Some Aspects on the Synthesis and Characterization of Dodecenyl Succinic Anhydride (DDSA) — a Curing Agent for Epoxy Resins

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Synopsis

Dodecenyl succinic anhydride (DDSA), a liquid anhydride curing agent for epoxy resins, was synthesised from C_{12} olefin and maleic anhydride by the "ene synthesis" reaction. C_{12} olefin was prepared by the dehydration of lauryl alcohol using Al_2O_3 (acidic) catalyst. The dehydration was carried out in a flow type reactor. The olefin collected was found to be a mixture of positional isomers of C_{12} olefin. Systematic studies were carried out by varying the dehydration temperature, mode of feeding and flow rate of lauryl alcohol, and the C_{12} olefin collected were converted into DDSA and mechanical properties of an epoxy resin–DDSA system were evaluated. The C_{12} olefins and DDSA were characterized, and the properties correlated with structure and composition. It was found that DDSA derived from C_{12} olefin with double bond near to the center of the chain gave better tensile strength than the DDSA derived from C_{12} olefin with terminal double bond.

INTRODUCTION

Epoxy resins, because of their low shrinkage during cure and superior mechanical, electrical, and adhesive properties, are used for various applications in industry such as reinforced plastics, surface coatings, adhesives, encapsulation of electronic components, castings, etc.[1,2] Useful properties of epoxy resin appear only after curing. The curing process involves the transformation of low molecular weight epoxy resin to crosslinked material. The most commonly used curing agents are amines, polyamides, anhydrides, BF_3–amine complex, etc. Anhydride curing agents are widely used with epoxy resins for various applications in industry. The majority of the anhydrides used are cyclic which transform low molecular weight epoxy resin to crosslinked material by epoxy–anhydride reaction. In the absence of an accelerator, anhydride will not react with the epoxy group. Various accelerators can be used with the epoxy–anhydride system to promote cure. These include tertiary amines, organic ammonium salts, and imidazoles and are used in the range of 1–5 phr.[3] The mechanism of curing reaction of epoxy resin with anhydride has been investigated by several authors,[4–6] and the mechanism well accepted in the literature for tertiary amine accelerators is given in Figure 1. Most of the anhydrides used are solids and are soluble in epoxy resins only at elevated temperatures. To overcome this limitation, liquid anhydrides are employed as they are miscible with epoxy resins at room
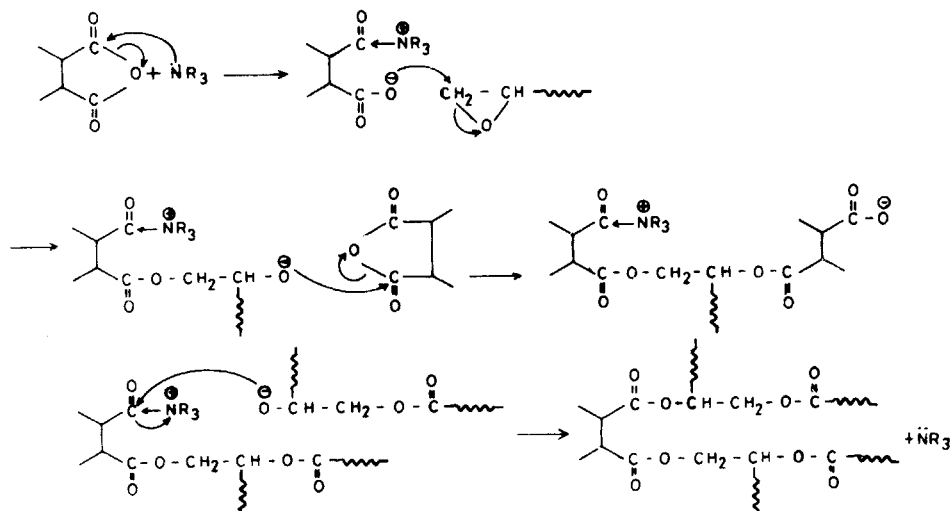
Fig. 1.   Cure reaction of epoxy resin with anhydride in presence of tertiary amine accelerator.

temperature in all proportions. The liquid anhydride curing agents used with epoxy resins exhibit long pot life, low exothermic temperature profile, low to moderate cost, and reduced irritation. Nadic methyl anhydride (NMA), methyl tetrahydrophthalic anhydride (MTHPA), methyl hexahydrophthalic anhydride (MHPA), and dodecenyl succinic anhydride (DDSA) are the commonly used liquid anhydrides.[3] Dodecenyl succinic anhydride is of interest because of its long aliphatic chain which reduces the brittleness of the cured epoxy system. Epoxy–DDSA compositions are useful for encapsulating and impregnating electronic components.[7] Akenyl succinic anhydrides also find utility as lubricating oil additive for corrosion inhibition.[8]

DDSA can be prepared by the "ene synthesis" reaction of maleic anhydride and C_{12} olefin. The reaction is shown in Figure 2. Maleic anhydride serves as an efficient enophile in the reaction.[9,10] We prepared C_{12} olefin by the dehydration of C_{12} linear primary alcohol (lauryl alcohol) over Al_2O_3 catalyst and the C_{12} olefin collected was converted into DDSA by the "ene synthesis" reaction with maleic anhydride. The dehydration of lauryl alcohol was carried out in a flow type glass reactor. The C_{12} olefin collected was a mixture of positional isomers having different positions for the double bond. In order to find the most suitable condition, we have carried out systematic study by
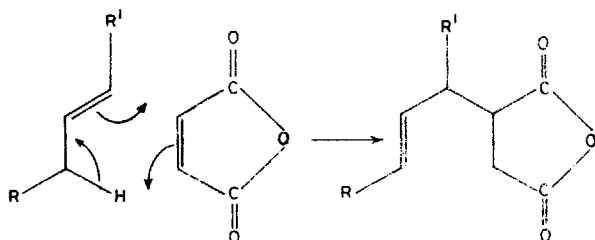

Fig. 2.   "Ene synthesis" reaction of maleic anhydride with olefin.

varying the dehydration temperature, mode of feeding, and flow rate of lauryl alcohol. The olefins collected were converted into DDSA, and the mechanical properties (stress–strain) of epoxy resin–DDSA systems were evaluated. The olefins and DDSA were characterized and the mechanical properties correlated with structure and composition. DDSA from C_{12} α-olefin and maleic anhydride was also prepared and compared.

