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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Donor-Acceptor Complexes in Copolymerization. XXXV. Alternating Diene-Dienophile Copolymers. 3. Copolymerization of cis- and trans-1, 3-Pentadiene with Maleic Anhydride and Acrylonitrile... $AlEt_{1.5}Cl_{1.5}$

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To cite this Article Gaylord, Norman G. , Stolka, Milan and Patnaik, Birendra K.(1972) 'Donor-Acceptor Complexes in Copolymerization. XXXV. Alternating Diene-Dienophile Copolymers. 3. Copolymerization of cis- and trans-1, 3-Pentadiene with Maleic Anhydride and Acrylonitrile... $AlEt_{1.5}Cl_{1.5}$ ', *Journal of Macromolecular Science, Part A*, 6: 8, 1435 – 1457

To link to this Article: DOI: 10.1080/10601327208056909

URL: <http://dx.doi.org/10.1080/10601327208056909>

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**Donor-Acceptor Complexes in Copolymerization.
XXXV. Alternating Diene-Dienophile
Copolymers. 3. Copolymerization of cis- and
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and Acrylonitrile. . . AlEt_{1.5}Cl_{1.5}**

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ABSTRACT

The copolymerization of the cis or trans isomers of 1,3-pentadiene with maleic anhydride in the presence of a peroxide catalyst yields identical equimolar, alternating copolymers in which the pentadiene units have a cis-1,4 configuration (IR, NMR). The copolymerization of the cis or trans isomers of 1,3-pentadiene with acrylonitrile in the presence of ethyl aluminum sesquichloride yields identical equimolar, alternating copolymers in which the pentadiene units have a trans-1,4 configuration (IR, NMR). Although the trans isomer forms cyclic adducts with both maleic anhydride and acrylonitrile, the cis isomer does not undergo the Diels-Alder reaction with these dienophiles. The formation of identical copolymers from cis- and trans-1,3-pentadiene is attributed to isomerization of the diene-dienophile charge transfer complex in the excited state, resulting in the generation of the same homopolymerizable exciplex from both isomers.

INTRODUCTION

Butadiene, isoprene, and other conjugated dienes have been found to yield alternating copolymers on reaction with maleic anhydride under γ [1] or UV [2] radiation as well as in the presence of peroxides or azo compounds [3-6]. Alternating copolymers are also obtained in the copolymerization of butadiene as well as isoprene with acrylonitrile in the presence of Lewis acids, such as zinc chloride and ethyl aluminum sesquichloride, in the absence as well as in the presence of peroxides [7-11] or under UV irradiation [12, 13].

The thermal reaction of conjugated dienes such as butadiene and isoprene with maleic anhydride in the absence of catalysts yields the Diels-Alder adduct. The adduct is also produced in the thermal reaction of butadiene and acrylonitrile, in the absence as well as in the presence of aluminum chloride [14].

The *cis* and *trans* isomers of piperylene, i.e., *cis*-1-methyl- and *trans*-1-methylbutadiene or *cis*- and *trans*-1,3-pentadiene, differ markedly in their behavior toward maleic anhydride and acrylonitrile. Thus, in the reaction with maleic anhydride, the *trans* isomer readily forms the Diels-Alder adduct while the *cis* isomer reacts very reluctantly and at 100°C yields a polymeric product accompanied by a small amount of adduct [15-18]. The Diels-Alder adduct is obtained from the reaction of acrylonitrile with the *trans* isomer while no reaction occurs with the *cis* isomer [16].

Dimerization of pentadiene through the Diels-Alder reaction occurs slowly with the *trans* isomer and does not occur with the *cis* isomer [16].

In order to gain further insight into the precursor in the formation of alternating copolymers and the relationship between the copolymerization and the Diels-Alder reaction, the copolymerization of *cis*- and *trans*-1,3-pentadiene with maleic anhydride and with acrylonitrile complexed with ethyl aluminum sesquichloride was investigated.

EXPERIMENTAL

Materials

Maleic anhydride, acrylonitrile, and technical piperylene were distilled before use. The technical piperylene contained 80% of

trans-1,3-pentadiene, as determined by Diels-Alder reaction with maleic anhydride in the presence of picric acid [16]. cis-1,3-Pentadiene (Chemical Samples Co.), 99% purity and trans-1,3-pentadiene (Matheson, Coleman & Bell Co.), 99.63% purity chromatography reagent, were used as received. 2-Methylpentanoyl peroxide (MPP) and t-butyl peroxyvalate (BPP) (Lupersol 11) (Lucidol Division, Pennwalt Corp.) were used as 50 and 75% solutions, respectively, in mineral spirits. Ethyl aluminum sesquichloride (EASC) (Texas Alkyls Co.) was used as a 25% solution in toluene.

Pentadiene-Maleic Anhydride Copolymerization

A solution of pentadiene and the catalyst in a small amount of peroxide-free dioxane was added to a solution of maleic anhydride in dioxane in a 3-necked flask equipped with condenser, thermometer, and stirrer and maintained at 80°C. The addition time was 10 min, during which the temperature was maintained $\pm 2^\circ\text{C}$. The reaction was terminated 20 min after the addition was complete by pouring the reaction mixture into dry benzene. The precipitated polymer was washed with benzene and hexane and dried in vacuo at 50°C. The polymer was purified by precipitation with hexane from acetone solution, softening point 140°C. Analysis: Calculated for $\text{C}_9\text{H}_{10}\text{O}_3$ (1:1 copolymer): C, 65.05; H, 6.07. Found: C, 65.00; H, 6.10.

The filtrates from the reaction mixture and the reprecipitation were partially concentrated on a rotating evaporator. The Diels-Alder adduct which crystallized from the solution was twice recrystallized from benzene solution, mp 63°C. Analysis: Calculated for $\text{C}_9\text{H}_{10}\text{O}_3$ (1:1 adduct): C, 65.05; H, 6.07. Found: C, 64.93; H, 6.00.

