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Synthesis and characterization of polymers from cashewnut shell liquid (CNSL), a renewable resource III. Synthesis of a polyether

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Abstract

A novel polyether was synthesized by cationic polymerization of glycidyl 3-pentadecenyl phenyl ether (GPPE) in the presence of a latent thermal initiator, *N*-(benzyl) *N*,*N*-dimethyl anilinium hexafluoroantimonate (BDAHA). The monomer, GPPE, was synthesized from cardanol, a naturally occurring meta-substituted long chain monoene phenol. Cardanol has been recently characterized by CHN analysis, IR, ^{1}H NMR and ^{13}C NMR spectroscopic techniques by the authors. The polyether was examined with ^{1}H NMR, FTIR, differential scanning calorimetry (DSC), and thermogravimetry (TGA). Gel permeation chromatography (GPC) indicated the weight average molecular weight ($\bar{M}_w$) to be 3790 g/mol and polydispersity index was found to be 1.148.

1. Introduction

Cashewnut shell liquid (CNSL), an agricultural by-product, is a source of a long chain *m*-substituted phenol which promises to be an excellent monomer for polymer production. CNSL occurs as a reddish brown viscous fluid in the soft honeycomb structure of the shell of cashewnut. Many researchers have investigated its extraction [1, 2], chemistry and composition [3–12]. The CNSL contains four major components namely, 3-pentadecenyl phenol (cardanol), 5-pentadecenyl resorcinol (cardol), 6-pentadecenyl salicylic acid (anacardic acid) and 2-methyl, 5 pentadecenyl resorcinol (2-methyl cardol). The polymers from CNSL and cardanol have been prepared either by condensation with electrophilic agents, such as formaldehyde or by chain polymerization at the unsaturation sites in the side chain using acid catalysts, or by functionalization at the phenolic hydroxyl group and subsequent oligomerization to get functionalized prepolymers. Cardanol is functionalized with orthophosphoric acid and oligomerized, the resulting prepolymers acting as multifunctional additives [13–18]. Functionalization of cardanol with acrylate moiety gives rise to crosslinked polymers of uniform bead size [19, 20]. There have been a few attempts at synthesis, chemical modification and functionalization of cardanol and its polymers. Ghatge and Patil [21] have synthesized epoxy novolac resins based on cardanol and studied their water, acid and alkali resistance properties. Similarly, Chakrawarti and Mehta [22] have prepared *m*-cresol novolac with epichlorohydrin for improving the surface coating properties of varnishes, but no

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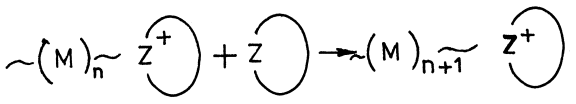
attempt has been made to prepare polymers from these glycidyl ethers by ring opening polymerization.

A wide variety of cyclic monomers have been successfully polymerized through ring-opening polymerization. Cyclic ethers or epoxides are the most important monomers in such polymerization. Epoxides are polymerized by both anionic and cationic initiators because of the high degree of strain in the three-membered ring. In recent years, cationic homopolymerization of epoxides has been intensively studied. The reaction being very fast, the polymerization is suitable for reaction injection moulding [23, 24]. Most cationic ring-opening polymerization involve the formation and propagation of oxonium ion centers. The reaction involves nucleophilic attack of the monomer on the oxonium ion.



Where Z represents reactive functional groups, such as O—C, N—C, Si—O, CO—O, CO—NH, in ethers, amines, siloxanes, esters and amides, respectively. Cationic initiators show activities by external stimulation such as heating or photo-irradiation. Photo-induced cationic polymerization of epoxy resins with triaryl sulphonium salts has been studied by Crivello and his co-workers [25]. It has been shown by Pappas et al. and Endo et al. that sulphonium salts can act as excellent latent thermal catalysts in the curing and polymerization of epoxy resins [26], spiro ortho carbonates [27], bicyclo ortho esters [28], and styrene [29]. Further, Endo et al. [30–37] have demonstrated that benzylpyridinium salts act as latent initiators in cationic polymerization which can be initiated by benzyl cations generated from the benzylpyridinium salts. They have also demonstrated that *p*-substituted benzylanilinium hexafluoroantimonates act as thermal latent initiators in the cationic polymerization of glycidyl phenyl ether [38].

The present paper deals with the synthesis of the latent thermal initiator, *N*-(benzyl) *N*,*N*-dimethyl anilinium hexafluoroantimonate (BDAHA) in the laboratory and cationic polymerization of glycidyl 3-pentadecenylphenyl ether (GPPE) obtained from cardanol by treating with epichlorohydrin. The synthesized polyether has been characterized by IR, NMR and thermal techniques.

