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Poly-2,3- and 2,7-Bicyclo[2.2.1]hept-2-enes: Preparation and Structures of Polynorbornenes

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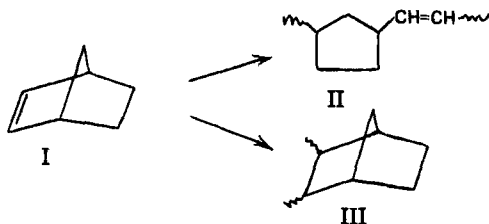
ABSTRACT

The polymerization of norbornene in the presence of either radical catalysts having a short half-life at the polymerization temperature or ethylaluminum dichloride yields a saturated polymer having a rearranged structure with 2,7 linkages. Polymerization in the presence of either $\text{Pd}(\text{C}_6\text{H}_5\text{CN})_2\text{Cl}_2$ or Ziegler-Natta catalysts containing TiCl_4 and AlR_3 or R_2AlCl yields a saturated polymer with 2,3 linkages.

INTRODUCTION

Bicyclo[2.2.1]hept-2-ene (2-norbornene) (I) undergoes ring-opening polymerization in the presence of Ziegler-Natta catalysts where Al/Ti or $\text{Al/Mo} > 1$ [1-6], reduced oxides of Cr, Mo, and W [7], and hydrated halides of Ru, Os and Ir [8-10], to yield polymers containing cyclopentane rings and cis and/or trans unsaturation (II).

Ziegler-Natta catalysts based on $\text{TiCl}_4\text{-R}_3\text{Al}$ [4, 6] and $\text{TiCl}_4\text{-R}_2\text{AlCl}$ [11], as well as $\text{C}_2\text{H}_5\text{ AlCl}_2$ [12] and Pd compounds such as $\text{Pd}(\text{C}_6\text{H}_5\text{ CN})_2\text{ Cl}_2$ [13] yield saturated polymers, presumably by "vinyl-type" double bond addition (III).



The polymerization of norbornene at 130°C in the presence of di-*tert*-butyl peroxide under 6000 atm pressure is reported to yield a polymer of unelucidated structure [14].

The effective polymerization of 5-norbornene-2,3-dicarboxylic anhydride in the presence of *tert*-butyl hydroperoxide [15, 16] prompted an investigation of the polymerization of norbornene in the presence of free radical catalysts and a determination of the structure of the resultant polynorbornene [17]. Subsequently, the structures of the saturated polymers produced by cationic, palladium and Ziegler-Natta catalysts were compared [17, 18].

EXPERIMENTAL

Materials

Norbornene (Pfaltz & Bauer) was used as received. Azobisisobutyronitrile (AIBN) was recrystallized twice from ethanol. Di-*sec*-butyl peroxydicarbonate (DsBPDC), *tert*-butyl peroxyvalate (75% in mineral spirits) (tBPP) and *tert*-butyl peracetate (75% in mineral spirits) (tBPA) were used as received (Lucidol Division, Pennwalt Corp.). Triisobutylaluminum (TIBA), triethylaluminum (TEA), diethylaluminum chloride (DEAC) and ethylaluminum dichloride (EADC) were used as received (Texas Alkyls Inc.). Titanium tetrachloride was distilled before use. Bis(benzonitrile)palladium (II) chloride (Research Organic/Inorganic Chemicals Co.) was used as received. Solvents were purified and dried by standard procedures.

Polymerization

"Radical" Polymerization. A test tube containing norbornene was flushed with nitrogen, sealed with a rubber serum cap, and placed in an oil bath which was maintained at the desired temperature. Except where indicated otherwise, the catalyst was added by hypodermic syringe in four portions over a period of 20 min. The mixture was kept in the oil bath for an additional 40 min, diluted with 3 ml benzene, and then poured into methanol. The precipitated polymer was washed with methanol and dried in vacuo at 50°C. The polymer was purified by reprecipitation from benzene solution with methanol.

Cationic Polymerization. Norbornene was charged into a test tube which was flushed with nitrogen and sealed with a rubber serum cap. Heptane or methylene chloride was injected by syringe and the tube was placed in a Dry Ice-methanol mixture which was maintained at -76°C. EADC was injected into the tube as a 20% solution in the reaction solvent. After 24 hr, chilled methanol was introduced into the tube. The reaction mixture was poured into methanol and the precipitated polymer was purified by reprecipitation from benzene solution.