Pentadiene-Acrylonitrile Copolymerization

The reactions were carried out in rubber cap-sealed tubes which were purged with nitrogen. After acrylonitrile and pentadiene were injected into the tube by hypodermic syringe, a toluene solution of EASC was added slowly with occasional stirring. The temperature was maintained at 20°C for 1 hr. The solution became yellow and viscous. The polymerization was terminated by pouring the reaction mixture into methanol. The precipitated copolymer was purified by precipitation with methanol from benzene solution.

Spectroscopy

The IR spectra of the copolymers were obtained in a Perkin-Elmer Model 21 spectrophotometer on films cast from acetone solution.

The NMR spectra of the pentadiene-maleic anhydride copolymers were measured in deuterated acetone at 75°C at 100 MHz using tetramethylsilane as internal standard. The NMR spectra of the pentadiene-acrylonitrile copolymers were measured in CDCl_3 at 72°C.

RESULTS

Copolymerization of 1,3-Pentadiene with Maleic Anhydride

The reaction of either the trans, cis, or mixed isomers of 1,3-pentadiene with maleic anhydride in dioxane in the presence of a peroxide initiator yielded a soluble equimolar copolymer (Table 1). When the reaction was carried out in toluene the copolymer prepared from the trans isomer was initially soluble in acetone but became insoluble on standing in air or on precipitation from acetone solution, while the copolymer from the cis isomer was insoluble even when initially isolated.

In the absence of the peroxide, the product of the reaction of maleic anhydride with either trans-pentadiene or the isomeric mixture of pentadienes at 35 or 70°C was exclusively the Diels-Alder adduct, mp 63°C, i.e., cis-3-methyl-cis,cis-1,2,3,6-tetrahydrophthalic anhydride [8]. No product was isolated from the reaction of cis-pentadiene with maleic anhydride at 35°C.

The equimolar copolymer obtained in the presence of a peroxide was accompanied by the adduct in all reactions involving the trans isomer or the isomer mixture. No adduct was isolated from copolymerizations involving the cis isomer.

Copolymerization of 1,3-Pentadiene with Acrylonitrile

The reaction of either the cis, trans, or mixed isomers of 1,3-pentadiene with acrylonitrile (PD/AN mole ratio = 1/3) was carried

TABLE 1. Copolymerization of 1,3-Pentadiene with Maleic Anhydride

	trans		cis		mixed
Pentadiene isomer, g (mole)	6.8(0.1)	6.8(0.1)	3.4(0.05)	14.7(0.22)	36.8(0.54) 22.9(0.34)
MAnh, g (mole)	9.8(0.1)	9.8(0.1)	4.9(0.05)	20.3(0.21)	52.9(0.54) 32.7(0.33)
BPP, ml (mmole)	0.3(1.0)	1.3(4.3)	0.15(0.5)	2.5(8.3)	6(20) 5.5(18.3) ^a
Medium, ml ^b	D, 10	T, 18	D, 6	T, 40	T, 100 T, 60
Addition time, min	10	25	10	30	45 60
Temperature, °C	80	70	80	70	70 35
Copolymer					
Yield, %	70.0	35.4	81.7	73.3	64.0 22.0
$[\eta]$, 30°C, MEK	0.23		0.35		

^aMPP.^bD = dioxane; T = toluene.

out at 20°C in the presence of EASC. No solvent was added other than the toluene which was the solvent for the EASC. As shown in Table 2, the essentially equimolar copolymer was obtained in all of the reactions. The equimolar copolymer was previously reported as the product of the reaction of the mixed isomers of 1,3-pentadiene with acrylonitrile (PD/AN = 1/3 and 3/1) at 0°C in the presence of $\text{EtAlCl}_2\text{-VOCl}_3$ [11].

TABLE 2. Copolymerization of 1,3-Pentadiene with Acrylonitrile

	trans	cis	mixed
Pentadiene isomer, g (moles)	3.4 (0.05)	6.8 (0.1)	6.8 (0.1)
AN, g (moles)	8.0 (0.15)	16.0 (0.3)	16.0 (0.3)
EASC, ml (mmoles)	5.0 (9.0)	10 (18.0)	10 (18.0)
Temperature, °C	20	20	20
Time, hr	1	1	1
Copolymer			
Yield, %	4.7	5.0	7.9
AN, mole %	47.7	49.9	47.3

Structure of 1,3-Pentadiene—Maleic Anhydride Copolymers

The IR spectra of the maleic anhydride copolymers prepared from cis- and trans-1,3-pentadiene are almost identical. The anhydride unit appears as two peaks at 1840 and 1765 cm^{-1} due to the asymmetric and symmetric stretching frequencies, respectively, whose absorbance ratios are equal to 3.2 and 3.4 for the copolymers derived from cis- and trans-pentadiene, respectively. A small peak at 1705 cm^{-1} is probably due to traces of COOH group resulting from hydrolysis of the anhydride group during handling. The presence of traces of COOH group is evident from the nonbroadening of the absorption of 2900 cm^{-1} .

The CH_2 and CH_3 stretching frequencies are observed at 2900 cm^{-1} . The presence of the double bond is not evident in this region because of the absence of absorption beyond 3000 cm^{-1} . Similarly, the characteristic absorption at $\sim 1640\text{ cm}^{-1}$ was not observed. The CH_2 and CH_3 deformation frequencies of the pentadiene units are observed at 1440 and 1360 cm^{-1} , respectively.

The other absorptions at 1215 , 1075 , 975 , 940 , 915 , 755 , and 735 cm^{-1} are characteristic of diene-maleic anhydride copolymers. Some of these absorptions overlap the absorptions due to the various configurations of the pentadiene unit (975 cm^{-1} for 1,4- and 1,2-trans, 915 cm^{-1} for 3,4, and 755 and 735 cm^{-1} for 1,4- and 1,2-cis).

