

Preparation and Properties of Mahua Oil-Based Liquid Crystalline Pentalkyds

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ABSTRACT: Medium oil length Mahua oil-based pentalkyds are prepared with varying degree of excess hydroxyl. These alkyds are subsequently converted into liquid crystalline form by copolymerizing with *p*-hydroxy benzoic acid (*p*-HBA). Esterification is facilitated by dicyclohexyl carbodiimide (DCC). Graft efficiencies of copolymers are calculated and reported. Characterization of grafted alkyds is carried out using IR, DSC, and polarizing microscope techniques. A sharp melting point indicates liquid crystalline characteristic of *p*-HBA grafted alkyds. DSC and

polarizing microscope study results further substantiated the observation. Mechanical film properties of LC resins viz., hardness, impact resistance, and adhesion are also reported and compared with the amorphous counterparts. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 2648–2654, 2009

Key words: Mahua oil; alkyds; coatings; liquid-crystalline polymers (LCP)

INTRODUCTION

Liquid crystalline polymers (LCPs) have gained importance in the last few decades because of their unique properties of toughness and weatherability. These materials exhibit mechanical properties, which are significantly superior to those, exhibited by conventional amorphous resins. Structurally, these comprise of rigid rod-like materials containing predominantly symmetrical aromatic components known as mesogens. Generally, there are two types of LCPs, one with mesogens in the main chain and others with mesogens in the side chain. Behavior of polymer with mesogen in side chains is influenced by the nature of polymeric backbone and its proximity to the mesogenic group in the side chain.¹

Extensive studies have been carried out in the past on synthesis, rheological properties, and structure property relationship of side chain LCPs.^{2–4} Their applications as coatings have also been studied.^{5–7} The purpose of these studies is to enhance properties of LC coatings in terms of curing time, applicability, mechanical properties, etc. LC copolymers of terphthalic acid and dihydroxy diphenyl sulfone have been prepared.⁸ Bruggemen et al.⁹ synthesized high molecular weight liquid crystalline polyhydroxyethers containing functional hydroxyl

groups from an aromatic diol and the diglycidylether of an aromatic diol. Side chain LC acrylic copolymers were prepared using *p*-HBA as mesogenic group.¹⁰ Work has been reported on synthesis and characterization of LC polymers from *p*-HBA, PET, and third monomers like vanillic acid, *p*-aminobenzoic etc.¹¹ Preparation of LC alkyd resins has also been reported.¹²

This article describes the conversion of an amorphous pentalkyd based on Mahua oil to liquid crystalline (LC) resin. Medium oil length alkyd was prepared using fatty acids derived from Mahua oil. Other raw materials used were pentaerythritol and phthalic anhydride. Mahua oil is a nondrying and nonedible oil available abundantly. Its major components are myristic, palmitic stearic, arachidic, oleic, and linoleic acids.¹³ Its other uses are limited and therefore can be potentially exploited in preparation of resins. The alkyd was copolymerized with *p*-HBA to impart liquid crystallinity, and its characterization was carried out using techniques like IR, DSC, polarized microscopy, and its mechanical properties were determined and compared with its amorphous counterpart.

EXPERIMENTAL

Materials

Mahua oil was obtained from the local market. Phthalic anhydride (Impex Chemical Corp., India), pentaerythritol (Merck, India), *p*-hydroxy benzoic acid or *p*-HBA (Merck, India), *p*-toluene sulfonic

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acid or *p*-TSA (Merck, India), dicyclohexyl carbodiimide or DCC (Merck, India) were used as such. Pyridine (Merck, India) was distilled and dried with anhydrous Na₂SO₄ before use.

Isolation of fatty acids from Mahua oil

The oil was saponified by refluxing with alcoholic KOH. The excess alcohol was removed under reduced pressure. The saponified oil was acidified with HCl, washed, and recrystallized. Acid value was calculated for oil as well as the fatty acid, and other properties of Mahua oil were also determined like specific gravity, iodine value, and saponification value.¹³

Preparation of pentalkyds based on Mahua fatty acids

Pentalkyds were prepared in three different compositions (MPAL1, MPAL2, and MPAL3) by varying the percentage of excess hydroxyl as 15, 18, 22 and keeping the oil length constant to 60%. Fusion method was adopted for preparation.¹⁴ For preparing 200 g resin (MPAL1), 149.6 g MFA, 32.4 g phthalic anhydride, and 18 g pentaerythritol were heated to 180°C in a resin kettle fitted with a stirrer, condensing system, a charge hole, and pipes for passing inert gas over the charge, for 1 h. Water produced during the reaction was removed with the help of water separator attached to the condenser. The temperature was then raised to 270°C in an oil bath and maintained till the completion of the reaction. The reaction was followed by measuring acid value and viscosity at regular intervals till the acid value falls below 10. Other compositions MPAL2 and MPAL3 were prepared in a similar manner.