2. Experimental

2.1. Materials

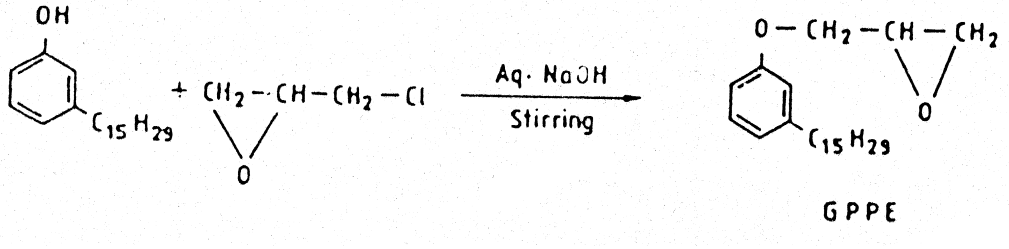
Technical-grade CNSL of Indian Standard specification IS:840 (1964) [39] was obtained from the Cashew Development Corporation, Kollam, Kerala, India. The chemicals epichlorohydrin, benzylchloride, acetonitrile, *N*,*N*-dimethylaniline (AR, S.D. Fine Chem, India) and sodium hexafluoroantimonate (Aldrich) were used as received without purification. The solvents, dimethyl formamide (DMF), dimethyl sulphoxide (DMSO), (Merck, India), chloroform, methanol and acetone, (SRL, India) were dried by standard methods [40, 41] and vacuum distilled.

2.2. Procedure

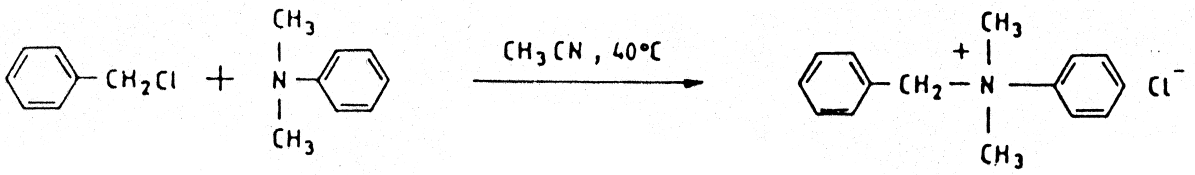
Cardanol was recovered from CNSL by direct double vacuum distillation at 5–10 mm of Hg in the temperature range of 180–240°C as reported earlier [42]. It was found to have a refractive index of 1.509 and Brookfield viscosity of 950–520 cp at 30°C. The pH of cardanol was measured to be 6.5, which agrees well with that of pure cardanol [39].

2.3. Synthesis of glycidyl 3-pentadecenylphenyl ether (GPPE) from 3 pentadecenylphenol (cardanol)

The monomer synthesis (Scheme 1) was carried out according to the modified procedure of Vernekar [43]. 30 g of 3-pentadecenylphenol (cardanol) was taken in a 250 ml three necked round bottom flask and 13 ml of epichlorohydrin was added to it while stirring. Then 8% NaOH solution was added dropwise to the above mixture in a period of 6 h at room temperature. The



Scheme 1.



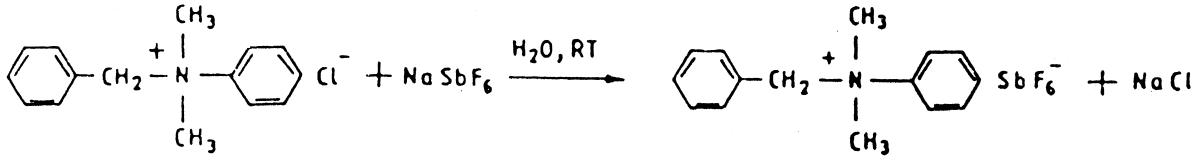
Scheme 2.

stirring was continued at room temperature for 12 h and the mixture was kept aside for 24 h at room temperature. The product was extracted into ether, which was washed with water and dried over anhydrous sodium sulphate. The ether solution was filtered and evaporated. The product was distilled under reduced pressure. The yield was 73% (22 gm).

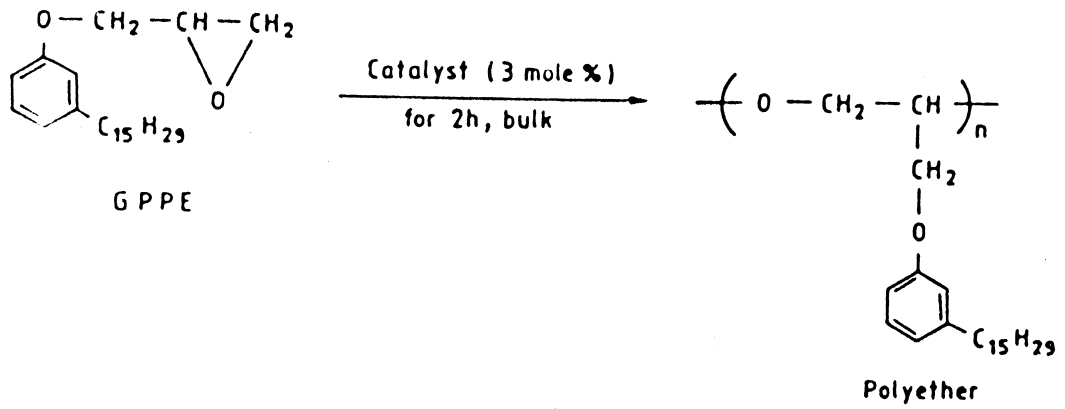
2.4. Synthesis of N-benzyl N,N-dimethyl anilinium hexafluorantimonate (BDAHA) catalyst