Figure 1 shows the IR spectra of the maleic anhydride copolymers derived from cis- (Fig. 1a) and trans-pentadienes (Fig. 1b), isoprene (Fig. 1c), and butadiene (Fig. 1d) in the 1000 - 700 cm^{-1} range where the absorptions for the various diene configurations are observed. The strong absorptions in the 900 - 970 cm^{-1} range would suggest the presence of 1,4- and 1,2-trans and 3,4 configurations for the pentadiene units. However, the NMR spectra (Fig. 2) indicate the absence of 3,4 structures. Further, maleic anhydride copolymers also exhibit absorptions in this range even when the comonomer is not a diene, e.g., the alternating ethylene-maleic anhydride copolymer [19] and maleic anhydride grafted polyethylene [20] exhibit strong absorptions in this range. Nevertheless, the presence of trans configurations cannot be ruled out.

The bands at 730 - 750 cm^{-1} have been attributed to the cis configuration of butadiene units in its homopolymer and copolymers with acrylonitrile, sulfur dioxide, maleic anhydride, fumaronitrile, maleates, and fumarates, and on the basis of the above assignment the copolymers with sulfur dioxide and maleic anhydride were found to have high cis-1,4 content while the others had predominantly trans configurations [3]. The butadiene-maleic anhydride copolymer prepared in the presence of radical catalysts has also been reported as having predominantly cis-1,4 configuration [5].

It is, therefore, probable that the 1,3-pentadiene-maleic anhydride copolymers have predominantly cis-1,4 configurations. It is also evident that the copolymers derived from cis- and trans-1,3-pentadiene have essentially identical configurations.

The NMR spectra of the maleic anhydride copolymers prepared from cis- and trans-1,3-pentadiene (Fig. 2) are essentially identical. The olefinic protons of the pentadiene unit appear at 4.30τ as a single peak. The peak centered at 6.85τ is attributed to the methine protons of the maleic anhydride unit present in the copolymer. The peaks centered at 7.20 and 7.37τ are due to the methine and

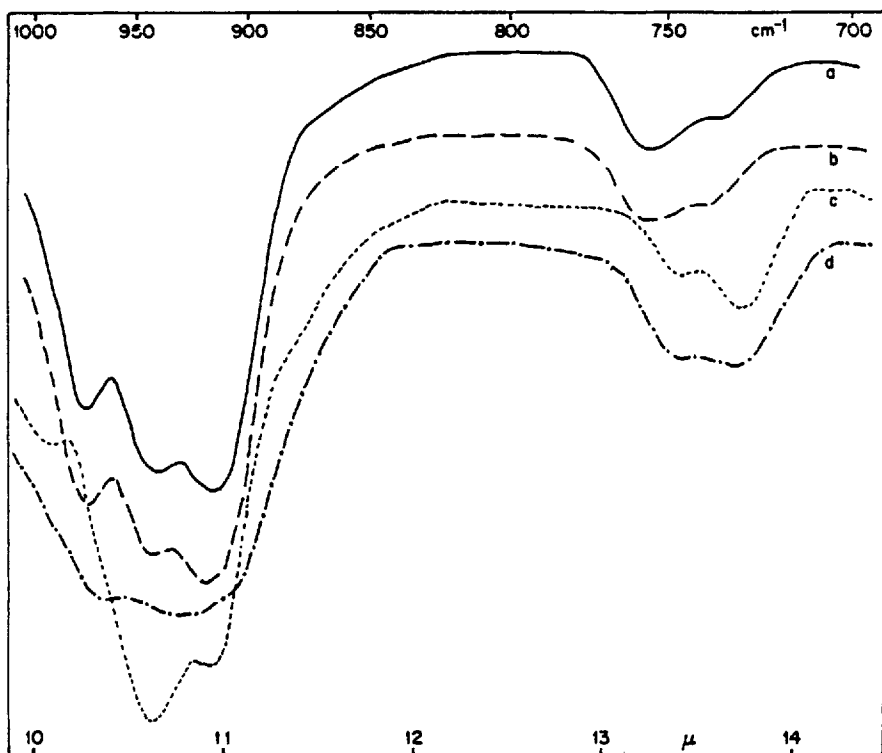


FIG. 1. IR spectra of alternating copolymers from maleic anhydride and (a) *cis*-1,3-pentadiene, (b) *trans*-1,3-pentadiene, (c) isoprene, and (d) butadiene.

methylene protons of the pentadiene unit. The multiplet at 8.75τ is due to the methyl group protons of the pentadiene unit. The assignments are made on the basis of chemical shift and relative peak area measurements.

It is evident that the copolymers have an alternating structure since the peak positions for the pentadiene sequences (corresponding to each type of proton), i.e., olefinic protons at ~ 4.70 - 4.90τ , methylene and methine protons at $\sim 8.0 \tau$, and $C-CH_3$ protons at $\sim 9.1 \tau$, are absent. This also explains the considerable downfield shift of each of the pentadiene protons because of the neighboring

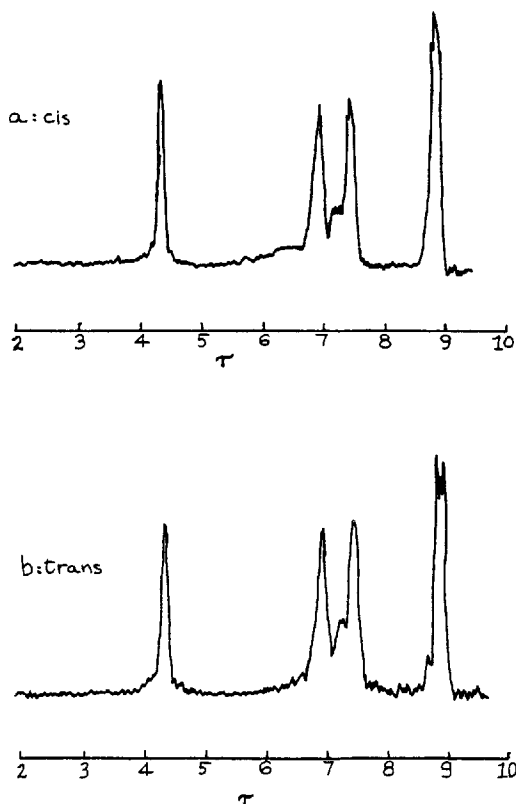


FIG. 2. NMR spectra of alternating copolymers from maleic anhydride and (a) *cis*-1,3-pentadiene and (b) *trans*-1,3-pentadiene.

maleic anhydride unit. The absence of the other types of olefinic protons and the ratio of the methyl and olefinic protons being not less than 1.5 rules out the presence of 3,4 or 1,2 configurations of the pentadiene unit.

