to differences in the size of similar molecules than is spin-spin relaxation or chemical shift.

(6) It is conceivable that the methodology presented here could be used as a fractionation technique of laboratory-scale samples.

Model PDMS networks of this kind after sol extraction are eminently suitable as host materials in the study of molecular kinetics and dynamics in the presence of topological constraints. Work along these lines is in progress in our laboratories.

Acknowledgment. We thank G. Iannacchione and D. Mahoney for their help with the preparation of the NMR samples and with data entry. E.D.v.M. gratefully acknowledges support of this work by the National Science Foundation.

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Registry No. Si(OEt)$_4$, 78-10-4.

Cationic Transannular Polymerization of 1,5,9-Cyclododecatriene

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ABSTRACT: The cationic transannular polymerization of 1,5,9-cyclododecatriene initiated by $Al_2Et_3Cl_3$ or $AlEtCl_2$ is studied, and the effects of reaction conditions on the polymer yield are investigated. In accordance with the experimental infrared and nuclear magnetic resonance spectroscopic data, GC-MS analysis, and the solubility of the products, the resulting polymer is determined to be a linear oligomer consisting of tricyclic repeat units, of which the number-average molecular weight is ca. 1100-2200. The intramolecular cyclization of 1,5,9-cyclododecatriene reported earlier by Tolstikov et al. corroborated the conclusion given in this paper. The experimental results also indicate that *cis,trans,trans*-1,5,9-cyclododecatriene is much more prone to polymerize than *trans,trans,trans*-1,5,9-cyclododecatriene.

Introduction

The field of cationic transannular polymerization was opened by investigations concerning the polymerization of 2-methylene-5-norbornene[1] and 2,5-norbornadiene.[2] Typical examples of transannular polymerization are shown in Table I. However, no research work has been reported hitherto on the cationic transannular polymerization of 1,5,9-cyclododecatriene (CDT), although the ring-opening polymerization of CDT occurs in the presence of some chlorides of transition metals.[8,9]

In this work, the transannular polymerization of CDT initiated by $AlEtCl_2$ and $Al_2Et_3Cl_3$ was studied. The effects of reaction conditions, such as the kind of cationic initiator and coinitiator and the concentration of monomer, on the polymer yield were investigated. Combining the results of infrared and nuclear magnetic resonance spectroscopy and GC-MS analysis with the experimental data on isomerization of CDT reported by Tolstikov[10] and Antropimsova,[11] we concluded that the resultant polymer consists of tricyclic repeat units.

Experimental Section

Materials. 1,5,9-Cyclododecatriene was purified by shaking with concentrated sodium hydroxide solution three times at room temperature. It was then washed with dilute sulfuric acid and with water and predried with calcium chloride. The predried monomer was distilled at reduced pressure under an argon

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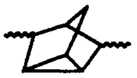
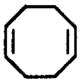
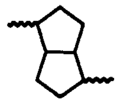
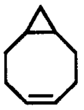
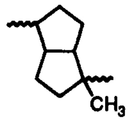
Table I
Typical Examples of Transannular Polymerization

monomer	repeat unit of resulting polymer	refs
		1
		2
		3–5
		6, 7

atmosphere from CaH_2, and a fraction was collected at 62 °C/10 mmHg. Then it was stored under an argon atmosphere at −30 °C. The purified monomer was shown by ^{13}C NMR spectroscopy and gas chromatography to be a mixture of 96% *cis,trans,trans*-1,5,9-cyclododecatriene and 4% *trans,trans,trans*-1,5,9-cyclododecatriene. Benzyl chloride, iodomethane, and 1-chlorobutane were dried with CaH_2 for more than 24 h and distilled from CaH_2 under an argon atmosphere (benzyl chloride was distilled at reduced pressure). Solvent, dichloromethane, was refluxed over CaH_2 for 24 h and distilled under an argon atmosphere. $AlEt_3$, $AlEt_2Cl$, $AlEtCl_2$, and $Al_2Et_3Cl_3$ were kindly provided by the Changchun Institute of Applied Chemistry, Academia Sinica of China, and were used as received. The water content in CDT and CH_2Cl_2 should be within 15 ppm for CDT and <6 ppm for CH_2Cl (by the Karl Fischer method).

