would not have changed the apparent heptane quantum yield.

Other possible reactions of the heptyl radical are (a) recombination with another heptyl radical to give tetradecane

$$R\cdot + R\cdot \longrightarrow RR \quad (6)$$

or (b) recombination with a solvent radical formed by hydrogen abstraction in the sequence

$$R\cdot + SH \longrightarrow RH + S \quad (7)$$

$$S\cdot + R\cdot \longrightarrow RS \quad (8)$$

$$S\cdot + S\cdot \longrightarrow SS \quad (9)$$

Tetradecane was definitely not formed in the reaction (it is easily detectable in the reaction mixture by gas chromatography) and consequently no heptyl radicals are consumed by process a. This is not unexpected, since the concentration of primary radicals is very low and their lifetime short, so the probability of recombination of primary radicals after the escape from the solvent "cage" is negligible.

On the other hand the radical formed by attack on the solvent, mineral oil (a highly branched saturated hydrocarbon), is likely to be much more stable, and consequently the processes described by eq 8 and 9 are much more favorable under the experimental conditions. Unfortunately, the products formed would not be detectable by gas chromatography, and hence final proof of this mechanism is not available from experiments of this type. However, in the absence of a plausible alternative it does seem reasonable to attribute the discrepancy between the carbon monoxide and heptane quantum yields to removal of heptyl radicals by reaction 8. It is obvious that in such a case, the yield of heptane is not a good measure of the quantum yield for the type I process. This difficulty could be resolved by carrying out the photolysis in a solvent in which the product RS could be estimated by gas chromatography or other means.

From the above results, it may be concluded that for linear, symmetrical, aliphatic ketones, the type I and type II quantum yields are functions of chain length, and that both decrease with increasing chain length. The type I quantum yield decreases rapidly and reaches a limiting value of 0.012. The major change occurs between R = 3 and R = 4 (4-heptanone and 5-nonanone). The type II quantum yield decreases slowly and appears to be still decreasing in ketones of about 40 carbon atoms in length, where it has a value of 0.06. The type II process is not sensitive to changes in temperature or solution viscosity. The type I quantum yield, on the other hand, is temperature dependent, but also does not appear to be affected by solvent viscosity. The type I quantum yields and activation energies for the two higher ketones studied are quite similar to those obtained for ketone polymers, and hence no additional effect would be expected from a further increase in molecular weight. On the other hand ϕ_{II} appears to be still a function of chain length even for the largest ketone used in this study and a further reduction may be expected as the molecular weight is increased.

Acknowledgment. This work was supported by research grants from Dunlop Research Ltd. and the Province of Ontario, whose support is gratefully acknowledged.

Polymerization and Structure of Allyl-Substituted Cyclopentadienes

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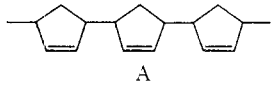
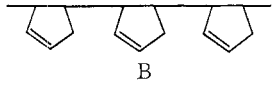
ABSTRACT: The related diene monomers, allylcyclopentadiene, methallylcyclopentadiene, and allylmethylcyclopentadiene, the last two of which have not previously been reported in the literature, were synthesized and characterized as their Diels–Alder adducts with tetracyanoethylene. Polymerizaton of these monomers was carried out with boron trifluoride as catalyst; all three polymers were soluble in organic solvents such as benzene. The structures of the polymers were determined by nmr spectroscopy and it was shown that the proportion of the 1,4 structure increased with increasing steric hindrance in the monomer.

Two extremes of structure are observed in the polymerization of cyclopentadiene under normal conditions. These are a 1,4 enchainment (A) and a 1,2 enchainment (B). The proportions of these two



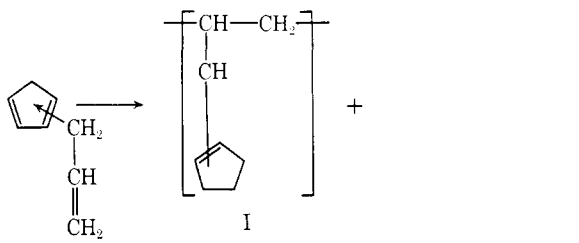
A



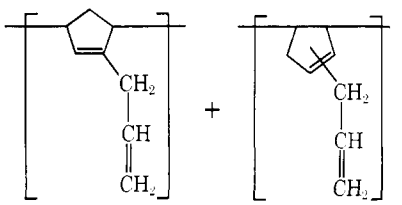
B

units can be estimated by using nmr spectra of the polymer.[1] Aso and Ohara have also determined the structure of polyallylcyclopentadiene prepared by a cationic mechanism and found it to consist of about equal amounts of the 1,4 structure (II) and the 1,2 structure (III), and no other structures such as I.[2] The isomer distribution in allylcyclopentadiene, however, was not determined.

(1) C. Aso, T. Kunitake, K. Ito, and Y. Ishimoto, *J. Polym. Sci., Part B*, **4**, 701 (1966).
(2) C. Aso and O. Ohara, *Kobunshi Kagaku*, **23**, 895 (1966).