It is apparent that the *cis*-1,3-pentadiene- and *trans*-1,3-pentadiene-maleic anhydride copolymers have essentially identical alternating structures in which the pentadiene units have a *cis*-1,4 configuration.

Structure of 1,3-Pentadiene-Acrylonitrile Copolymers

The IR spectra of the acrylonitrile copolymers prepared from *cis*- and *trans*-1,3-pentadiene (Fig. 3) are essentially identical. The spectrum of the copolymer from the *trans* isomer (Fig. 3b) is quite straightforward. The nitrile group absorbs at 2240 cm^{-1} .

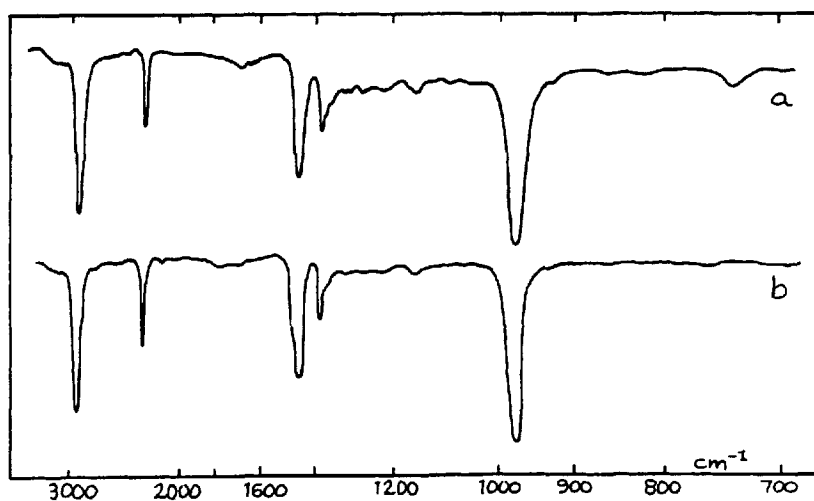


FIG. 3. IR spectra of alternating copolymers from acrylonitrile and (a) *cis*-1,3-pentadiene and (b) *trans*-1,3-pentadiene.

A single strong peak at 970 cm^{-1} is attributed to the C-H out-of-plane deformation of the olefinic double bond present in *trans* configuration. This is also consistent with the very weak C=C stretching observed at 1665 cm^{-1} . There are no absorptions indicating the presence of either the 3,4 unit ($\sim 915\text{ cm}^{-1}$) or the *cis* double bond ($\sim 740\text{ cm}^{-1}$). However, it is not possible to distinguish between the 1,4- and 1,2-*trans* configurations since both absorb at 970 cm^{-1} . Since the NMR spectrum (Fig. 4) indicates that the pentadiene units have a 1,4 configuration, it can be concluded that the unsaturation is *trans*-1,4. This is in agreement with the *trans*-1,4 structure of the equimolar butadiene-acrylonitrile

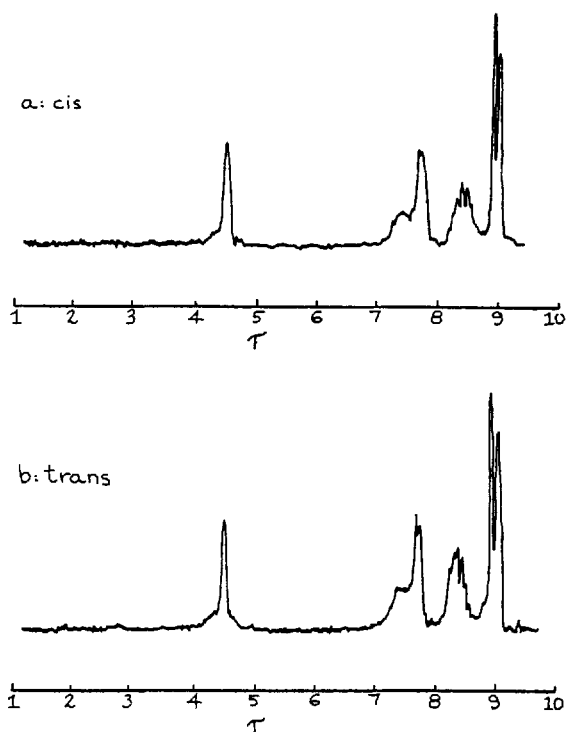


FIG. 4. NMR spectra of alternating copolymers from acrylonitrile and (a) *cis*-1,3-pentadiene and (b) *trans*-1,3-pentadiene.

copolymers prepared in the presence of zinc chloride [8], EASC [8], and $\text{EtAlCl}_2\text{-VOCl}_3$ [11].

The IR spectrum of the copolymer from the *cis* isomer (Fig. 3a) is essentially the same as that of the copolymer from the *trans* isomer (Fig. 3b) except for a small absorption at 735 cm^{-1} . The strong absorption at 970 cm^{-1} and the absence of any absorption at 915 cm^{-1} indicates the *trans* configuration of the double bond and the absence of 3,4 units. The absorption at 735 cm^{-1} is attributed to the presence of a *cis* double bond to a small extent. This is supported by a slightly increased absorption, as compared to that in Fig. 3b, in the $\text{C}=\text{C}$ stretching frequency range with the appearance of small peaks at 1620 and 1665 cm^{-1} . Considering

the absorptivity of the *cis* configurations in diene polymers, the proportion of this configuration is quite low and is probably due to the presence of 1,2-*cis* units of pentadiene.

