

Kinetics and Mechanism of Oligomerization of Cardanol Using Acid Catalysts

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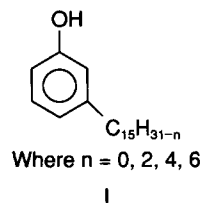
SYNOPSIS

The kinetics and mechanism of oligomerization of cardanol over acid catalysts were studied. GPC results showed the formation of a mixture of oligomers such as dimer, trimer, tetramer, etc. IR spectra of the products of oligomerization showed a decrease in the intensity of the double bond absorption band at 1630 cm^{-1} and the disappearance of terminal vinyl bands at 895 cm^{-1} and 907 cm^{-1} . ^1H NMR spectra showed drastic changes in the unsaturated proton resonance signals at 5.5δ with respect to saturated protons at $0.2\text{--}2.5\delta$. The ratio of resonance integrals of unsaturated to saturated protons decreased from 1 : 6.5 to 1 : 20 after oligomerization. GPC studies showed that the rate of formation of the dimer, trimer, tetramer, etc. follow an identical path and that the individual oligomers are formed in the same weight percentage at any time during the reaction. A kinetic scheme is proposed to explain this phenomenon. Kinetic studies showed that the oligomerization reaction follows first order kinetics with respect to the monomer concentration and the rate constant is $K = 6.6 \times 10^{-5}\text{ s}^{-1}$. A probable mechanism for the oligomerization of cardanol is proposed.

INTRODUCTION

There has been, of late, much interest in the development of speciality polymer products from cardanol (I) (37330-39-5),¹⁻¹⁰ a monophenol with a C_{15} unsaturated side chain at the *meta* position. Although there is a vast patent base^{11,12} for cardanol and cashew-nut shell liquid (CNSL, 8007-24-7), from which cardanol was obtained by distillation, the gap between technology and the scientific understanding of such systems is quite substantial. Cardanol can be polymerized either by condensation with aldehydes or by chain reaction polymerization using the side chain unsaturation.¹³ Mishra and Pandey¹⁴ recently reported the kinetics of the alkaline catalyzed formaldehyde condensation of cardanol, but few attempts have been made to study the nature and mechanism of the chain reaction polymerization through the double bonds in the side chain. Many of the patents^{11,12} cite a cationic polymerization involving acid catalysts such as sulphuric acid, phos-

phoric acid, diethyl sulphate, etc. There are also examples of the use of Lewis acids such as aluminium chloride in the polymerization of cardanol. Certain patents even cite uses of metallic powders or their oxides. However, there has been no attempt to make a fundamental study of the polymerization characteristics and structures and/or properties of the polymer. In this paper we report the results of a study on the kinetics and mechanism of the oligomerization of cardanol through the side chain using acid catalysts.



EXPERIMENTAL

Materials

Cardanol was obtained by double distillation of cashew-nut shell liquid (8007-24-7) of Indian Stan-

Table I Optimization of Conditions for Oligomerization of Cardanol

Reaction No.	Catalyst (% v/v)	Temp. (°C)	Duration of Oligomerization (mins)	Intrinsic Viscosity (η) (dl/g)
1	Nil	30	30	0.005
2	Nil	180	30	0.009
3	DES-H ₂ SO ₄ (6%)	180	30	0.032
4	DES-H ₃ PO ₄ (10%)	180	20	0.021

standard Specification IS : 840 (1964). The distillation was carried out at 3–4 mm Hg and the fraction collected at 228°C gave a refractive index of 1.509 and a Brookfield viscosity of 450–520 cp at 30°C as reported for pure cardanol.¹³

Methods

Synthesis

Oligomerization Using Diethylsulphate-Sulfuric Acid (DES-H₂SO₄ Catalyst System). A 25% solution (v/v) of sulfuric acid (British Drug House [BDH], Analar grade) in diethyl sulfate (BDH, Genreal Research Purpose [GRP] grade) was prepared. In a typical procedure 50 g (0.166 mole) of cardanol was mixed with 3 mL of this reagent (containing 0.014 mole of sulfuric acid and 0.017 mole of diethyl sulfate) in a 3-necked flask fitted with a mechanical stirrer, N₂-inlet, and a reflux condenser. The whole assembly was kept in a thermoregulated bath kept at 180°C and the mixture was stirred for 30 min. After the reaction, the monomer and catalysts were removed by washing with methanol, and the polymer was dried and weighed. The experiment was repeated varying the temperature, reaction time, and catalyst concentration and the conditions were optimized with respect to yield.