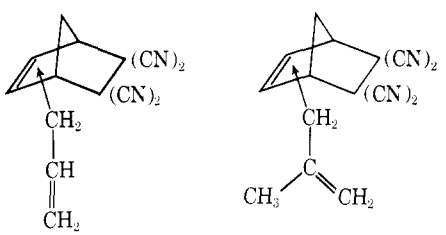
I



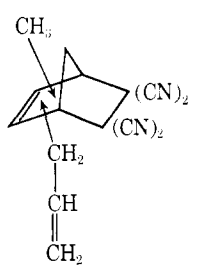
II III

In a later study, Aso and Ohara examined the polymerization of methylcyclopentadiene, whose isomer distribution can be determined by chromatographic methods, and described the relationship of the polymer structure to the polymerization conditions and the difference in reactivity between isomers.[3]

In the present work, the identity of the three monomers, allylcyclopentadiene, methallylcyclopentadiene, and allylmethylcyclopentadiene, was established by analysis of the nmr spectra of their tetracyanoethylene (TCE) adducts, IV → VI, respectively.



IV V



VI

Experimental Section

1. Preparation of Allylcyclopentadiene (ACPD), Methallylcyclopentadiene (MACPD), and Allymethylcyclopentadiene (AMCPD). All of the cyclopentadiene monomers were prepared by the reaction of cyclopentadienylsodium or methylcyclopentadienylsodium (0.25 mol) with allyl bromide or methallyl chloride (0.25 mol) in tetrahydrofuran.

Cyclopentadiene and methylcyclopentadiene were prepared by cracking the commercial dimers and could be stored at Dry Ice temperatures until ready for use. The appropriate diene was added dropwise with stirring to a sodium suspension (0.25 g-atom) in tetrahydrofuran, under a stream of prepurified nitrogen. When the evolution of hydrogen ceased, the reaction flask was packed in ice and the appropriate alkenyl halide was added dropwise with stirring over the course of about 1 hr. The reaction mixture was filtered and the solvent removed at 0° under reduced pressure. The resultant crude product was distilled under vacuum and the temperature of the water bath about the distilling flask was gradually raised. The vapor temperatures and pressures at which monomers sufficiently pure for use in cationic polymerization could be collected are as follows for the three monomers: ACPD, 25–27° (13 mm); MACPD, 39–42° (13 mm); AMCPD, 52–55° (15 mm).

(3) C. Aso and O. Ohara, *Makromol. Chem.*, **109**, 161 (1967).

TABLE I
ASSIGNMENT OF NMR SPECTRUM OF MACPD

Range, ppm	No. of protons integrated	Assignment
1.7	3	Methyl protons
3.0–3.15	2	Ring methylene protons
2.7–3.0	2	Side-chain methylene protons
4.7–4.85	2	Terminal olefinic protons
5.8–6.5	3	Ring olefinic protons

The ir, uv, and nmr spectra of the three monomers were examined; Figures 1–3 show the nmr spectra of ACPD, MACPD, and AMCPD, respectively.

The ACPD exhibited λ_{max}^{EtOH} 248 mμ (lit.[2] $\lambda_{max}^{heptane}$ 249.5 mμ). The ir and nmr spectra show the same patterns as reported by Aso and Ohara.[2]

MACPD. The distilled material showed λ_{max}^{EtOH} 245 mμ. Infrared absorptions of analytical importance are as follows: 6.07 μ ($CR_1R_2{=}CH_2$ double bond stretch), 6.23μ (conjugated C=C), 6.9–7.0 μ doublet (CH deformations of vinylidene group). An intense, broad absorption about 11.2 μ is characteristic of a $CR_1R_2{=}CH_2$ system.

The assignments made for the nmr spectrum (Figure 2) are as tabulated in Table I.

It seems reasonable that the ring methylene protons, being doubly allylic to a pair of conjugated double bonds, should exhibit a somewhat greater chemical shift than the side-chain $-CH_2-$ protons, which are doubly allylic to a pair of double bonds not in conjugation; the assignments have been made accordingly. Impurity peaks appear in this spectrum at 2.35 and 7.13 (toluene) and at 5.48 (unknown, but could not be ascribed to any isomer of MACPD).

AMCPD. The distilled monomer showed λ_{max}^{EtOH} 252 mμ. In the infrared region the allyl group shows strong absorptions at 6.20 and 7.12 μ. The absorption due to conjugated C=C comes at 6.24 μ and that due to the =C—H stretch of the allyl group appears as a strong double peak at 3.27 μ.

The assignments made for the nmr spectrum (Figure 3) are as tabulated in Table II.

2. Preparation of Monomer Derivatives. The Diels–Alder adducts of the monomers with tetracyanoethylene were prepared by the following method which has been

TABLE II
ASSIGNMENT OF NMR SPECTRUM OF AMCPD

Range, ppm	No. of protons integrated	Assignment
1.8–2.07	3	Methyl protons
2.65–2.92	2	Side-chain methylene protons
2.92–3.25	2	Ring methylene protons
4.75–5.25	2	Terminal olefinic protons
5.6–5.88	1	Internal olefinic proton of the allyl group
5.9–6.4	2	Ring olefinic protons