The *N*-(benzyl) *N*,*N*-dimethyl anilinium chloride salt was synthesized using the method of Nakano and Endo [38]. Into a four-necked flask equipped with a stirrer and a reflux condenser 1 mol of *N*,*N*-dimethylaniline and 80 ml of acetonitrile were introduced. The mixture was stirred and maintained at 40°C for 20 h. Acetonitrile was removed under vacuum. The solid product was washed with acetone and dried. The yield was 90%. The greenish-white product obtained was *N*-(benzyl) *N*,*N*-dimethyl anilinium chloride (Scheme 2).

Anilinium chloride salt, 5 g (0.02 mol), was dissolved in 50 ml of water, and 5.2 g (0.02 mol) of sodium hexafluoroantimonate was then added to this solution to obtain the crude *N*-(benzyl) *N*,*N*-dimethyl anilinium hexafluoroantimonate, a white solid. The product was recrystallized from methanol (Scheme 3). The yield was 90% (9 g).



Scheme 3.



Scheme 4.

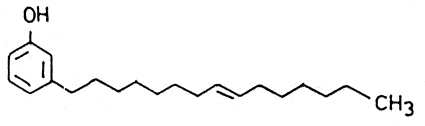


Fig. 1. Structure of cardanol.

2.5. Cationic polymerization of glycidyl 3-pentadecenylphenyl ether (GPPE)

A homogenous mixture of 25 g (0.07 mol) of GPPE and 0.95 gm (0.0021 mol) of the initiator was placed in a two-necked round bottom flask fitted with a magnetic stirrer, a thermometer, and a nitrogen inlet tube. Nitrogen was allowed to flow through the flask continuously at a constant rate. The temperature was then raised to 190°C in an oil bath and maintained for 1 h. The reaction mixture was then dissolved in methylene chloride, and the resulting solution was poured into methanol (50 ml) to precipitate the polymer. The methanol layer was decanted and the viscous polymer was dried at 60°C in vacuum. The polyether thus formed was characterized by ^{1}H NMR and FTIR spectroscopic study (Scheme 4).

2.6. Characterization

The characterization of the cardanol and polyether was carried out through elemental analysis (Heracus CHN-rapid analyser), IR spectrophotometer (Model: Perkin–Elmer 843), FTIR (model: Perkin–Elmer Pragon-1000). ^{1}H NMR and ^{13}C NMR spectra were recorded with a Bruker 200 MHz, and the chemical

