Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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Norman G. Gaylord[a]; Milan Stolka[a]; Akio Takahashi[a]; Sukumar Maiti[a]
[a] Gaylord Research Institute Inc., Newark, New Jersey

To cite this Article Gaylord, Norman G. , Stolka, Milan , Takahashi, Akio and Maiti, Sukumar(1971) 'Donor-Acceptor Complexes in Copolymerization. XVIII. Alternating Diene-Dienophile Copolymers. 1. Conjugated Diene-Maleic Anhydride Copolymers through Radical-Catalyzed Polymerization', Journal of Macromolecular Science, Part A, 5: 5, 867 — 881

To link to this Article: DOI: 10.1080/00222337108061068

URL: http://dx.doi.org/10.1080/00222337108061068

J. MACROMOL. SCI.–CHEM., A5(5), pp. 867-881, August, 1971

Donor-Acceptor Complexes in Copolymerization. XVIII. Alternating Diene—Dienophile Copolymers. 1. Conjugated Diene—Maleic Anhydride Copolymers through Radical-Catalyzed Polymerization

NORMAN G. GAYLORD, MILAN STOLKA, AKIO TAKAHASHI, and SUKUMAR MAITI

Gaylord Research Institute Inc.
Newark, New Jersey 07104

SUMMARY

The copolymerization of isoprene, butadiene, and other conjugated dienes with maleic anhydride was readily initiated in polar solvents by conventional free radical catalysts, including peroxides, hydroperoxides, and azobisisobutyronitrile, at high concentrations or at temperatures at which the catalyst had a half-life of 1 hr or less and the total reaction time was 0.5-1 hr. Decreasing the reaction temperature or the rate of catalyst addition resulted in increased yields of Diels-Alder adduct and decreased yields of copolymer. The molecular weight decreased as the temperature increased. Dioxane and tetrahydrofuran peroxides, obtained by the passage of oxygen or UV irradiation in air, also initiated the copolymerization. The soluble diene–maleic anhydride copolymers were equimolar and alternating, had [η] 0.1-6 (cyclohexanone) and contained 75-95% 1,4 structure according to ozonolysis, titration with ICl and NMR. The IR spectrum of the butadiene–maleic anhydride copolymer indicated 75-95% cis-1,4, 5-20% trans-1,4 and 0-5% 1,2-vinyl unsaturation. The proposed mechanism of polymerization involves a donor-acceptor (diene-dienophile) interaction generating a ground-state charge transfer complex

which is readily converted to the cyclic adduct. Under the influence of radicals the ground-state complex is transformed into an excited complex which undergoes polymerization. High concentrations of radicals are necessary to generate polymerizable excited complexes in competition with adduct formation.

INTRODUCTION

The interaction of a strong electron donor with a strong electron acceptor results in a spontaneous one-electron transfer and the formation of a charge transfer complex. The latter may undergo an intra-complex reaction to yield a cyclic adduct or an inter-complex reaction to yield an alternating copolymer [1].

The Diels-Alder reaction wherein a diene and a dienophile undergo a spontaneous reaction to form a cyclic adduct is one of the most widely recognized examples of donor-acceptor interaction [2, 3]. The reaction is accelerated at elevated temperatures and, in some cases, in the presence of Friedel-Crafts catalysts such as aluminum chloride [4].

The thermal reaction of a conjugated diene, such as butadiene or isoprene with maleic anhydride, yields the corresponding tetrahydrophthalic anhydride. However, it has recently been shown that alternating copolymers are formed under the influence of ionizing radiation [5] or free radical initiators [5-8]. Since the formation of the Diels-Alder adduct is accelerated at elevated temperatures, the rate of copolymer formation under ionizing radiation reached a maximum at about 20°C [5].

