

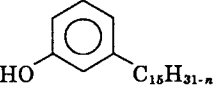
GPC Studies on the Cationic Polymerization of Cardanol Initiated by Borontrifluoridediethyletherate

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Synopsis

The cationic polymerization of cardanol using borontrifluoridediethyletherate as initiator has been investigated by gel permeation chromatographic techniques. The molecular weight and molecular weight distribution of the polymer at different temperatures and various initiator concentrations were studied, and the polymerization conditions have been optimized as 140°C with an initiator concentration of 1%. The reaction was found to follow first-order kinetics with respect to the monomer. The activation energy and rate constants for the system have also been evaluated. The polymer has been characterized by IR, ^1H and ^{13}C -NMR spectra.

INTRODUCTION

Cardanol  where $n = 0, 2, 4, 6$ (37300-39-5), obtained from the plant *Anacardium occidentale L.* can be considered to be an alternate source for the manufacture of special phenolic resins such as surface coatings, brake lining resins, epoxy resins, etc.¹⁻⁵ Recent developments also emphasize the potential of cardanol as a monomer source for the preparation of speciality polymers.⁶⁻⁹ Although there are innumerable patents¹⁰⁻¹³ and reports^{3,4} describing the manufacture of various resins from cardanol, a wide gap exists between the technology and the scientific understanding of such systems. Being an inexpensive raw material, large-scale manufacturers prefer cardanol without resorting to separation¹⁰ into its individual components. Cardanol is a mixture of four components, varying in the degree of unsaturation in the side chain [3-(pentadecyl)-phenol 10%, 3-(8-pentadecenyl)-phenol 52%, 3-(8,11-pentadecadienyl)-phenol 20%, and 3-(8,11,14-pentadecatrienyl)-phenol 18%].^{7,14,15} But basic studies on the polymerization characteristics of cardanol and its components are limited, and there is scarcity of data for development of improved materials.

The polymerization of cardanol can be accomplished either by formaldehyde condensation or through the unsaturation in the side chain. Recently Misra and Pandey¹⁶ reported the kinetics of formaldehyde condensation of cardanol. Manjula¹⁷ studied the oligomerization of cardanol using acidic catalysts such as sulfuric acid and phosphoric acid and indicated that $\text{BF}_3 \cdot \text{OEt}_2$ is a good

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cationic initiator for the polymerization of cardanol. This article reports the results of a detailed study on the polymerization characteristics of the unseparated cardanol using $\text{BF}_3 \cdot \text{OEt}_2$ as initiator. Subsequent articles will describe in detail studies on the kinetics and mechanism of polymerization of the individual components of cardanol.

EXPERIMENTAL

Materials

Cardanol was obtained by double vacuum distillation of cashew nut shell liquid (CNSL-8007-24-7) at 3–4 mm Hg, and the fraction distilled at 230–235°C gave a refractive index of 1.509 and Brookfield viscosity of 450–520 cps at 30°C as reported for pure cardanol.^{18,19} CNSL was purchased from Kerala State Cashew Development Corporation, Quilon, and was of standard specification, IS : 840 (1964). Borontrifluoridediethyletherate (48% BF_3 , Fluka Chemicals, Germany) was used as supplied without further purification.

Polymerization

One typical polymerization procedure is given below. Cardanol (20 g, 0.67 mol) was taken in a 100-mL three-necked flask fitted with a mechanical stirrer, reflux condenser, and N_2 inlet, kept in a constant temperature oil bath at $140 \pm 1^\circ\text{C}$. The contents were allowed to attain the temperature of the bath, and $\text{BF}_3 \cdot \text{OEt}_2$ (0.2 g, 1%) was added with vigorous stirring under nitrogen atmosphere. Samples (1 mL) were withdrawn at definite intervals of time, chilled, and were analyzed by GPC.