Polymerization. The polymerization was carried out in a predried 20-mL ampule under highly purified argon. The solvent, the monomer, and the catalysts were added to the reaction bottle by hypodermic syringes. Then the bottle was sealed and left alone at the desired temperature with stirring. The polymerization was stopped by pouring the reaction mixture into ca. 100 mL of ethanol and hydrochloric acid. The precipitated white powder was collected, dissolved in a small amount of dichloromethane, and precipitated again in the same way mentioned. Finally, the polymer generated was dried to constant weight in vacuo at 40 °C.

Characterization of Poly(1,5,9-cyclododecatriene). The number-average molecular weight was measured with a Knauer VPO using chloroform as a solvent. The gel permeation chromatogram (GPC) was recorded on a Hitachi 635TR chromatograph using chloroform as eluent. $CDCl_3$ solutions of the polymer obtained by transannular polymerization of CDT (5% concentration) were examined with a JEOL 100 MC NMR spectrometer at room temperature. The infrared spectra of polymers were recorded on a Perkin-Elmer B599 spectrometer. GC–MS analyses were performed with JEOL JMS D100 and C25 GC–MS spectrometers.

Results and Discussion

Selection of Coinitiators. Several Lewis acids were used to initiate the polymerization of CDT. The relevant data from these polymerizations are presented in Table II. When the polymerization of CDT initiated by $AlEtCl_2$ and $Al_2Et_3Cl_3$ was carried out at 0 °C or room temperature, the reaction proceeded violently, the temperature of the polymerization system rose instantaneously, and the product exhibited a brown or black color and lower molecular weight. On the other hand, the reaction rate was very slow at much lower temperature, −78 °C.

Table II indicates that $AlEt_3$ and $AlEt_2Cl$ failed to initiate the polymerization of CDT, and the order of the initiation activity of the coinitiators used is as follows: $BF_3{\cdot}OEt_2 < AlCl_3 < AlEtCl_2 < Al_2Et_3Cl_3$, which is just opposite to their order of acidity.

Table II
Polymerization of CDT Initiated by Several Lewis Acids[a]

coinit	coinit/CDT molar ratio	temp, °C	polym yield, %
$BF_3{\cdot}OEt_2$	0.06	24	32.2
$AlCl_3$	0.025	24	48.8
$AlEt_3$	0.10	24	0.0
$AlEt_2Cl$	0.05	24	0.0
$AlEtCl_2$	0.05	−18	69.0
$AlEtCl_2$	0.0125	−18	34.6
$Al_2Et_3Cl_3$	0.05	−18	86.8
$Al_2Et_3Cl_3$	0.0125	−18	50.8
$Al_2Et_3Cl_3$	0.05	−25	>80.0[b]
$Al_2Et_3Cl_3$	0.05	−50	50.0[c]

[a] Solvent, CH_2Cl_2; (CDT) = 2.8 mol/L; reaction time, 70 h except those marked by *b* and *c*. [b] Reaction time, 1 week. [c] Reaction time, 2 weeks.

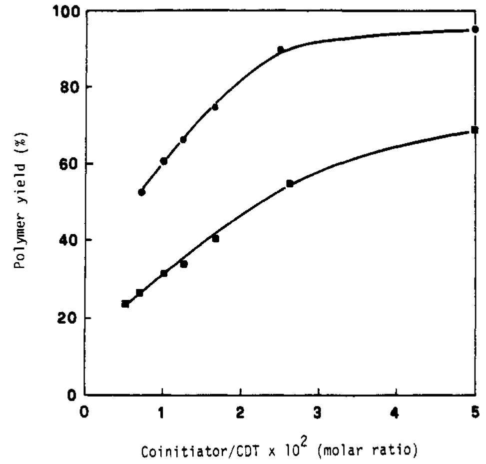


Figure 1. Relationship between polymer yield and molar ratio of coinitiator to CDT: (1) $Al_2Et_3Cl_3$; (2) $AlEtCl_2$. [CDT] = 2.8 mol/L; solvent, CH_2Cl_2; reaction time, 72 h; temperature, −18 °C.