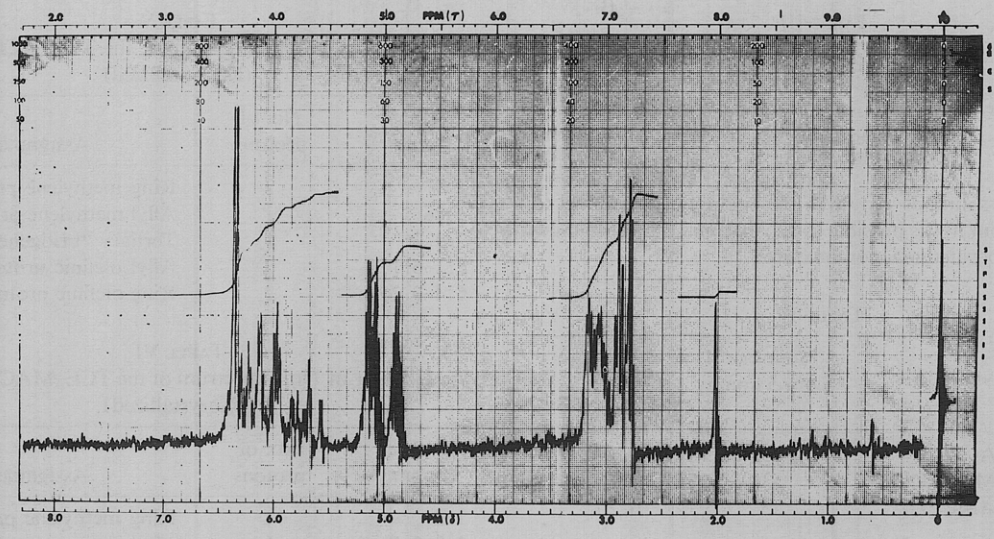


Figure 1. Allylcyclopentadiene.

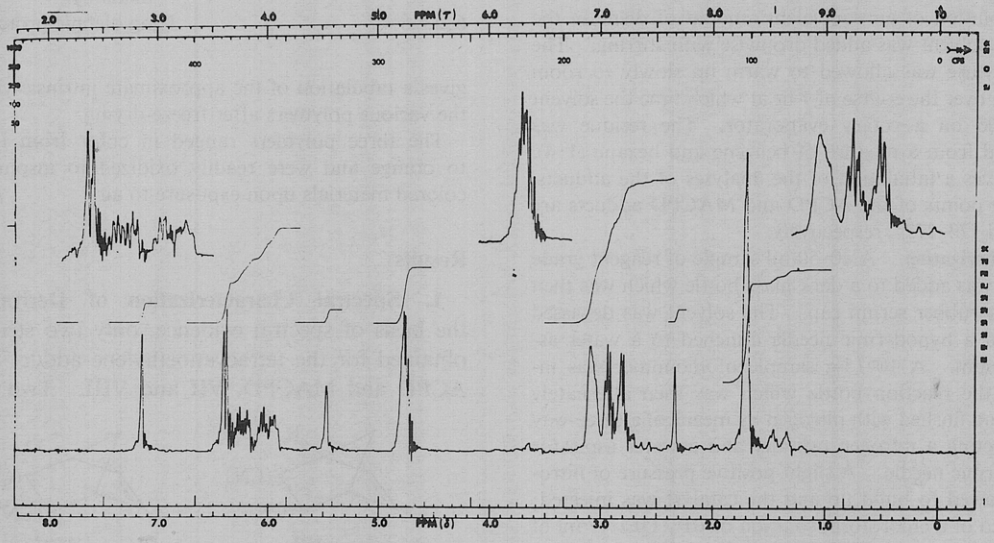


Figure 2. Methallylcyclopendadiene.

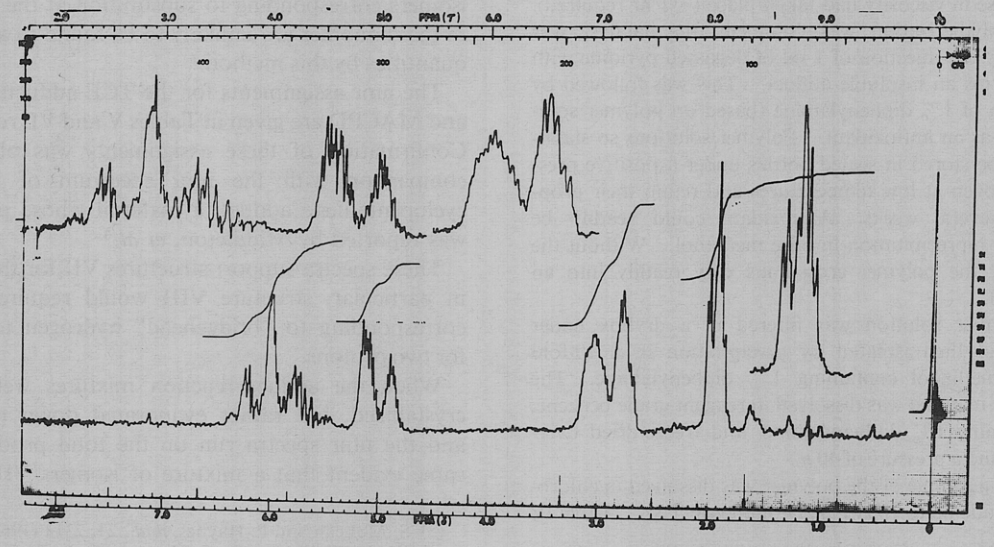


Figure 3. Allylmethylcyclopentadiene.