Measurements

The GPC data were obtained using Hewlett-Packard 1081B HPLC, equipped with an automatic sample injection system and a differential RI detector. The GPC columns used in this work were styrene-divinyl benzene copolymers based microstyragel 100 and 500 Å (Waters Associates) connected in series. An additional column with a large porosity (10^3 Å) was used along with the present set of columns to get better resolution. THF (HPLC grade) was used as the eluent. The GPC columns were calibrated²⁰⁻²² by the linear calibration method (least-square approximation) with monodisperse polystyrene standards, supplied by M/s. H. Knauer & Co., West Germany. Polystyrene standards used had molecular weight in the range of 800–19,000 with a polydispersity of 1.08 ± 0.02 .

The transmission infrared spectra were recorded on Perkin-Elmer IR spectrophotometer Model 882 as neat films on NaCl windows by the smear techniques. $^1\text{H-NMR}$ spectra were recorded on Hitachi R-24B high-resolution NMR spectrometer in CCl_4 using TMS as internal reference. $^{13}\text{C-NMR}$ spectra were recorded on a JEOL FX-90 Q FT spectrometer.

RESULTS AND DISCUSSION

The polymerization of cardanol initiated by $\text{BF}_3 \cdot \text{OEt}_2$ was studied. Initial optimization studies showed that addition of $\text{BF}_3 \cdot \text{OEt}_2$ polymerizes cardanol

within a few minutes and that the optimum temperature of polymerization is 140°C.

Effect of Time and Temperature

Figure 1 gives the GPC patterns of the polymerization products of cardanol at 140°C for 4 min and for 5 h, in comparison to that of cardanol alone. Peaks marked I and II in the product mixture of cardanol correspond to monomer (cardanol) and dimer, respectively, as evidenced by spiking the product mixture with authentic samples of monomer and dimer. Peak III corresponds to the polymer having a molecular weight of 3500–4000. (All molecular weights reported here are with respect to polystyrene standards.) In no experiment was 100% conversion of the monomer to polymer observed. Even after a period of 5 h, the product mixture was found to contain 8–12% monomer.

The concentrations of the different reaction products (monomer, dimer, and polymer) as a function of time for the polymerization of cardanol at various temperatures obtained from GPC measurements are presented in Figure 2(a)–(c). It was observed that at all temperatures, the polymerization reaction was rapid as revealed by the sudden disappearance of the monomer and the quick formation of the polymer.

The variation of the GPC patterns of the polymerization products of cardanol with temperature is given in Figure 3(a). It is evident that as temperature increases, peak I decreases in intensity, reaches a minimum at 140°C, and then increases. Hence 140°C can be taken as the optimum temperature for the formation of the polymer. Further increase in temperature increases the monomer content indicating that possibly there is thermal decomposition or depolymerization taking place above 140°C. Cardanol has been reported to be quite stable even at 180°C.¹⁸ When the polymer obtained at 140°C was heated to 180°C

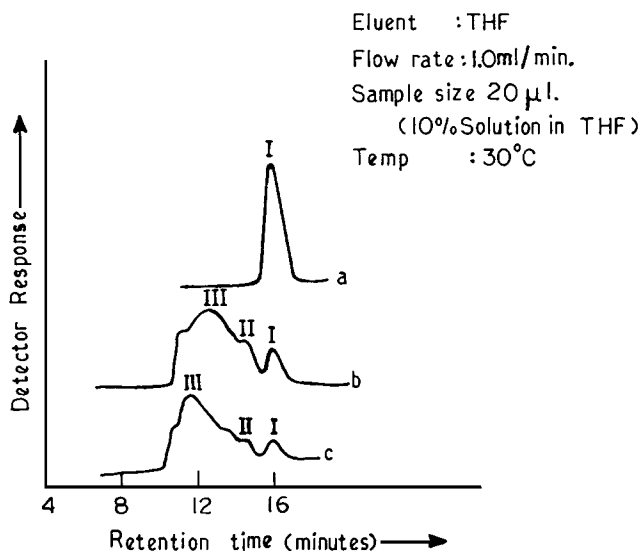


Fig. 1. Gel permeation chromatograms of (a) cardanol (I); (b) polymerization product of I (140°C, 4 min); (c) polymerization product of I (140°C, 5 hr).