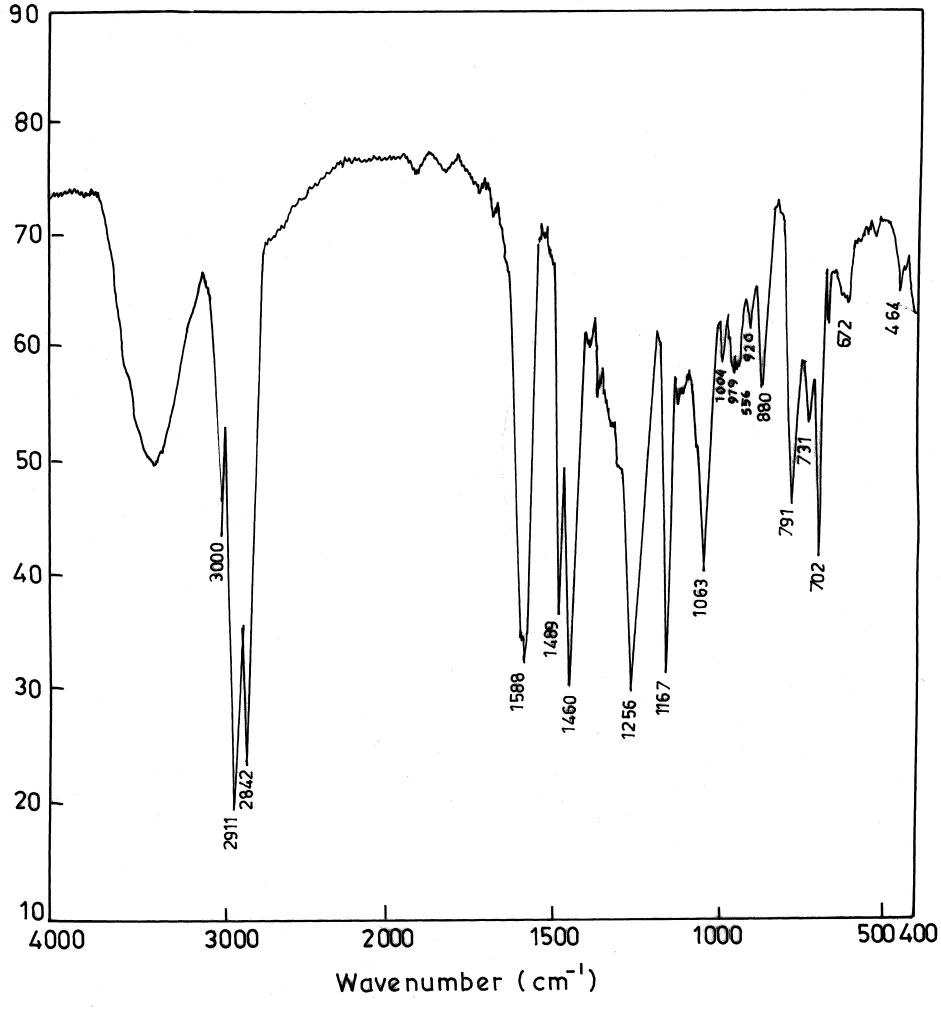


Fig. 2. IR spectrum of glycidyl 3-pentadecenyl phenyl ether.

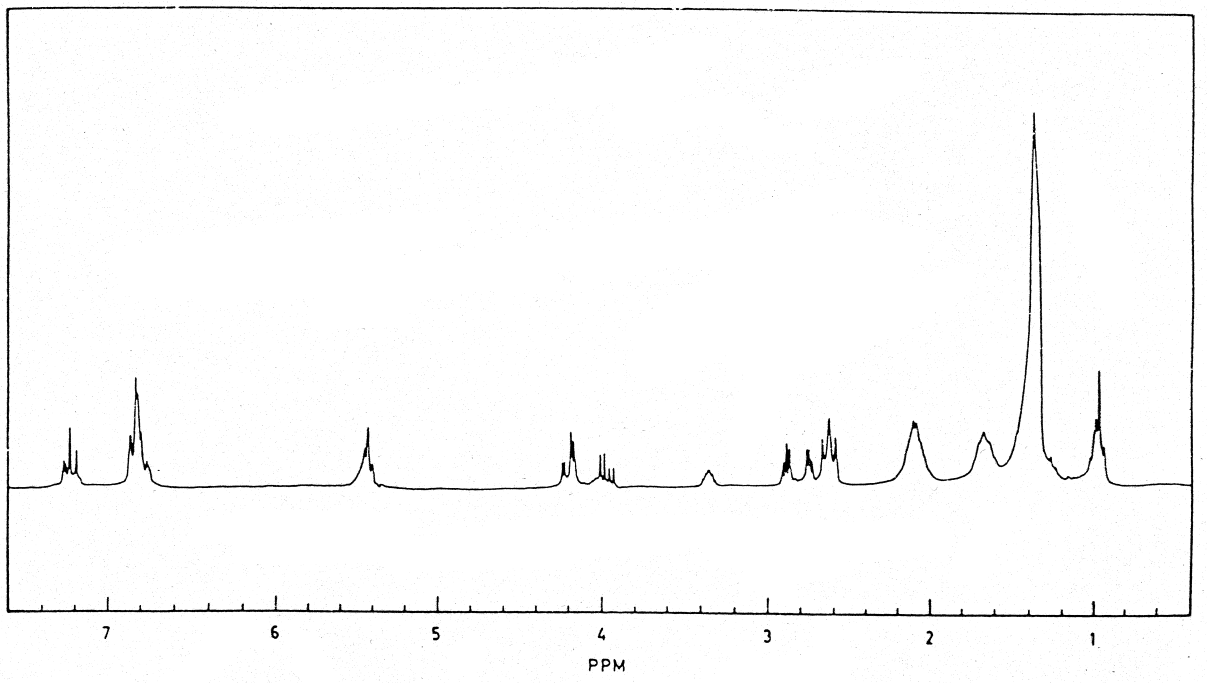


Fig. 3. ^{1}HNMR spectrum of glycidyl 3-pentadecenyl phenyl ether.

shifts were reported in ppm units with tetramethylsilane as internal standard. Deuterated chloroform ($CDCl_3$) or dimethylsulphoxide (CMSO-d_6) was used as solvent for recording the NMR spectra. The thermal analysis measurements were performed in a DuPont 9000 thermal analyser employing a 20 ml/min flow of dry nitrogen as purge gas for the sample and reference cells. The intrinsic viscosity of the polymer was determined at 35°C in DMF by using Ostwald viscometer. Molecular weight and molecular weight distribution (MWD; M_w/M_n) were determined by gel permeation chromatography (GPC) on a 510 HPLC, equipped with three polystyrene gel columns (ultrastyragel liner, 10^3, 500, 100 Å), using tetrahydrofuran as an eluent, a flow rate of 1.0 ml min^{-1}, polystyrene calibration, and refractive index (RI) detectors.

