Cyclo- and Cyclized Diene Polymers. XXI. Polymerization of Isoprene by Stable Carbonium Ion Salt Catalysts

N. G. Gaylord[a]; M. Švestka[b]

[a] Gaylord Associates, Inc., Newark, New Jersey [b] Institute of Physical Chemistry Czechoslovak Academy of Science, Prague, Czechoslovakia

PLEASE SCROLL DOWN FOR ARTICLE

Cyclo- and Cyclized Diene Polymers. XXI. Polymerization of Isoprene by Stable Carbonium Ion Salt Catalysts

N. G. GAYLORD

Gaylord Associates, Inc.
Newark, New Jersey

M. ŠVESTKA

Institute of Physical Chemistry
Czechoslovak Academy of Science
Prague, Czechoslovakia

SUMMARY

The cyclopolymerization of isoprene was readily effected with the stable carbonium ion salts $C_7H_7^+SbCl_6^-$ and $(C_6H_5)_3C^+SbCl_6^-$ in nitrobenzene. Little or no polymerization occurred when n-heptane, benzene, toluene, acetonitrile, methylene chloride, or nitromethane were used as reaction media. The molecular weights of the polymers obtained by light-scattering were in the range of 6,000–70,000 although the intrinsic viscosities in benzene were extremely low, i.e., 0.03–0.06. Triphenylmethyl groups were detected in cyclopolyisoprene prepared with $(C_6H_5)_3C^+SbCl_6^-$ as catalyst. No tropylium residues were detected in polymers prepared with $C_7H_7^+SbCl_6^-$. All polymers contained 10–45% unsaturation (trans-1,4 and 3,4). The unsaturation decreased with increasing trityl ion concentration but was independent of tropylium ion concentration. At constant isoprene concentration, a limiting conversion was reached; polymerization resumed on the addition of monomer. $SbCl_5$ in nitrobenzene was an effective catalyst for the cyclopolymerization of isoprene in the absence of cocatalyst. The proposed initiation mechanism involves the

formation of a catalyst-nitrobenzene charge transfer complex which undergoes a one-electron transfer with isoprene monomer to yield a monomer cation-radical. The latter generates a fused ring structure by successive cation and radical additions to monomer, as proposed for cyclopolymerizations initiated by $C_2H_5AlCl_2$ and $C_2H_5AlCl_2-TiCl_4$.

INTRODUCTION

Stable carbonium ion salts such as cycloheptatrienyl (tropylium) or triphenylmethyl (trityl) hexachloroantimonate have been shown to initiate nonterminating cationic polymerization of cyclic ethers and various vinyl monomers. Tropylium salts with anions such as $SbCl_6^-$, BF_4^-, and ClO_4^- have been utilized in the polymerization of cyclic ethers such as tetrahydrofuran as well as alkyl vinyl ethers, N-vinylcarbazole, alkoxystyrenes, vinyl naphthalene, and acenaphthylene. Triphenylmethyl cation salts with anions such as $SbCl_6^-$, SbF_6^-, PF_6^-, and AsF_6^- have effectively initiated the polymerization of cyclic ethers such as tetrahydrofuran, dioxolane, and sym-trioxane as well as alkyl vinyl ethers, N-vinylcarbazole, and alkoxystyrenes [1-5].

It has been proposed that initiation by the tropylium ion, in the case of alkyl vinyl ethers [1] and N-vinylcarbazole [6], proceeds through the formation of a donor (vinyl monomer)-acceptor (tropylium ion) charge transfer complex, leading to a monomer cation-radical which can react with free monomer and ultimately propagates through dication species as a result of radical coupling.

In contrast, it was originally [2] proposed that the trityl ion initiation of tetrahydrofuran polymerization proceeded through the formation of an oxonium ion salt, followed by oxonium ion propagation. It was later proposed [5] that the initiation step involves hydride ion abstraction by the trityl ion to form a cyclic tetrahydrofuran cation which can, per se or after cleavage to an open chain carbonium ion, propagate by a carbonium ion mechanism.