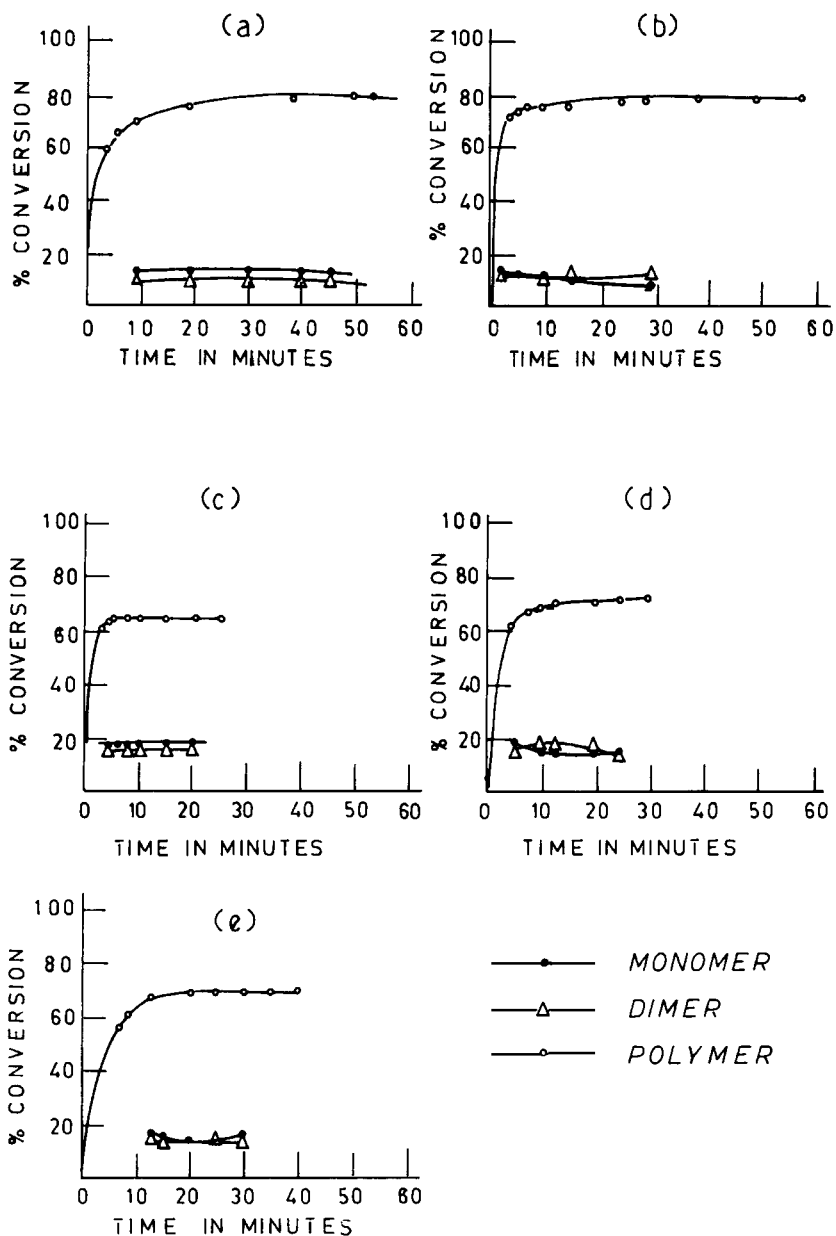


Fig. 2. Concentration of the components appearing in the polymerization of cardanol determined by GPC: (a) 130°C; (b) 140°C; (c) 150°C; (d) 160°C; (e) 180°C.

and then analyzed by GPC, the GPC pattern was found to be exactly similar to that obtained by direct polymerization reaction at 180°C. The total percentages of the monomer, dimer, and the polymer were identical, and there was no other loss due to decomposition. This possibly indicates depolymerization of the polymer above 140°C. Similar depolymerization reactions have been