"Palladium" Polymerization. A mixture of norbornene and $\text{Pd}(\text{C}_6\text{H}_5\text{CN})_2\text{Cl}_2$ was heated under nitrogen in a tube immersed in an oil bath while the temperature was slowly increased from 107 to 132°C over 17 hr. The solidified reaction mixture was slurried with benzene and activated carbon and heated to reflux for 30 min. The mixture was poured into methanol with stirring. The resultant white powder (31% yield) was soluble in benzene and was purified by reprecipitation from benzene into methanol.

A reaction carried out at 50-120°C for 22 hr resulted in a higher molecular weight polymer (56% yield) which was isolated without the use of activated carbon and was insoluble in heptane, cyclohexane, benzene, toluene, CCl_4 , chlorobenzene, and DMF below 100°C.

Ziegler-Natta Polymerization. The organoaluminum compound was added to TiCl_4 in 10 ml toluene and the mixture was stirred at 0°C for 20 min. A solution of norbornene in 5 ml toluene was added to the dark brown catalyst mixture at 25 or 60°C. The reaction mixture was stirred for 26-168 hr and then poured into a 1:3 acetone-isopropanol mixture. The precipitated white polymer was dried in vacuo and then stirred with toluene at 25°C for 5 days. The toluene-soluble fraction was isolated by precipitation in methanol.

Polymer Characterization

Molecular weights were obtained by vapor-phase osmometry or cryoscopy in benzene.

NMR spectra were recorded at 60 MHz at ambient temperature in CDCl_3 using tetramethylsilane as internal standard.

Infrared spectra were recorded as Nujol mulls on a Beckman IR 12 spectrophotometer.

RESULTS AND DISCUSSION

"Radical" Polymerization

The polymerization of norbornene was successfully carried out over the temperature range 50-130°C by use of free-radical catalysts having a short half-life at the polymerization temperature (Table 1). When catalysts were used under normal conditions, i.e., at temperatures where the half-life was at least 5 hr, little or no polymer was obtained. The yield increased with increasing catalyst concentration.

The molecular weights of the polymers were between 500 and 700, essentially independent of catalyst concentration, under the conditions investigated. However, the softening points decreased with increasing catalyst concentration.

The presence of solvents greatly reduced the yield of polymer (Table 2). Thus, an approximately 20% (w/v) solution of norbornene in dioxane gave no polymer at 80°C in the presence of 2 and 5 mole % tBPP, whereas the corresponding bulk reactions gave polymer yields of 1.3 and 11.7%, respectively. Polymer was obtained when the solvent concentration was reduced.

"Radical" polynorbornene was soluble in petroleum ether, benzene, toluene, and CCl_4 and insoluble in methanol, acetone, and ethyl acetate.

The failure to obtain polymer under normal conditions, i.e., by using a radical precursor at a temperature where it has a half-life of 3-5 hr, and successful polymerization at a temperature where the catalyst has a half-life of 1 hr, suggest that effective polymerization is dependent upon the propagation step as well as the initiation step.

It has been demonstrated that the copolymerization of conjugated dienes and maleic anhydride [19-21] and the homopolymerizations of maleic anhydride [22], ethylene [23], and 5-norbornene-2,3-dicarboxylic anhydride [15, 16] proceed readily in the presence of radical precursors at temperatures where the latter have a short

TABLE 1. Bulk Polymerization of Norbornene with Radical Catalysts^a

Type	Catalyst		$t_{1/2}$ (hr)	Temp (°C)	Time (hr)	Polymer		
	mmoles	mole-%				Yield (%)	Softening range (°C)	\bar{M}_n
DsBPDC	1	5	5	50	1	3.5	157-188	
	1	5	0.5	70	1	12.2		
AIBN	0.02	0.1	5	70	5	trace		
tBPP	0.4	2	0.5	80	1	1.3	180-235	
	1	5		80	1	11.7	150-210	640
	2	10		80	1	19.0	125-185	510
tBPA	0.6	3	1.1	120	1	6.0	185-235	
	1	5		120	1	10.0 ^b		
	1	5		120	1	13.2	140-198	580
	1.25	6.25		120	1	38.7		
	1	5	0.5	130	1	58.3		

^aCatalyst added in four portions over 20-min period to 20 mmole norbornene; total reaction time 60 min.