TABLE III[a]

Diene	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N
ACPD	71.98	4.48	23.91	71.78	4.30	23.67
MACPD	72.56	4.87	22.57	73.01	5.05	21.96

[a] Adduct solutions of AMCPD could not be made to crystallize, but it was possible to run an nmr spectrum on the syrupy, evaporated reaction mixture.

TABLE IV

	Monomer conversion, %	$[\eta]$
Poly-ACPD	65	0.19
Poly-MACPD	53	0.16
Poly-AMCPD	85	0.20

employed for the maleic anhydride adducts of the methylcyclopentadienes.[4]

A 1- or 2-g sample of tetracyanoethylene was suspended in a 1:1 mixture of benzene–hexane and cooled in an ice–salt bath. A solution of an equivalent amount of diene in the same mixed solvent was added dropwise with stirring. The reaction mixture was allowed to warm up slowly to room temperature over the course of 1 hr at which time the solvent was removed on a rotary evaporator. The residue was recrystallized from a mixture of benzene and hexane (1:4). Table III gives a tabulation of the analyses of the adducts. The melting points of the ACPD and MACPD adducts are 142–143 and 170–172°, respectively.

3. Polymerization. A 40–50-ml sample of reagent grade chloroform was added to a dark glass bottle which was then fitted with a rubber serum cap. The solvent was degassed by means of a hypodermic needle attached to a water aspirator vacuum. A 10–15-g sample of monomer was injected into the reaction bottle which was then alternately evacuated and flushed with nitrogen by means of a three-way valve connecting a nitrogen cylinder and a water aspirator to a hypodermic needle. A slight positive pressure of nitrogen was allowed to build up and the catalyst was injected; this consisted of a chloroform solution of $BF_3 \cdot OEt_2$ (7 ml of catalyst to 93 ml of $CHCl_3$) and a sufficient amount of this solution was used to bring the catalyst concentration up to 0.5% (based on polymer solution). The reaction bottle was left at room temperature until it became obvious that a large increase in viscosity had taken place (~1 hr required).

When polymerization was complete, the catalyst was destroyed by the injection of 1 ml of degassed pyridine with which it forms an insoluble adduct. This was followed by the addition of 1% diphenylamine (based on polymer solution) to act as an antioxidant. Polymer solutions so stabilized could be stored in sealed bottles under a positive pressure of nitrogen at low temperatures and retain their properties for several weeks. Antioxidant could readily be removed by reprecipitation in pure methanol. Without the antioxidant, the polymer cross-links very readily into an insoluble gel.

The polymer solution was filtered in a drybox under nitrogen and then isolated by precipitation in a 20-fold excess of methanol containing 1% diphenylamine. The precipitated material was dissolved in reagent grade benzene, also containing 1% diphenylamine, and freeze-dried overnight at 0° and a pressure of 40 μ.

A 1- or 2-g sample of the polymer was dissolved in chloroform and made up to 100 ml in a volumetric flask. Table IV gives a tabulation of the approximate intrinsic viscosities of the various polymers after freeze-drying.

The three polymers ranged in color from light yellow to orange and were readily oxidized to insoluble, deeply colored materials upon exposure to air.

(4) V. A. Mironov, E. V. Sobolev, and A. N. Elizarova, *Tetrahedron*, **19**, 1939 (1963).

TABLE V
Assignment of Nmr Spectrum of the TCE–ACPD Adduct (Recrystallized)

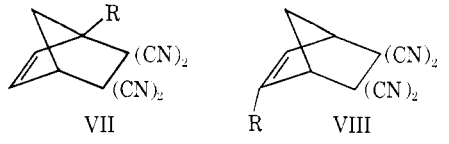
Range, ppm	No. of protons	Assignment
2.07	2	Ring methylene protons
2.88	2	Allyl methylene protons
3.9	1	Tertiary "bridgehead" proton
5.1–6.1	3	Allyl olefinic protons
6.4–6.75	2	Ring olefinic protons

TABLE VI
Assignment of Nmr Spectrum of the TCE–MACPD Adduct (Recrystallized)

Range, ppm	No. of protons	Assignment
1.89	2	Ring methylene protons
2.0–2.3	3	Methyl protons
2.8–3.0	2	Methallyl methylene group
3.94	1	Tertiary "bridgehead" proton
5.03	2	Terminal olefinic protons of methallyl
6.53–6.77	2	Ring olefinic protons

Results

1. Spectral Characterization of Derivatives. On the basis of spectral evidence, only two structures are obtained for the tetracyanoethylene adduct of each of ACPD and MACPD, VII and VIII. Two additional



VII VIII

R = allyl or methallyl

isomers corresponding to substitution at the 5 position in the monomer are unlikely to be found in appreciable quantities by this method.[5]

The nmr assignments for the TCE adducts of ACPD and MACPD are given in Tables V and VI, respectively. Confirmation of these assignments was obtained by comparison with the nmr spectrum of the TCE–cyclopentadiene adduct, a material whose preparation was reported by Middleton, *et al.*[6]

These spectra support structures VII for the adducts; in particular, structure VIII would require the peak corresponding to "bridgehead" hydrogen to integrate for two protons.

When the adduct reaction mixtures were not recrystallized, but rather evaporated down to dryness, and the nmr spectra run on the total product, it became evident that a mixture of isomers VII and VIII

(5) S. McLean and P. Haynes, *ibid.*, **21**, 2313 (1965).
(6) W. J. Middleton, R. E. Heckert, E. L. Little, and C. G. Krespan, *J. Amer. Chem. Soc.*, **80**, 2783 (1958).