The present paper reports the effect of reaction variables, namely catalyst nature and reaction time and temperature, on the competitive formation of the Diels-Alder adduct and the alternating copolymer in the free radical catalyzed copolymerization of conjugated dienes and maleic anhydride [8]. Although numerous conjugated dienes including butadiene, isoprene, chloroprene, 2,3-dimethylbutadiene, piperylene, 1-methoxybutadiene, and 2,4-hexadiene were successfully copolymerized to alternating copolymers with maleic anhydride, the characteristics of the copolymerization of isoprene and butadiene with maleic anhydride are presented as representative of the general reaction.

EXPERIMENTAL

The polymerization was generally carried out by adding a solution of the catalyst and the conjugated diene to a solution containing the maleic anhydride. When the latter solution was initially at room temperature, the temperature was rapidly raised and then maintained at the desired level by means of external cooling, if necessary. Alternatively, the solution of maleic anhydride was preheated before the addition of the solution containing the catalyst and diene. The addition generally required 30-60 min and attempts to control the temperature by extending the addition time resulted in increased yields of Diels-Alder adduct and decreased yields of alternating copolymer.

The reaction was extremely exothermic and the temperature rise was accompanied by an increase in the viscosity of the solution. In most cases the reaction was complete as soon as the addition of the diene was completed. The copolymer was isolated by precipitation with toluene and purified by extraction with toluene to remove the cyclic adduct and reprecipitated.

Poly(Isoprene–alt–Maleic Anhydride)

A 500-ml round-bottomed three-necked flask equipped with a mechanical stirrer, a thermometer, and a reflux condenser was charged with 98 g (1.0 mole) of sublimed maleic anhydride and 80 ml of dioxane. Solution was achieved by heating the mixture to 80°C with continuous stirring on a hot water bath. A solution containing 102 ml (1.02 mole) of distilled isoprene and 1 g of t-butyl peroxypivalate (TBPP) was added carefully through the open end of the condenser over a total period of 20 min with continuous stirring. The reaction was exothermic and external cooling was required to maintain the temperature at 80 ± 2°C. The onset of polymerization was instantaneous and copolymer formation was visible at the surface of the reaction mixture. The solution became extremely viscous and the stirrer speed was gradually increased to maintain efficient stirring. After approximately one-half of the isoprene-TBPP solution had been added, the viscosity was so increased that periodic addition of dioxane was necessary to keep the mixture stirrable. A total of 60 ml dioxane was added for this purpose. After addition of all of the isoprene-TBPP solution, stirring was continued for an additional 45 min to complete the reaction. The viscous solution was diluted with 60 ml of acetone and slowly poured with stirring into 2000 ml of dry benzene. The copolymer was precipitated in fibrous form, filtered, washed with petroleum ether, and dried at 50°C in vacuo overnight. The dried, tan colored fluffy copolymer was obtained in a yield of 84 g (50%). The copolymer was purified by solution in acetone and then pouring the acetone solution in a thin stream into excess benzene (4 volumes of benzene per volume of acetone solution) with vigorous stirring. The copolymer was washed with petroleum ether and dried in a vacuum oven at 50°C. The recovery of purified copolymer was 75-80%.

The intrinsic viscosity was 0.80 dl/g in cyclohexanone at 30°C. The copolymer had a stick temperature of 145-150°C.

Analysis calculated for $C_9H_{10}O_3$ (1:1 copolymer): C, 65.1; H, 6.1. Found: C, 64.7; H, 6.1.

Poly(Butadiene–alt–Maleic Anhydride)

A 500-ml round-bottomed flask equipped with a dropping funnel, a mechanical stirrer, a thermometer, a condenser (cold finger) packed with Dry Ice, and a nitrogen inlet and outlet was charged with 49 g (0.5 mole) of maleic anhydride and 76 g of distilled cyclohexanone. The mixture was heated to 60-70°C under nitrogen to effect solution. A solution containing 35 g of butadiene, 76 g of cyclohexanone, and 1.5 g of TBPP was added to the reaction flask through the dropping funnel over a period of 40 min with continuous stirring while maintaining the temperature at 60-70°C. The solution became extremely viscous within 10 min after the addition of the monomer-catalyst solution was started. The solution was stirred for 1 hr after the monomer addition was completed and then cooled to room temperature with external cooling. The viscous solution was poured with stirring into 1000 ml of dry benzene to precipitate the copolymer. The latter was filtered, washed with 200 ml of petroleum ether, and dried to constant weight in vacuo at 50°C. The yield of copolymer was 40 g (53% based on maleic anhydride).