^bReaction carried out in air atmosphere.

half-life. It has been proposed [24] that when radical precursors undergo rapid decomposition in the presence of certain monomers, the latter undergo excitation. Effective polymerization involves the participation of excited monomers or dimers in the propagation step. The polymerization of norbornene under these conditions presumably involves the homopolymerization of excited norbornene monomer or dimer.

The failure to effect polymerization in the presence of substantial amounts of dioxane appears to be a dilution effect since polymerization does occur when the dioxane concentration is reduced. Further, dioxane does not interfere in conjugated diene-maleic anhydride copolymerization [20] and other reactions involving excited species. The dilution effect may have become apparent in the present instance due to an extremely short lifetime for the excited norbornene. A

TABLE 2. Solution Polymerization of Norbornene with Radical Catalysts^a

Type	Catalyst		$t_{1/2}$ (hr)	Solvent (ml) ^b	Temp (°C)	Time (hr)	Yield (%)
	mmoles	mole-%					
DsBPDC	1	5	5	A, 0.3	50	1	2.5
AIBN	1	5	5	B, 2.0	70	5	trace
tBPP	0.4	2	0.5	D, 10.0	80	1	0
	0.8	4		D, 1.85	80	1	3.2
	1	5		D, 10.0	80	1	0
	1	5		B, 0.045	80	1	11.3
tBPA	1	5	1.1	B, 0.045	120	1	19.6
	1.25	6.25		MS, 0.045	120	1	34.2

^aCatalyst added in four portions over 20 min to 20 mmole norbornene.

^bSolvents: A, acetone; B, benzene; D, dioxane; MS, mineral spirits.

similar dilution effect has been noted in the cyclocopolymerization of cyclopentadiene and maleic anhydride [25].

Cationic Polymerization

The polymerization of norbornene with EtAlCl_2 as catalyst at -76°C gave a 2.2% yield of polymer when heptane was used as solvent and an 18.7% yield with dichloromethane as solvent (Table 3). Although the polymer prepared in heptane had a softening range similar to that of the "radical" polymer, probably due to its low molecular weight, the polymer prepared in CH_2Cl_2 had a higher softening point, similar to that obtained by Kennedy and Makowski [12] using $\text{C}_2\text{H}_5\text{Cl}$ as solvent. The cryoscopic molecular weight of the polymer prepared in CH_2Cl_2 was 1370, comparable to the molecular weights of 1475 and 1945 reported for the polymer prepared in $\text{C}_2\text{H}_5\text{Cl}$.

TABLE 3. Cationic Polymerization of Norbornene^a

Type	Solvent Vol (ml)	Polymer		
		Yield (%)	Softening range (°C)	\bar{M}_n
Heptane	7.8	2.2	155-226	
Methylene chloride	7.5	18.7	239-298	1370

^aNorbornene, 4.0 g (42.5 mmole); EtAlCl₂, 1.2 mmole; -76°C; 24 hr.

TABLE 4. Polymerization of Norbornene with Pd(C₆H₅CN)₂Cl₂

Norbornene (g)	Pd catalyst (mg)	Temp (°C)	Time (hr)	Polymer		
				Yield (%)	Benzene solubility	\bar{M}_n
2.5	17	50-120	22.5	56	Insoluble	
2.0	12	107-132	17	31	Soluble	1290

"Palladium" Polymerization

McKeon and Starcher [13] have disclosed the polymerization of norbornene in the presence of palladium (II) compounds in which the metal is capable of forming dsp^2 hybrid orbitals. The catalysts cited include palladium bis(benzonitrile) dichloride and palladium acetate.

As shown in Table 4, the polymerization of norbornene in the presence of Pd(C₆H₅CN)₂Cl₂ gave a benzene-insoluble polymer, presumably of high molecular weight, when the reaction was initiated at 50°C and the maximum temperature was 120°C. The polymer prepared at higher temperature, i.e., 107-132°C, was benzene-soluble and had a molecular weight of 1290, comparable to that of the cationic polymer.