Table III
Effect of Initiators with $Al_2Et_3Cl_3$ as Coinitiator[a]

initiator	polym yield, %
benzyl chloride	explosive polymerization
iodomethane	46.9
1-chlorobutane	33.2

[a] Temperature, −18 °C; $Al_2Et_3Cl_3$/CDT molar ratio = 0.017; organic halide/$Al_2Et_3Cl_3$ molar ratio = 3; bulk polymerization.

Effect of the Molar Ratio of Coinitiator to Monomer. 1,5,9-Cyclododecatriene was polymerized by $AlEtCl_2$ and $Al_2Et_3Cl_3$ in dichloromethane solvent under fixed conditions. Figure 1 shows these results and indicates that the polymer yield increases with the elevation of the molar ratio of coinitiator to monomer.

Effect of Initiators. It is well-known that the activity of an initiator–coinitiator complex depends on its ability to donate a proton or cation to the monomer, which, in turn, depends on the initiator and coinitiator used.

It is evident from Table III that the activity of initiator in the polymerization of CDT with $Al_2Et_3Cl_3$ as coinitiator is in the following order: $C_6H_5CH_2Cl > CH_3I >$ *n*-BuCl.

Effect of Solvent. Great increase in the rate of polymerization is generally observed as one increases the solvating power of the reaction medium.[12–14] Figure 2 shows the relationship between the polymer yield and molar ratio of CH_2Cl_2/CDT. These plots exhibit a maximum polymer yield at a certain molar ratio of dichloromethane to monomer. The polymer yield increases with increasing CH_2Cl_2/CDT, reaches a maximum, and then

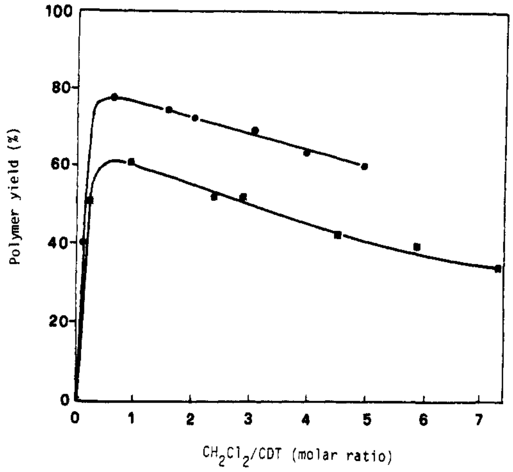


Figure 2. Relationship between polymer yield and CH_2Cl_2/CDT molar ratio: Coinitiator/CDT molar ratio = 0.017; solvent, CH_2Cl_2; temperature, −18 °C; reaction time, 96 h. (1) $Al_2Et_3Cl_3$; (2) $AlEtCl_2$.

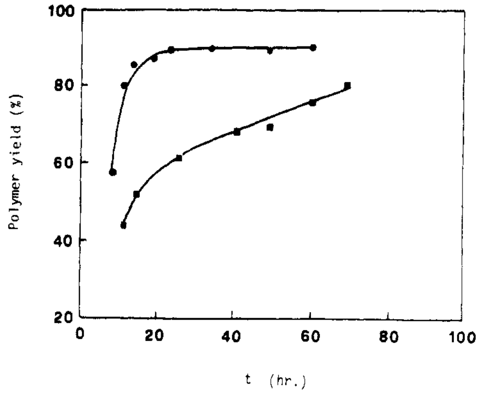


Figure 3. Relationship between polymer yield and duration of polymerization: (1) $Al_2Et_3Cl_3$; (2) $AlEtCl_2$. Coinitiator/CDT molar ratio = 0.017; solvent, CH_2Cl_2; temperature, −18 °C; [CDT] = 2.8 mol/L.