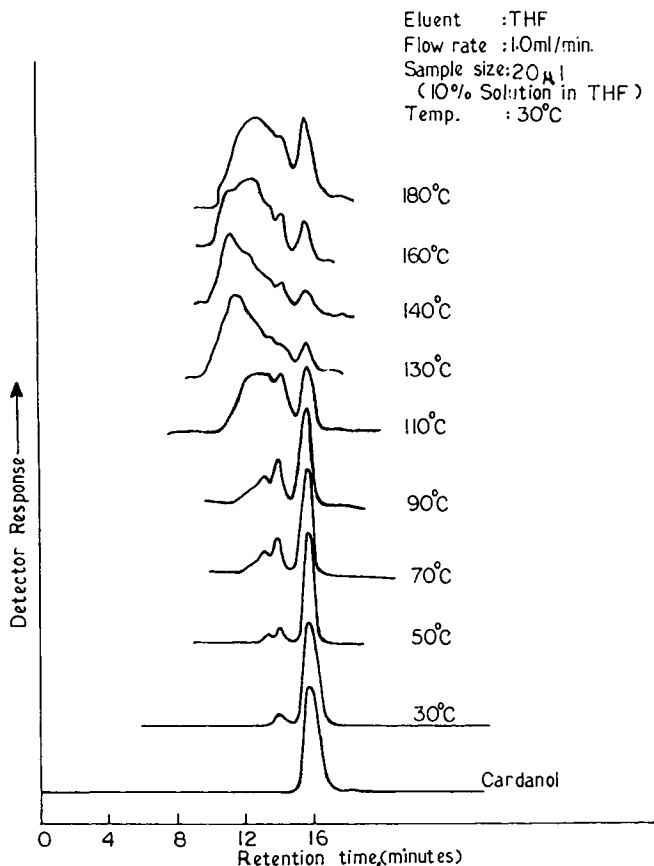


Fig. 3(a). Gel permeation chromatograms of polymerization products of cardanol at different temperatures.

reported in the cationic polymerizations of α -methyl styrene,^{23,24} aliphatic olefins,^{25,26} and styrene.²⁷

Similar trends were observed when the concentrations of monomer, dimer, and polymer (obtained by integrating the area under the respective GPC peaks) were plotted against temperature as shown in Figure 3(b).

The rate of polymerization at different temperatures was calculated from the slope of the corresponding percentage conversion-time curve, and is shown in Figure 3(c). It was observed that R_p increases with reaction temperature reaching the maximum value of 17.015×10^{-3} m/L s at 140°C and then decreases.

Figure 4 shows that the polymerization reaction follows first-order kinetics with respect to monomer concentration. The rate constants were found to be 6.67×10^{-3} s⁻¹ at 130°C and 8.75×10^{-3} s⁻¹ at 140°C. Using the Arrhenius equation, activation energy was calculated to be 8.98 kcal/mol.

Effect of Initiator Concentration on Polymerization

It is observed that the percent conversion of the monomer to polymer is unaffected by the variation of the initiator concentration up to 2%. Beyond 2%