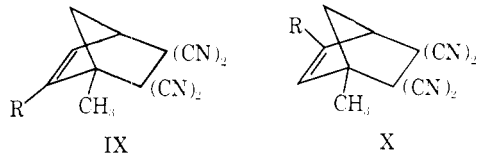
was present. A spectrum of the unrecrystallized reaction mixture for the ACPD–TCE adduct showed that the chemical shifts of the ring methylene protons and the allyl methylene protons occur at an appreciably lower field for isomer VIII than for VII. By subtraction of the spectrum of VII (*i.e.*, the recrystallized adduct) from the total spectrum, the following assignments could be made with certainty for the VIII isomer of the TCE–ACPD adduct: 2.2 ppm (2 H), ring methylene protons; 3.17 ppm (2 H), alkyl methylene protons.

As a further consequence of this large (0.15 ppm) separation in the chemical shifts for the two isomers, it is possible to estimate their relative abundance in the distilled monomer by relative integrations in the total adduct spectrum.

The above procedure is allowed because of the high yields and fast reaction rates which typify TCE additions to conjugated dienes.[6] Typically the yields of addition reactions carried out in this work were greater than 95% (based on monomer). Furthermore, reaction times as gauged by the decolorization of yellow TCE solution were of the order of a few seconds; this is very rapid as compared with the expected isomerization times between 1- and 2-substituted cyclopentadienes.[5]

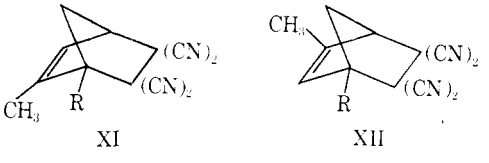
A simple analysis suggests that the ratio of VIII to VII is approximately 1.3. This proportion might have been expected in view of the work done on isomeric methylcyclopentadienes.[5] For this last system, the equilibrium mixture of isomers was found to contain approximately equal amounts of the 1- and 2-substituted isomers with very little (1%) of the 5-substituted species.

The nmr spectrum of the TCE adduct of AMCPD is rather complex. As before, bridgehead hydrogen absorption is assigned to the closely spaced multiplet centered at 3.79 (1 H). The integration of this region as one hydrogen implies that the only important adduct structures are those containing exactly one bridgehead substituent, *i.e.*, structures IX → XII. The



IX

X



XI

XII

R = allyl

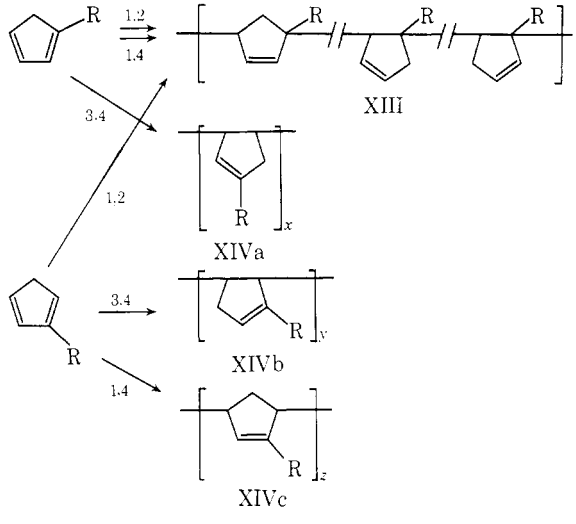
extensive splitting pattern of the allyl methylene group, 2.7–3.25 (2 H), could not be rationalized on the basis of any one structure; it appears that some allyl groups are joined to the bridgehead and some to the double bond of the ring. The assumption that a mixture of isomers is present explains the difficulty encountered in attempts to obtain a crystalline adduct. It also accounts for the appearance of *two* methyl peaks (1.72 + 1.97 ppm = 3 H) corresponding to methyl substitution on the bridgehead position or on the double bond, respectively. The ring methylene protons appear as a weakly split singlet at 2.07 ppm (2 H). As with the other adducts, the vinyl protons come in the range 4.95–6.55 (4 H).

2. Polymer Structure. The ultraviolet spectra of dilute chloroform solutions of all three polymers exhibited primarily a continuously increasing absorption between 450 mμ with neither a peak nor a shoulder.

Infrared spectra were measured as solutions in carbon disulfide and carbon tetrachloride (0.2 mm NaCl). In the monomer spectra absorption due to the cyclopentadiene ring is found at 6.2 μ; this is absent in the polymer spectra in which peaks appear to suggest the presence of a trisubstituted double bond in the case of poly-ACPD and poly-MACPD, and of a tetrasubstituted double bond in the case of poly-AMCPD.

Nmr spectra of poly-ACPD, poly-MACPD and poly-AMCPD are shown in Figures 4, 5, and 6, respectively. Spectral analysis of the polymers shows that an appreciable percentage of the monomer is incorporated as the 2 isomer. The most general starting point in the analysis of the polymer spectra is to consider the ACPD and MACPD monomers as equilibrium mixtures of the 1- and 2-substituted species as is the case with the isomeric methylcyclopentadienes.[5] The polymerization scheme may then be described as in Scheme I (after Aso and Ohara[2]).