The NMR spectra of the acrylonitrile copolymers prepared from the *cis*- and *trans*-1,3-pentadiene (Fig. 4) are also essentially identical. It is evident that the copolymers have an alternating structure since the resonances characteristic of pentadiene sequences, i.e., olefinic protons at ~ 4.70 - 4.90τ , methylene methine protons at $\sim 8.0 \tau$, and C-CH₃ protons at $\sim 9.1 \tau$, or acrylonitrile sequences (methine and methylene protons at ~ 7.0 and $\sim 8.0 \tau$, respectively) are absent. The olefinic protons appear as a single peak at 450τ which is attributed to the 1,4 units of pentadiene. A small resonance in the 4.65 - 4.80τ range might be due to some 1,2 structures. No 3,4 structure is evident since olefinic proton resonance at higher field strengths is absent.

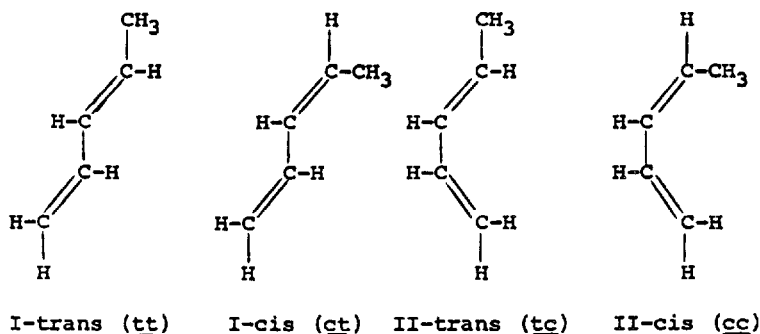
The downfield shift of the olefinic protons is due to the adjacent acrylonitrile units. The resonances for the methine proton (=CH) of acrylonitrile and the methine and methylene protons of pentadiene units are partly overlapped and appear as a broader peak in the 7.10 - 7.85τ range. The upfield shift of the methine protons of acrylonitrile and the downfield shift of the backbone protons in the pentadiene unit are due to the corresponding neighboring units. The multiplet observed at $\sim 8.40 \tau$ is assigned to the methylene protons of acrylonitrile and the $\begin{array}{c} | \\ =\text{C}-\text{CH}_3 \end{array}$ protons of pentadiene present in 1,2 structure. The $\begin{array}{c} | \\ =\text{C}-\text{CH}_3 \end{array}$ protons in the 1,2 structure in poly-1,3-pentadiene shows resonance at 8.3 - 8.5τ which is expected to shift downfield due to the neighboring acrylonitrile units. The $\geq\text{C}-\text{CH}_3$ protons of the pentadiene units in the 1,4 structure appear as a doublet centered at 8.93τ .

The presence of the 1,2 structure is also evident from the ratios of the areas under the methyl protons and the olefinic protons which is slightly less than 1.5. The coupling constant for the C-CH₃ splitting was found to be 6 Hz. Since the coupling constant for the C-CH₃ splitting in both *cis*- and *trans*-poly-pentadiene is 6 Hz, it is not possible to distinguish between them.

It is apparent that the *cis*-1,3-pentadiene- and *trans*-1,3-pentadiene-acrylonitrile copolymers have essentially identical alternating structures in which the pentadiene units have a *trans*-1,4 configuration.

DISCUSSION

A random examination of the literature reveals that the geometric isomers of 1,3-pentadiene have been considered to have several possible structures. Thus the geometric isomers have been represented as having *cis* and *trans* methyl groups with *trans* unsaturation (I) [21] as well as *cis* and *trans* methyl groups with *cis* unsaturation (II) [22]. It has also been suggested [17] that *cis*-pentadiene has



conformation I-*cis* and *trans*-pentadiene has conformation II-*trans*. However, it is now generally accepted that conjugated dienes such as butadiene, isoprene, pentadiene, 2,3-dimethylbutadiene, and other acyclic dienes possess the *transoid* conformation I [23, 24]. Therefore, I-*trans* is considered to represent *trans*-1,3-pentadiene, i.e., *trans*-1-methyl-1,3-*trans*-butadiene (*tt*), while I-*cis* represents *cis*-1,3-pentadiene i.e., *cis*-1-methyl-1,3-*trans*-butadiene (*ct*).

Notwithstanding the differences in monomer structure, it has now been found that in the copolymerizations with maleic anhydride in the presence of a free radical initiator and with acrylonitrile in the absence of a free radical initiator but in the presence of EASC, the same copolymer is obtained with *trans*-1,3-pentadiene as with *cis*-1,3-pentadiene.

It has been proposed [25] that alternating copolymers result from the homopolymerization of charge transfer complexes generated by the interaction of electron donor monomers, e.g., conjugated dienes, with strong electron acceptor monomers, e.g., maleic anhydride or acrylonitrile complexed with EASC. It has

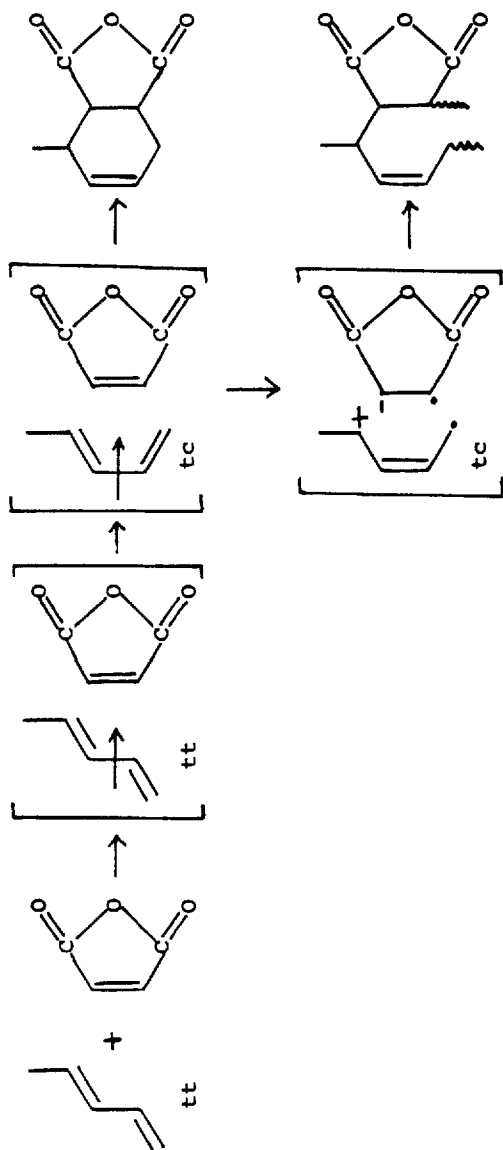
also been proposed that the Diels-Alder adduct and the alternating copolymer result from a common intermediate, i.e., the charge transfer complex [1, 3, 26], but that the cyclic adduct is formed from the complex in the ground state and the alternating copolymer from the complex in the excited state [2, 6, 27].