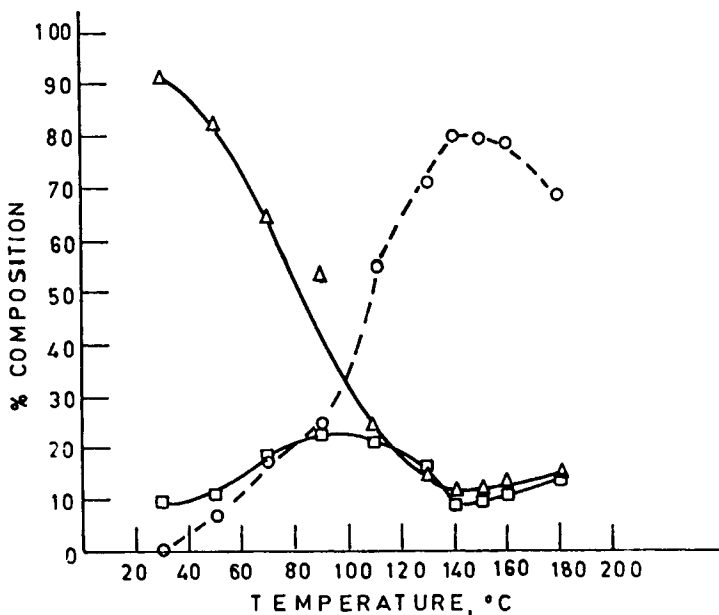


Fig. 3(b). Percentage composition of monomer ($-\triangle-\triangle-\triangle-$) dimer ($-\square-\square-\square-$) and polymer ($-\circ-\circ-\circ-$) vs. temperature.

initiator concentration, the reaction system was found to gel instantaneously, and so the products could not be analyzed by GPC. The molecular weights obtained (\bar{M}_n and \bar{M}_w) with varying initiator concentrations are presented in Table I. It is found that maximum molecular weight (\bar{M}_n) is obtained at 1% initiator concentration.

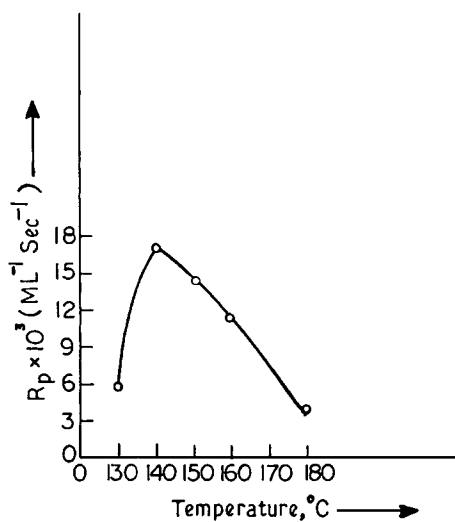


Fig. 3(c). Rate of polymerization vs. temperature.

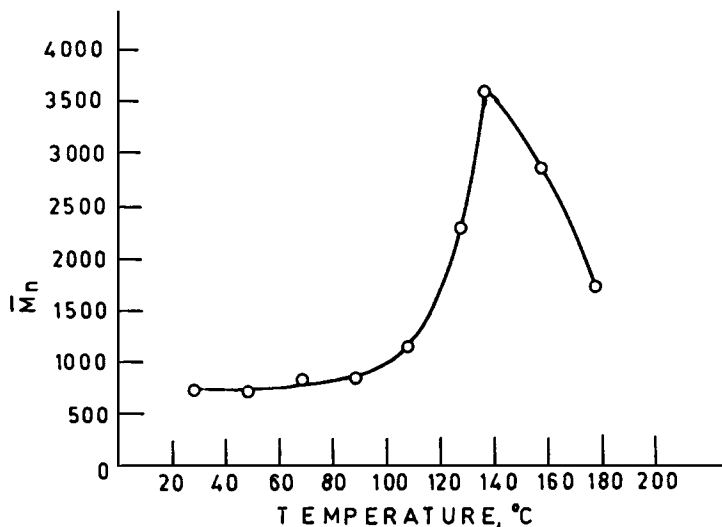


Fig. 3(d). Number average molecular weight vs. temperature.

Molecular Weight and Molecular Weight Distribution

The plot of the number average molecular weight vs. temperature [Fig. 3(d)] indicates that the average molecular weight increases from 730 at 30°C to 3575 at 140°C and then decreases to 1720 at 180°C. Polydispersity was found to increase from 1.2 at 30°C to 3.4 at 140°C.

Many patents cite the polymerization temperature of cardanol as 180°C, when cationic initiators such as H₂SO₄, H₃PO₄, AlCl₃, etc. have been used.