The intrinsic viscosity was 0.7 dl/g in cyclohexanone at 25°C. The copolymer had a softening point of 150-155°C on a melting point bar.

Analysis calculated for $C_8H_8O_3$: C, 62.6; H, 5.5. Found: C, 62.6, H, 5.5.

RESULTS

Polymerizations without Added Catalyst

A conventional free radical catalyst was not necessary to initiate polymerization of a mixture of isoprene and maleic anhydride if a solvent such as dioxane which forms a peroxide was used. Thus, aged dioxane, i.e., allowed to stand exposed to air, dioxane through which oxygen had been bubbled, or dioxane which was exposed to irradiation in air under a germicidal UV lamp initiated an exothermic polymerization reaction at room temperature. The reaction was even more effective at 60°C. Freshly distilled dioxane failed to initiate polymerization. The preparation of aged or oxygenated dioxane could be carried out in the presence or absence of maleic anhydride. In either case the solution gave a strong positive peroxide test with potassium iodide.

When diethyl ether containing maleic anhydride was irradiated under the UV lamp under nitrogen, no polymerization was initiated on the addition of isoprene. However, when the irradiation was carried out in air, the addition of isoprene resulted in an exothermic polymerization. Similar results were obtained with tetrahydrofuran.

The results obtained in the absence of an added catalyst are summarized in Table 1.

Polymerization in the Presence of a Radical Catalyst

The polymerization of isoprene, butadiene, and other conjugated dienes with maleic anhydride was readily initiated by any conventional free radical catalyst, e.g., benzoyl peroxide, lauroyl peroxide, 2,4-dichlorobenzoyl peroxide, di-t-butyl peroxide, dicumyl peroxide, t-butyl peroxypivalate, cumene hydroperoxide, t-butyl hydroperoxide, and azobisisobutyronitrile.

The relative efficiency of the various free radical sources was directly related to the polymerization temperature. Although catalyst concentrations could be maintained at catalytic levels, e.g., 0.005-1.5 wt % based on monomer concentration, the highest yields were obtained when the reaction was carried out at a temperature at which the catalyst had a half-life of 60 min or less.

Table 2 compares the results obtained with various catalysts in the copolymerization of isoprene and maleic anhydride in dioxane at 100-125°C. The yields increased with decreasing half-life of the catalyst.

The molecular weight of the copolymer was relatively independent of the initial catalyst concentration within the indicated range but was dependent upon the reaction temperature, i.e., the molecular weight decreased as the temperature increased. Therefore, although all of the catalysts initiated polymerization, the preferred catalyst was selected on the basis of the desired molecular weight of the copolymer. In order to obtain higher molecular weight copolymer, a low temperature catalyst was used at an elevated temperature. Thus, whereas azobisisobutyronitrile at 100°C gave a 30% yield of poly(isoprene–alt–maleic anhydride) with $[\eta]$ 0.1-0.3, under the same conditions t-butyl peroxypivalate at 80°C gave a 50% yield of

Table 1. Copolymerization of Isoprene–Maleic Anhydride in the Absence of Added Catalyst

MAnh (moles)	Isoprene (moles)	Solvent (moles)	Temp. (°C)	Time (hr)	Polymer (%)	Remarks [a]
0.31	0.5	D, 0.3	60	0.3	28	Dioxane aged in air 3 days.
0.05	0.005	D, 0.05	25	2.0	0	Distilled dioxane.
0.05	0.05	D, 0.05	25	0.3	18	Dioxane aged in air 3 days.
0.05	0.05	D, 0.005	25	0.3	11	Dioxane aged in air 3 days, reaction under N_2.
0.075	0.075	E, 0.075	35	2.0	0	MAnh and ether refluxed 20 min before I added.
0.090	0.10	E, 0.140	25	2.0	20	MAnh and ether irradiated in air 1 hr before I added.
0.90	0.10	E, 0.140	25	2.0	0	MAnh and ether irradiated under N_2 before I added.