EXPERIMENTAL

Materials and Instruments

Lauryl alcohol was supplied by Wilson's laboratories, Bombay, and used as such. Al_2O_3 (acidic) catalyst was obtained from Indian Institute of Petroleum, Dehradun. The catalyst was activated at 500–700°C for 5 h before use. Fresh catalyst was used for each experiment. Commercial maleic anhydride was purified by refluxing with acetic anhydride, followed by distillation. The epoxy resin and curing accelerator used were the liquid glycidyl ether of bisphenol A (tradename Araldite GY-250) and tris(dimethyl amino methyl) phenol (tradename Hardner HY 960), respectively, obtained from Hindustan Ciba Geigy Ltd., Bombay. C_{12} α-olefin (b.p. = 208–212°C) was procured from Indian Petrochemicals Corp. Ltd., Baroda.

A JEOL-MH-100 instrument was used for recording ^{1}H-NMR spectra. ^{13}C-NMR was recorded using a JEOL-FX-90Q instrument. The spectra were recorded in $CDCl_3$ solution. Gas chromatograms were obtained by using a Shimadzu gas chromatographic instrument Model GC 5A, with an SE 52 column. A DuPont 990 Thermal Analyzer was used to take the DSC thermogram. Viscosities were measured by a microviscometer, Brookfield Model HAI 55550. An Instron Model 4202 was used for determining mechanical properties.

Preparation of C_{12} Olefin and DDSA

C_{12} olefin was prepared by the dehydration of lauryl alcohol using Al_2O_3 (acidic) catalyst. The reaction was carried out in an ordinary flow type glass reactor of 50 cm length and 1.5 cm inner diameter with provisions for heating and measuring temperature. Activated Al_2O_3 catalyst (100 g) was packed into the reactor. The reactor was heated, and 500 g lauryl alcohol was allowed to flow through the catalyst. The olefin formed was condensed and collected. The olefin was then fractionally distilled, and the fraction boiling in the range 208–212°C was collected. The yield was 80–82%. C_{12} olefins were characterized by iodine value, GC and ^{13}C-NMR.

DDSA was synthesized by heating C_{12} olefin and maleic anhydride in a 1 : 1 molar ratio under N_2 atmosphere. The reaction temperature was fixed at 180–185°C, below the boiling point of maleic anhydride. The reaction was carried out in a three-necked flask fitted with a stirrer, a nitrogen inlet, and a water condenser. The flask was heated in an oil bath, and the reaction temperature was controlled with a thermostat. The reaction was monitored by iodine value, and the optimum time for the reaction was found to be 15 h. The unreacted materials were removed by distillation at 180–185°C under reduced pressure (below 10 mm Hg). The residual liquid was used as such. The yield of

the product was around 70–75%. The liquid anhydrides were characterized by anhydride content, iodine value, and ^{1}H-NMR.

Curing of Epoxy Resin with DDSA and Determination of Mechanical Properties

The cure temperature of the epoxy resin–DDSA–HY 960 system was determined by recording the DSC thermogram. Epoxy resin (Araldite GY 250) (100 g) was mixed with a stoichiometric amount of DDSA (80 g) and HY 960 (2 g). An approximately 10-mg sample was weighed in an open aluminum pan and cured in N_2 atmosphere under dynamic conditions at a heating rate of 10°C/min.

For evaluating the mechanical properties (stress–strain) of the cured system, dumbbells were cast directly in a silicone mold, since the volumetric shrinkage of epoxy resin is negligible. Araldite GY 250 (100 g), DDSA (varies), and HY 960 (2 g) were mixed well, deaerated, poured into the mold, and then cured in a hot air oven at 120°C for 3h. The specimens were allowed to stand for 24 h at room temperature, and the mechanical properties were determined in an Instron at a cross head speed of 10 mm/min. To learn the optimum mix ratio, DDSA concentration was varied from 60 to 120 phr.

To study the effect of dehydration temperature of lauryl alcohol on the mechanical properties of the epoxy system cured with DDSA derived from the olefin obtained by the dehydration of lauryl alcohol, three temperature ranges, 200–250°C, 250–300°C, and 300–350°C, were selected. To know the effect of flow rate of lauryl alcohol, 1 mL/min, 3 mL/min, and 5 mL/min were chosen, and the dehydration was carried out at 300–350°C. Another experiment was carried out by feeding lauryl alcohol vapor from the bottom of the reactor at 300–350°C. The C_{12} olefins collected in all the cases were converted into DDSA, and the mechanical properties determined as cited previously. DDSA made from C_{12} α-olefin was also evaluated for comparison.