SCHEME I



Poly-ACPD. The assignments made for this material and tabulated in Table VII are the same as those of Aso and Ohara.[2] It is to be noted that in all the polymer spectra depicted, absorption in the range 6.7–7.45 ppm is due to the aromatic protons of diphenylamine, the antioxidant employed. The unimportance of structure XIII as a contributor to the make-up of polymer chains has been demonstrated by infrared spectroscopy in poly(methylcyclopentadiene).[3] When the amount of the trisubstituted double bond in this polymer was determined using the 1660-cm^{-1} peak of 1-methylcyclopentadiene as reference, the polymer was found to contain more than 90% of the trisubstituted ring double bond (*i.e.*, structures XIV). Similar ir evidence was obtained in the case of poly-ACPD by Aso and Ohara.[2]

As a further, though negative, piece of evidence, it might be noted that the allyl $-CH_2-$ region in the nmr spectrum of poly-ACPD is very broad and flat with no

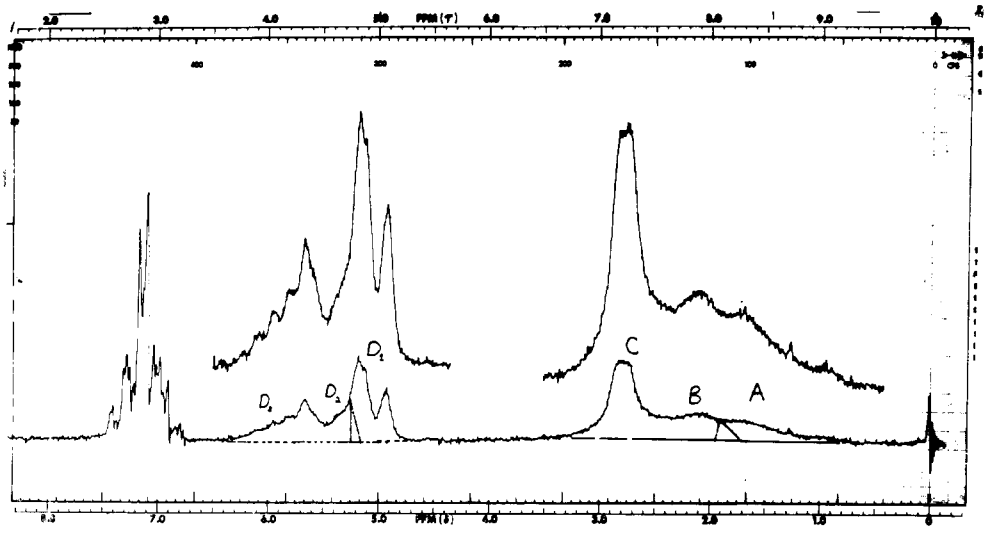


Figure 4. Poly(allylcyclopentadiene).

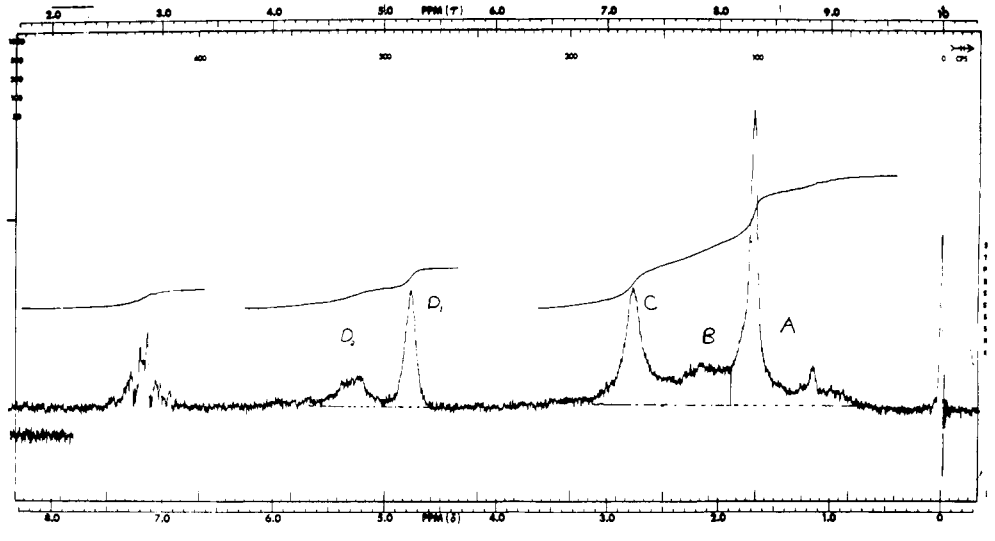


Figure 5. Poly(methallylcyclopentadiene).