[a] The Diels-Alder adduct accompanied the copolymer or was the sole product.

Table 2. Copolymerization of Isoprene and Maleic Anhydride at 100-125°C[a]

MAnh (g)	Dioxane (ml)	Isoprene (g)	Catalyst[b] Nature	Catalyst[b] Amt.	Catalyst[b] $t_{1/2}$(100°C) (hr)	Copolymer yield (%)
4.9	5	3.4	BHP	0.05 ml	165[c]	< 2
504	439	345	DCP	2.52 g	100[c]	6.9
527.5	460	336	BPO	2.64 g	0.40[c]	19.4
509	458	354	AIBN	2.54 g	0.12[d]	30[e]

[a] Solution of catalyst in isoprene added over 35 min to preheated solution of anhydride in dioxane.

[b] BHP = t-butyl hydroperoxide, DCP = dicumyl peroxide, BPO = benzoyl peroxide, AIBN = azobisisobutyronitrile.

[c] From published curve [9].

[d] Calculated from k_d [10].

[e] $[\eta] = 0.15$ (cyclohexanone, 25°C).

alternating copolymer with [η] 0.8-1.0 and at 70°C a 35% yield of copolymer with [η] 2.5-3.0.

Attempts to increase the size of the reaction mixture while maintaining the ratio of reaction components and temperature constant indicated an apparent effect of batch size on copolymer yield. As the total amount of reactants was increased, the yield of copolymer decreased and the yield of Diels-Alder adduct increased. However, the scale-up effect was found to be an artifact.

Due to the use of catalysts at temperatures where they have an extremely short half-life, the rate of radical generation was rapid and the reaction was extremely exothermic. If the rate of catalyst addition was decreased in order to maintain temperature control more readily, e.g., in carrying out large scale reactions, the yield of copolymer decreased and the yield of adduct increased. To maintain the yield of copolymer at a maximum level and minimize adduct formation, external cooling was generally needed to maintain the temperature at the desired level for radical generation and molecular weight control. The preferred catalyst addition time, in the concentration range of 0.25-1.5 wt % based on monomers, was 30-60 min.

When copolymerizations of isoprene and maleic anhydride were carried out in distilled dioxane using benzoyl peroxide (BPO) and t-butyl perbenzoate (tBPB) as catalysts at 80 and 100°C with rapid catalyst addition, the yield of copolymer increased and the molecular weight decreased with increasing catalyst concentration (Table 3).

Although the reaction could be carried out in hydrocarbon as well as well as polar solvents, the latter were preferred since the copolymers are insoluble in hydrocarbon solvents. In addition to maintaining a homogeneous phase throughout the period, polar solvents such as dioxane, cyclohexanone, and tetrahydrofuran accelerated the rate of decomposition of peroxide-type catalysts.

UV irradiation of a mixture of isoprene and maleic anhydride in tetrahydrofuran under nitrogen at room temperature gave the Diels-Alder adduct. In the presence of benzoyl peroxide, either under irradiation or in the absence of radiation, the alternating copolymer was formed.

Aromatic hydrocarbons such as toluene and xylene per se or in admixture with polar solvents decreased the yield of alternating copolymer, probably due to competitive complex formation with maleic anhydride. In addition, copolymers produced in aromatic hydrocarbon media precipitated during the polymerization and were generally insoluble in the polar solvents, indicative of cross-linking.