RESULTS AND DISCUSSIONS

C_{12} olefin was prepared by the dehydration of lauryl alcohol over Al_2O_3 (acidic) catalyst. The C_{12} olefin obtained was reacted with maleic anhydride and DDSA synthesized by "ene synthesis" reaction. Characterization of DDSA was done by ^{1}H-NMR, anhydride content, iodine value, and viscosity (Figs. 3(a) and 3(b)) and Table II). The δ values of ^{1}H-NMR are in agreement with structure (Table I). The fractional values of protons indicates that the product can be a mixture. The anhydride content (theoretical 27%) of DDSA prepared is close to the theoretical value (Table II). However, the iodine value (theoretical 95.4 g/100 g) is low probably due to the polymerization through double bonds. This is further indicated by increased viscosities. DDSA synthesized from C_{12} olefin obtained by the dehydration of lauryl alcohol by vapor feeding at 300–350°C has low viscosity whereas DDSA synthesized from C_{12} olefin obtained by liquid feeding has a higher viscosity. This difference in viscosities of the product might be due to the difference in polymerization rate of the double bond. Terminal double bond can be more reactive compared to the interior one. It is evident from C^{13}-NMR (discussed later) that C_{12} olefin obtained by dehydration of lauryl alcohol by vapor feeding at 300–350°C has
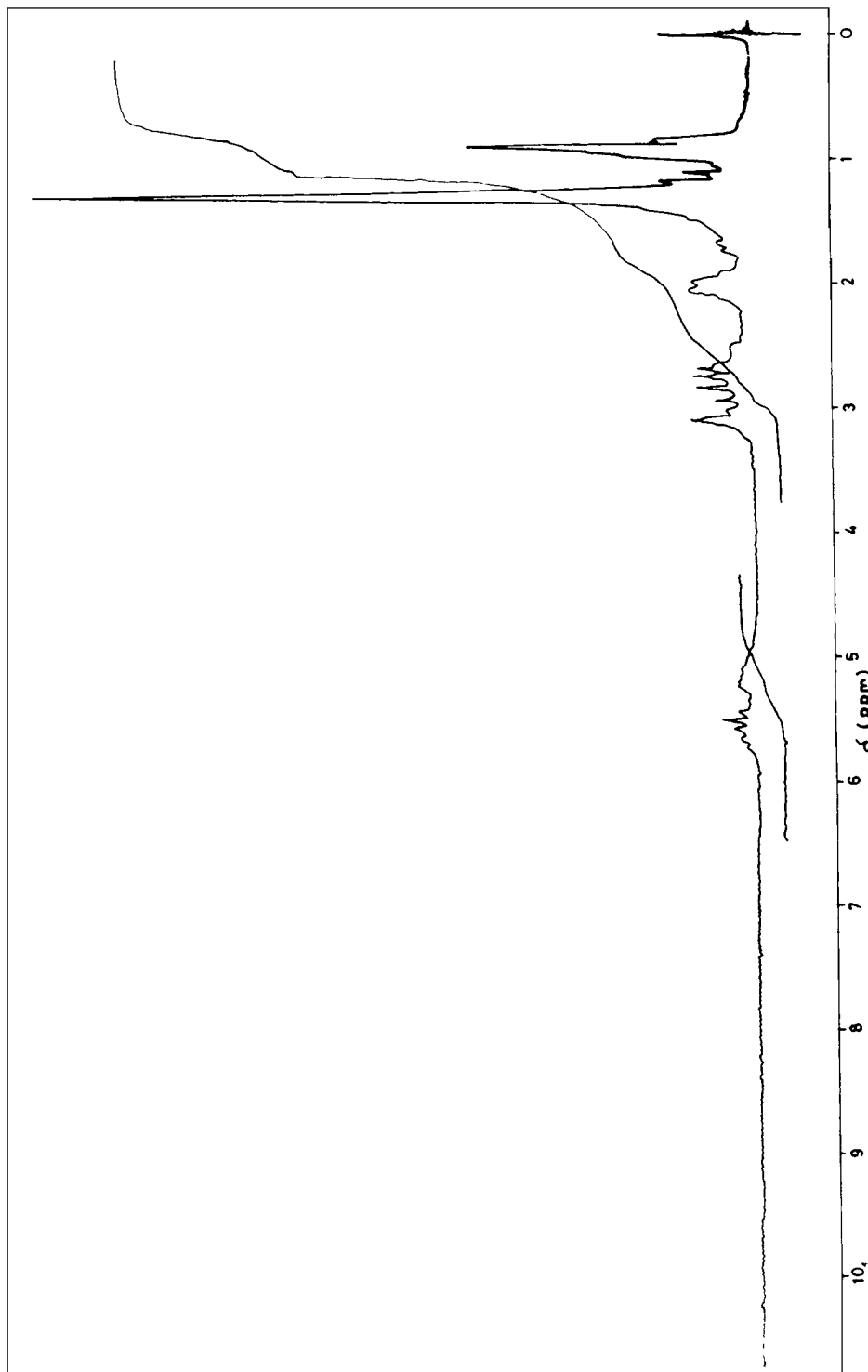
Fig. 3(a). ^{1}H-NMR spectrum of DDSA prepared fom maleic anhydride and C_{12} olefin obtained by the dehydration of lauryl alcohol over Al_2O_3 catalyst at 300–350°C by liquid feeding (solvent $CDCl_3$).
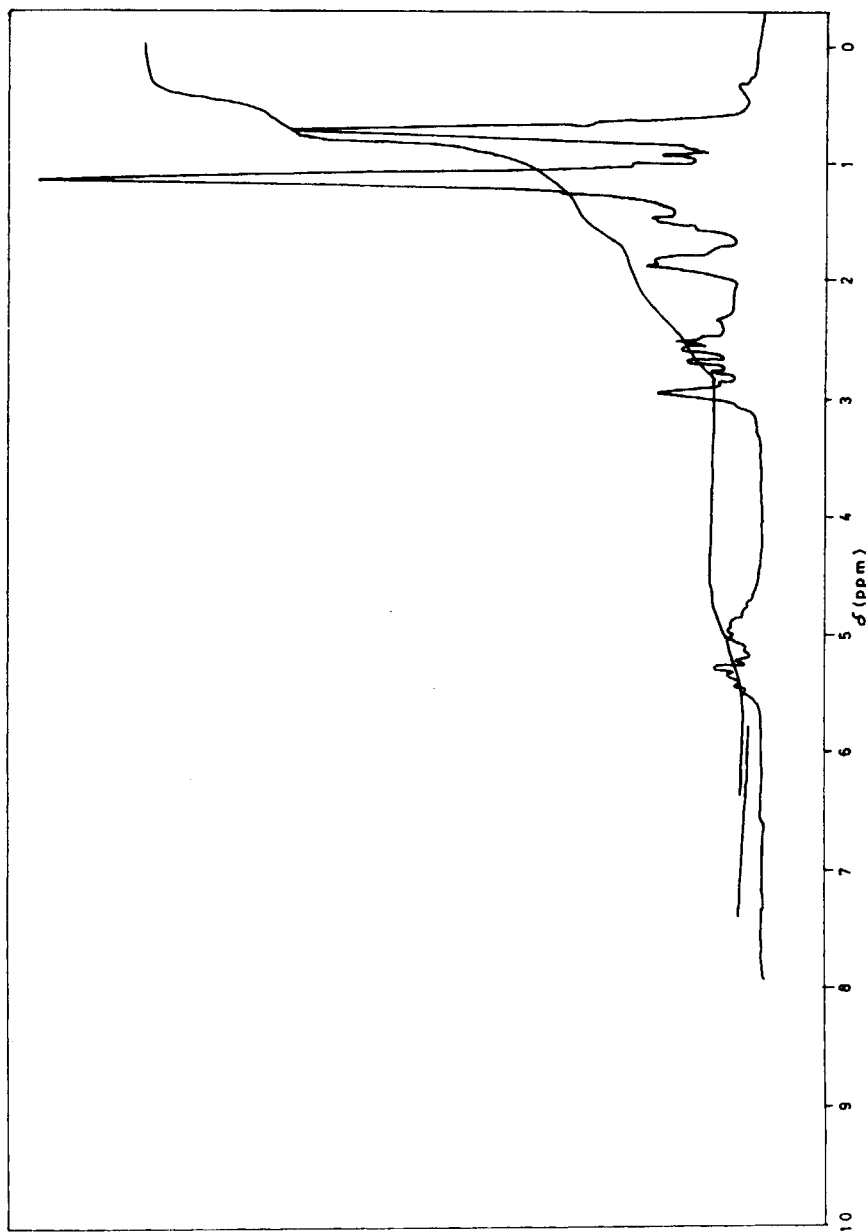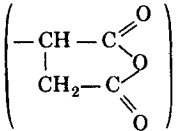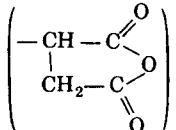
Fig. 3(b). ^{1}H-NMR spectrum of DDSA prepared from maleic anhydride and C_{12} olefin obtained by the dehydration of lauryl alcohol over Al_2O_3 catalyst at 300–350°C by vapor feeding (solvent $CDCl_3$).