Characterization of resins

The characterization of the amorphous resins was done for properties like acid value, excess OH, viscosity, and specific gravity¹⁴. IR analysis of the polymer samples was carried out on IR spectrophotometer (Perkin-Elmer, Model 1430) at 4 cm⁻¹ resolution. A thin layer of polymer was spread over KBR plate and dried under an infrared lamp before analysis. Film characteristics and mechanical properties of the resins like drying time, scratch hardness, impact resistance, and adhesion were determined by application of resin in the form of film over mild steel panels with the help of a brush.¹⁵

Grafting *p*-HBA to Mahua oil-based pentalkyds

One of the Mahua oil-based pentalkyd (MPAL2) was converted to liquid crystalline form by grafting *p*-HBA, in hydroxy equivalent ratios (*p*-HBA : pental-

kyd) of 3 : 1 (LC1), 4 : 1 (LC2), and 5 : 1 (LC3). For example, preparation of LC1 is described. A mixture of 10 g (0.0046 equiv) of Mahua oil-based pentalkyd, 3.5 g (0.16 mol) of DCC, and 0.18 g of *p*-TSA (5 mol % of DCC) in 100 mL pyridine was stirred in a 500 mL Erlenmeyer flask with magnetic stirrer. About 1.906 g (0.0138 mol) of *p*-HBA in 50 mL pyridine was added drop by drop to the polymer solution while stirring at 25°C. The time of addition was varied as 4, 8, 12, and 16 h to study its effect on graft efficiency. By-products dicyclohexyl urea (DCU) and oligo *p*-HBA started forming within minutes of the reaction. The process was continued for 24 h after which by-products were removed by filtration, washed with methylene chloride, and dried to constant weight (A). The filtrate was concentrated on a rotary evaporator. The residue was dissolved in methylene chloride and filtered to separate a small amount of insoluble precipitate (B) which is then dried and weighed. Filtrate was then washed with 10% HCl and water. The solution was concentrated, and the residue was dissolved in acetone and kept at -5°C overnight. Traces of precipitate appeared, which were filtered, washed with methylene chloride, dried, and weighed (C). Filtrate was evaporated in a rotary evaporator when pale yellow colored resin was obtained. The yield was 10.2 g (85.6%). The weight of by-products (A+B+C) was 3.6 g. IR and DSC indicated that these are mixtures of DCU and oligo *p*-HBA. Assuming the recovery of DCU to be 100% (other materials absent), the yield of oligo *p*-HBA and the graft efficiency was calculated as described below. A similar procedure was followed to prepare LC2 and LC3 resins.

Estimating graft efficiency

The following formula was used to calculate percentage graft efficiency (GE) of copolymers¹⁶:

$$\begin{aligned} \text{\%Graft Efficiency (\%GE)} \\ = \frac{\text{mols of } p\text{-HBA grafted}}{\text{mols of } p\text{HBA incharge}} \times 100 \quad (1) \end{aligned}$$

weight of grafted *p*-HBA was calculated by subtracting the weight of solid by-products (ungrafted oligo *p*-HBA and DCU) from the weight of *p*-HBA monomer and DCC in charge. After converting to moles and dividing by moles of *p*-HBA in charge, graft efficiency was calculated.

Determination of properties of LC copolymers

Viscosity of the resins was determined using Ubbelohde viscometer.¹⁷ Solution of the copolymer was prepared in a concentration of 0.5 g/100 mL in 60

TABLE I
Properties of Mahua Oil

S.No.	Property	Observed value
1	Color	Light yellow
2	Specific gravity	0.86
3	Acid value	18.5
4	Iodine value	74.1
5	Saponification value	140.2

: 40 ratio of trichloroacetic acid and methylene chloride. Efflux time was recorded for different polymer compositions at 25°C. For IR analysis, LC resins were made into thin pellets with KBr and analyzed on Perkin–Elmer (model 1430) spectrophotometer. Melting points of the resins were determined by capillary method in a melting point apparatus and were further confirmed by differential scanning calorimeter (DSC). A DSC (Dupont 9900) was used to study the thermal behavior of polymer samples at a heating rate of 20°C/min in a nitrogen flow of 50 mL/min. Morphological studies of the LC copolymers were carried out using LEICA MPS 30 photo-automat polarizing microscope with heating stage. The resin samples were subjected to heating slightly above the temperature corresponding to the endotherms of DSC and consecutive cooling. Pictures were taken at different magnifications. To determine the coating properties, resin was applied on mild steel panels as 20- μ thick film.¹⁸ Mechanical film properties such as scratch hardness, impact resist-

TABLE II
Composition of Mahua-Based Amorphous Pentalkyds

S.No.	Raw materials	% by weight		
		MPAL1	MPAL2	MPAL3
1	Mahua fatty acid	74.8	67.5	60.0
2	Phthalic anhydride	16.2	18.5	22.5
3	Pentaerythritol	9.0	14.0	17.5

ance, and adhesion were determined¹⁵ for amorphous resins, and the results were compared.