The formation of the Diels-Alder adduct and the alternating copolymer from the reaction of trans-1,3-pentadiene with maleic anhydride is outlined in Scheme 1. The conversion of the trans,-trans (tt) ground state complex to the trans,cis (tc) ground state complex is followed by the formation of the cyclic adduct. Under suitable activation, e.g., peroxide decomposition or UV light, the tc ground state complex is converted to the tc excited state complex which then undergoes homopolymerization to form the alternating copolymer having cis-1,4 unsaturation.

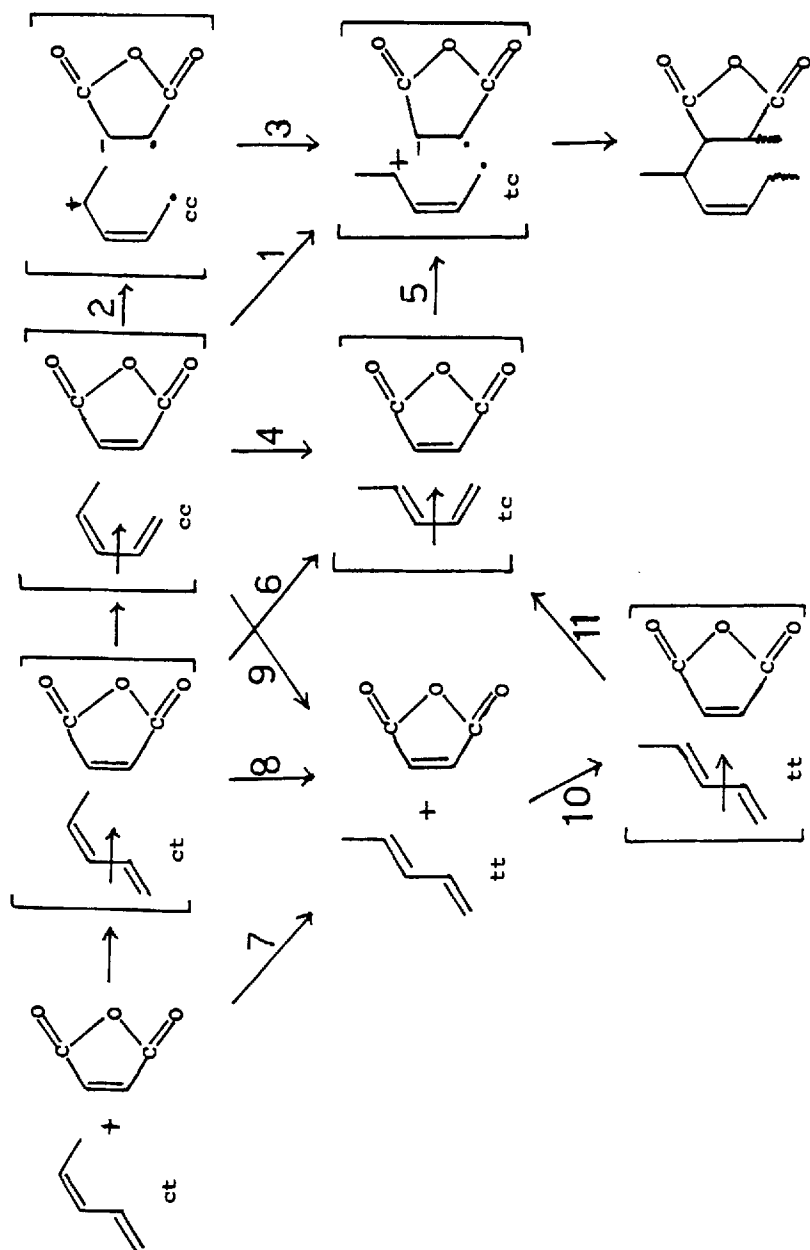
The formation of the same alternating copolymer from the reaction of cis-1,3-pentadiene with maleic anhydride is outlined in Scheme 2. The copolymer apparently results from the polymerization of the tc excited state complex. The latter may be generated

- a) directly from the cis,cis (cc) ground state complex (Path 1),
- b) by isomerization of the cc excited state complex which results from the excitation of the cc ground state complex (Path 2,3) or
- c) directly from the tc ground state complex which results from
 - (1) isomeration of the cc ground state complex (Path 4,5),
 - (2) isomerization of the ct ground state complex (Path 6,5) or
 - (3) generation of trans-pentadiene from
 - (i) cis-pentadiene (Path 7),
 - (ii) reversion of the ct ground state complex (Path 8) or
 - (iii) reversion of the cc ground state complex (Path 9),
 followed by the formation of the tt ground state complex (Path 10) and its conversion to the tc ground state complex (Path 11) which undergoes excitation (Path 5).