It has been shown that isoprene can be polymerized by many Friedel-Crafts catalysts to polymers with essentially fused cyclic structures with varying, though small, amounts of trans-1,4 unsaturation [9]. The cyclic structures apparently arise as a result of initiation by a one-electron transfer from monomer to catalyst, yielding a monomer cation-radical which propagates by consecutive cation and radical additions to the diene

double bonds [10]. The linear unsaturation results from conventional cation or radical addition to monomer.

Since tropylium ions and trityl cations form relatively stable salts, moieties derived therefrom can be readily detected when present in polymer structures, and cationic polymerizations are initiated by different species and mechanisms, i.e., cation-radical and cation, respectively. The stable hexachloroantimonates of these carbonium ions were investigated in order to obtain more insight into the mechanism of the initiation of the cyclopolymerization of isoprene.

EXPERIMENTAL

The polymerization of isoprene was carried out under a nitrogen atmosphere using tropylium hexachloroantimonate [7] and triphenylmethyl hexachloroantimonate [8] as catalysts and distilled benzene, toluene, heptane, methylene chloride, acetonitrile, nitromethane, and nitrobenzene as reaction media. The solvents and isoprene were dried over calcium hydride and charged into the reaction vessel by means of hypodermic syringes.

In a typical polymerization, 50 ml of nitrobenzene and 1 mmole of tropylium hexachloroantimonate were stirred at $20°C$ in a 250-ml three-necked flask equipped with a magnetic stirrer, thermometer, reflux condenser, and a nitrogen inlet and outlet. The polymerization was started by adding 10 ml of isoprene, and the temperature was maintained at $20°C$ for 100 min. The reaction mixture was poured into 150 ml of methanol. Although a portion of the polymer coagulated, the major part remained as an emulsion in the methanol-nitrobenzene mixture. After distillation of the solvents in vacuo, the residual polymer was dissolved in benzene and precipitated by methanol. After a reprecipitation from benzene by methanol, the solid polymer was dried in vacuo and weighed.

Viscosity measurements were carried out in benzene solution at $25°C$ with a Ubbelohde viscometer. Infrared analyses were carried out using KBr pellets. The absorption bands at 845 and 1145 cm^{-1} were used to determine the trans-1,4 content of the polymers.

RESULTS

Both $C_7H_7^+SbCl_6^-$ and $\phi_3C^+SbCl_6^-$ failed to initiate the polymerization of isoprene when n-heptane, benzene, toluene, or acetonitrile was used as

the reaction medium. Only trace amounts of solid polymers were isolated
when reaction was carried out in methylene chloride or nitromethane.
This is in marked contrast to the successful polymerization of vinyl ethers,
alkoxystyrenes, N-vinylcarbazole, etc., with $\phi_3 C^+ SbCl_6^-$ in methylene chlor-
ide and acetonitrile [1]. This is also in contrast to the successful polymer-
ization, particularly cyclopolymerization, of isoprene with Lewis acids,
$R_2 AlX\text{-}TiCl_4$, $RAlCl_2$, and $RAlCl_2\text{-}TiCl_4$ in benzene and heptane [9, 10].

When n-heptane or methylene chloride was mixed with nitrobenzene, the
yield of polymer increased in proportion to the nitrobenzene content of
the solvent mixture, pure nitrobenzene giving the highest polymer yield.
Table 1 summarizes the results with $\phi_3 C^+ SbCl_6^-$ as catalyst. Similar results
were obtained with $C_7 H_7^+ SbCl_6^-$.

The yields of polymer obtained in nitrobenzene were essentially the
same whether the crystalline salt $\phi_3 C^+ SbCl_6^-$ was added or was formed in
situ by the addition of separate solutions of trityl chloride and $SbCl_5$.