Table IV
Number-Average Molecular Weight of Resulting Polymers[a]

expt no.	coinit	CDT concn, mol/L	polym yield, %	$\bar{M}_n$(VPO)
B17	$Al_2Et_3Cl_3$	2.8	86.8	2230
B53	$AlEtCl_2$	2.6	69.6	1140

[a] Solvent, CH_2Cl_2; reaction time, 72 h; temperature, −18 °C; coinitiator/CDT molar ratio = 0.05.

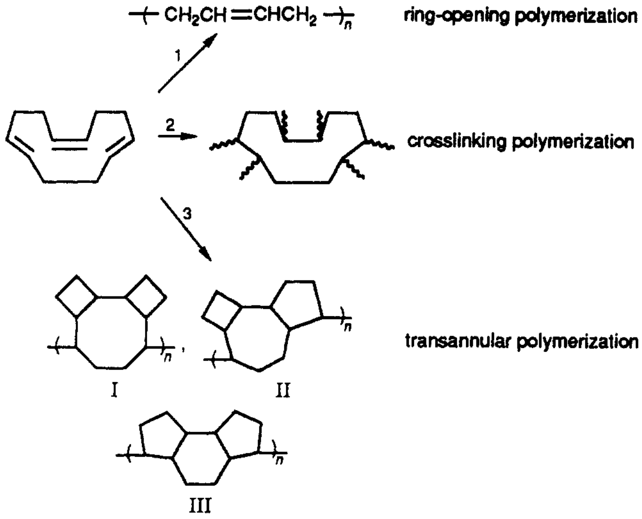
either decreases or levels off. The decrease in polymer yield at higher molar ratio of CH_2Cl_2/CDT should be ascribed to the fact that the decrease in monomer concentration leads to decreasing propagation rate; thus at constant reaction duration, one observes a decrease in polymer yield.

Dependence of Polymer Yield on Reaction Time. A plot of polymer yield versus polymerization time with $AlEtCl_2$ and $Al_2Et_3Cl_3$ as coinitiators is shown in Figure 3, which indicates that the polymer yield increases with polymerization time.

Characterization of Polymer and Mechanism of Transannular Polymerization. Table IV shows the number-average molecular weights ($\bar{M}_n$) of the polymers obtained. It is found from Table IV that coinitiators $AlEtCl_2$ and $Al_2Et_3Cl_3$ can polymerize CDT, yielding oligomers only.

The number-average molecular weights measured by GPC are in approximate agreement with those from VPO listed in Table IV.

Scheme I



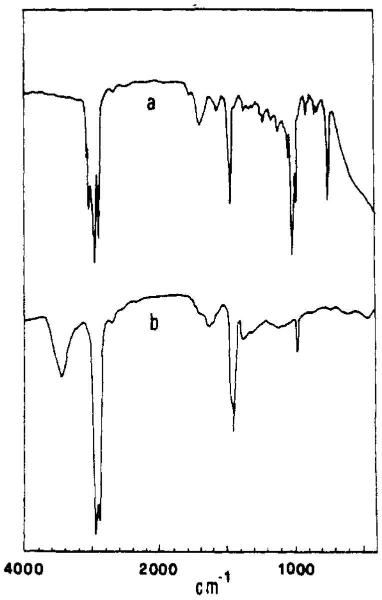


Figure 4. IR spectra of 1,5,9-cyclododecatriene and poly(1,5,9-cyclododecatriene): (a) 1,5,9-cyclododecatriene; (b) poly(1,5,9-cyclododecatriene). Coinitiator/CDT molar ratio = 0.017; temperature, −18 °C; solvent, CH_2Cl_2; [CDT] = 2.8 mol/L; coinitiator, $AlEtCl_2$; reaction time, 72 h.

It is interesting to examine the mechanism of polymerization of CDT. This monomer offers at least three possibilities for homopolymerization, as shown in Scheme I.

Route 1 is the ring-opening polymerization. This type of polymerization of CDT is usually carried out by using some chlorides of transition metals,[8,9] and the polymer formed is identical with a polybutadiene of all-1,4 structure.

Route 2 involves a polymerization that results in a cross-linked material.