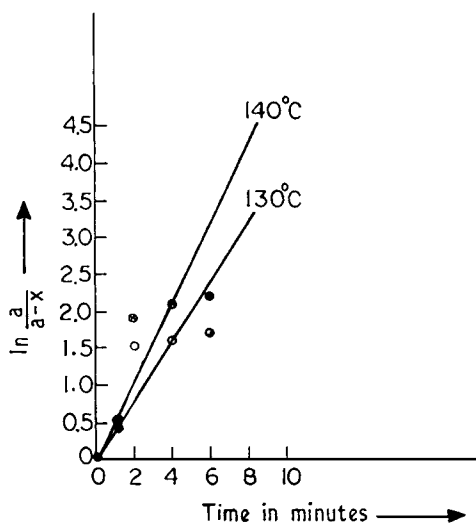


Fig. 4. $\ln \frac{a}{a-x}$ vs. time for the polymerization of cardanol. a is the concentration of the monomer and x is the amount reacted during polymerization.

TABLE I
Effect of Initiator Concentration on Polymerization of Cardanol^a

BF ₃ · OEt ₂ (%)	Monomer (%)	Dimer (%)	Polymer			
			%	\bar{M}_n	\bar{M}_w	D^b
0.25	18	14	68	3000	8633	2.88
0.5	15	13	72	3376	9542	2.83
1.0	12.6	12.6	74.6	3763	11507	3.06
2.0	14	14	72	3184	10045	3.15
3.0 ^c						

^a Polymerization was carried out at 140°C for 10 min.

^b $D = \bar{M}_w/\bar{M}_n =$ polydispersity.

^c Gelled instantaneously.

Further studies have to be done to see whether depolymerization occurs or not with these catalysts at this temperature.

Spectral Studies

The infrared spectra of pure cardanol and polymerized cardanol are given in Figures 5(a) and 5(b), respectively. The peaks at 1620 cm⁻¹ (C=C Str), 3040 cm⁻¹ (C-H Str of alkene) and 790 cm⁻¹ (C-H out of plane deformation)²⁸ were found to diminish in intensity in the spectrum of polymer, indicating that polymerization has taken place through the double bonds in the side chain. The ¹H-NMR spectra of cardanol and polycardanol are shown in Figures 6(a) and 6(b). The multiplet at 5.2–5.4 ppm (CH=CH)¹⁴ was found

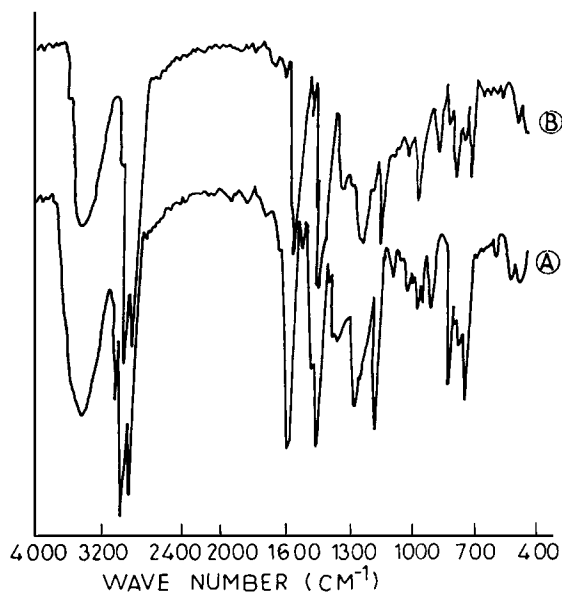


Fig. 5. Infrared absorption spectra of cardanol (A) and cardanol after polymerization (B).