The molecular weights of the polymers increased with increasing nitro-
benzene content of the reaction medium. As discussed later, polymers
prepared with trityl ion initiation contained triphenylmethyl groups. The
amount of such groups in the polymer was inversely proportional to the
nitrobenzene content of the reaction medium (Fig. 1).

Table 1. Influence of Solvent Composition on Isoprene Polymerization [a]

No.	Catalyst	Solvent, vol/vol	Temp., °C	Conversion, %	$[\eta]$,[b] dl/g	Polymer appearance
1	$\phi_3 CCl + SbCl_5$	$CH_2 Cl_2$	0	2.0	—	Tacky
2		$CH_2 Cl_2 /\phi NO_2$				
		(4/1)	0	6.9	—	Tacky
3		ϕNO_2	20	51.5	0.057	Powdery
4	$\phi_3 C^+ SbCl_6^-$	$n\text{-}C_7 H_{16}$	20	0	—	
5		$n\text{-}C_7 H_{16} /\phi NO_2$				
		(4/1)	20	0	—	
6		(2/3)	20	4.4	0.035	Tacky
7		(3/7)	20	22.0	0.040	Tacky
8		ϕNO_2	20	44.0	0.056	Brittle
9	$SbCl_5$	ϕNO_2	20	33.8	0.055	Tacky

a [Isoprene] = 1.6 moles/liter; [catalyst] = 0.016 mole/liter.
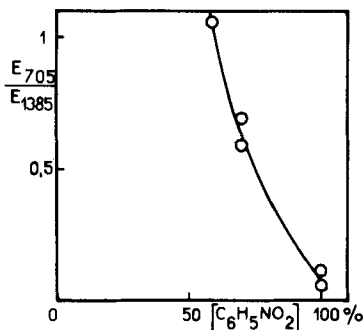
b Benzene, 25°C.

Fig. 1. Phenyl group content of cyclopolyisoprene as a function of the volume-per cent of nitrobenzene in the reaction medium. [Isoprene] = 1.6 moles/liter; $[\phi_3 C^+ SbCl_6^-]$ = 0.016 mole/liter; solvent: n-heptane/nitrobenzene; E_{705} = phenyl group absorptivity; E_{1385} = methyl group absorptivity.

Polymerization initiated by the tropylium salt was slower than that in-itiated by the trityl salt, as indicated by the lower yields in the former case (Table 2). Antimony pentachloride per se also initiated the polymer-ization of isoprene in nitrobenzene. Under the same conditions, i.e., [isoprene] = 1.6 moles/liter, [catalyst] = 0.016 mole/liter, the yields and the intrinsic viscosities of the polymers were as shown in Table 3.

When the concentration of isoprene was maintained at a constant level during the entire course of polymerization in nitrobenzene with $C_7 H_7^+$ $SbCl_6^-$ as catalyst, a limiting conversion was reached, characterized by the presence of free monomer and active catalyst (Fig. 2). Similar results

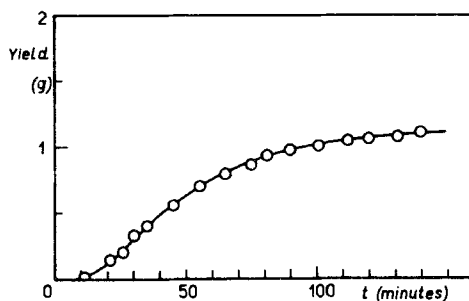

Fig. 2. Polymerization of isoprene in nitrobenzene at 20°C catalyzed by $C_7 H_7^+ SbCl_6^-$. Nitrobenzene 50 ml; $[C_7 H_7^+ SbCl_6^-]$ = 0.02 mole/liter. Iso-prene concentration maintained constant during polymerization at 0.1 mole/liter.

Table 2. Influence of Monomer and Catalyst Concentrations on
Isoprene Polymerization in Nitrobenzene at 20°C.