TABLE 5. Polymerization of Norbornene with Ziegler-Natta Catalysts^a

Al compound		Polymer						
Type	Amt (mmole)	TiCl ₄ (mmole)	Temp (°C)	Time (hr)	Yield (%)	Toluene		Softening range (°C) ^b
						Soluble (%)	Insoluble (%)	
\bar{M}_n^b								
Al (iBu) ₃	2	5	25	168	8	100	0	70-83
AlEt ₃	5	2	25	43	52	51	49	220-235
Et ₂ AlCl	4	2	25	44	55	45	55	260-270
Et ₂ AlCl	4	2	60	26	65	93	7	220-230

^aNorbornene, 100 mmole; toluene, 15 ml.^bToluene-soluble fraction.

Ziegler-Natta Polymerization

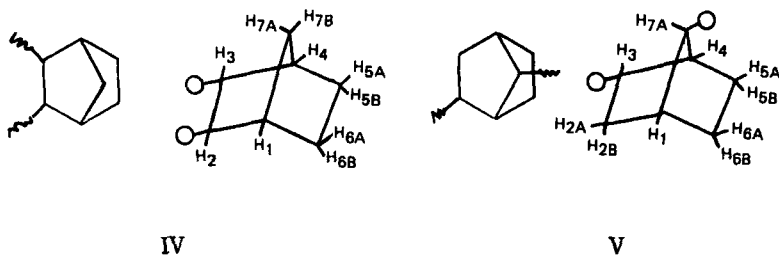
Polynorbornenes were prepared with an $\text{Al}(\text{iBu})_3\text{-TiCl}_4$ (1:2) catalyst, as reported by Sartori et al. [4], an $\text{AlEt}_3\text{-TiCl}_4$ (2.5:1) catalyst, as reported by Tsujino et al. [6], and an $\text{Et}_2\text{AlCl-TiCl}_4$ (2:1) catalyst, as reported by Koinzer et al. [11]. As shown in Table 5, the highest yield of toluene-soluble, reportedly [6] saturated, polymer was obtained with the latter composition at 60°C . The cryoscopic molecular weight of the polymers prepared with the $\text{Et}_2\text{AlCl-TiCl}_4$ catalyst was 550-750, comparable to that of the "radical" polymer. However, the softening point of over 200°C was much higher than that of the "radical" polymer and comparable to that of the cationic polymer.

Structure of Polynorbornenes

NMR Analyses. The NMR spectra of polynorbornenes prepared with "radical" (Fig. 1A), cationic (Fig. 1B), and "palladium" (Fig. 2c) catalysts are devoid of absorption below 7.5τ , indicating the absence of unsaturation. The NMR spectra of the toluene-soluble polymers prepared with Ziegler-Natta catalysts (Figs. 2D, 2E, 3F, and 3G) have a small amount of absorption at $2.7\text{-}3.0 \tau$, indicating some unsaturation.

The radical and cationic polymers have similar spectra, with the exception of the absorption peak at 9.1τ in the spectrum of the former, due to the presence of the primary hydrogens from the tert-butyl moiety from the catalyst (Fig. 1). In contrast to the two major peaks, exclusive of the catalyst peak, in these spectra, the spectra of the "palladium" polymer (Fig. 2C) and the Ziegler-Natta polymers (Figs. 2 and 3) contain three major peaks.

Two possible structures, IV and V, may be considered for a saturated polynorbornene.