Oligomerization Using Diethylsulfate-Phosphoric Acid (DES-H₃PO₄ Catalyst System). Since orthophosphoric acid (BDH, Analar grade) was not soluble in diethylsulfate, the reagents were added separately in the required molar ratios as in the case of DES-H₂SO₄ system, and the experiments were conducted in a similar manner.

Characterization

The relative viscosities of oligomerized samples were measured using a suspended type Ubbelohde viscometer at 40°C with toluene as the solvent. Relative viscosity (η_r) and the intrinsic viscosity (η) were calculated using the following equation:

$$\eta_r = t/t_0$$

where t is the time (sec) of flow for the solution and t_0 is that for the solvent.

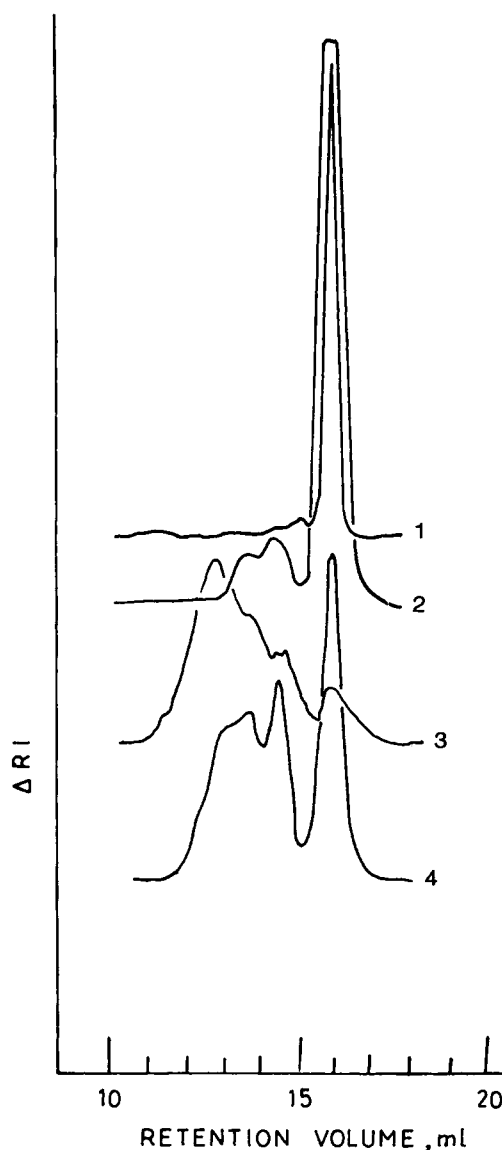


Figure 1 GPC of products 1, 2, 3, and 4.

Table II Percentage Composition of Cardanol Oligomers

Reaction No.	Monomer %	Dimer %	Trimer %	Tetramer %
1	100.0	—	—	—
2	94.13	2.68	3.19	—
3	9.90	9.30	21.41	59.39
4	21.07	35.50	17.11	26.30

$$\eta_{sp/c} \text{ (specific viscosity)} = \eta_r - 1$$

when $\eta_{sp/c}$ was plotted against C , where C is the concentration of the solution of g/dL and the graph was extrapolated to $(\eta_{sp/c})_{C=0}$ the intercept gives the value of the intrinsic viscosity (η).

Hydroxyl number, acid value, and iodine value were determined by standard methods.

Infrared (IR) spectra were recorded as a neat film or a Nujol mull on a Perkin-Elmer Model 2993 B I infrared spectrophotometer. ^1H NMR spectra were recorded with tetramethylsilane as internal standard in CCl_4 using a JEOL FX-902 spectrometer.

Gel permeation chromatograms (GPC) were recorded on a Waters 244 instrument fitted with a 6000A pump system and a column combination of 100 Å, 500 Å (microstryro gel) with tetrahydrofuran

as solvent at a flow rate of 1 mL/minute. A differential refractometer R 40 with sensitivity setting 8× was used as the detector.