Table 3. Effect of Temperature and Radical Concentration on Copolymerization of Isoprene and Maleic Anhydride[a]

Catalyst		Temp.	Copolymer	
Nature	mmole	(°C)	Yield (%)	[η] (dl/g)[b]
BPO	1.00	80	49.5	0.70
	7.23	80	92.0	0.43
	1.00	100	43.0	0.21
tBPB	1.00	100	24.6	0.53
	22.60	100	52.0	0.20

[a] Isoprene (0.25 mole) solution containing catalyst added over 15 min to 20 ml dioxane containing maleic anhydride (0.25 mole). Total reaction time 2 hr. Additional dioxane added to keep mixture stirrable. Copolymer isolated by precipitation in benzene and washing with benzene and petroleum ether. Dried copolymer precipitated with benzene from acetone solution.

[b] Cyclohexanone, 30°C.

Although free radical inhibitors such as N-phenyl-2-naphthylamine and di-t-butyl-p-cresol inhibited polymerization, hydroquinone reduced the yields but did not prevent polymer formation.

Copolymer Characterization

Elementary analyses of the copolymers prepared by the reaction of maleic anhydride and the various conjugated dienes indicated an essentially equimolar composition, irrespective of the monomer charge from 90/10-45/55 diene/maleic anhydride ratio. However, the maximum yield never exceeded that corresponding to an equimolar charge.

IR spectra of soluble polymers recorded from films cast from acetone solution and of insoluble polymers from KBr pellets indicated the presence of 75-95% cis-1,4, 5-20% trans-1,4, and 0-5% 1,2-vinyl unsaturation in the butadiene–maleic anhydride copolymers. In contrast, the IR spectra of isoprene–maleic anhydride copolymers indicated the presence of less than 5% unsaturation.

NMR spectra of the butadiene–maleic anhydride and the isoprene–maleic anhydride copolymers in deuterated acetone or deuterated acetic acid at 25°C at 60 Mc using tetramethylsilane as the internal standard indicated 85-90% 1,4 unsaturation and an alternating structure (absence of diene-diene diads).

Ozonolysis of the isoprene–maleic anhydride copolymers indicated 85% unsaturation while titration with iodine monochloride indicated 70-86% unsaturation. Attempts to hydrogenate the isoprene copolymers using platinum oxide and palladium on charcoal as catalysts were unsuccessful.

The diene–maleic anhydride copolymers were soluble in polar solvents such as dimethylformamide, dimethylacetamide, tetrahydrofuran, dioxane, acetone, methyl ethyl ketone, cyclohexanone, acetonitrile, and nitrobenzene and insoluble in aliphatic, aromatic, and chlorinated hydrocarbons. The solubility of the copolymers was dependent upon the molecular weight. Thus, isoprene–maleic anhydride copolymers having intrinsic viscosities of 1-6 in cyclohexanone were insoluble in methyl isobutyl ketone while copolymers with intrinsic viscosities of 0.1-0.3 were soluble.

Although dimethylformamide was a good solvent for the copolymers, its miscibility with water made it difficult to obtain reproducible viscosity measurements. In the presence of water the copolymers behaved as typical polyelectrolytes and the η_{sp}/c vs. c plots gave parabolic curves. The low miscibility of cyclohexanone with water made it a better solvent for viscosity determinations.

DISCUSSION

Tetrahydrofuran and maleic anhydride form a charge transfer complex which on irradiation in the presence of a monomer capable of undergoing free radical polymerization yields homopolymers, e.g., methyl methacrylate, or copolymers with maleic anhydride, e.g., vinyl acetate and isobutyl vinyl ether [11]. In the presence of a conjugated diene, irradiation under nitrogen yields the Diels-Alder adduct while irradiation in the presence of oxygen or benzoyl peroxide yields the diene–maleic anhydride copolymer. Benzoyl peroxide, which undergoes rapid induced decomposition in tetrahydrofuran at room temperature, also initiates the copolymerization in the absence of irradiation. It is apparent that the irradiated tetrahydrofuran–maleic anhydride complex, which is a radical initiator in the absence of peroxide or irradiation under oxygen, is not effective in the diene–maleic anhydride copolymerization.