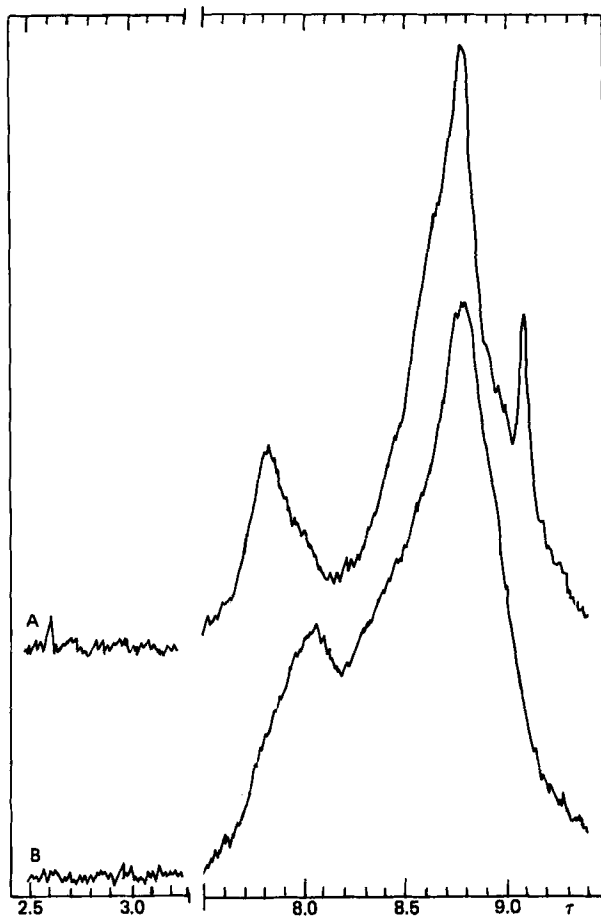


FIG. 1. NMR spectra of polynorbornenes prepared with (A) tert-butyl peroxyvalate at 80°C; (B) EtAlCl_2 at -76°C.

The assignments of absorption peaks in the polynorbornenes may be made by utilizing the assignments in the NMR spectra of norbornane [26], norbornene dimers [27], and other norbornene and norbornane derivatives.

The area under the major peak(s) centered between 8.6 and 9.0 τ is four times the area under the minor peak centered between 7.7

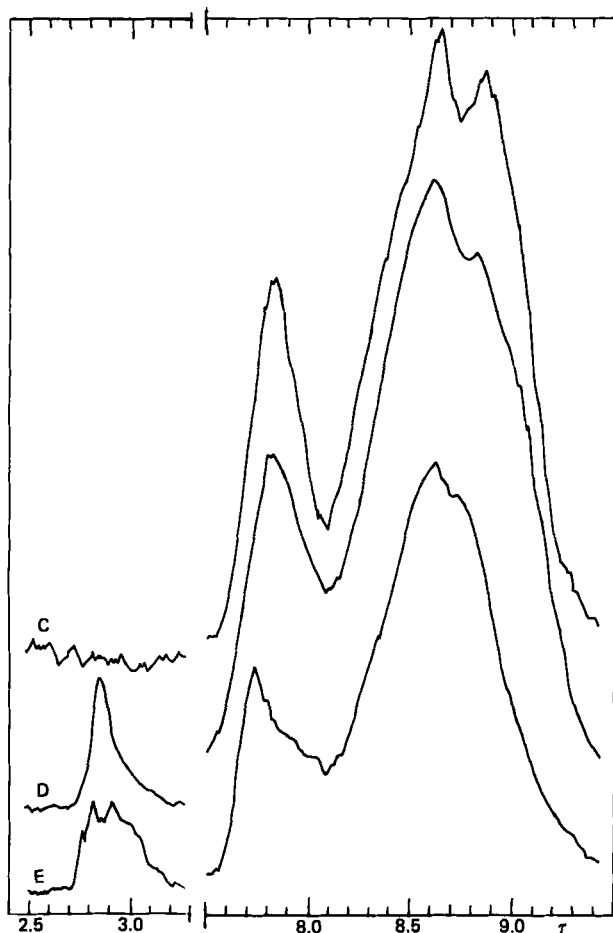


FIG. 2. NMR spectra of polynorbornenes prepared with (C) $\text{Pd}(\text{C}_6\text{H}_5\text{CN})_2\text{Cl}_2$ at 120°C ; (D) $\text{AlEt}_3\text{-TiCl}_4 = 2.5$ at 25°C ; (E) $\text{Al}(\text{i-Bu})_3\text{-TiCl}_4 = 0.5$ at 25°C .

and 8.1τ . Since the ratio of the other hydrogens to the hydrogens at positions 1 and 4 is 8:2, the peak at 8.10τ in the cationic polymer, at 7.83τ in the radical and palladium polymers and at $7.73\text{-}7.83\tau$ in the Ziegler-Natta polymers is assigned to H_1 and H_4 .