3. Results and discussion

Cardanol as recovered from CNSL was characterized by elemental analysis using a CHN-analyser, and by IR (Table 1), ^{1}H NMR and ^{13}C NMR spectroscopy techniques as reported recently [42]. It has been confirmed that cardanol thus obtained is basically a monoene meta-substituted phenol having empirical formula $C_{21}H_{29}O$ (Fig. 1). The other component of CNSL double distillation is a highly viscous dark plastic mass which remains as a residue in the flask. It has also been confirmed from ^{1}H NMR (proton decoupled) spectra that cardanol exists in the *cis*-configuration. The results agree with that of Tyman [13], who reported that the total percentage of unsaturated constituents in CNSL remained almost the same when recovered from various sources, but the distribution of triene, diene and monoene varied widely. The CHN-analysis also supported this view.

The purity of the monomer GPPE was first checked by thin layer chromatography (TLC) and elemental analysis. The elemental analysis result showed the constituents as 79.58% carbon and 10.14% hydrogen for the monomer thus synthesized. Theoretical values were found to be 80.45% carbon and 10.61% hydrogen respectively. From IR spectroscopy (Fig. 2) it is difficult to identify ether bands because many other strong

Table 1
IR absorption frequency and vibrational assignment of cardanol

Vibration assignments	Absorption frequency (cm^{-1})
Phenolic (—OH) group	3375–3000
C—H stretching	2922–2858
Aromatic ring (C=C)	1538, 1554, 1587, 1611
Monosubstitued phenol	1915, 1832, 1784, 1697
m-substitued phenol	966, 873
> C=C <	770

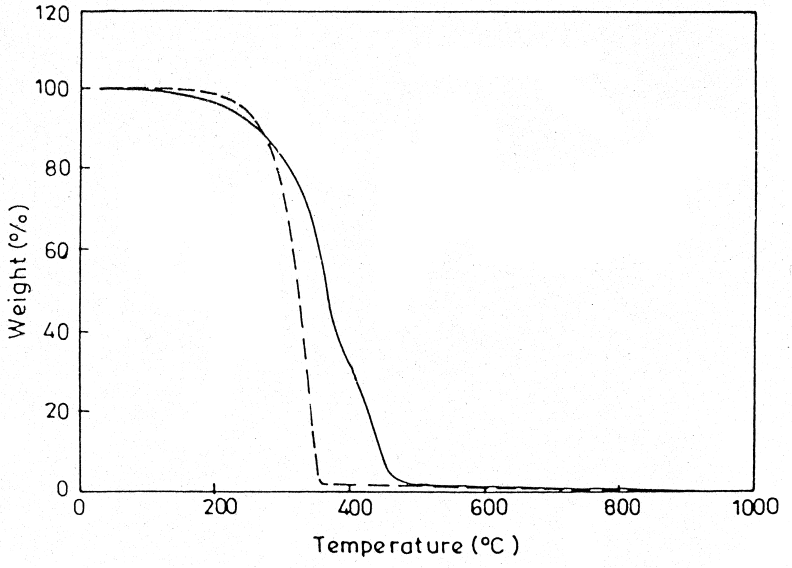
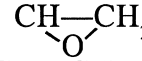
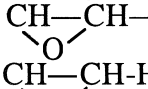
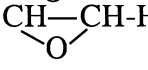


Fig. 4. Thermogravitograms of cardanol (.....) and glycidyl 3-pentadecenyl phenyl ether ——).

bands appear in the region from 1050–1300 cm^{-1} [44]. Although new peaks appear at 1260 and 1047 cm^{-1} due to the presence of cyclic C—O—C asymmetric and symmetric stretching vibrations, respectively, there is strong evidence for presence of an ether group. In the ^{1}HNMR spectrum (Fig. 3), apart from the characteristic signals for the aromatic nucleus and C_{15} side chain protons, the presence of the glycidyl moiety was confirmed by the appearance of the following signals: δ4.0–4.2 (1H, *dd*, J = 3.3, 10.9 Hz, ArOCH-H), 3.92–4.0 (1H, *dd*, J = 5.8, 11.4 Hz, ArOCH-H), 3.33–3.37 (1H, *m*, ), 2.80–2.88 (1H, *t*, J = 4.6, 4.5 Hz, ), 2.73 2.79 (1H, *dd*, J = 5.2, 6.2 Hz, ).

