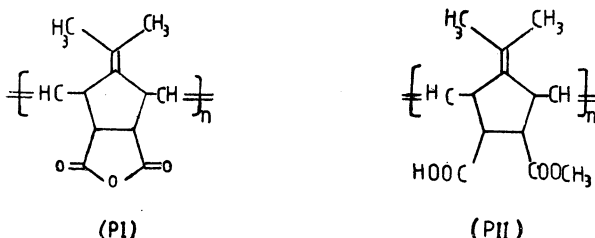


Fig. 1.  $^{13}\text{C}$ Nmr spectrum of monomer (I)



Scheme 1

previously<sup>14</sup>. The monomer is believed to polymerize to give polymer PI as shown in Scheme 2.



Scheme 2

Polymer (PI) was easily soluble in acetone. It was precipitated using methanol. The IR spectra of the polymeric material were obtained as a films cast from acetone and was consistent with the expected structure; it showed that C—H stretching ( $2870\text{--}3000\text{ cm}^{-1}$ ) and the two bands at  $1890\text{ cm}^{-1}$  (low intensity) and at  $1790\text{ cm}^{-1}$  (high intensity) corresponding to the C=O stretching frequency in cyclic acid anhydrides (Fig. 2(a)). <sup>1</sup>Hnmr spectrum of the polymer collected from  $\text{WCl}_6/(\text{CH}_3)_4\text{Sn}$  showed two ill resolved broad bands at 1.2 and 1.6 ppm due to the methyl  $\text{CH}_3$  protons; at 3 ppm two methine protons adjacent to C=O and at 3.58 ppm two methine protons adjacent to the olefinic groups. The vinylic protons resolved into two distinct bands with the cis vinylic H at 5.48 and trans at 5.75 ppm.

Although this polymeric material was evacuated for 3 hrs drying, it still captured some of the solvent, it seemed that the solvent effected the opening of the acid anhydride ring with the formation of a half methyl ester Polymer P. II, (Scheme 2). This was concluded from IR spectrum of the polymer collected from  $\text{MoCl}_5/(\text{CH}_3)_4\text{Sn}$  catalyst measured two weeks thereafter, Fig. 2(b). The spectrum shows a broad band at  $3650\text{--}2400\text{ cm}^{-1}$  (OH acid), a strong band at  $1750\text{ cm}^{-1}$  (C=O ester) and a strong band at  $1705\text{ cm}^{-1}$  (C=O acid). The <sup>1</sup>Hnmr spectrum of this polymer shows the two  $\text{CH}_3$  protons broad band at 1.6 ppm, the two methine protons adjacent to CO at 3.6 ppm, the two methine protons adjacent to olefinic bonds at 3.58 ppm, the  $\text{CH}_3\text{O}$  protons at 3.8 ppm,

the olefinic protons at 5.6 ppm and a proton at about 7.8 ppm probably corresponding to the OH proton.