Mixtures of dioxane and maleic anhydride irradiated with gamma or

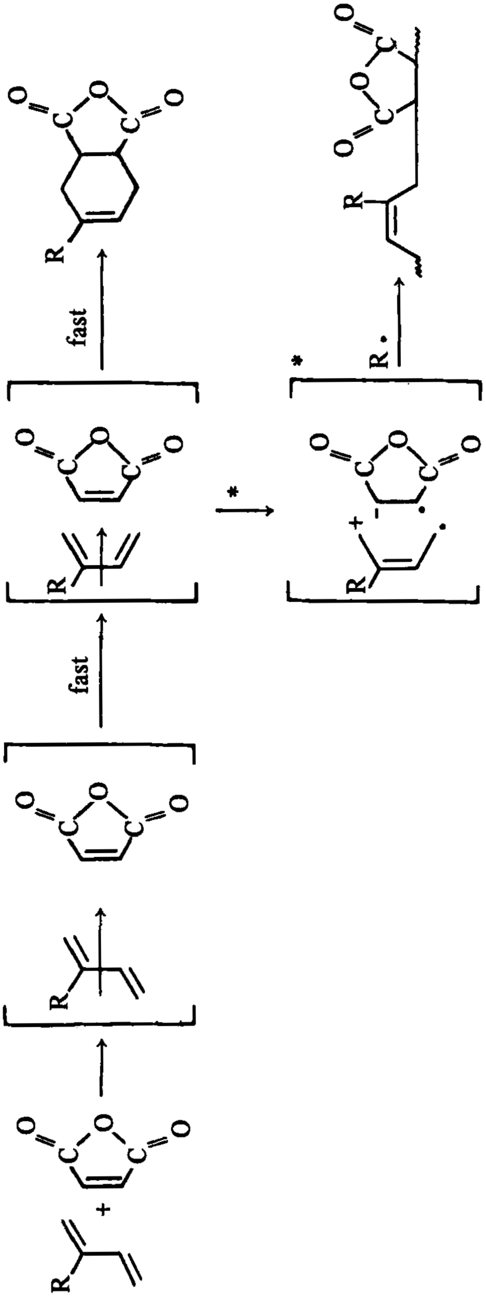
UV radiation in the presence of oxygen or heated with acyl peroxides in the absence of oxygen are capable of initiating cationic polymerization [12, 13]. Although the alternating conjugated diene–maleic anhydride copolymers are produced under these conditions, the effectiveness of dialkyl peroxides, hydroperoxides, and azobisisobutyronitrile in the copolymerization and their ineffectiveness in the cationic polymerization suggests that the copolymerization involves radical rather than cationic initiation.

The high cis-1,4 unsaturation of the alternating diene–maleic anhydride copolymers, in contrast to the trans structures of the conjugated diene monomers and the alternating diene–acrylonitrile copolymers prepared in the presence of zinc chloride, ethyl aluminum sesquichloride, and ethyl aluminum dichloride–transition metal compound [14-21], suggests that a cisoid charge transfer complex is involved in the formation of both the cyclic Diels-Alder adduct and the alternating copolymer.

If the cyclic adduct and the equimolar copolymer arise from alternative or competing one step reactions from a common intermediate, e.g., a cisoid charge transfer complex, the need to generate high concentrations of radicals to increase the yield of copolymer and the decrease in yield when the concentration of radicals per unit time is decreased indicates that the conversion of the complex to the adduct is a fast reaction. Rapid polymerization decreases the complex concentration and the yield of adduct. However, the failure to obtain diene–maleic anhydride copolymer in the irradiated tetrahydrofuran–maleic anhydride mixture, in the absence of oxygen or peroxide, indicates that the simple presence of radical species is not sufficient to account for copolymer formation.

If the cyclic adduct and the equimolar copolymer arise from different complexes, which may have a common precursor, the effect of radicals may be more readily interpreted. Donor-acceptor charge transfer complexes may exist in a ground state and several excited states. The transformation of a ground state to an excited state generally occurs on the absorption of light. However, it has recently been shown that chemically generated excited states may act as sensitizers for photochemical reactions [22, 23]. The thermal decomposition of an oxaoxetane [22] and oxidation of a diacyl hydrazide [22] and a diketooxaoxetane [23] have been shown to generate electronically excited states which can transfer their excitation energy to acceptors which subsequently undergo photochemical reactions.