Thermogravimetric analysis of GPPE shows that it degrades in two steps (Fig. 4). The first step in degra-

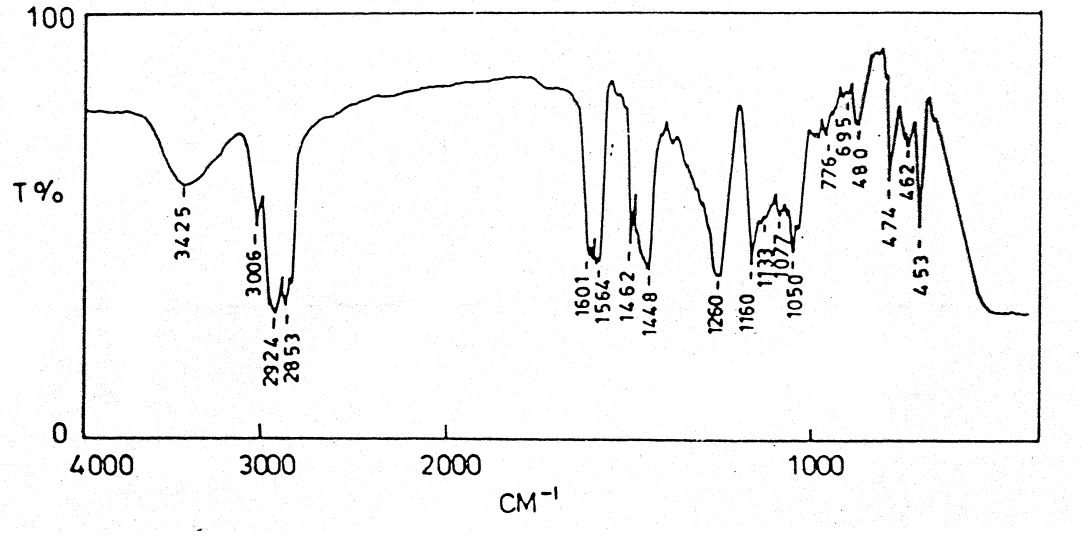


Fig. 5. FTIR spectrum of the polyether.

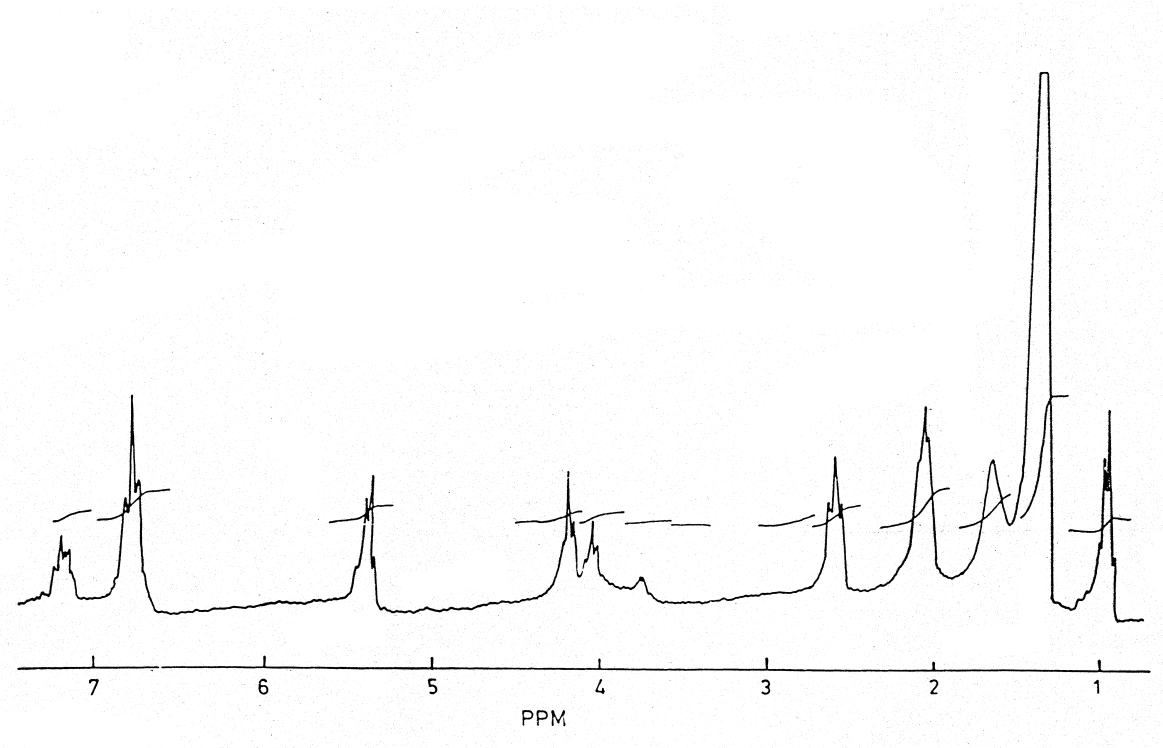


Fig. 6. ^{1}HNMR spectrum of the polyether.