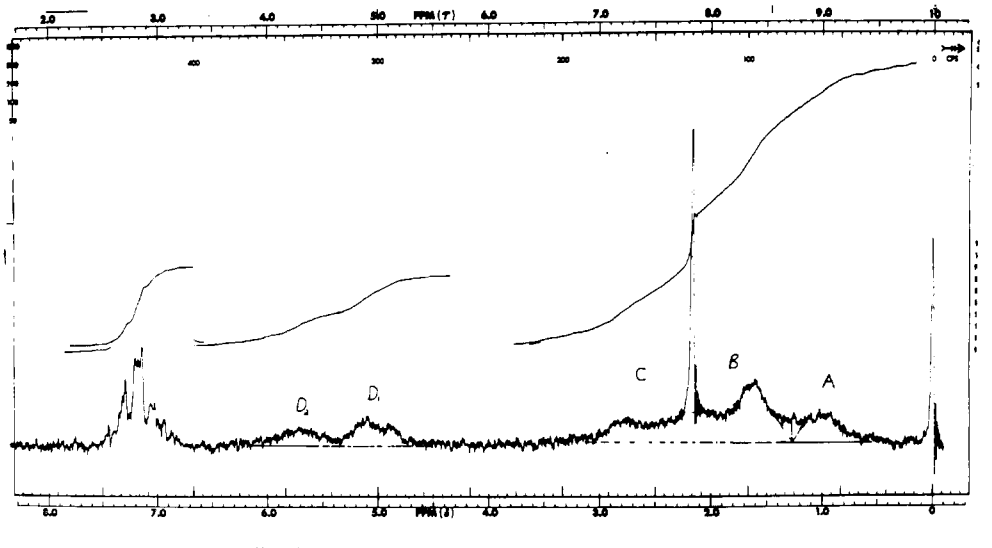


Figure 6. Poly(allylmethylcyclopentadiene).

TABLE VII
ASSIGNMENT OF THE NMR SPECTRUM OF POLY-ACPD

	δ, ppm	Assignment
A	1.0–1.95	β-Methylene protons in the ring
B	1.7–2.2	Methylene protons of the allyl group,
C	2.2–3.1	methine and α-methylene protons of the ring
D_1	4.8–5.25	Olefinic protons in the ring and in-
D_2	5.15–5.5	ternal olefinic proton of the allyl
D_3	5.5–6.0	group

evidence of the rather sharper peaks that might be predicted for the singly allylic $-CH_2-$ of the side chain in the structure XIII. In structures XIVa–c the side chain $-CH_2-$ is doubly allylic and would be expected to give the severe, unstructured splitting actually observed. It will be assumed in the following treatment that for the above reasons structure XIII is not an important contributor and only structures XIV will be considered.

The relative amounts of structures XIVa, XIVb, XIVc (*i.e.*, x, y, z) contributing to the structure of poly-ACPD are obtainable by the same sort of analysis which has been used for polycyclopentadiene.[1]

Normalizing the integrated spectral areas in Figure 4 to a basis of ten protons one obtains for A 1.03, for B + C 4.81, for D ($D_1 + D_2 + D_3$) 4.19. If the total integrated spectral area ascribed to structures XIVa, b, c is represented by the symbols [*a*], [*b*], and [*c*], then the ratio $z/(x + y)$ may be obtained as

$$\frac{z}{x+y} = \frac{[c]}{[a]+[b]} = \frac{3A}{B+C-2A} = 1.12$$

or, expressed as a percentage, the sample examined contained about 53% of the 1,4 linkages and about 47% of the 1,2 structures.

The assignment of polymer peaks by comparison with those of model compounds (the isomeric methylcyclopentenes) may not be very precise since the methylene peaks of the model compounds which were used overlap somewhat, and the peaks of the polymer spectra are broad. Fortunately, it has been shown that the overlap between the β-methylene peaks is less than 10% of the total methylene–methine area.[1]

Poly-MACPD. The assignments for the nmr spectrum (Figure 5) are given in Table VIII. As with poly-ACPD, structure XIII may be neglected for this material.

The normalized spectral areas observed were for A 4.45, for B + C 4.85, for D 2.70. Using the previous notation

$$\frac{z}{x+y} = \frac{[c]}{[a]+[b]} = \frac{3(2A-(B+C))}{5(B+C)-4A} = 1.89$$

or, expressed as a percentage, about 65% of the 1,4 linkages and about 35% of the 1,2 structures.

Poly-AMCPD. The nmr spectrum of this material is shown in Figure 6, and assignments are given in Table IX. The absence of a reasonably sharp methyl peak around 1 ppm suggests that almost all of the methyl groups must be substituted on the ring double bond. Furthermore, the singlet corresponding to the methyl protons is not perceptibly split; this

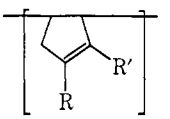
TABLE VIII
ASSIGNMENT OF THE NMR SPECTRUM OF POLY-MACPD

	δ, ppm	Assignment
A	0.9–1.9	β-Methylene protons of the ring and methyl protons of the side chain
B	1.9–2.4	Methine and α-methylene protons of
C	2.4–3.1	the ring; methylene protons of the allyl group
D_1	4.6–5.0	Terminal olefinic proton of the allyl
D_2	5.0–5.6	group; olefinic proton of the ring

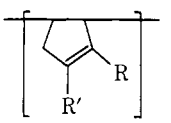
TABLE IX
ASSIGNMENT OF THE NMR SPECTRUM OF POLY-AMCPD

	δ, ppm	Assignment
A	0.8–1.3	β-Methylene protons in the ring
B	1.3–2.25	Methylene protons of the allyl group,
C	2.25–3.0	methyl protons, methine and α-methylene ring protons
D_1	4.75–5.35	Terminal olefinic protons of allyl
D_2	5.35–6.0	group, internal olefinic proton of the allyl group

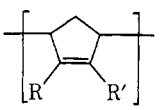
provides strong evidence that its neighboring group on the double bond is allyl rather than hydrogen, an observation in accord with the infrared spectrum of this material. Thus the only structural units which need to be considered are XVa, b, and c.