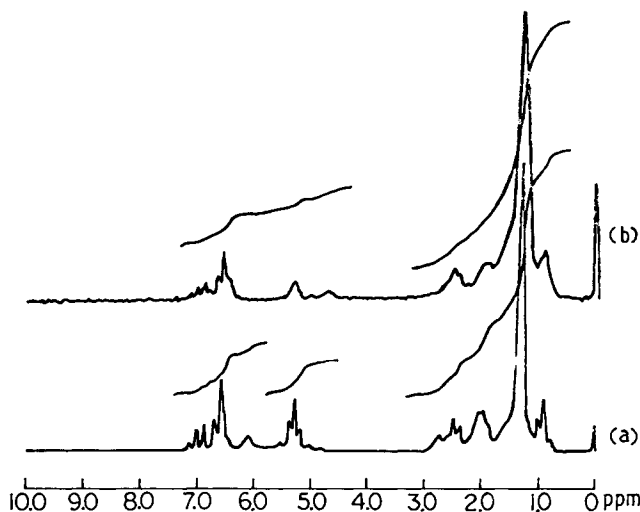


Fig. 6. ^1H -NMR spectra of (a) cardanol and (b) cardanol polymer.

to decrease in intensity in the spectrum of the polymer. From Table II it is clear that the intensity of ^{13}C -NMR spectral absorption bands of olefinic carbons at ($\delta 111$ – 115 ppm)²⁹ of polycardanol is less than that of cardanol. These observations indicate that polymerization has taken place through the side chain double bonds.

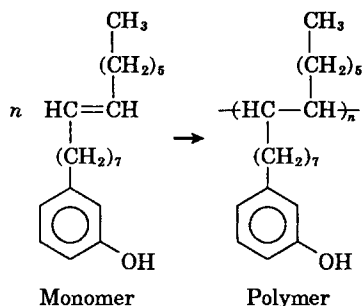
As revealed by the time-conversion curves [Fig. 2(a)–(c)] polymerization reaction was rapid, suggesting a chain mechanism.³⁰ The IR and NMR spectra also indicate involvement of unsaturation in polymerization. $\text{BF}_3 \cdot \text{OEt}_2$ is often used in the polymerization of olefins, vinyl ethers, etc. Worsfold and Bywater³¹ investigated the polymerization of α -methyl styrene, and Giustip³² studied that of styrene using $\text{BF}_3 \cdot \text{OEt}_2$ in the presence and absence of H_2O . These studies showed that BF_3 etherate is less reactive but more convenient than $\text{BF}_3 : \text{H}_2\text{O}$.

TABLE II
 ^{13}C -NMR Absorption Bands with Relative Intensities

Cardanol		Polymer	
ppm	Intensity	ppm	Intensity
108.24	164	112.628	1467
112.737	2968	113.874	125
114.741	399	114.308	111
115.500	4237	115.445	1911
121.080	2830	116.962	97
126.822	209	120.759	1824
127.635	354	122.00	151
128.068	1063	123.788	174
128.231	999	128.176	234
129.422	3869	129.26	2428
129.964	2446	129.856	659

In both cases the formation of a protonated species appears to be the initial step.

GPC data show that the percentage weight of the monomer that remained unpolymerized under optimum conditions is only 8–12%, which is equivalent to the percentage of the saturated component present in cardanol. So this indicates conversion of all the unsaturated components into dimer/polymer. Taking monoene (which is the major component, 52%)⁷ as example, the polymerization could be depicted as follows:



Tyman¹ has proposed that the polymerization of cardanol under acidic conditions might involve the formation of an allylic carbonium ion from the more reactive triene component. However, Tyman does not provide any experimental evidence regarding the involvement of the triene component alone. As the present data indicate conversion of all the monoene, diene, and triene components into the polymer, further understanding of the system requires data on the rates of reaction of the individual components. Manjula¹⁷ also proposed a carbocationic mechanism with the addition of a hydrogen ion to one of the double bonds of the side chain. Thus the complex nature of the system cautions not to make conjectures on the nature of the mechanism of polymerization. However, it appears that the polymerization of cardanol under $\text{BF}_3 \cdot \text{OEt}_2$ could be said to be carbocationic³⁰ in nature and might involve protonation of cardanol as the initiation step. With first-order kinetics it is probable that the termination would involve a transfer to the monomer.

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