TABLE I
^{1}H-NMR Characteristics of DDSA

	δ (ppm)
a) DDSA synthesized from C_{12} olefin collected by the dehydration of lauryl alcohol at 300–350°C by liquid feeding	0.8 (5.8H, —CH$_3$), 1.2 (12.3 H, —CH$_2$), 1.6–2 (3.04H, allyl proton), 2.5–3.1 (3.19H, 4.8–5.6 (1.74H, vinyl proton) $\left(\begin{array}{c} -CH - C\!\!\diagup^{\displaystyle O}_{\diagdown O} \\ \mid \\ CH_2 - C\!\!\diagdown^{\displaystyle }_{\displaystyle O} \end{array} \right)$
b) DDSA synthesized from C_{12} olefin collected by the dehydration of lauryl alcohol at 300–350°C by vapor feeding	0.8 (5.74H, —CH$_3$), 1.2 (12.8H, CH$_2$), 1.5–2 (3.02H, allyl proton), 2.5–3(2.87H, 4.8–5.6 (1.86H, vinyl proton) $\left(\begin{array}{c} -CH - C\!\!\diagup^{\displaystyle O}_{\diagdown O} \\ \mid \\ CH_2 - C\!\!\diagdown^{\displaystyle }_{\displaystyle O} \end{array} \right)$

more concentrations of C_{12} olefins with double bond near to the center of the chain, whereas at low dehydration temperatures high concentrations of C_{12} olefin with terminal double bond are formed (Table III). Hence a greater extent of polymerization and an increase in viscosity can be expected for the product with the decrease of dehydration temperature. The DSC thermogram (Fig. 4) of epoxy resin–DDSA–HY 960 system indicates a strong polymerization exotherm commencing from 100°C. Hence it is obvious that curing has to be carried out above 100°C. Various compositions for determining the mechanical properties were cured at 120 ± 2°C for 3 h. The effect of variation of DDSA concentration on the tensile strength of the cured system is given in Figure 5. It can be seen that maximum tensile strength was obtained at a concentration of 75 phr DDSA. This optimum mix ratio was used for evaluating the DDSA prepared under different conditions.

Table II illustrates the effect of dehydration temperature, flow rate, and mode of feeding of lauryl alcohol on the characteristics of C_{12} olefin and DDSA derived from lauryl alcohol and on the mechanical properties of the epoxy–DDSA system. It is evident from Table II that mechanical properties are dependent on the dehydration conditions of lauryl alcohol. Maximum tensile strength was obtained with DDSA prepared from C_{12} olefin obtained by the dehydration of lauryl alcohol over Al_2O_3 catalyst at 300–350°C by vapour feeding. Even though the flow rate of lauryl alcohol has no appreciable effect, the dehydration temperature has a substantial effect on the characteristics of liquid anhydride and on the mechanical properties. The difference in properties might be due to variation in structure and composition of C_{12} olefin as a function of temperature. In the presence of acidic catalyst, the double bond can migrate towards the interior of the chain, and the thermodynamically most stable olefin will be the one predominantly formed.[11] A gas chromatogram of olefin (fig. 6) revealed that olefins collected by dehydration

TABLE II
Effect of Dehydration Temperature, Flow Rate, and Mode of Feeding of Lauryl Alcohol on the Characteristics of C_{12} Olefin and DDSA Derived from Lauryl Alcohol and on the Mechanical Properties of Epoxy-DDSA System

Mode of feeding of lauryl alcohol	Dehydration (°C)	Flow rate of lauryl alcohol (mL/min)	Iodine value of C_{12} olefin (g/100 g)	Characteristics of DDSA		mechanical properties of epoxy-DDSA system		
				Anhydride content (%)	Iodine value (g/100)	Viscosity at 25°C (cps)	Tensile strength (kg/cm²)	Elongation (%)
Liquid feeding	300–350	1	158.6	24.5	64	2414	303	4.5
	300–350	3	154.6	23.2	67	2334	285	5.5
	250–300	3	155	23.6	55.5	8600	254	7
	200–250	3	151.6		Semisolid; properties not determined			
	300–350	5	151.6	23.9	63.4	2560	313	5.4
Vapor feeding	300–350	—	157	25.4	74	570	422	6

TABLE III

Olefinic ^{13}C-Chemical Shifts of C_{12} Olefins and Their Intensities[a]

Position isomers of dodecene and the ^{13}C-chemical shifts			C_{12} olefin obtained from lauryl alcohol by liquid feeding									C_{12} olefin obtained from lauryl alcohol by vapor feeding		
			Dehydration temp 200–250°C			Dehydration temp 250–300°C			Dehydration temp 300–350°C			dehydration temp 300–350°C		
			Olefinic ^{13}C-chemical shifts	Intensity	% of dodecene calculated	Olefinic ^{13}C-chemical shifts	Intensity	% of dodecene calculated	Olefinic ^{13}C-chemical shifts	Intensity	% of dodecene calculated	Olefinic ^{13}C-chemical shifts	Intensity	% of dodecene calculated
1-Dodecene	C-1	114.8	114.5	1567	39.8			2.8						2.8
	C-2	139	139.3	1326		139	309					139.1	258	
2-Dodecene	C-2	123.3	123.5	776	32.3	123.6	473	44	123.6	421	41.8			27.9
		(125.2)	(124.5)	885		(124.6)	848		(124.6)	783		(124.5)	739	
	C-3	130.6	130.4	291		130.5	2309		130.5	2405		130.7	848	
		(132.6)	(131.9)	422		(132)	1226		(132)	903		(131.9)	933	
3-Dodecene	C-3	132.1	131.7	618	13.2	131.8	812	14.4	131.8	875	16.8	131.8	809	19
	C-4	129.7	129.4	338		129.5	779		129.7	947		129.47	907	
4-Dodecene	C-4	130.8				130.2	1585	38.7	131.6	416	41.3	130.1	390	
		(131.8)				130	1127		130.9	592		129.96	972	
		130.8							130.77	1271		130.45	1723	
	C-5	(131.1)												
5-Dodecene	C-5	130.1	130.1	274	14.6	130.5	1556		130.2	1239		130.9	437	50.1
		130.9	130.9	792					130	936				
		(131.1)												
6-Dodecene	C-6	130												
		(130.5)												