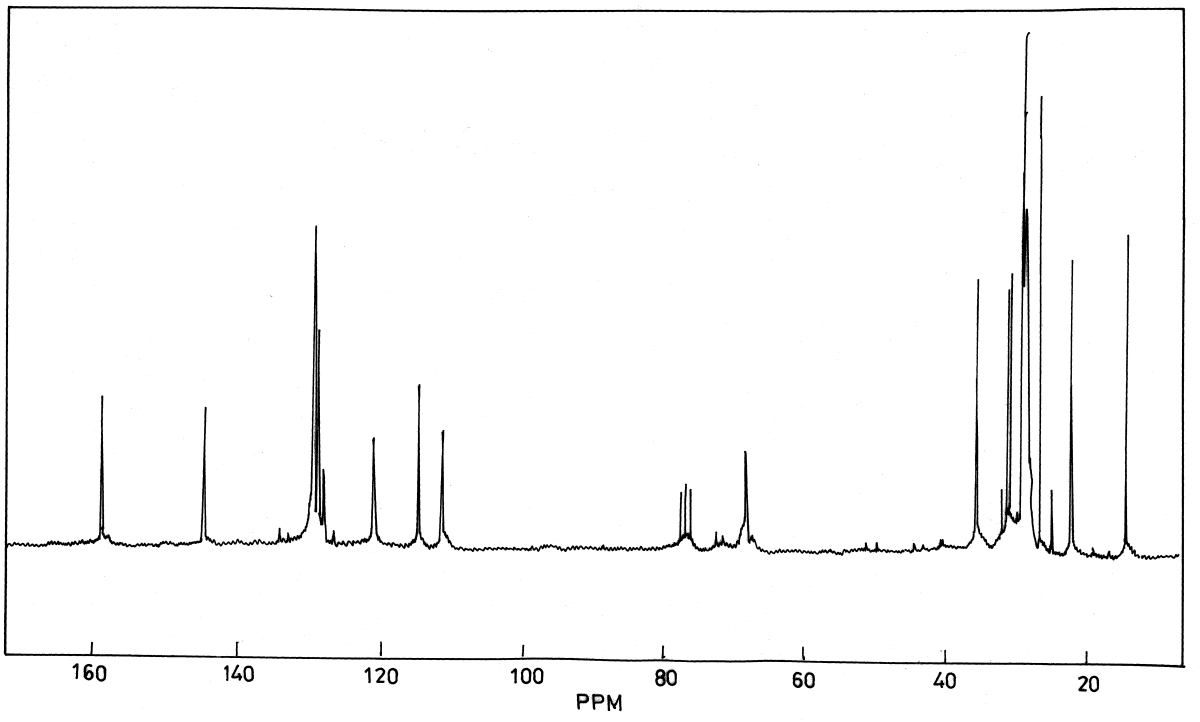


Fig. 7. ^{13}CNMR spectrum of the polyether.

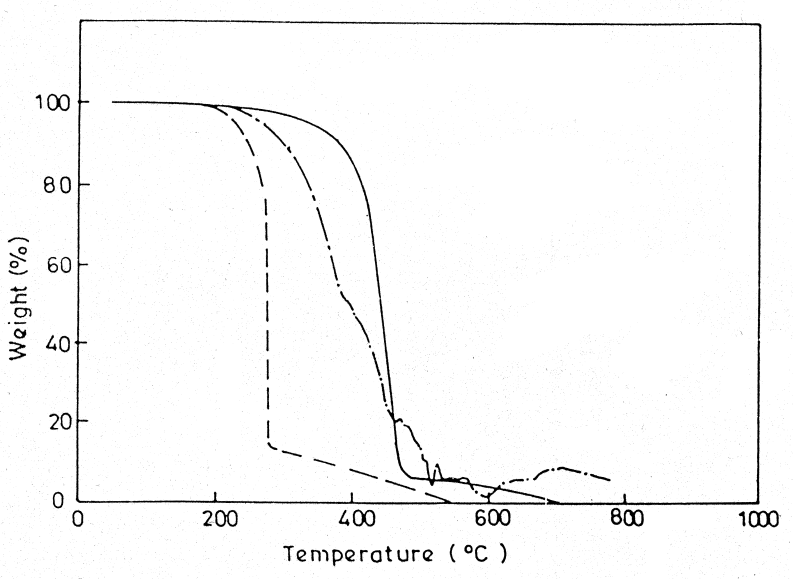


Fig. 8. Thermogram of the polyether, (– –) in N_2 atmosphere, (.....) in O_2 atmosphere and (——) in air.

dation (41%) begins at 265°C and continues up to 405°C, while the T_{max} occurs at 365°C. The second step in degradation commences at 405°C and continues up to 1000°C with the T_{max} ocurring at 443°C. The degradation is carried out in N_2 at a heating rate of 10°C min^{-1} (Table 1).