RESULTS AND DISCUSSION

Table I gives the optimum conditions for the oligomerization of cardanol.

The products of oligomerization were analyzed by GPC and the results are given in Figure 1. The oligomerization of cardanol gives a mixture of dimer, trimer, tetramer of molecular weights 600, 900, and 1200, respectively, and also of higher oligomers. The percentage composition of the oligomers as computed from GPC is given in Table II. The formation of dimer and trimer in small quantities in product from reaction 2 where no catalyst was used, indicates thermal polymerization (see Table II).

Figure 2 gives the IR spectra and Figure 3 gives the ^1H NMR spectra of products from reactions 1 and 3. Comparison of the IR spectra indicates the partial loss of unsaturation from cardanol. The decrease in the 1630 cm^{-1} peak and disappearance of the terminal vinyl bands¹⁵ at 895 cm^{-1} and 907 cm^{-1} are expected as the oligomerization takes place through the double bonds of cardanol. The reso-

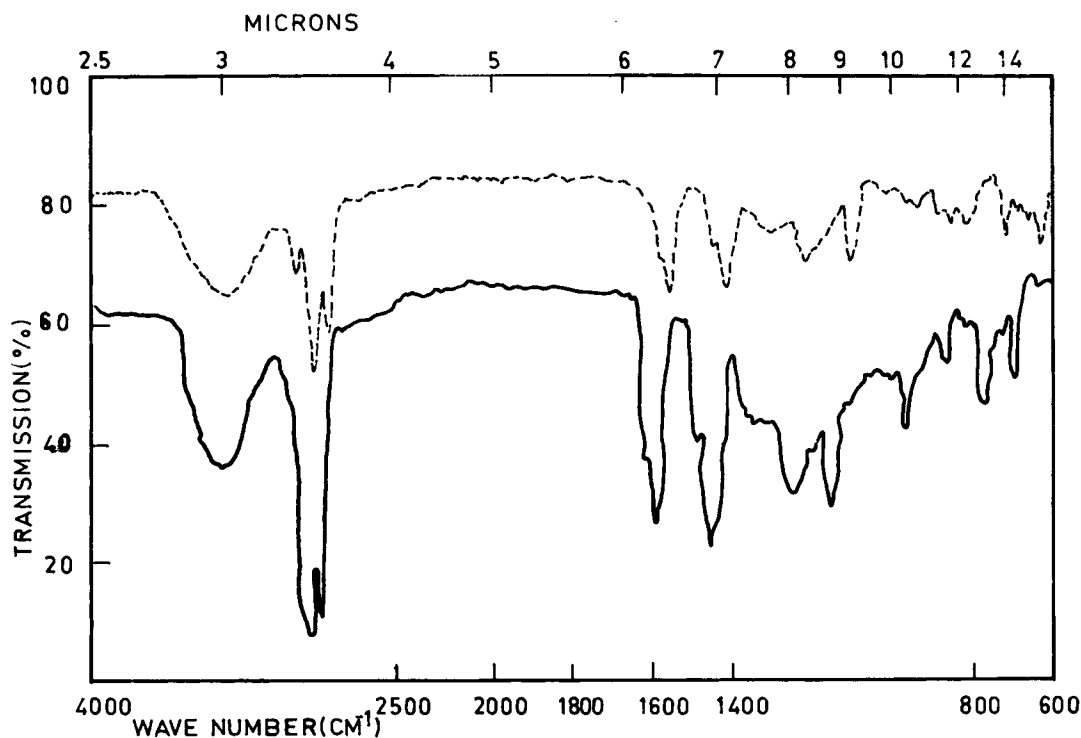


Figure 2 IR spectra of products 1 (----) and 3 (—).