No.	[Catalyst], mole/liter	[Isoprene], moles/liter	Conversion, %	$[\eta]$,[a] dl/g	Polymer appearance
	$\phi_3 C^+ SbCl_6^-$				
10	0.008	1.6	35.3	0.040	Tacky
11	0.016	1.6	44.1	0.056	Tacky
12	0.024	1.6	45.6	0.053	Powdery
13	0.032	1.6	60.3	0.050	Powdery
	$C_7 H_7^+ SbCl_6^-$				
14	0.016	1.6	26.3	0.049	Tacky
15	0.032	1.6	54.4	0.056	Tacky
16	0.048	1.6	61.7	0.052	Tacky
17	0.016	0.8	20.6	0.042	Powdery
18	0.016	1.6	26.5	0.049	Tacky
19	0.016	2.4	41.2	0.063	Tacky
20	0.016	3.2	42.6	0.053	Tacky

[a] Benzene, 25°C.

Table 3

Catalyst	Conversion, %	$[\eta]$, dl/g [a]
$(C_6 H_5)_3 C^+ SbCl_6^-$	44.0	0.056
$SbCl_5$	33.8	0.055
$C_7 H_7^+ SbCl_6^-$	26.3	0.049

[a] Benzene, 25°C.

were obtained with $\phi_3 C^+ SbI_6^-$ as catalyst. When additional monomer was added, further polymerization occurred, analogous to the results obtained in the cyclopolymerization of isoprene in benzene or heptane with $C_2 H_5 AlCl_2$ or $C_2 H_5 AlCl_2$-$TiCl_4$ catalysts.

Both tropylium and trityl ion catalysts gave increased yields of polymer with increasing catalyst concentration at constant monomer concentration

(Table 2). The intrinsic viscosities, within experimental error, were apparently independent of catalyst concentration.

With $\phi_3 C^+ SbCl_6^-$ as catalyst, higher concentrations yielded polymers with decreased linear, i.e., trans-1,4, structure content (Fig. 3). However, with
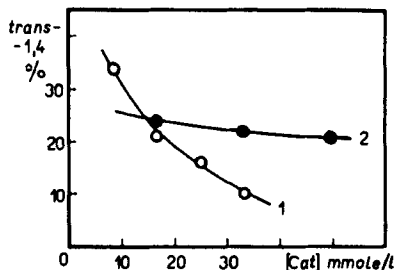

Fig. 3. Percentage of trans-1,4 units in cyclopolyisoprene as a function of catalyst concentration. [Isoprene] = 1.6 moles/liter; nitrobenzene, 20°C.
(1) $\phi_3 C^+ SbCl_6^-$; (2) $C_7 H_7^+ SbCl_6^-$.

$C_7 H_7^+ SbCl_6^-$ as catalyst, the trans-1,4 content was essentially independent of catalyst concentration.

At constant $C_7 H_7^+ SbCl_6^-$ concentration, the yield of polymer, and possibly the intrinsic viscosity, increased with increasing monomer concentration. The amount of linear unsaturation also increased; e.g., increasing the isoprene concentration from 0.8 to 3.2 M increased the trans-1,4 content from 18 to 26%.

In all cases, the polymers isolated by precipitation with methanol, were powders or tacky solids with extremely low intrinsic viscosities (Tables 1 and 2). However, analogous to the previously reported results in the cyclopolymerization of isoprene with cationic catalysts, molecular weights determined by light-scattering were in the range of 6,000–70,000. Infrared and chemical analysis showed that all polymers contained 10–45% unsaturation (trans-1,4 and 3,4), independent of the nature of the catalyst. No cis-1,4 units could be detected.

When the catalyst contained trityl moieties, in all cases triphenylmethyl groups were detected in the polymer by the presence of characteristic absorption bands at 700, 742, 760, 1595, and 1600 cm^{-1}. These bands did not disappear even after repeated precipitation of very dilute solutions with methanol. On the other hand, no cycloheptatrienyl groups were found in polymers prepared with the tropylium salt catalyst.