The essentially similar height and area of the peaks at 8.87τ

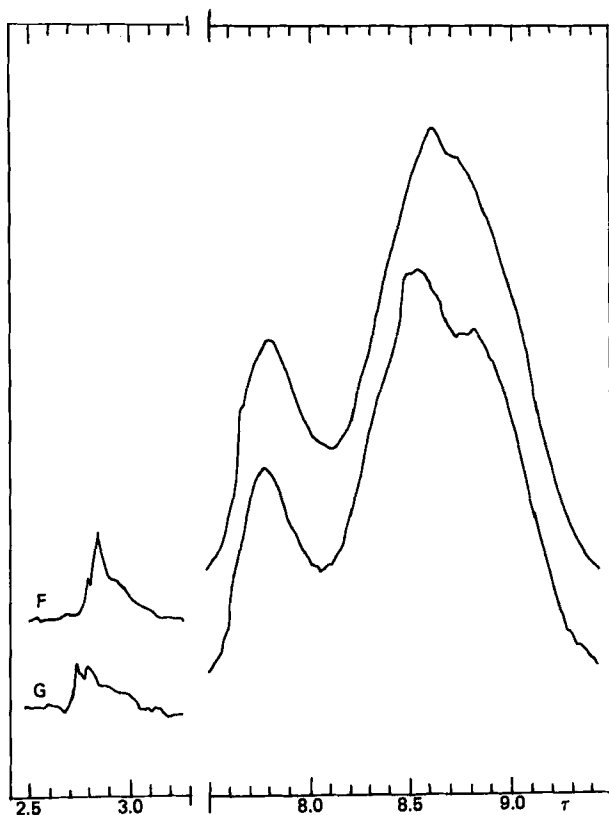


FIG. 3. NMR spectra of polynorbornenes prepared with $\text{Et}_2\text{AlCl-TiCl}_4 = 2.0$ at (F) 60°C ; (G) 25°C .

and 8.65τ in the spectrum of the palladium polymer (Fig. 2C) indicate the presence of two pairs of hydrogen atoms with a sterically similar environment, i.e., $\text{H}_{6\text{A},6\text{B}}$ and $\text{H}_{5\text{A},5\text{B}'}$, respectively in structure IV.

The $\text{H}_{6\text{A},6\text{B}}$ peaks in the spectra of the radical and cationic polymers, at 8.78τ and 8.80τ , respectively, are similar to that in the palladium polymer. However, the $\text{H}_{5\text{A},5\text{B}'}$ peaks in these spectra, at 8.73τ and 8.70τ , respectively, are only shoulders on the $\text{H}_{6\text{A},6\text{B}}$

TABLE 6. NMR Absorption Assignments in Polynorbornene

	τ							
	H _{1,4}	H _{2A}	H _{2B}	H ₃	H _{5A,5B}	H _{6A,6B}	H _{7A}	H _{7B}
Radical	7.83	8.67	8.62	8.47	8.73	8.78	8.35	-
Cationic	8.10	8.60	8.57	8.50	8.70	8.80	8.33	-
Palladium	7.83	-	8.53	8.47	8.65	8.87	8.32	8.32
Al(iBu) ₃ -TiCl ₄	7.73	-	8.52	8.47	8.63	8.75	8.34	8.34
AlEt ₃ -TiCl ₄	7.83	-	8.54	8.43	8.63	8.82	8.30	8.30
Et ₂ AlCl-TiCl ₄								
At 25°C	7.78	-	8.55	8.49	8.65	8.84	8.40	8.40
At 60°C	7.83	-	8.52	8.43	8.62	8.75	8.36	8.36

peaks. In contrast, the H_{6A,6B} peaks in the spectra of the Ziegler-Natta polymers at 8.75-8.84 τ are distinct peaks, although as shoulders on the H_{5A,5B} peaks at 8.62-8.65 τ .

These and other assignments are summarized in Table 6. Based on these assignments, it may be concluded that the polynorbornenes prepared with palladium and Ziegler-Natta catalysts have the "vinyl" polymer structure IV with 2,3 linkages, while the radical and cationic polymers have the 2,7 linkages of structure V.

The cationic and "radical" polymers apparently differ sterically, i.e., based on the assignments for the norbornene dimers [27], wherein H_{1,4} peaks are at 9.07 τ in the exo-exo dimer and at 7.75 τ in the endo-endo dimer, the cationic polymer with an absorption peak at 8.1 τ has exo substitution at carbon 3 while the "radical" polymer with an absorption peak at 7.83 τ has endo substitution at carbon 3.

The areas under the absorption peak centered at 7.83 τ in the palladium polymer and at 7.73-7.83 τ in the Ziegler-Natta polymers are twice that of the area centered at 7.83 τ in the radical polymer, suggesting that the substituents at both carbons 2 and 3 are endo and confirming the assignment of structure IV to these polymers.