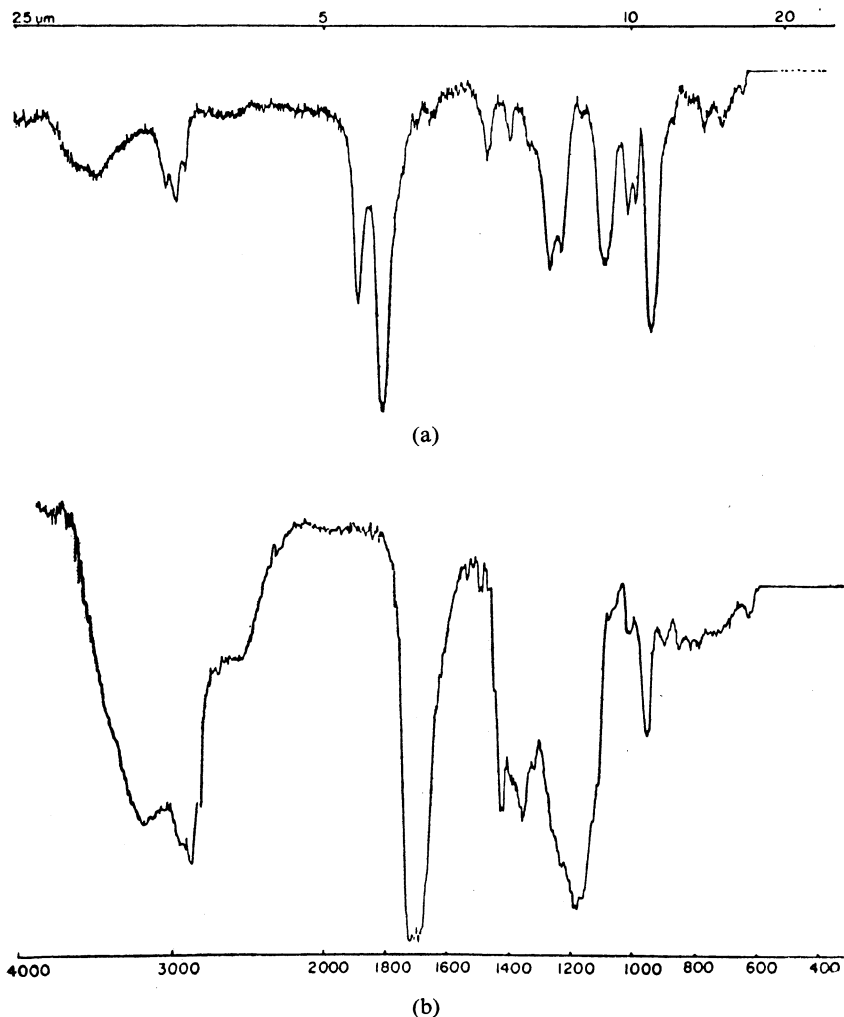


Fig. 2. IR spectra of polymer PI (a) and polymer PII (b)

The data are consistent along with the assumption that the products are formed by ring-opening polymerization.  $^{13}\text{C}$ nmr spectra provide the major part of the evidence for the structure of the monomer and the polymers. In the  $^{13}\text{C}$ nmr spectrum of the monomer seven signals are observed. The proposed structure is shown in Figure 2, along with the numbering system. The high field signal at 19.48 ppm is assigned to the methyl carbon ( $\text{C}_{9,9'}$ ) and the other two signals at 46.60 and 49.00 ppm are assigned to the methine carbon  $\text{C}_{1,4}$  and  $\text{C}_{5,6}$ , respectively. The down

field signals at 118.82 and 139.52 ppm are assigned to the  $C_7$  and  $C_8$  respectively. The vinylic carbon of the six membered ring has appeared