Figure 4b shows the IR spectrum of the polymer obtained, which is simple, merely exhibiting two main peaks from methylene at 1448 and 2940 cm^{-1} and a small peak at 1630 cm^{-1} from residual unsaturation which results from chain-terminating reactions (see ref 1). The NMR spectrum shown in Figure 5 indicates that the resonance peaks of the unsaturated protons essentially disappeared. Only the peaks at 2.64, 1.55, and 1.27 ppm from the protons of methylene and methine remained. Therefore, it can be concluded from Figures 4 and 5 that CDT does not undergo ring-opening polymerization with $AlEtCl_2$ or $Al_2Et_3Cl_3$ as coinitiators (cf. route 1).

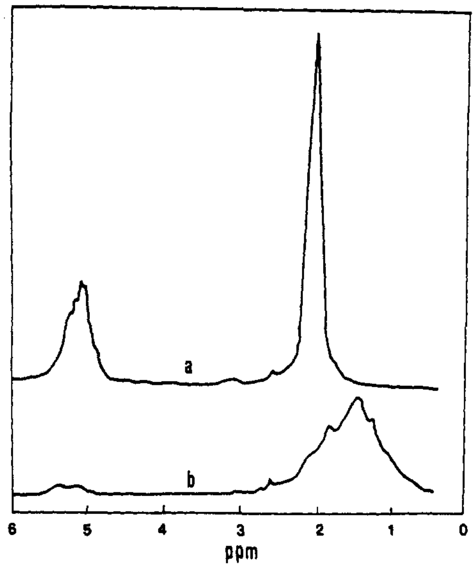


Figure 5. NMR spectra of 1,5,9-cyclododecatriene and poly(1,5,9-cyclododecatriene): (a) 1,5,9-cyclododecatriene; (b) poly(1,5,9-cyclododecatriene). Coinitiator, $Al_2Et_3Cl_3$; other conditions are identical with those of Figure 4.

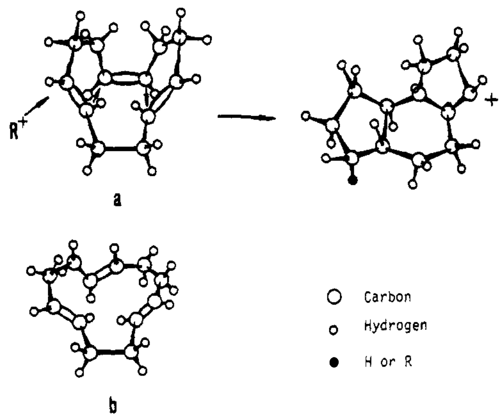


Figure 6. Steric configuration of the isomers of 1,5,9-cyclododecatriene: (a) cis,trans,trans isomer; (b) trans,trans,trans isomer.

The polymer obtained is a white powder, soluble in benzene, THF, chloroform, dichloromethane, and other chlorinated hydrocarbons, and these facts indicate that the polymer is linear instead of a cross-linked polymer (cf. route 2).

All of these experimental data demonstrate that the polymerization of CDT should fall within the third possibility, i.e., the transannular one shown in route 3.

It is worth mentioning the isomerization of CDT reported by Tolstikov[10] and Antropimsova.[11] According to Tolstikov,[10] the intramolecular cyclization of CDT, catalyzed by $AlEt_3$ or triisobutylaluminum at 200 °C, gives a mixture of tricyclo[6.4.0.0^{3,7}]- and tricyclo[7.3.0.0^{3,7}]dodec-4-ene. Antropimsova[11] pointed out that the isomerization of CDT, catalyzed by Cp_2TiCl_2–$LiAlH_4$ (Cp is η^5-cyclopentadienyl), results in a mixture of C_{12} hydrocarbons consisting mainly of the two isomers of tricyclo[7.3.0.0^{2,6}]dodec-7-ene and 5,6,7,8,9,10-hexahydrobenzocyclooctene. These experimental data corroborated the mechanism of transannular polymerization. Furthermore, the results of intramolecular cyclization of CDT[10,11] illustrated that the stereoconfiguration of the monomeric units and ring strain favor structure III among the products of route 3.

It was determined by ^{13}C NMR and GC analyses that the monomer used was a mixture of 96% *cis,trans,trans*-1,5,9-cyclododecatriene (IV) and 4% *trans,trans,trans*-1,5,9-cyclododecatriene (V).