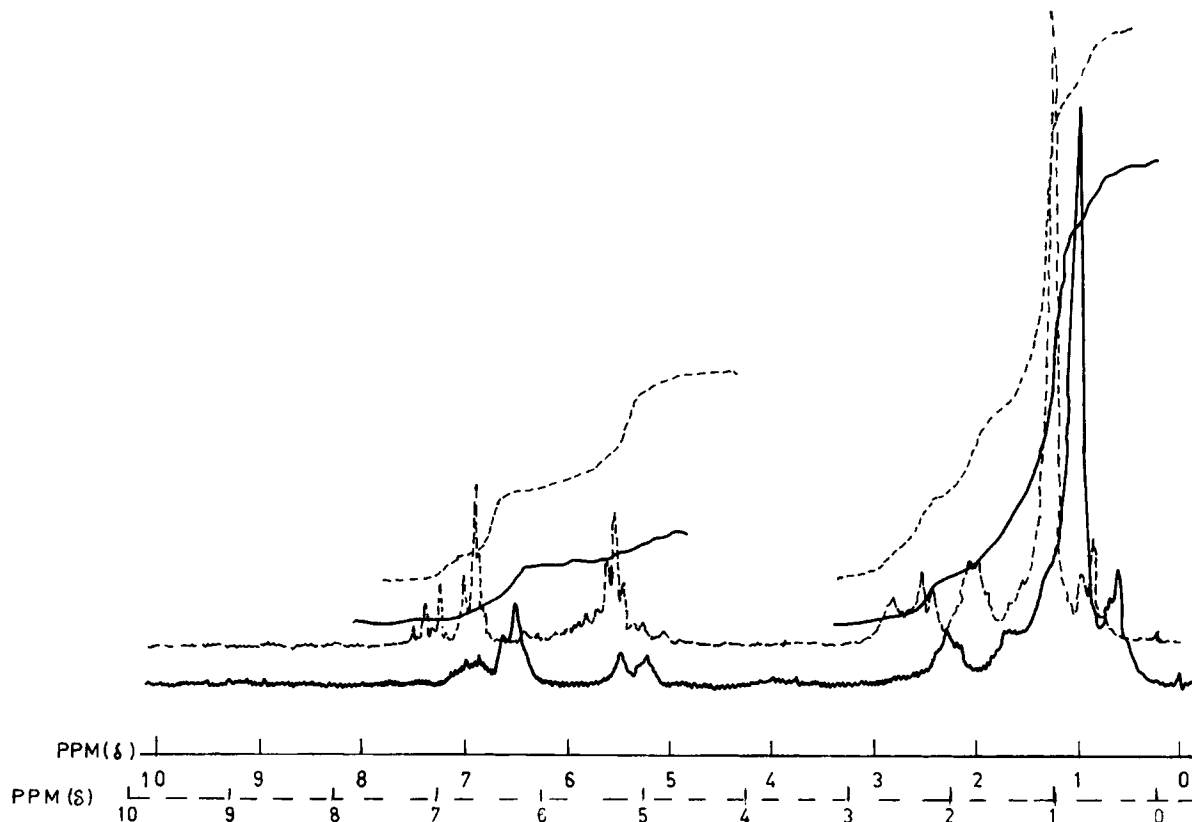


Figure 3 NMR spectra of products 1 (----) and 3(—).

nance due to the unsaturated protons (5.5δ) in the ^1H NMR spectrum is also observed to decrease with respect to saturated protons ($0.9\text{--}2.5\delta$). The ratio of the integration of unsaturated proton to saturated proton resonances decreases from a value of 1 : 6.75 to 1 : 20 after oligomerization in the case of the DES- H_2SO_4 and DES- H_3PO_4 catalyst systems for reactions 3 and 4. The decrease in the unsaturated protons was minimal in thermal polymerization.