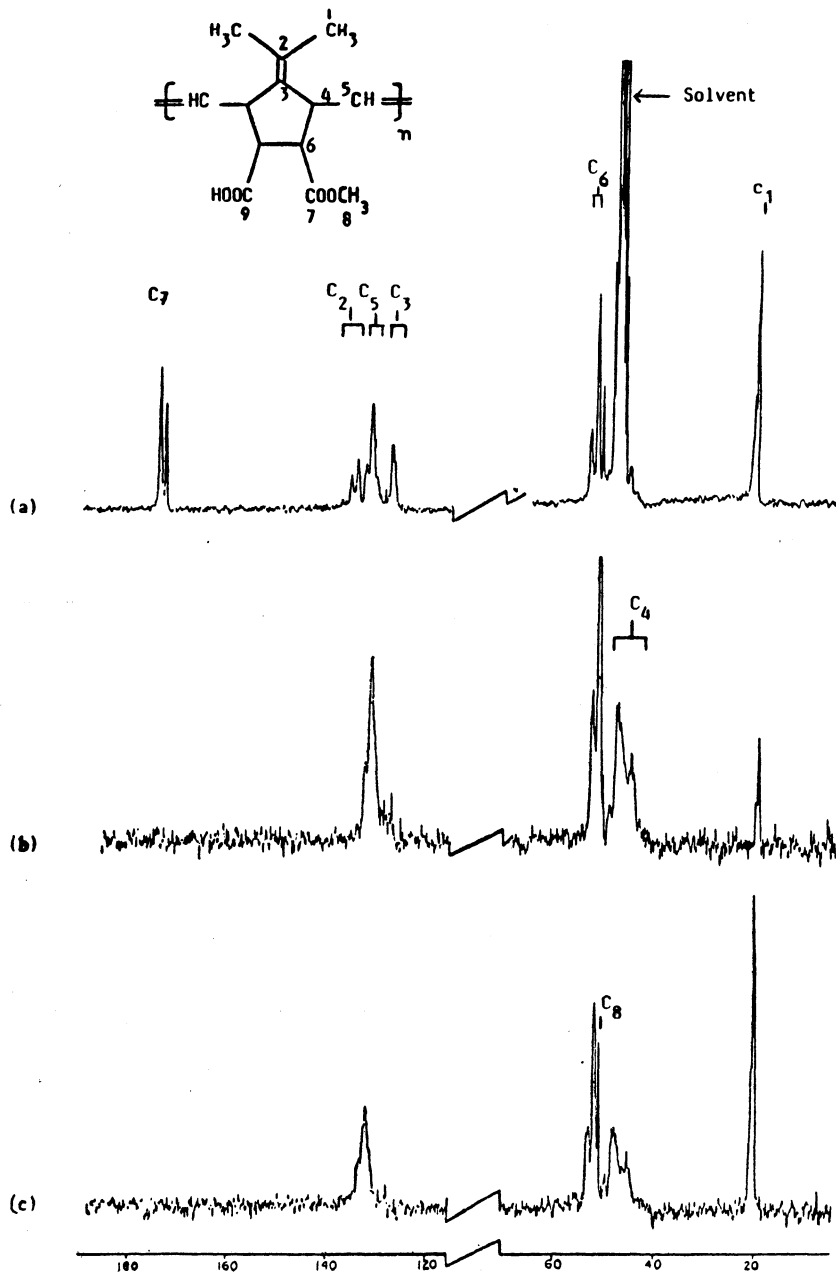
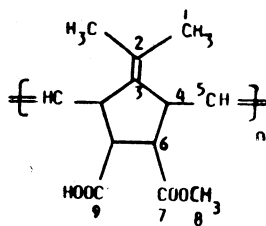


Fig. 3.  $^{13}\text{C}$  NMR spectrum of polymer PII prepared via  $\text{WCl}_6/\text{Me}_4\text{Sn}$  initiation, recorded at 50.32 MHz, in  $(\text{CD}_3)_2\text{CO}$  solution with TMS as internal reference.

at 137.77 ppm, and the signal at 171.07 ppm is assigned to C=O. The  $^{13}\text{C}$ nmr spectrum of the polymer PII obtained via  $\text{WCl}_6/(\text{CH}_3)_4\text{Sn}$  catalyst is shown in Figure 3(a). Figure 3(b) records its DEPT spectrum in which only CH signals are observed. Figure 3(c) shows the DEPT spectrum in which both methyl and methine signals are recorded. In both DEPT spectra quaternary carbon atoms did not appear. The  $^{13}\text{C}$ nmr chemical shifts and their assignments are summarized in Table 1. On the basis of

TABLE I  
 $^{13}\text{C}$ NMR LINE POSITIONS AND ASSIGNMENTS  
OF POLYMER PIIW AND PIIMo



Line Position (ppm)		Assignment	Integral		$\sigma_c$	
PIIW	PIIMo		PIIW	PIIMo	PIIW	PIIMo
19.74	19.748	1 t	6.54	8.60		
20.22	20.30	1 C	3.83	5.20	0.36	0.38
44.62	—	4 C	0.91	—	—	—
44.84	44.86	4 t	0.95	2.82	—	—
50.29	50.34	8 t	2.398	4.48	—	—
51.33	51.29	6 t	8.04	9.37	—	—
52.64	52.70	6 C	3.33	4.37	0.29	0.32
127.28	127.32	3 C	0.68	1.894		
127.56						
127.77	127.75	3 t	1.44	2.18	0.2	0.46
130.82	130.76	5 t	1.04	0.94		
131.72	131.72		5.34	8.03		
132.89	132.97	5 C	1.83	2.27	0.22	0.2
134.51	134.47	2 t	1.74	1.81		
	135.39			0.58	0.4	0.36
135.75	135.63	2 C	1.2	1.37		
173.08	173.10	9 t	2.09	2.80		
174.29	174.41	7 t	4.46	6.39		

the DEPT spectrum, the signals at about 20 and 50 ppm can be assigned to methyl carbons,  $\text{C}_1$  and  $\text{C}_8$  respectively. The cis content determined from  $\text{C}_1$  was 0.36. The spectra in the range of 43–50 ppm are very complicated. It consists of three broad unresolved bands assigned to  $\text{C}_4$ .