Although the polymers have a predominantly cyclic structure,

irrespective of the nature of the catalyst, it would appear that the initiation mechanisms differ.

It has been proposed [1] that initiation of the polymerization of alkyl vinyl ethers with the trityl cation involves classical cationic initiation. This could account for the presence of triphenylmethyl groups in the cyclopoly-isoprene, e.g.,

$$
\phi_3 C^+ + \quad \underset{CH_3}{\diagup\diagdown} \quad \longrightarrow \quad \phi_3 C \dots \qquad (1)
$$
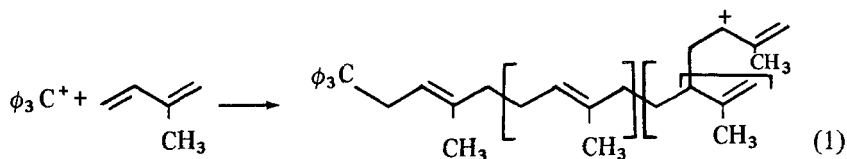
However, it has been proposed [10] that cyclopolymerization under the in-fluence of $C_2H_5AlCl_2$ or $C_2H_5AlCl_2$–$TiCl_4$ catalysts involves not a class-ical two-electron transfer but a one-electron transfer from the donor diene monomer to the acceptor cation derived from the catalyst, resulting in the formation of a monomer cation-radical. The latter then initiates cyclo-polymerization by successive cation and radical additions, e.g.,

$$
A^+ + \quad \underset{R}{\diagup\diagdown} \quad \longrightarrow \quad A^{\oplus} \quad \underset{R}{\diagup\diagdown} \qquad (2)
$$

$$(3)$$
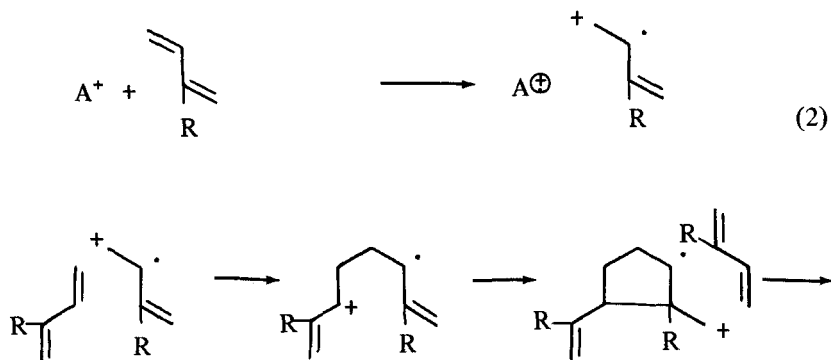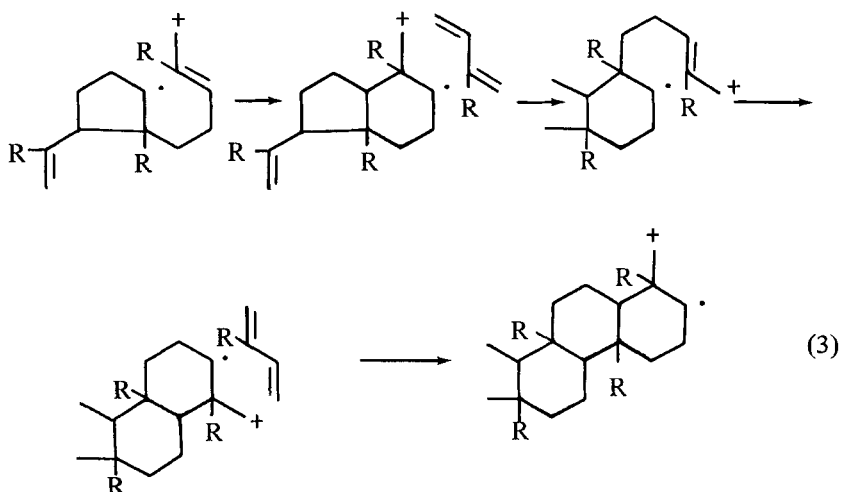
It has been proposed [10] that conventional cationic addition by the polymeric cation, unaccompanied by the radical addition, results in residual linear, mainly trans-1,4, unsaturation. However, the monomer cation-radical can initiate cyclopolymerization by addition to such polymeric unsaturation as well as to monomeric unsaturation.