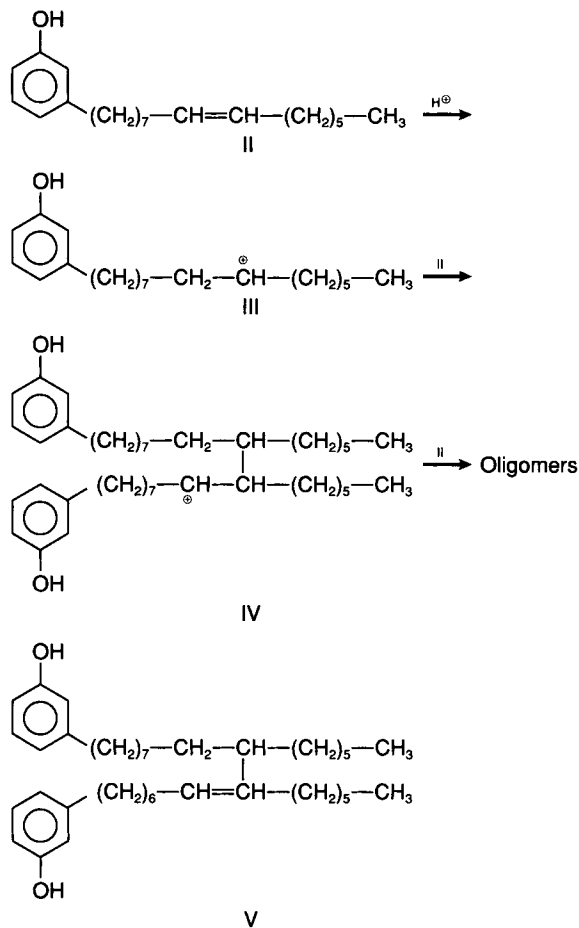
Two possible mechanisms for the oligomerization came to mind. One mechanism involves the formation of a 4-membered carbon ring from two separate cardanol molecules each having a double bond. In this, the oligomerization should stop at the dimer stage. However, GPC analysis of the products show the presence of higher oligomers. This result, when viewed in combination with the fact that the IR spectra of the oligomerized products did not show peaks at 960 cm^{-1} and 1000 cm^{-1} (expected for cyclobutane ring)¹⁶, suggest the absence of the mechanism during oligomerization.

The other possible route involves protonation of the side chain of cardanol under the highly acidic

conditions, followed by a cationic chain growth mechanism.

As cardanol consists of four components differing in the degree of unsaturation of the side chain (saturated 8–10%; 8'-monoene 52%; 8', 11'-diene 20–22%; and 8', 11', 14'-triene 18%), the complexity of the system cautions against proposing any detailed mechanism unless other data on the polymerization of the individual components are available (efforts to separate the individual components by argentation chromatography¹⁷ did not yield sufficient quantities for polymerization). Moreover, there is a strong probability that isomerization will occur under these strongly acidic conditions. However, an attempt has been made to depict protonation and oligomerization as shown in Scheme II using the structure of the monoene (II) (the major component) of cardanol.

It is also probable that structure IV can deprotonate to give a stable dimer (V) which, being reactive, can again protonate to form higher oligomers. This is evident from a study on the composition and the trend in the formation of dimer, trimer and tet-


Scheme I

ramer species. Figure 4 gives the plots of weight % against time of formation for monomer, dimer, trimer, and tetramer species for the DES-H₂SO₄ catalyst system at 50°C. The monomer concentration decreases with time and dimer, trimer, and tetramer concentrations increase correspondingly. The decrease of monomer concentration and the increase in dimer, trimer, and higher oligomers attain a plateau after 30–40 minutes reaction and reach a saturation equilibrium during this period. The rate of formation of dimer, trimer, and higher oligomers follows an identical trend and this suggests a chain mechanism for the oligomerization reaction. As the dimer is the first product of the reaction between two monomers, at least during the initial stages of the reaction, a higher concentration of the dimer is expected. However, the dimer, trimer, and higher oligomers are formed in the same weight percentage at any time during the reaction. This is possibly explained by the following kinetic scheme for the reaction (Scheme II).