The absence of unsaturation in the NMR spectra of the radical, cationic, and "palladium" polymers is consistent with a mechanism involving double bond addition, per se, or followed by a rearrangement,

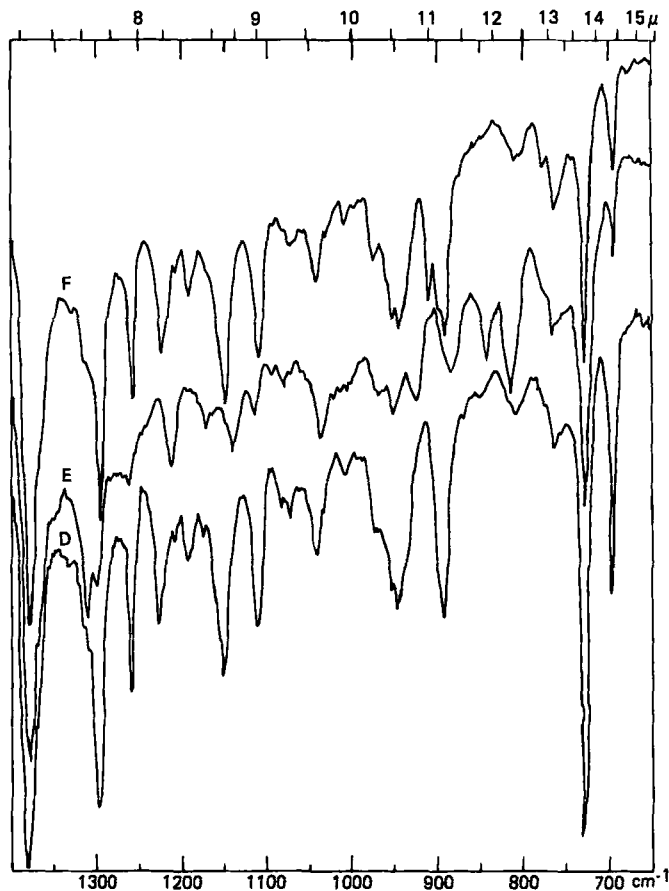


FIG. 4. IR spectra of polynorbornenes prepared with (A) tert-butyl peroxyvalate at 80°C; (B) EtAlCl_2 at -76°C; (C) $\text{Pd}(\text{C}_6\text{H}_5\text{CN})_2\text{Cl}_2$ at 120°C.

as discussed in a later section. The small amount of unsaturation in the polymers obtained with the Ziegler-Natta catalysts is attributable to the vinylcyclopentane structure II, as a monomer unit in a chain which is predominantly IV, or as a unit in a chain which is predominantly or all-II, not separated from the polymer IV by the toluene extraction.