XVa



XVb



XVc

The normalized spectral areas observed were for A 1.47, for B + C 8.13, for D 2.40. Proceding, as before

$$\frac{z}{x+y} = \frac{[c]}{[a]+[b]} = \frac{9/2A}{B+C-(7/2A)} = 2.21$$

or, expressed as a percentage, about 69% of the 1,4 linkages and about 31% of the 1,2 linkages.

Discussion

It is observed that the general increase in the content of 1,4 structure follows the order poly-ACPD < poly-MACPD < poly-AMCPD. This is the order of increasing steric hindrance in the 1,2 structural unit. Observed variations in the structure of polycyclopentadienes must therefore be due to structural differences in the propagating ion pair; all other conditions being equal, addition of a 2-substituted cyclopentadiene should be most readily achieved in a 1,4 addition (XIVc) and become more favored over the

3,4 addition (XIVb) as the bulkiness of the substituent increases. The addition of 1-substituted cyclopentadienes was seen to occur primarily, if not entirely, by 3,4 addition and the rate of this process should be relatively insensitive to the size of the substituent, which is two carbons removed from the polymer chain.

A more exact estimation of the relative amounts of isomers in the monomer mixtures than can be obtained by nmr techniques would require efficient chromatographic conditions under which ACPD and the related dienes studied are stable with respect to isomerization and thermal polymerization. Determination of the isomer ratio in the monomer and subsequent examination of polymer structural units with varying compositions of the monomer feed would then establish the relative importance of isomerization in the polymerization process.

Conclusions

In conclusion, it appears that the cationic polymerization of allyl-substituted cyclopentadienes occurs almost entirely through the double bond in the cyclopentadiene ring. The amount of 1,4 structure increases with increasing steric hindrance around the conjugated double bond system. Although the monomers are obtained as an approximately equimolar mixture of two isomers, some isomerization seems to take place under polymerization conditions. The detailed structure of both monomers and polymers may be established by nmr analysis.

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Poly(ferrocenylazomethines)[1a]

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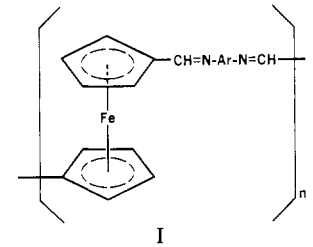
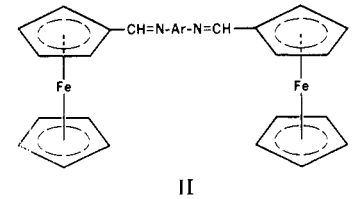
ABSTRACT: Polycondensation of *p*-phenylenediamine with 1,1′-diformylferrocene in N,N-dimethylformamide solution with or without an acidic catalyst leads to soluble polymeric azomethines of the type [-1,1′-$C_{10}H_8FeCH$=N-1,4-C_6H_4N=CH-]$_n$ (I). Inherent viscosities are in the range 10–13 ml g^{-1}. Polymers of the same composition and chain lengths are obtained from the two reactants in glacial acetic acid solution or from the two Schiff bases, $C_{10}H_9FeCH$=N-1,4-C_6H_4N=$CHC_{10}H_9Fe$ (II) and C_6H_5N=CH-1,1′-$C_{10}H_8FeCH$=NC_6H_5 (III), in a melt exchange reaction at temperatures ultimately reaching 325°. Solid-state postcondensation of these polyazomethines at 350° *in vacuo* produces polymers of unchanged elemental composition, but with inherent viscosities increased to 12–16 ml g^{-1}. Electronic spectral findings indicate that no substantial enhancement in π-electron delocalization is achieved in the polymeric Schiff base I. This confirms earlier reports on 1,1′-ferrocenylene-containing polymers with conjugated substituent links, in which the lack of appreciable conjugation across the central iron atoms was demonstrated spectroscopically. The polyazomethines I exhibit a thermostability behavior only marginally superior to that of ferrocenoyl or ferrocenoylbenzoyl polymers of previous studies; relative residual weights are 70 and 60% at 600 and 800°, respectively.

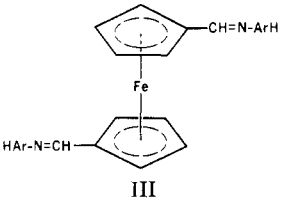
Polyazomethines of the type I (Ar = 1,4-phenylene in all formulas), in which the internuclear connecting segments provide uninterrupted conjugation,



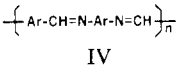
I



II

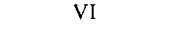


III



IV

V



VI

should lend themselves well to studies of the problem of electron delocalization across the central metal atom in polyconjugated systems with intrachain type 1,1′-ferrocenylene units. Sonogashira and Hagihara,[2] recognizing this possibility, prepared the polymeric Schiff

(1) (a) Metallocene Polymers. XXIV. Part XXIII: E. W. Neuse, *J. Org. Chem.*, **33**, 3312 (1968); (b) McDonnell Douglas Corp.; (c) Air Force Materials Laboratory.

(2) K. Sonogashira and N. Hagihara, *Kogyo Kagaku Zasshi*, **66**, 1090 (1963).