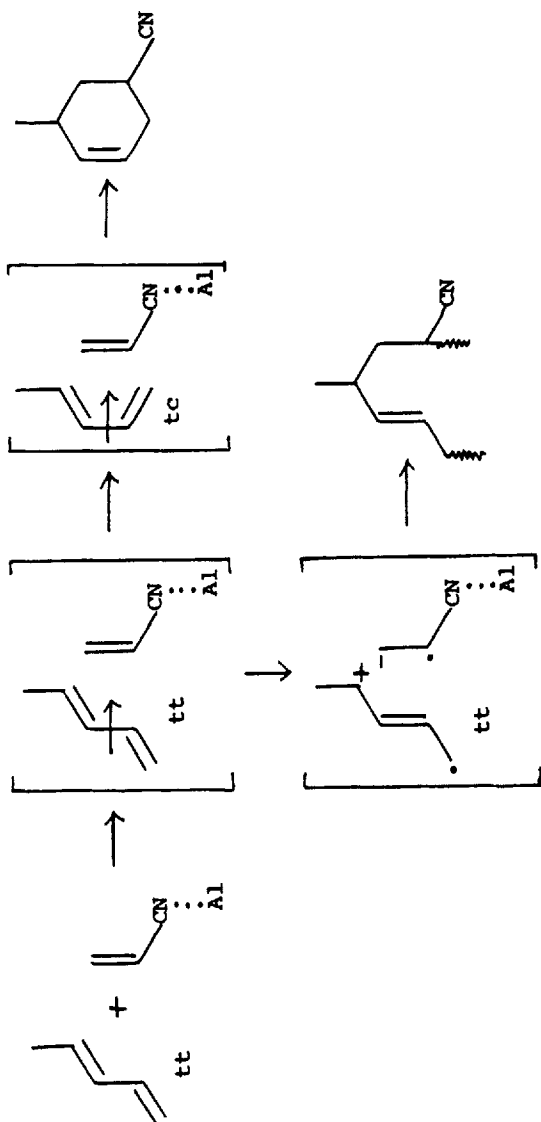
The formation of the alternating copolymer from the reaction of trans-1,3-pentadiene with acrylonitrile complexed with EASC is outlined in Scheme 3. The conversion of the tt ground state complex to the tc ground state complex is followed by the formation of the cyclic adduct. However, in contrast to the reaction with maleic



SCHEME 1.



SCHEME 2.



SCHEME 3.

anhydride, this conversion is slow and possibly occurs to only a limited extent at the reaction temperature of 20°C. The presence of EASC per se or the high concentration of tt ground state complexes resulting from the presence of EASC results in excitation to the tt excited state complex which then undergoes homopolymerization to form the alternating copolymer having trans-1,4 unsaturation.

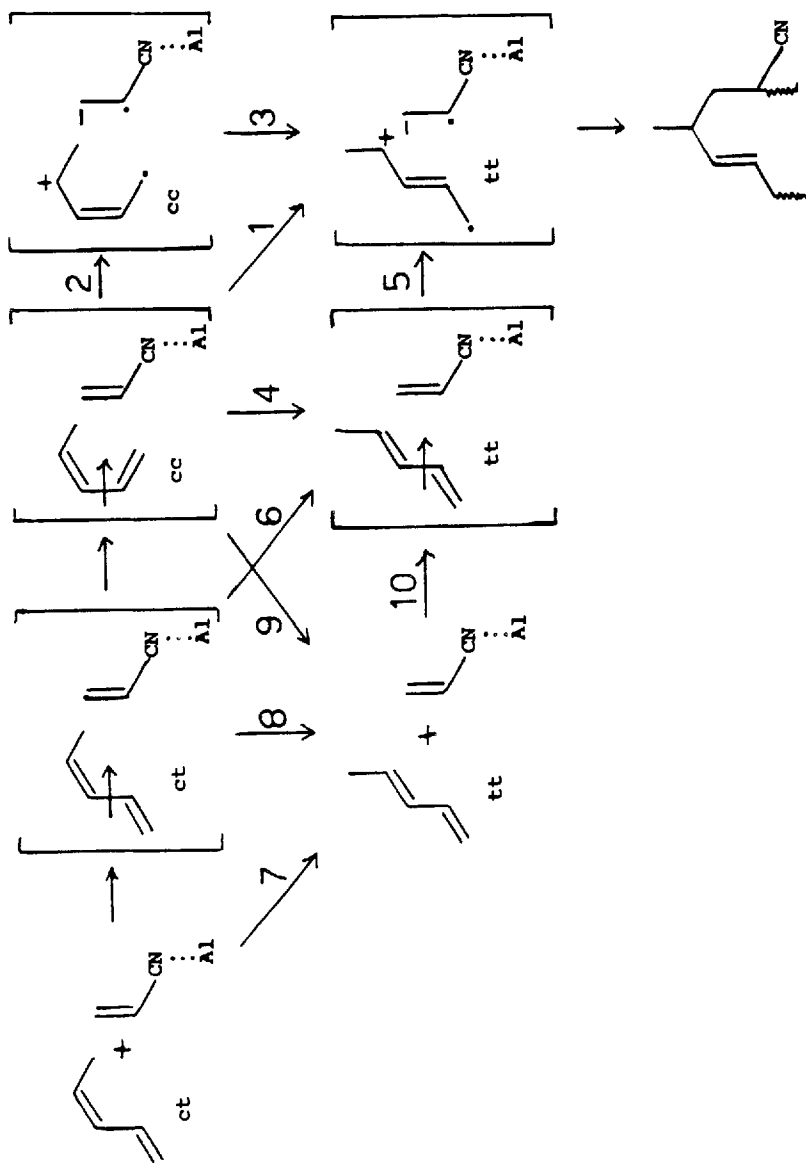
The formation of the same alternating copolymer from the reaction of cis-1,3-pentadiene with the EASC-complexed acrylonitrile is outlined in Scheme 4. The copolymer results from the polymerization of the tt excited state complex. The latter may be generated

- a) from the cc ground state complex
 - (1) directly (Path 1), or
 - (2) by isomerization of the cc excited state complex which results from the excitation of the cc ground state complex (Path 2,3),
- b) directly from the tt ground state complex which results from
 - (1) isomerization of the cc ground state complex (Path 4,5),
 - (2) isomerization of the ct ground state complex (Path 6,5), or
 - (3) generation of trans-pentadiene from
 - (i) cis-pentadiene (Path 7),
 - (ii) reversion of the ct ground state complex (Path 8) or
 - (iii) reversion of the cc ground state complex (Path 9),
 followed by formation of the tt ground state complex (Path 10) which undergoes excitation (Path 5).