Applying this sequence of reactions to polymerization systems containing the trityl cation in nitrobenzene: See Eqs. (4) and (5).

$$\phi_3 C^+ \quad + \quad \overset{}{\underset{R}{\diagup}} \quad \longrightarrow \quad \phi_3 C \cdot \quad \overset{+}{\underset{R}{\diagup}} \qquad (4)$$
$$(\phi NO_2) \qquad\qquad\qquad (\phi NO_2)$$
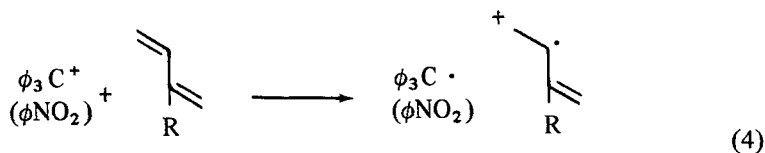
The resultant polymer has cyclic structures, linear unsaturation, and triphenylmethyl moieties, consistent with the experimental data.

The failure to initiate isoprene polymerization in benzene, toluene, or heptane may be indicative of the decreased electron-accepting characteristics of the trityl cation as compared with the cations derived from $C_2H_5AlCl_2$, $C_2H_5AlCl_2-TiCl_4$, or other Lewis acids in these solvents. The failure to initiate isoprene polymerization in methylene chloride, acetonitrile, or nitromethane may be indicative of the decreased electron-donating characteristics of the isoprene as compared with the alkyl vinyl ethers, N-vinylcarbazole, or alkoxystyrenes in these solvents. Both effects

(5)
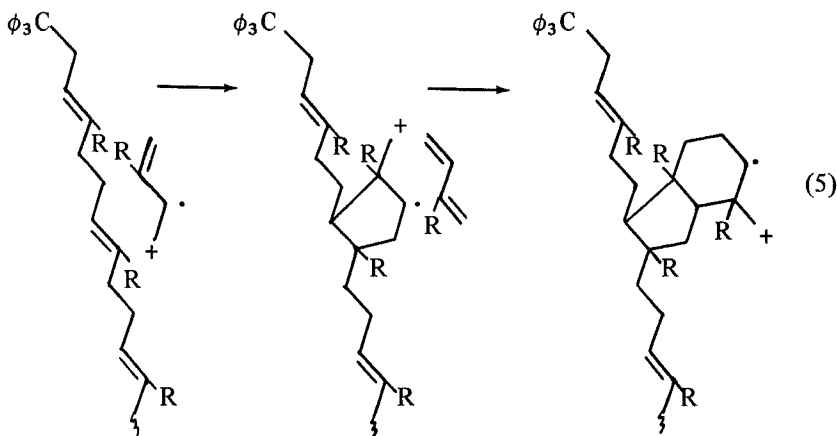
may be related to the extreme stability of the triphenylmethyl cation or the lack of dissociation of the triphenylmethyl cation salt. Thus, the cation salt may dissociate insufficiently in the hydrocarbon solvents to act as an electron acceptor. However, its effectiveness in initiating the polymerization of the oxygen- and nitrogen-containing monomers in the nonhydrocarbon solvents indicates that dissociation occurs readily in these solvents. The inactivity of the trityl cation must therefore be related to the inherent stability of the trityl cation or the so much greater stability of the trityl cation than the cation derived from the isoprene so that the latter cannot exist in the presence of the former.