The generation of excited states in the decomposition of organic peroxides and azo compounds has been demonstrated [24-27]. Therefore, the transformation of the ground-state charge transfer complex to the excited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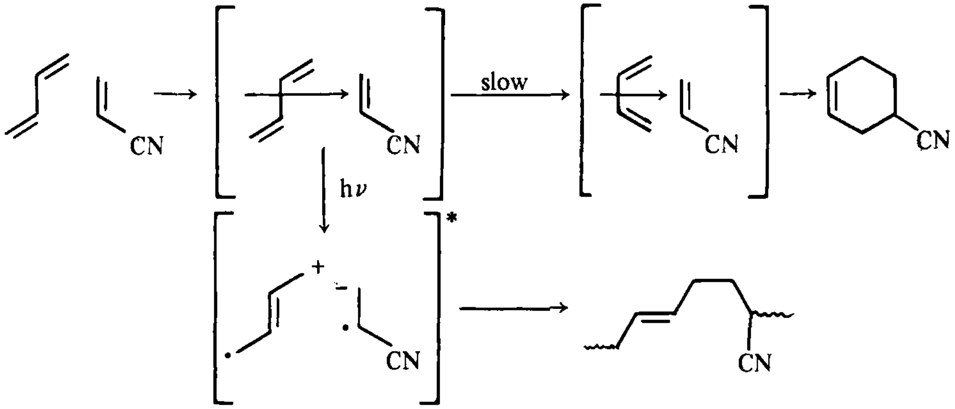
charge transfer complex under the influence of the products from the decomposition of radical precursors may be postulated.

The formation of alternating copolymer and cyclic adduct in the diene–maleic anhydride reaction may be accounted for by assuming the generation of different complexes from a common precursor complex. Thus, the interaction between the donor diene and the acceptor dienophile results in the formation of a ground state charge transfer complex. The latter is rapidly transformed into the cyclic adduct. Transfer of the excitation energy from the peroxide or azo decomposition products to the ground state charge transfer complex results in the formation of the excited charge transfer complex (singlet or triplets). The latter then undergoes spontaneous or radical initiated polymerization. The results shown in Table 3, wherein the dependence of yield and molecular weight on catalyst concentration are in agreement with the behavior in a normal radical polymerization, suggest that the polymerization of the complex is radical initiated. (See structure on preceding page.)

UV radiation has been reported to promote rapid copolymerization of butadiene and acrylonitrile to alternating copolymer at room temperature whereas reaction in the dark at elevated temperatures yields the cyclic adduct. The formation of adduct is accelerated in the presence of $AlCl_3$. The latter and other metal halides also accelerate the formation of alternating copolymer under irradiation. It has been suggested that as a result of UV irradiation the comonomer complex undergoes excitation and polymerization rather than cyclization [28].

The trans-1,4 structure of the alternating butadiene–acrylonitrile copolymer in contrast to the cis-1,4 structure of the alternating diene–maleic anhydride copolymer may be due to the slow conversion of the trans ground state charge transfer complex to the cis ground state charge transfer complex. As a result the excitation of the former yields the trans excited state complex which undergoes polymerization.



The spontaneous polymerization of various donor and acceptor monomers per se as well as in the presence of metal halides to form alternating copolymers may be due to the rapid, spontaneous conversion of the ground state complex, at least in part, to the excited state complex. The catalytic effect of peroxides and other radical precursors may be due to the excitation of ground state complexes.

The essentially equal amounts of cis-1,4 and trans-1,4 unsaturation in the alternating butadiene–sulfur dioxide copolymer [6] suggest the existence of equal amounts of the cis and trans ground state charge transfer complexes which undergo excitation and copolymerization.

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Accepted by editor December 3, 1970
Received for publication January 13, 1971