The isomerization of cis-pentadiene to trans-pentadiene has been accomplished by heating at 600°C [16], by refluxing with a trace of iodine [16] and by irradiation under 2537 Å UV light [28, 29].

Isomerization has been proposed as a factor in the polymerization of cis-pentadiene in hydrocarbon solution with an $AlEt_3-Ti(OBu)_4$ catalyst [22]. The emulsion polymerization of cis- and trans-pentadiene with a benzoyl peroxide-ferrous sulfate catalyst system yields polymers with similar properties and essentially identical IR absorption spectra, resulting in the suggestion that the "activated monomer" during polymerization is the same for each monomer [16].

It was originally proposed that the failure to form the Diels-Alder adduct from the reaction of cis-pentadiene with maleic anhydride



SCHEME 4.

was due to the absence [17] or hindrance [24] of the cisoid conformation in the diene monomer. However, since the model of the adduct shows no hindrance [24] and the adduct is formed under forcing conditions [18, 24], it has been suggested that the slowness of the reaction is due to the slow formation of the cisoid (cc) transition state [24]. In contrast, the formation of the cyclic adduct from cis-pentadiene and sulfur dioxide indicates the relatively greater ease of formation of the cisoid transition state, i.e., the cc ground state complex, and its conversion to the tc ground state complex since the thermal decomposition of the sulfone adducts from both cis-pentadiene and trans-pentadiene results in the recovery of trans-pentadiene [17].

The rapid formation of the Diels-Alder adduct from trans-pentadiene and maleic anhydride and the failure to isolate any adduct from the copolymerization of cis-pentadiene and maleic anhydride indicates that the tc ground state is not a precursor in the formation of the tc excited state complex (Path 5 in Scheme 2).

Therefore, the generation of trans-pentadiene from cis-pentadiene (Path 7) or from the ct (Path 8) or cc (Path 9) ground states is unlikely. Similarly, the formation of the tc ground state complex from the cc ground state complex (Path 4) is unlikely. Therefore, the tc excited state complex arises from the cc ground state complex either directly (Path 1) or through the cc excited state complex (Path 2,3). Since direct conversion of the cc ground state complex to the isomeric excited state is unlikely, while the isomerization of excited states is well known [28, 29], Path 2,3 represents the probable route to the tc excited state complex which undergoes homopolymerization to the alternating copolymer having cis-1,4 unsaturation.

Although the more difficult formation of the cyclic adduct from trans-pentadiene and acrylonitrile, as compared to adduct formation from maleic anhydride, does not permit as easy a rejection of the formation of trans-pentadiene in the copolymerization of cis-pentadiene with acrylonitrile...EASC, it is unlikely that the trans monomer is formed from the ct (Path 8, Scheme 4) or cc (Path 9) ground state complexes or that these complexes isomerize to the tt ground state complex (Paths 6 and 4, respectively). Since the direct conversion of the cc ground state complex to the tt excited state complex (Path 1) is also unlikely, the route to the tt excited state complex is either through the tt ground state complex, which is formed from trans-pentadiene generated from cis-pentadiene isomerization (Path 7,10,5), or through the isomerization of the cc excited state complex, which is derived from the cc ground

state complex (Path 2,3) which is in turn generated from the ground state complex resulting from the monomer interaction.

The formation of identical copolymers in reactions involving *cis*- and *trans*-1,3-pentadiene provides further insight into the relationship between the Diels-Alder reaction and copolymerization resulting in alternating copolymers.

The thermal reactions of *trans*-1,3-pentadiene with maleic anhydride and with acrylonitrile yield the expected *cisoid* Diels-Alder adducts. The thermal reaction of *cis*-1,3-pentadiene with maleic anhydride proceeds reluctantly and yields an isomeric Diels-Alder adduct having the expected *cisoid* structure, but with a different orientation of the methyl group than the adduct from the *trans* isomer [18]. There is apparently no adduct formation from the reaction of *cis*-1,3-pentadiene with acrylonitrile [16].

Both *cis*- and *trans*-1,3-pentadiene readily yield identical copolymers with maleic anhydride and with acrylonitrile. Although the maleic anhydride copolymers have *cis*-1,4 unsaturation and the acrylonitrile copolymers have *trans*-1,4 unsaturation, the orientation of the methyl group in the copolymer is the same, irrespective of the starting diene.

Geometric isomerization involves rotation around a single bond. It is apparent that the conversion of the *transoid* diene structure to the *cisoid* diene structure occurs in the *transoid* ground state complex where a double bond rotates around the central single bond, resulting in the formation of the *cisoid* ground state complex. Similarly, the conversion of the *cis*-methyl to a *trans*-methyl involves rotation around the single bond which exists only in the excited state complex.

Since isomerization of the methyl group occurs only in the polymerization reaction, the latter apparently involves the excited state complex. The failure of the methyl group to isomerize in the ground state complex hinders the formation of the cyclic adduct from the *cis*-pentadiene. The adduct is readily formed from the *trans*-pentadiene where ring closure of the ground state complex is not hindered.

The *transoid* ground state complex is the common precursor of 1) the *transoid* excited state complex which yields the *trans*-1,4-diene-acrylonitrile copolymers, 2) the *cisoid* ground state complex which yields the Diels-Alder adduct, and 3) the *cisoid* excited state complex which yields the *cis*-1,4-diene-maleic anhydride copolymers.

The complexation of a metal halide, such as AlX_3 , with acrylonitrile or an acrylic ester promotes the formation of the *transoid*

ground state complex with a conjugated diene. Since this is the common precursor of both the Diels-Alder adduct and the alternating copolymer, both reactions are promoted in the presence of the metal halide. When this complex is subjected to activation, e.g., free radicals, UV light, or a vanadyl compound, excitation occurs and is followed by polymerization. Since the yield of adduct decreases when polymerization occurs, the metal halide is probably not a promotor in the isomerization of the transoid ground state complex to the cisoid complex. However, the thermal activation of the Diels-Alder reaction may enhance the transoid-cisoid isomerization in the ground state.

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Accepted by editor February 10, 1972

Received for publication June 15, 1972