One explanation for the effectiveness of the trityl cation salt in nitrobenzene is the possible presence of water in the latter. Hydrolysis of the salt to the acid would yield the protonic initiation common to conventional catalysts for cationic polymerization. While this may explain the initiation of isoprene polymerization with $SbCl_5$ and the tropylium ion salt where catalyst residues are absent from the polymer, it fails to explain the cyclic structure of the polymer in these cases and the presence of trityl moieties in the polymer when the trityl cation salt is used as catalyst.

A more satisfactory explanation is the interaction of the trityl cation or the salt with the strongly electron-accepting nitrobenzene to produce a charge transfer complex which is a better electron acceptor than the trityl cation and is the actual active species in the initiation.

This active species initiates cyclopolymerization by a one-electron transfer reaction, as shown in Eqs. (2) and (3). With increasing nitrobenzene content, the participation of conventional cationic addition in the reaction

scheme as shown in Eq. (1) becomes less significant, as evidenced by the decreasing trityl content of the polymer. Further evidence is found in the decreasing unsaturation with increasing concentration of trityl catalyst, i.e., catalyst-nitrobenzene charge transfer complex.

The increase in the yield and the molecular weight of the polymer with increasing nitrobenzene content, as well as the reinitiation of polymerization after the limiting conversion has been reached, are related to the formation of monomer cation-radical, as in Eq. (4), and its reaction with polymeric unsaturation, as shown in Eq. (5).

The characteristics of the tropylium ion-catalyzed isoprene polymerization are similar to those of the trityl cation-catalyzed polymerization with a few exceptions, i.e., lower rate of polymerization, absence of catalyst residues in polymer, and nondependence of trans-1,4 content of polymer on catalyst concentration. These are all indicative of the absence of the classical cationic addition reaction shown in Eq. (1).

Color formation on the addition of $C_7H_7^+SbCl_6^-$ to nitrobenzene is probably related to the formation of the charge transfer complex which is responsible for cyclopolymerization, as shown in Eqs. (2)–(5). The participation of nitrobenzene in charge transfer complex formation has been indicated in the photosensitized polymerization [11] of N-vinylcarbazole, both in the absence and in the presence of $NaAuCl_4$, as well as in the anodic polymerization [12] of styrene, isobutyl vinyl ether, and N-vinylcarbazole in the presence of $(C_2H_5)_4N^+BF_4^-$ and $(C_2H_5)_4N^+ClO_4^-$.

The trans-1,4 content of the cyclopolyisoprene prepared with the tropylium and trityl ion salts in nitrobenzene is higher than that of the cyclopolyisoprenes prepared previously with cationic catalysts in benzene of heptane.

The cation-radical generally considered to be operative in polymerizations initiated by one-electron transfer, i.e., through charge transfer intermediates, is not inhibited by conventional radical inhibitors such as air, 2,2-diphenyl-1-picrylhydrazyl, or nitrobenzene, and propagates by a cationic mechanism. This is also apparently true of the monomer cation-radical produced by the action of the carbonium ion salt-nitrobenzene charge transfer complex on isoprene. However, in the latter case propagation is not cationic but rather successive cation and radical. During propagation, as shown in Eq. (3), the radical passes consecutively from a monomer 1,2 cation-radical (allyl radical) to a 1,4 cation-radical (allyl radical) to a 1,3 cation-radical (no unsaturation) to a 1,7 cation-radical (allyl cation, unconjugated radical) to a 1,3 cation-radical, etc. It is probable that the radical in the 1,4, 1,3, or 1,7 cation-radical interacts with the nitrobenzene in the normal inhibition reaction. The residual cation can continue to add monomer in the conventional manner to yield linear unsaturation.

A further implication of the noninhibition of both the monomer cation-radical and the propagating cation and the inhibition of the propagating radical is a decrease in the length of cyclic sequences and probably in the extent of branching, e.g., that resulting from reinitiation or addition of monomer cation-radical to polymeric unsaturation. This is indicated by the tacky nature of many of the cyclopolyisoprenes (Table 1 and 2), probably due to linear polyisoprene segments, and the greatly reduced slope of the specific viscosity-concentration plot.