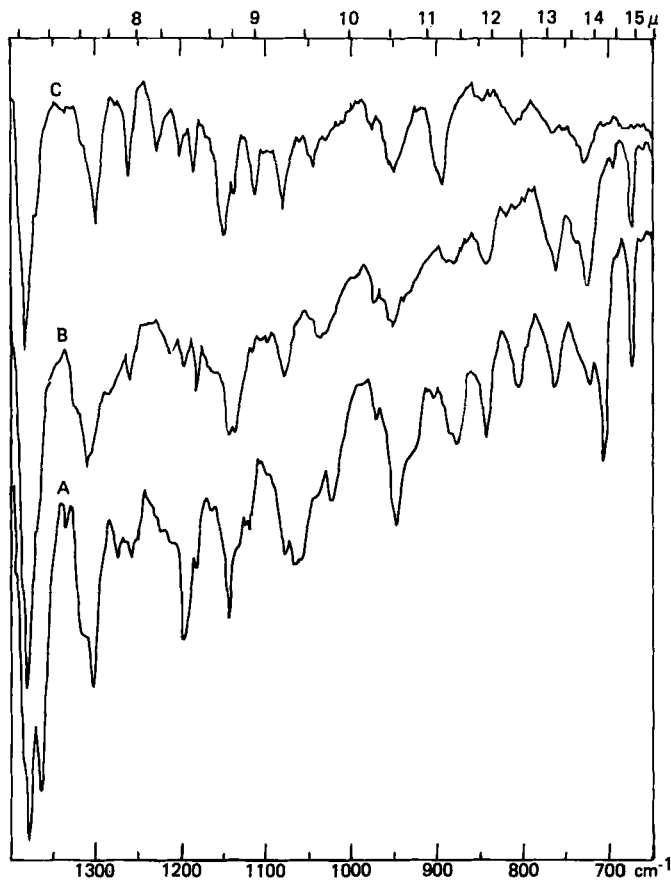


FIG. 5. IR spectra of polynorbornenes prepared with (D) $\text{AlEt}_3\text{-TiCl}_4 = 2.5$ at 25°C ; (E) $\text{Al}(\text{i-Bu})_3\text{-TiCl}_4 = 0.5$ at 25°C ; (F) $\text{Et}_2\text{AlCl-TiCl}_4 = 2.0$ at 25°C .

Infrared Analyses. The IR spectra of polynorbornenes prepared with radical, cationic, and palladium catalysts (Fig. 4) as well as those prepared with Ziegler-Natta catalysts (Fig. 5) contain numerous absorption peaks between 700 and 1500 cm^{-1} .

Absorption bands at 730 cm^{-1} and 960 cm^{-1} have been assigned to cis and trans double bonds, respectively, in vinylcyclopentane units (II), resulting from ring-opening polymerization with Ziegler-Natta

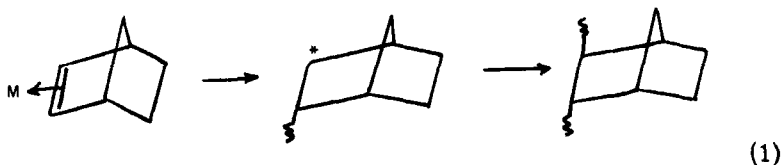
catalysts [5, 6]. The spectra of the polymers prepared with these catalysts (Fig. 5) show strong absorption peaks at 730 cm^{-1} while the spectra of the other polymers (Fig. 4) show weak or negligible absorption, consistent with the NMR spectra.

The absorption peak in the 960 cm^{-1} region in all of the polymers is relatively weak as compared to that peak in the spectra of polynorbornenes prepared by ring-opening polymerization [5, 6].

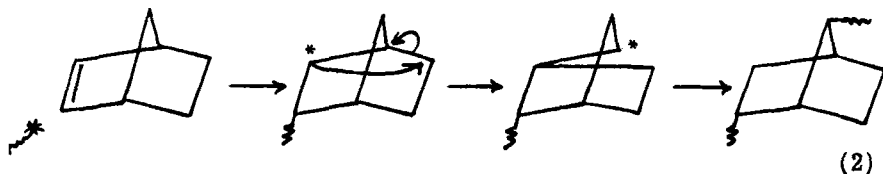
The absence of unsaturation in the NMR spectra of the radical, cationic, and palladium polymers, indicates that the absorption peak at 960 cm^{-1} in the IR spectra of these polymers is not related to the presence of trans unsaturation. Kennedy and Makowski [12] have noted the presence of this peak in the spectra of condensed ring structures such as bicyclo[2.2.1]heptane and cis-bicyclo[3.3.0]octane and have assigned the peak to such ring systems rather than to unsaturation. The present spectra are consistent with this assignment.

Mechanism of Polymerization

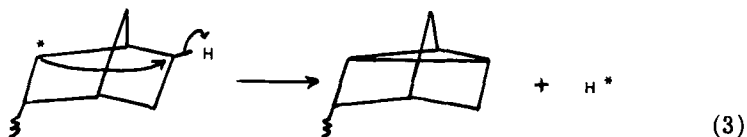
Catalysts which are known to complex with olefinic unsaturation yield polynorbornenes having structures derived from 2,3 or "vinyl-type" polymerization. Thus, catalysts containing palladium or Ti-Al reaction products result in double bond addition polymerization of norbornene [Eq. (1)].



In contrast, the reactive species derived from radical or cationic catalysts yield polynorbornenes having structures arising from a rearrangement following the double bond addition [Eq. (2)].



The low molecular weights of the latter polymers may be attributed to proton or hydrogen displacement in lieu of ring opening, i.e., nortricyclene formation [Eq. (3)].



This is consistent with the formation of 2,7-dichloronorborene and nortricyclene chloride as the major products in the chlorination of norbornene in CCl_4 solution in the presence of oxygen [28].

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