Although the computer did resolve separate lines for this carbon no value was calculated.  $C_6$  signal is resolved into cis and trans environments as indicated by the value of  $\sigma_C$  0.29. The vinylic carbon resonance is only partially resolved. The main peak is assigned to the trans vinylene unit and the other down field side is assumed to arise from the cis unit  $\sigma_C$  from these intensities is 0.22. The three bands which are absent in the DEPT spectrum, are assigned to  $C_2$ ,  $C_3$  and  $C_7$ . The signals at 127.28, 127.56 and 127.77 ppm have been assigned to  $C_3$ . The cis content determined was  $\sigma_C = 0.2$ , the peaks at 134.5 and 135.75 ppm have been assigned to  $C_2$ , and the remaining two signals at 173.08 and 174.29 ppm have been assigned to the two carbonyl carbons as indicated in Table 1. Unfortunately, the resolution is insufficient to say anything positive about the tacticity of the polymer, although the polymer is essentially atactic. An analogous analytical procedure was applied to the spectrum obtained from polymer PIIMo. The shifts and the assignments are recorded in Table 1. The spectrum is very similar to that obtained from polymerization using  $WCl_6/(CH_3)_4Sn$  as catalyst system. The  $\sigma_C$  values, Table 1, shows that the two polymers derived from  $WCl_6$  and  $MoCl_5$  initiators contain a higher proportion of trans vinylene units.

### CONCLUSIONS

7-Isopropylidenebicyclo [2, 2, 1] hept-2-ene-5, 6-dicarboxylic acid anhydride is readily polymerised by metathesis catalysts using  $MoCl_5/(CH_3)_4Sn$  and  $WCl_6/(CH_3)_4Sn$ . The polymerization occurs by ring-opening at the double bond rather than by vinyl polymerizations. Surprisingly, the  $^{13}C$ nmr spectral data for these pairs of polymers show that there is no difference in their microstructure with a tendency towards the formation of polymers having a high trans-vinylene content.

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### REFERENCES

1. K. J. Ivin, *Olefin Metathesis*, Academic Press, Ch. 15, pp. 190 et seq. (1983).
2. K. J. Ivin, J. J. Rooney, L. Bencze, J. G. Hamilton, L. M. Lam, G. Lapienis, B. S. R. Reddy and H. T. Ho, *Pure Appl. Chem.*, **54**, 447 (1982).
3. Jap. Pat. 77/63, 1977, 298 to Showa Denko, *Chem. Abstr.*, **87**, 102850 (1977).
4. A. B. Al Muniar, J. H. Edwards and J. W. Feast, *J. Mol. Catal.*, **28**, 313 (1985).
5. P. M. Blackmore and W. J. Feast, *J. Mol. Catal.*, **36**, 145 (1986).
6. ———, *J. Fluorine Chem.*, **40**, 331 (1988).
7. S. Matsumoto, K. Komatsu and K. Igarishi, *Am. Chem. Soc., Polymer Prepr.*, **18**, 110 (1977).

8. K. F. Castner and N. Calderon, *J. Mol. Catal.*, **15**, 47 (1982).
9. K. J. Ivin, J. Kress and J. A. Osborn, *J. Mol. Catal.*, **46**, 351 (1988).
10. S. Matsumoto, K. Komatsu and K. Igarishi, *Am. Chem. Soc. Symp. Ser.*, **59**, 303 (1977).
11. W. J. Feast and L. A. Shahada, *Polymer*, **27**, 1289 (1986).
12. W. J. Feast and I. S. Millichamp, *J. Mol. Catal.*, **28**, 331 (1985).
13. Alder and A. Ruhman, **17**, 566 (1950).
14. W. J. Feast and K. Harper, *J. Mol. Catal.*, **28**, 293 (1985).

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