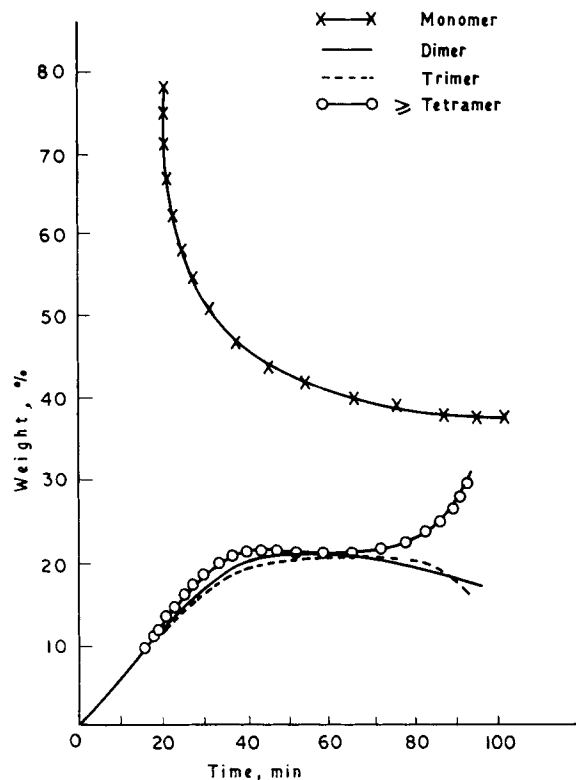
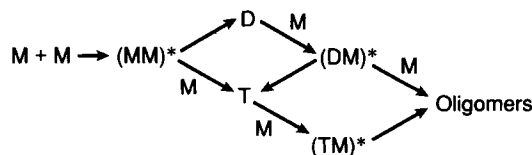


Figure 4 Plot of weight percentage vs. time of monomer, dimer, trimer, and tetramer species for DES-H₂SO₄ catalyst system.

The active intermediate (MM)* if formed in the first step could either convert into a dimer or it could react with another monomer leading to a trimer. Similarly the (DM)* active intermediate can form either a trimer or a tetramer. The composition of the dimer, trimer, and higher oligomers would thus be decided by the stability and high-life of the active intermediates (MM)*, and (DM)*, etc.

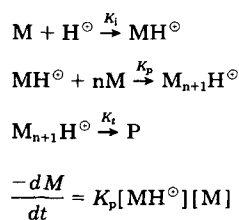
S. M. Kaback has reported a Friedel-Crafts type alkylation of the phenolic rings of cardanol during its acid catalyzed polymerization based on a comparison of the IR spectra of cardanol and polycardanol.¹⁸ The ratio of aromatic to saturated proton integrals is higher than the expected 1 : 7 in the case of product from reaction 3. This may be due to the


Scheme II

loss of aromatic protons during the oligomerization due to a possible side reaction.

The kinetics of the oligomerization reaction was studied with DES-H₂SO₄ catalyst system at 50°C. The monomer concentration was estimated from the GPC at different intervals of reaction time. A plot of $\ln a_0/a_0 - x$, where a_0 = initial concentration of monomer and x = amount of monomer reacted at any time t , versus time is given in Figure 5. A straight line plot is obtained which indicates that oligomerization follows first order kinetics and the rate constant at this temperature is estimated to be $k = 6.6 \times 10^{-5} \text{ s}^{-1}$.

The first order kinetics at 50°C can be explained by the following kinetic scheme (Scheme III):

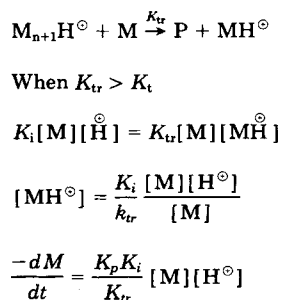


Scheme III

Assuming steady state,

$$\begin{aligned} K_i[M][H^{\oplus}] &= K_t[MH^{\oplus}] \\ [MH^{\oplus}] &= \frac{K_i}{K_t}[M][H^{\oplus}] \\ \frac{-dM}{dt} &= \frac{K_p K_i}{K_t}[H^{\oplus}][M]^2 \end{aligned}$$

The reaction is second order with respect to the monomer concentration whereas the experimental results at 50°C indicate a first order kinetics with respect to the monomer. This could be explained if the termination takes place by a transfer of H⁺ onto a monomer (Scheme IV).