It is thus apparent that the same initiation and propagation mechanisms are operative in the cyclopolymerization of isoprene with triphenylmethyl and tropylium ion salt catalysts. They differ only in that in the case of the triphenylmethyl carbonium ion salt the cyclopolymerization is accompanied by a classical two-electron initiation and propagation.

The effectiveness of antimony pentachloride in nitrobenzene in initiating the cyclopolymerization of isoprene in the absence of added cocatalyst is noteworthy. The yield of polymer was only slightly lower than when $\phi_3 C^+ SbCl_6^-$ was used as catalyst (Table 1), while the intrinsic viscosity and the extent of unsaturation were essentially the same. Although the presence of water as cocatalyst cannot be excluded from consideration, the active species in the $SbCl_5 - C_6H_5NO_2$ system may be $SbCl_4^+(C_6H_5NO_2)Cl^-$ due to the strong electron-accepting characteristics of nitrobenzene.

This is analogous to the increased catalytic activity of the $AlBr_3 - TiCl_4$ system [13] or $AlBr_3$ alone [14] in the absence of water in the polymerization of isobutylene in heptane. In these cases the active species are considered to be $TiCl_3^+ AlBr_3 Cl^-$ and $AlBr_2^+ AlBr_4^-$, respectively, and the addition of water causes a substantial decrease in polymerization rate. In contrast, $TiCl_4$ and BF_3 are ineffective in the absence of water in the polymerization of isobutylene in heptane [14].

The influence of nitrobenzene in diene polymerization is also seen in the effective cyclopolymerization of isoprene in nitrobenzene at 20°C using PF_5 or $TiCl_4$ as catalyst, in the absence of added cocatalyst. No catalytic activity is noted in nitromethane or acetonitrile. In heptane the cyclopolymerization of isoprene is catalyzed by $TiCl_4$ in the presence but not in the absence of water [9]. These catalytic effects are under further investigation.

REFERENCES

[1] C. E. H. Bawn, C. Fitzsimmons, and A. Ledwith, *Proc. Chem. Soc.,* **1964,** 391.

[2] C. E. H. Bawn, R. M. Bell, and A. Ledwith, *Polymer,* 6, 95 (1965).
[3] C. E. H. Bawn, R. M. Bell, C. Fitzsimmons, and A. Ledwith, *Polymer,* 6, 661 (1965).
[4] B. J. K. Smith, J. A. Dodd, A. T. Instone, and D. B. Partridge, *J. Polymer Sci.,* B5, 625 (1967).
[5] I. Kuntz, *J. Polymer Sci.,* A-1(5), 193 (1967).
[6] A. Ledwith, *J. Appl. Chem.,* 17, 344 (1967).
[7] H. J. Dauben, Jr., F. A. Gadecki, K. M. Harmon, and D. L. Pearson, *J. Am. Chem. Soc.,* 79, 4557 (1957).
[8] W. M. Pasika, *J. Polymer Sci.,* A(3), 4287 (1965).
[9] N. G. Gaylord, B. Matyska, K. Mach, and J. Vodehnal, *J. Polymer Sci.,* A-1(4), 2493 (1966).
[10] N. G. Gaylord, I. Kössler, and M. Štolka, *J. Macromol. Sci.,* A2, 421 (1968).
[11] S. Tazuke, M. Asai, S. Ikeda, and S. Okamura, *J. Polymer Sci.,* B(5), 453 (1967).
[12] J. W. Breitenbach and C. Srna, *Pure and Appl. Chem.,* 4, 245 (1962).
[13] M. Marek and M. Chmelír, *J. Polymer Sci.,* C23(1), 223 (1968).
[14] M. Chmelír, M. Marek, and O. Wichterle, *J. Polymer Sci.,* C16(2), 833 (1967).