The polyether thus synthesized was characterized by elemental analysis. The CHN analysis showed a value of 80.99% carbon, and 10.20% hydrogen, which agrees well with the theoretical values of 80.95% carbon and 10.61% hydrogen. FTIR spectra of the polyether shows a peak at 1259 cm^{-1} due to the C—O—C asymmetric stretching vibration (Fig. 5). The presence of $OCH_2CH—CH_2OPh$ unit was confirmed from ^1H NMR spectroscopic studies (Fig. 6). The signals at δ4.1–4.2(m,2H) were due to CH_2 attached to phenoxy moiety, while the signal at δ3.9(m,2H) was due to the —O—CH_2—CH— unit. The multiplet at δ3.7 was attributed to the >CH— group. The ^{13}C NMR spectroscopic study shows peaks in the range 68–73 due to the methylene carbon and methine carbon attached to oxygen (Fig. 7).

3.1. Polymer properties

The polyether synthesized from GPPE is a reddish viscous liquid. It is soluble in chloroform. The density of the polyether is 1.1 gm cm^{-3}. The intrinsic viscosity (η) was found to be 0.83 dl/g at 35°C. GPC study of the polyether shows a lower molecular weight of $\bar{M}_n$ 3300, $\bar{M}_w$ 3790 and $\bar{M}_z$ 4435 Da with a polydispersity of 1.148. The molecular weight distribution of the polyether synthesized is bimodal in nature. Thermogravimetric analysis of the polyether (Fig. 8) shows a single stage degradation. The degradation initiates at 347°C and completes at 485°C whereas T_{max} occurs at 442°C. TGA results of the polyether, cardanol and GPPE are summarized in Table 2. Comparing the data, one can say that polyether is more stable than the monomer (GPPE). The DSC thermogram (Fig. 9) of the polyether shows a shift in the base line at −25°C which indicated its transition to the glassy state. Thus −25°C may be considered as its glass transition temperature.

Table 2
Thermogravimetric analysis of cardanol, monomer and polyether

Components	T_i (°C)	T_{max} (°C)	T_f (°C)	Loss (%)
Cardanol	200	329	350	100
Glycidyl 3-pentadecenyl phenyl ether				
1st stage	295	365	405	41
2nd stage	405	443	1000	59
Polyether	347	442	485	100

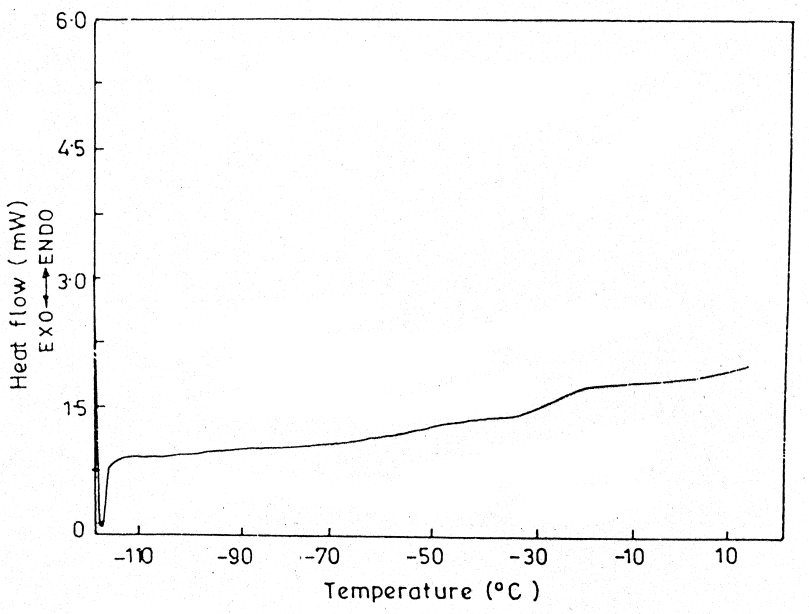


Fig. 9. DSC thermogram of the polyether.

4. Conclusions

The following conclusions have been drawn from the present study:

1. Double vacuum distillation of CNSL yields cardanol with a monoene substituent in the meta position.
2. A monomer glycidyl 3-pentadecenylphenyl ether could be synthesized from cardanol.
3. The monomer could be polymerized by cationic polymerization into a polyether.
4. The resulting polyether has low molecular weight of $\bar{M}_n = 3300$ and $\bar{M}_w = 3790$ and a polydispersity index of 1.148.
5. The thermal stability of the polyether thus synthesized is comparatively higher than that of the monomer.

Acknowledgements

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