[a] Olefinic ^{13}C-chemical shifts of dodecenes given in the first column of the table are taken from Ref. 9. Data listed for cis and (trans).
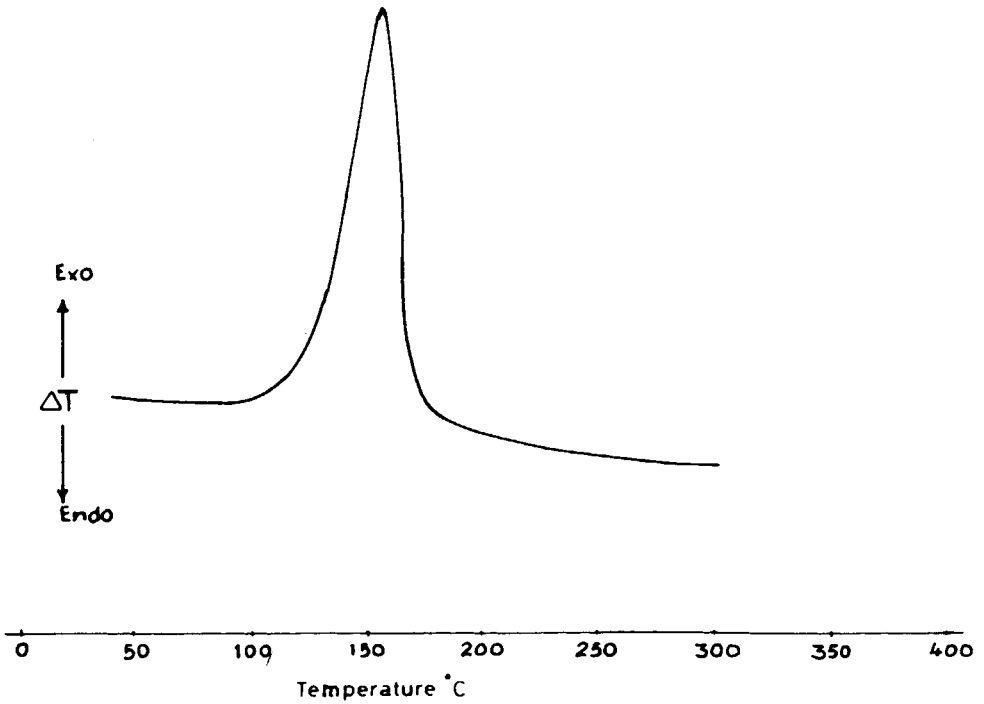
Fig. 4.   DSC thermogram of Araldite GY 250-DDSA HY 960 system in N_2 atmosphere at a heating rate of 10°C/min.
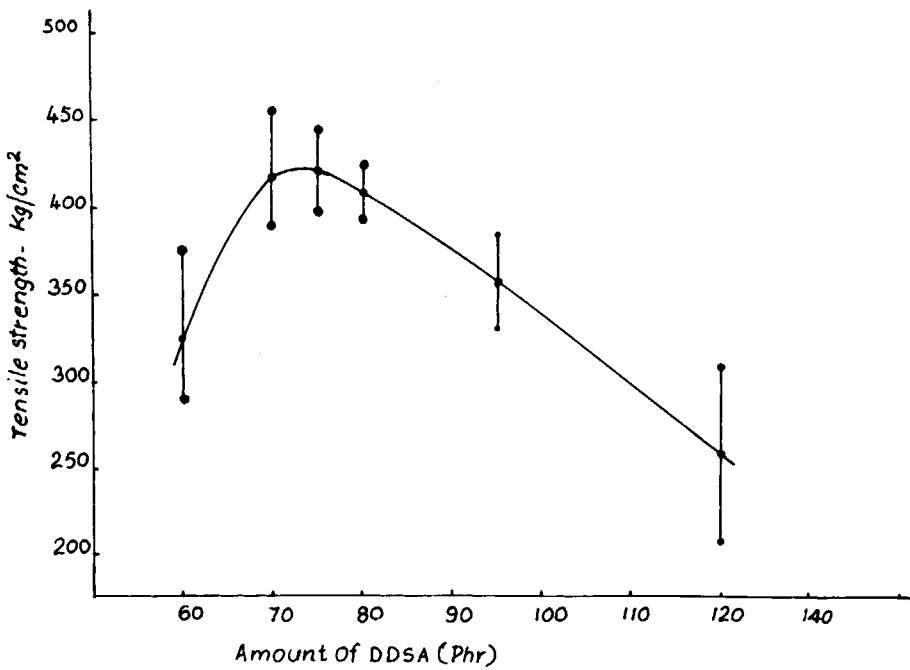
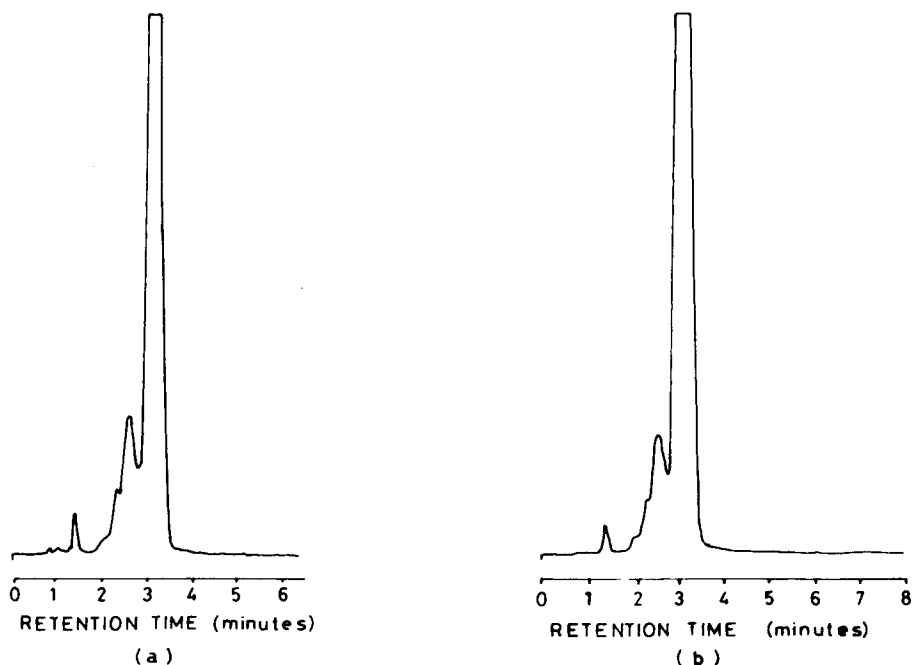Fig. 5.   Effect of DDSA concentration on the tensile strength of Araldite GY 250-DDSA-HY 960 system.