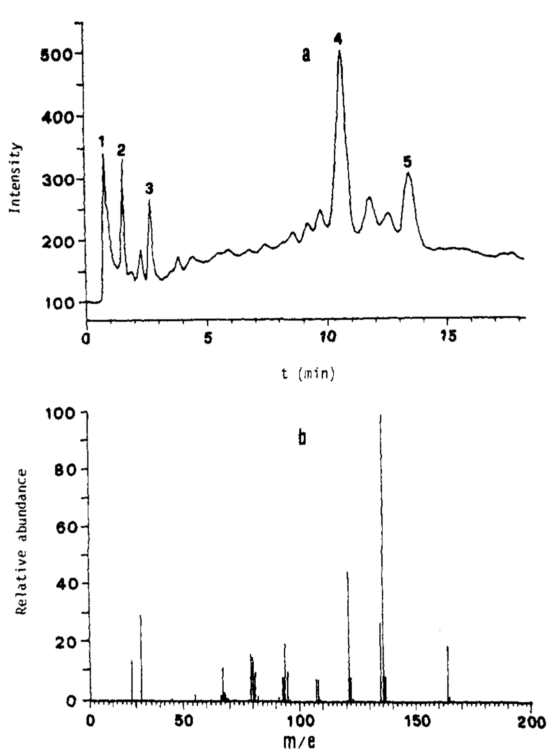


Figure 7. GC–MS of poly(1,5,9-cyclododecatriene): (a) TIM chromatogram; (b) mass spectrum of component 4 in TIM chromatogram. Cf. Figure 5 for reaction conditions.

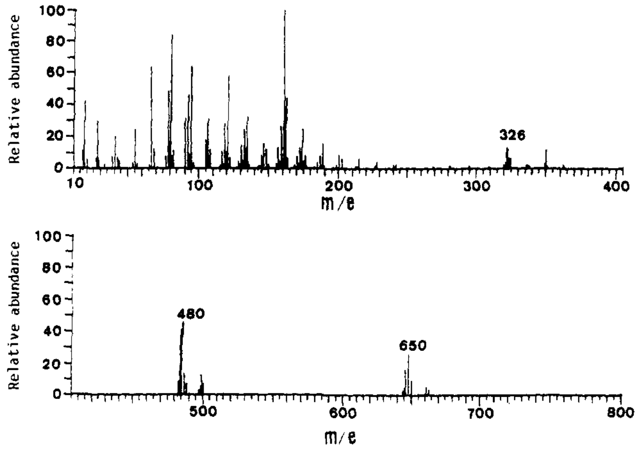
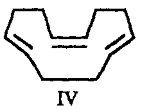
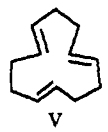


Figure 8. Mass spectrum of poly(1,5,9-cyclododecatriene). Cf. Figure 5 for reaction conditions.



IV
cis, trans, trans



V
trans, trans, trans

Table V indicates that the content of cis,trans,trans isomer IV in the remainder of the monomer decreases with increasing polymer yield, while the content of trans,trans,trans structure V increases. It is concluded from these data that the polymerizability of *cis,trans,trans*-1,5,9-cyclododecatriene is much larger than that of the trans,trans,trans isomer. This result may be explained by the stereoconfigurations of CDT (Figure 6). It is known from Figure 6 that the double bonds in the cis,trans,trans structure are very close together, and this configuration favors transannular polymerization. However, the double bonds in the trans,trans,trans isomer are far apart, and

Table V
Polymerization of *cis,trans,trans*-1,5,9-Cyclododecatriene and the *trans,trans,trans* Isomer[a]

expt no.	$Al_2Et_3Cl_3$/CDT molar ratio	init monomer IV, %	init monomer V, %	residual monomer IV, %	residual monomer V, %	polym yield, %
b-3	0.017	96	4	94.1	5.9	34
B57	0.017	96	4	91.3	8.7	56
e-1	0.02	0	100[b]			7.1
e-2	0.02	100[b]	0			80.8

[a] Structures IV and V were determined by GC analysis. [b] *trans,trans,trans*-1,5,9-Cyclododecatriene and *cis,trans,trans*-1,5,9-cyclododecatriene were supplied by Aldrich Chemical Co.

it is probable that in this configuration the double bonds are unable to undergo a transannular polymerization.