Scheme IV

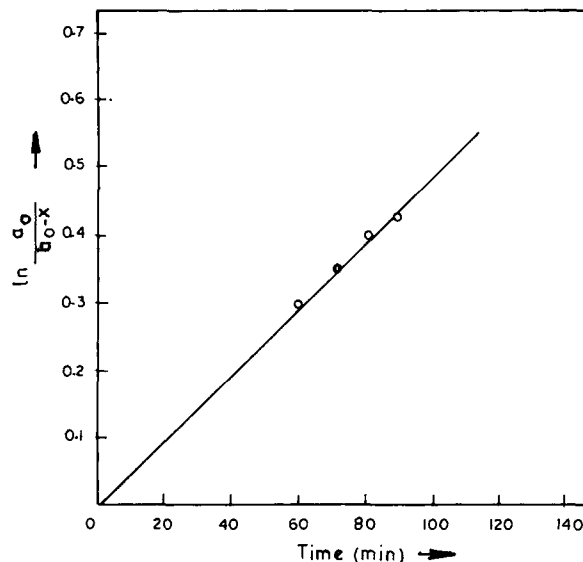


Figure 5 Plot of $\ln \frac{a_0}{a_0 - x}$ vs. time for oligomerization of cardanol over DES-H₂SO₄ catalyst system.

Hence at 50°C, in the case of the DES-H₂SO₄ system, the termination of oligomerization takes place through proton transfer. Thus when $K_{tr} > K_t$, the rate is proportional to $[M]$, i.e. first order with respect to the monomer concentration. Termination by transfer to monomer has been proposed as one of the major mechanisms in the cationic polymerization of bulk monomer.¹⁹

REFERENCES

1. J. H. P. Tyman, *Chem. Soc. Rev.*, **8**, 499 (1979).
2. A. R. R. Menon, C. K. S. Pillai, J. D. Sudha, and A. G. Mathew, *J. Sci. Ind. Res.*, **44**, 324 (1985).
3. P. H. Gedam and P. S. Sampathakumaran, *Prog. Org. Coatings*, **14**, 115 (1986).
4. R. J. Wilson, *The Market for Cashew Kernels and Cashew Nut Shell Liquid*, Report No. G91, Tropical Products Institute, London, 1975.
5. B. S. Sitaramam and P. C. Chatterjee, *J. Appl. Poly. Sci.*, **37**, 33 (1989).
6. C. K. S. Pillai, J. D. Sudha, V. S. Prasad, S. C. Bera, A. R. R. Menon, A. D. Damodaran, S. Alwan, S. K. Lakshmidasan, and K. N. Govindaraman, *Indian Pat.*, 1157/Del/88 (1988).
7. C. K. S. Pillai, V. S. Prasad, J. D. Sudha, S. C. Bera, and A. R. R. Menon, *J. Appl. Poly. Sci.*, **41**, 2487 (1990).
8. A. D. Damodaran, C. K. S. Pillai, S. C. Bera, V. S. Prasad, J. D. Sudha, and A. G. Mathew, *Indian Pat.*, 314/Del/87 (1987).

9. C. K. S. Pillai, *Rubber Reporter*, **12**, 145 (1988).
10. J. P. Pillot, J. Dunogues, J. Gerval, M. D. The, and M. V. Thanh, *Eur. Polym. J.*, **25**, 3, 285 (1989).
11. *Cashew Nut Shell Liquid Patents*; USA, Vol. 1; UK, India, and Japan, Vol. II; Cashew Export Promotion Council, Ernakulam (1964).
12. *Cashew Nut Shell Liquid, Extraction and Uses—A Survey of World Patents up to 1976*, Cashew Export Promotion Council, Ernakulam (1978).
13. B. G. K. Murthy, M. C. Menon, J. S. Agarwal, and S. H. Zaheer, *Paint Manuf.*, **31**, 47 (1961).
14. A. K. Misra and G. N. Pandey, *J. Appl. Poly. Sci.*, **30**, 969 (1985).
15. L. J. Bellamy, *The Infra-Red Spectra of Complex Molecules*, Chapman and Hall, London (1980).
16. H. A. Szymanski, *Interpreted Infrared Spectra, Vol. 1*, Plenum Press, New York (1964).
17. S. K. Sood, J. H. P. Tyman, A. Durani, and R. A. Johnson, *Lipids*, **21**, 241 (1986).
18. S. M. Kaback, *Dissertation Abstracts*, **21**(1-4), 759 (1960).
19. J. P. Kennedy, *Carbocationic Polymerization*, Wiley Interscience, New York (1982).

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