Fig. 6. The gas chromatograms of C_{12} olefin derived from lauryl alcohol: (a) dehydration over Al_2O_3 catalyst at 300–350°C by liquid feeding; (b) dehydration over Al_2O_3 catalyst at 300–350°C by vapor feeding.

of lauryl alcohol is not a pure single component. The iodine values of olefins obtained under different conditions (Table II) are close to the theoretical value (151.2 g/100 g) of C_{12} olefin, thus eliminating the possibility of low molecular weight fractions. GC did not furnish any conclusive result since the olefin with a very small difference in polarity and boiling point might not be resolved in the chromatogram. More conclusive results were provided by ^{13}C-NMR. ^{13}C-NMR spectra of the olefins collected under different conditions are shown in Figures 7–10. Correct assignment of the chemical shift is difficult since the olefin contains mixture of positional isomers. However, the possible olefinic ^{13}C-chemical shifts close to the reported literature values[12] are compiled in Table III, along with their intensities. 4, 5, 6-Dodecenes are considered together as they all have almost similar chemical shifts. In ^{13}C-NMR spectra, the peak intensities are not necessarily proportional to the number of carbons of each structural kind because of the nuclear Overhauser enhancement (NOE).[13] The molecule will yield accurate peak intensities only if the NOEs for all the carbons in the molecule are the same. For small molecules this will not be the case. Approximate estimation is possible in this case considering the relatively long chain of olefins which makes it possible to assume that the NOE of all the carbons in the molecule is approximately the same.[14] From Table III it can be stated that lower dehydration temperature results in a higher concentration of 1-dodecene, whereas, at higher temperatures, migration of the double bond to the interior of the chain occurs. It is evident that DDSA derived from C_{12} olefin with double bond near the center of the chain gives better tensile strength than the DDSA derived from C_{12} olefin with
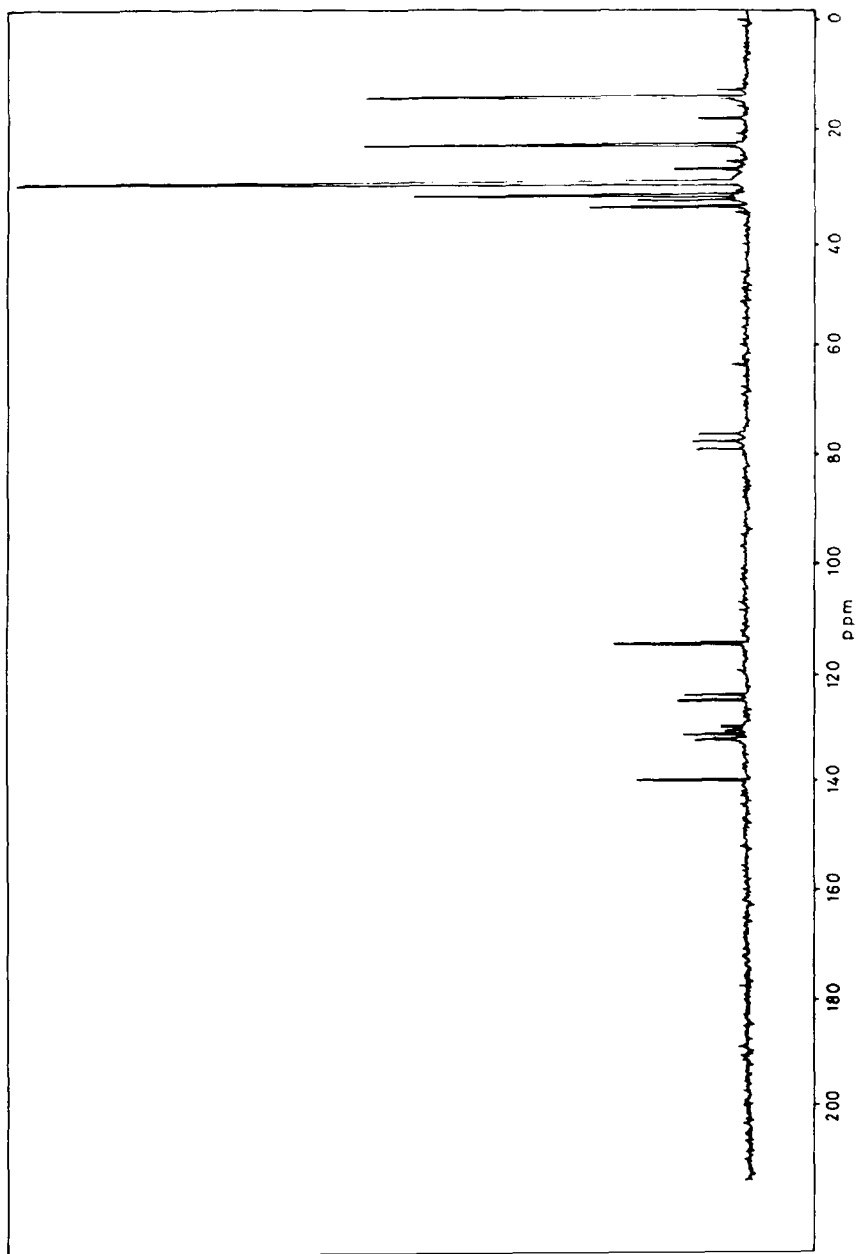
Fig. 7. ^{13}C-NMR spectrum of C_{12} olefin obtained by the dehydration of lauryl alcohol over Al_2O_3 catalyst by liquid feeding at 200–250°C (solvent CDCl$_3$).
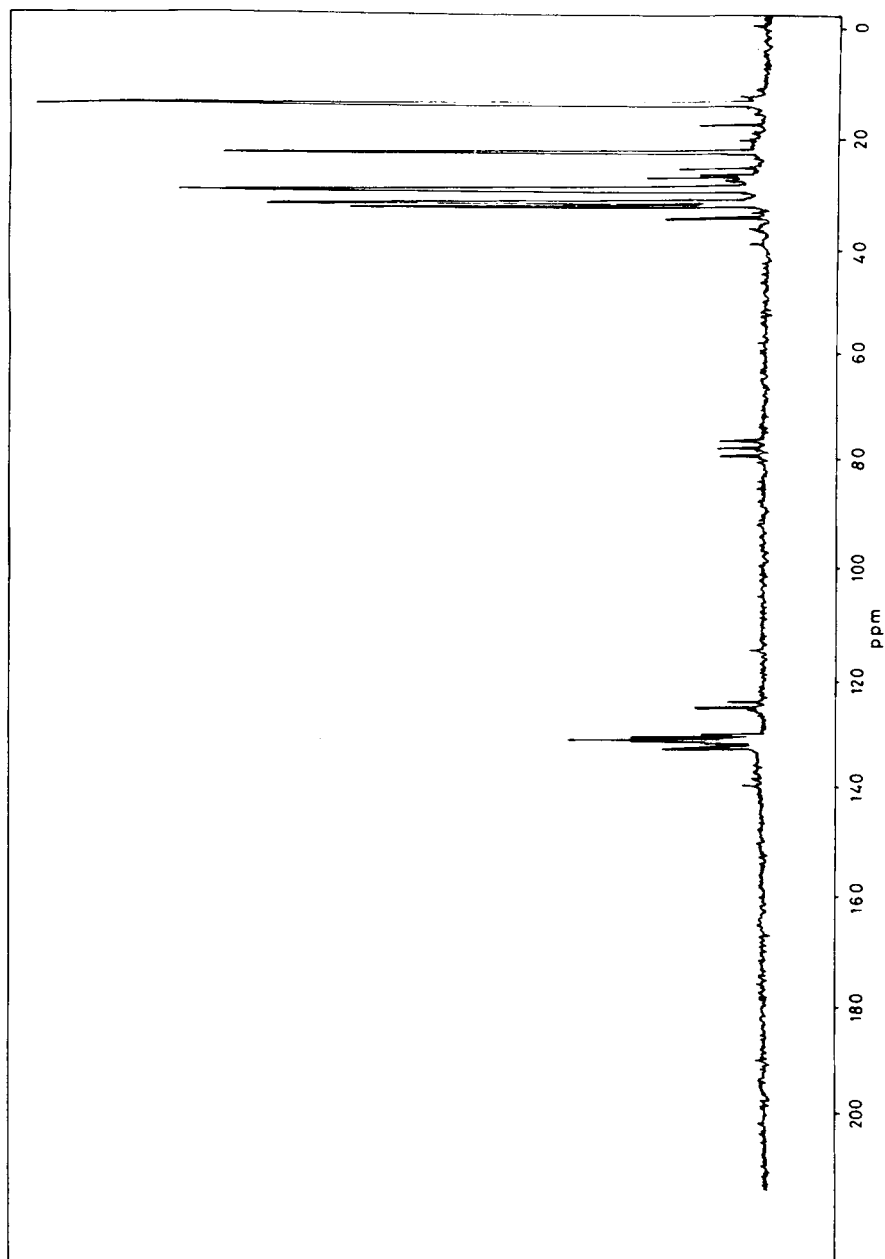
Fig. 8. ^{13}C-NMR spectrum of C_{12} olefin obtained by the dehydration of lauryl alcohol over Al_2O_3 catalyst by liquid feeding at 250–300°C (solvent $CDCl_3$).
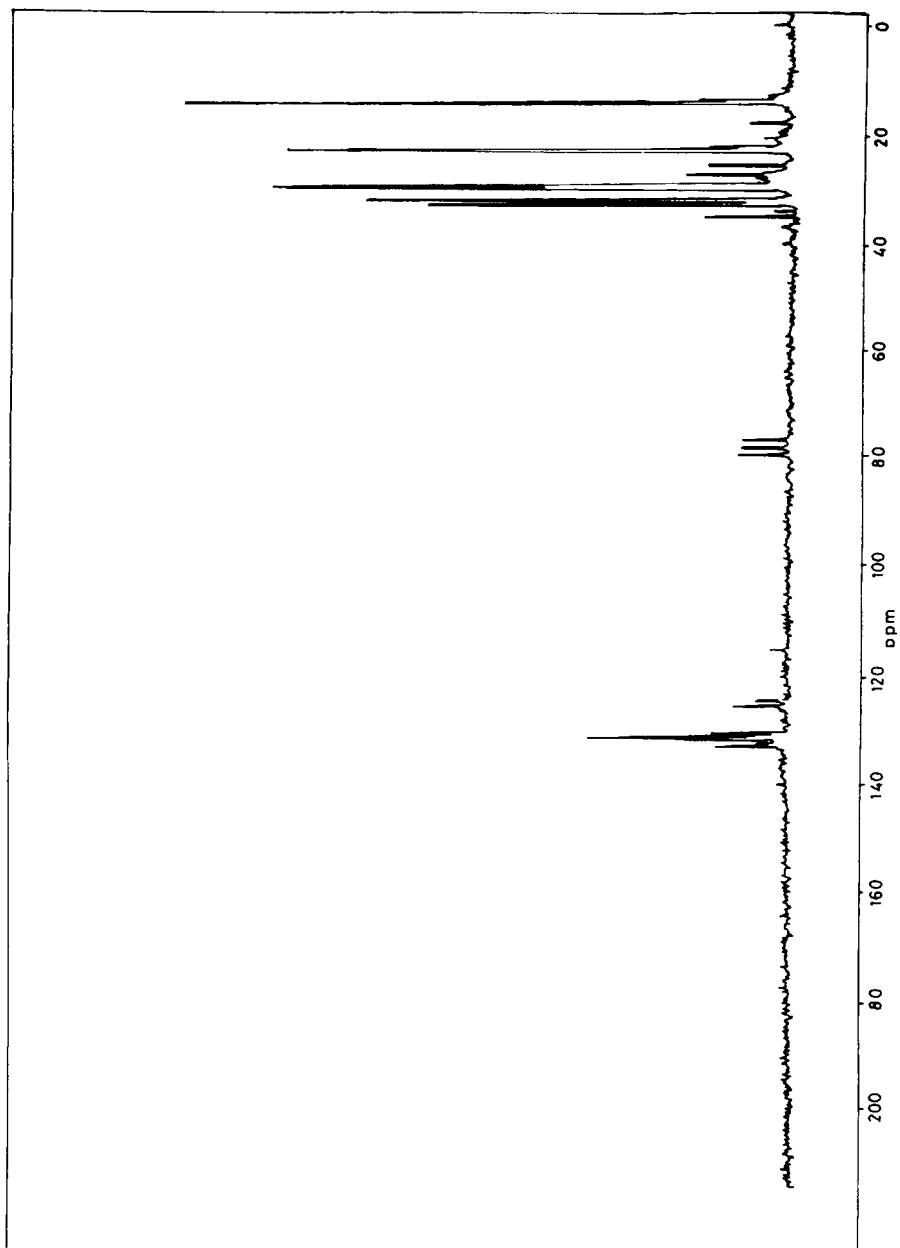
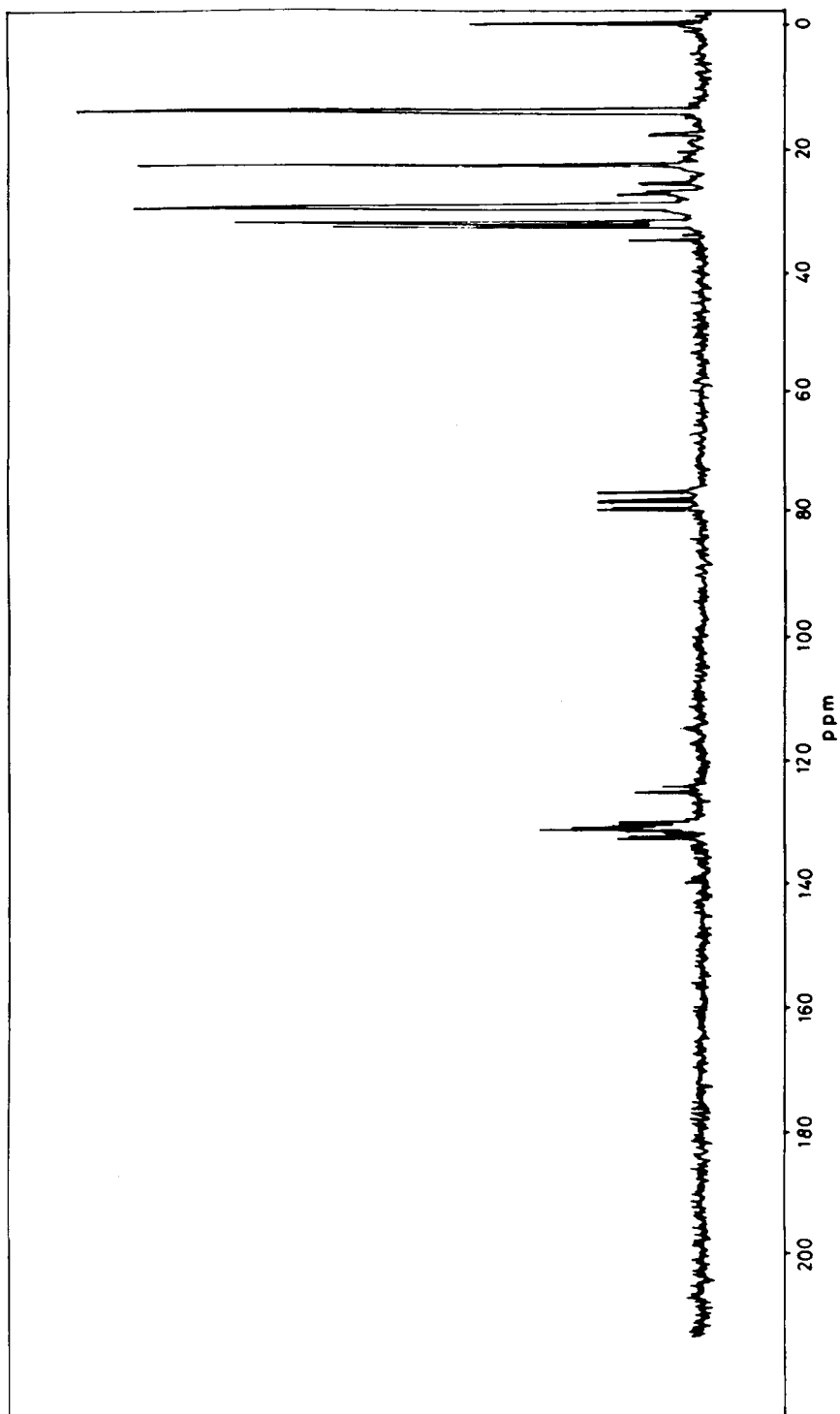Fig. 9. ^{13}C-NMR spectrum of C_{12} olefin obtained by the dehydration of lauryl alcohol over Al_2O_3 catalyst by liquid feeding at 300–350°C (solvent $CDCl_3$).