The possible structures of poly(1,5,9-cyclododecatriene) are shown in I, II, and III. Structures I and II can be eliminated in view of the stereoconfiguration of the monomer and the strain in the ring as mentioned. Only structure III is stable, which consists of five- and six-membered rings.

In order to further determine the structure of poly(1,5,9-cyclododecatriene) synthesized by electrophilic polymerization, we examined the GC-MS spectrum of the polymer, which is shown in Figure 7. It is known that the predominant component of the pyrolytic products of the polymer (component 4 in the TIM chromatogram of Figure 7) is

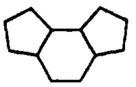
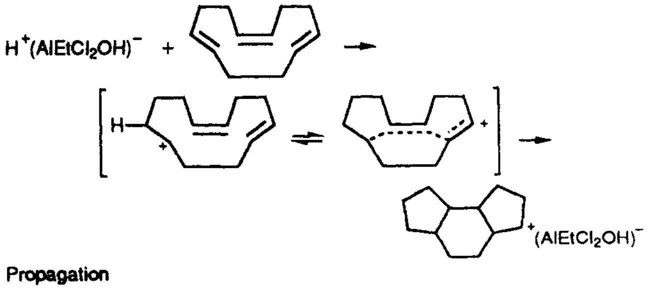


Figure 8 is the mass spectrum of poly(1,5,9-cyclododecatriene), which shows that there are compounds having molecular weights 326, 488, and 650, which correspond to those molecular weights of III when n = 2, 3, and 4, respectively. These data support that the resulting polymer has a tricyclic repeat unit as shown in III.

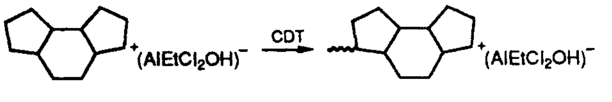
According to the structure of poly(1,5,9-cyclododecatriene) and the normal mechanism of cationic polymerization, it is not difficult to suggest that the mechanism of cationic transannular polymerization involves three steps in the reaction ($AlEtCl_2$ and H_2O are used in this example):

Initiation

$AlEtCl_2 + H_2O \rightarrow H^+(AlEtCl_2OH)^-$ (hypothetical acid)

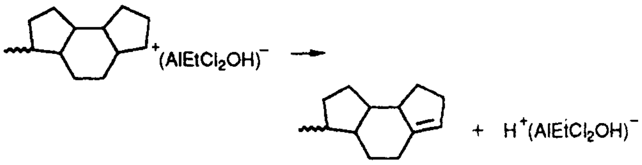


Propagation

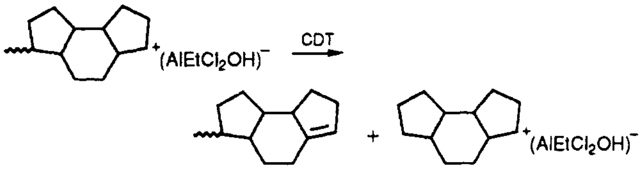


There are two forms of possible chain-terminating reactions:

(a) Spontaneous transfer



(a) Transfer to monomer



The NMR and IR spectra of poly(1,5,9-cyclododecatriene) show that there are traces of double bonds in the polymer. This fact indicates that the spontaneous transfer and transfer to monomer are both occurring in the chain-terminating reactions.

References and Notes

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Registry No. (IV)(V) (copolymer), 127356-78-9; CDT, 27070-59-3; $AlEtCl_2$, 563-43-9; $Al_2Et_3Cl_3$, 12075-68-2; $BF_3{\cdot}OEt_2$, 109-63-7; $AlCl_3$, 7446-70-0; benzyl chloride, 100-44-7; iodomethane, 74-88-4; 1-chlorobutane, 109-69-3.