Fig. 10. ^{13}C-NMR spectrum C$_{12}$ olefin obtained by the dehydration of lauryl alcohol over Al$_2$O$_3$ catalyst by vapor feeding at 300–350°C (solvent CDCl$_3$).

TABLE IV
Mechanical Properties of Epoxy Resin Cured with DDSA Derived from C_{12} α-Olefin

Mechanical properties	DDSA from C_{12} α-olefin	DDSA from C_{12} α-olefin after passing through Al_2O_3 at 300–350°C
Tensile strength (kg/cm^2)	92	378
Elongation (%)	85	6

terminal double bond. Maximum tensile strength obtained for the liquid anhydride prepared from C_{12} olefin obtained by the vapor feeding of lauryl alcohol at 300–350°C can be attributed to the presence of more concentrations of C_{12} olefin with double bond near the center of the chain. The difference in mechanical properties with the change of position of double bond might be due to the change in side chain length of DDSA. This is further substantiated by the studies with C_{12} α-olefin (1-dodecene). The product obtained with C_{12} α-olefin was solid. (This could be the reason for the semisolid product obtained from the C_{12} olefin collected from lauryl alcohol at 200–250°C, which contains more concentration of 1-dodecene). The mechanical properties of the epoxy system cured with DDSA derived from C_{12} α-olefin is given in Table IV. The low tensile strength and high elongation can be due to the long aliphatic side chain. When the C_{12} α-olefin is passed through the column of activated Al_2O_3 (acidic) catalyst at 300–350°C and the DDSA made from this ($\eta = 2370$ cps) gave mechanical properties (Table IV) similar to the one derived from lauryl alcohol dehydrated over Al_2O_3 at 300–350°C. The difference in properties for DDSA derived from C_{12} α-olefin and DDSA made after passing C_{12} α-olefin through Al_2O_3 catalyst at 300–350°C might be due to the migration double bond to the interior of the chain.

SUMMARY AND CONCLUSIONS

DDSA was synthesized by "ene synthesis" reaction of C_{12} olefin and maleic anhydride, and the mechanical properties of an epoxy resin cured with DDSA was evaluated. C_{12} olefin obtained by the dehydration of lauryl alcohol using Al_2O_3 (acidic) and C_{12} α-olefin obtained from petrochemical source were used for the study. ^{13}C-NMR indicated that dehydration of lauryl alcohol gives mixture of C_{12} olefins, and at low dehydration temperatures more concentration of 1-dodecene is formed, whereas, at higher temperatures, migration of the double bond to the interior of the chain occurs. The principal focus of this paper is that mechanical properties of epoxy–DDSA system is dependent on the position of the olefinic bond of C_{12} olefin from which DDSA is derived. This difference in mechanical properties can be attributed to the change in side chain length of DDSA.

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