RESULTS AND DISCUSSIONS

Properties of Mahua oil and its pentalkyds

Table I indicates the properties of Mahua oil, which is a light yellow colored oil having a specific gravity of 0.86 and a saponification value of 140.2, significant in calculation of KOH required for its saponification during conversion to fatty acids. Its acid value is 18.5, which rises to 193.98 when converted to its fatty acids. It has a low iodine value of 74.1 and is therefore nondrying in nature.¹⁹

Table II gives the compositions of pentalkyds prepared by varying excess hydroxyl percentage. Chemical reactions during preparation of pentalkyds are shown in Figure 1. The properties of amorphous resins are mentioned in Table III. An increase in average functionality as well as the intrinsic viscosity of

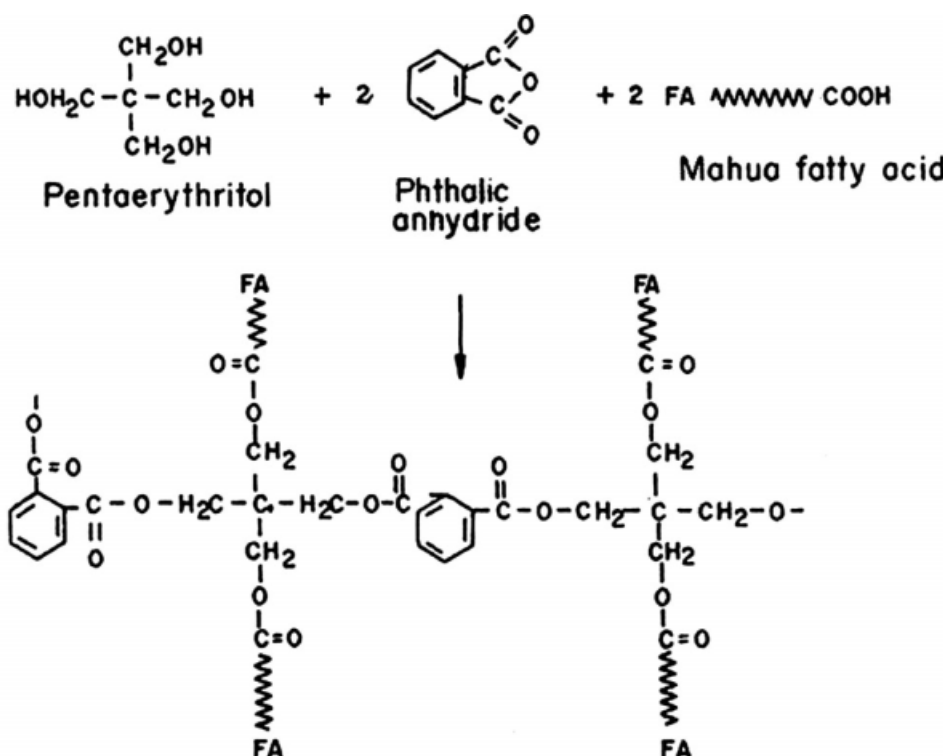


Figure 1 Stepwise reaction for the preparation of pentalkyds.

TABLE III
Properties of Amorphous Mahua-Based Pentalkyds

S.No.	Property	Observed values		
		MPAL1	MPAL2	MPAL3
1	Average functionality	1.98	1.92	1.83
2	Acid value	1.8	2.1	2.8
3	Excess hydroxyl (%)	15	18	22
4	Intrinsic viscosity (η)	0.62	0.50	0.45
5	Specific gravity	0.96	0.98	0.94

the resins was observed with decrease in excess hydroxyl percentage. A reverse trend was observed for acid value. Scratch hardness of the resins varied inversely with hydroxyl percentage (Table IV), that is, an increase in excess hydroxyl resulted in decrease in scratch hardness of the resin films. Impact resistance improved with increase in excess hydroxyl that can be attributed to an increase in flexibility of the resin films.

Grafting efficiency of resins

Figure 2 gives chemical reactions for grafting of *p*-HBA to alkyds. Maximum graft efficiency (95.2%) was obtained for LC pentalkyd prepared with 3 : 1 ratio of *p*-HBA to alkyd (LC1). The graft efficiency

TABLE IV
Mechanical Properties of Amorphous Pentalkyds

S.No.	Property	Observed values			
		MPAL1	MPAL2	MPAL3	
1	Scratch hardness (kgs)	1.52	1.47	1.41	
2	Impact resistance (inches)	Direct	15	16	16
		Indirect	18	19	20
3	Adhesion (kg/cm ²)	35	40	40	

was found to decrease with the increase in equivalents of *p*-HBA added (Table V). The reason may be attributed to the comparative rates of reactions for esterification of alkyd and homo polymerization of *p*-HBA to form oligo *p*-HBA. It has been observed that if homo polymerization occurs at a faster rate than grafting of *p*-HBA to alkyd, the graft efficiency is low and *vice versa*¹⁶. It was also seen that on increasing the time of addition of *p*-HBA to alkyd, the graft efficiency increases and becomes constant after 12 h as illustrated in Figure 3. Increasing the time of addition of *p*-HBA provides less opportunity for self-polymerization, and therefore, it is readily available for grafting. This study reveals that if the time of addition of *p*-HBA is maintained between 12 and 16 h, a ratio of 3 : 1 of *p*-HBA to alkyd gives highest graft efficiency.

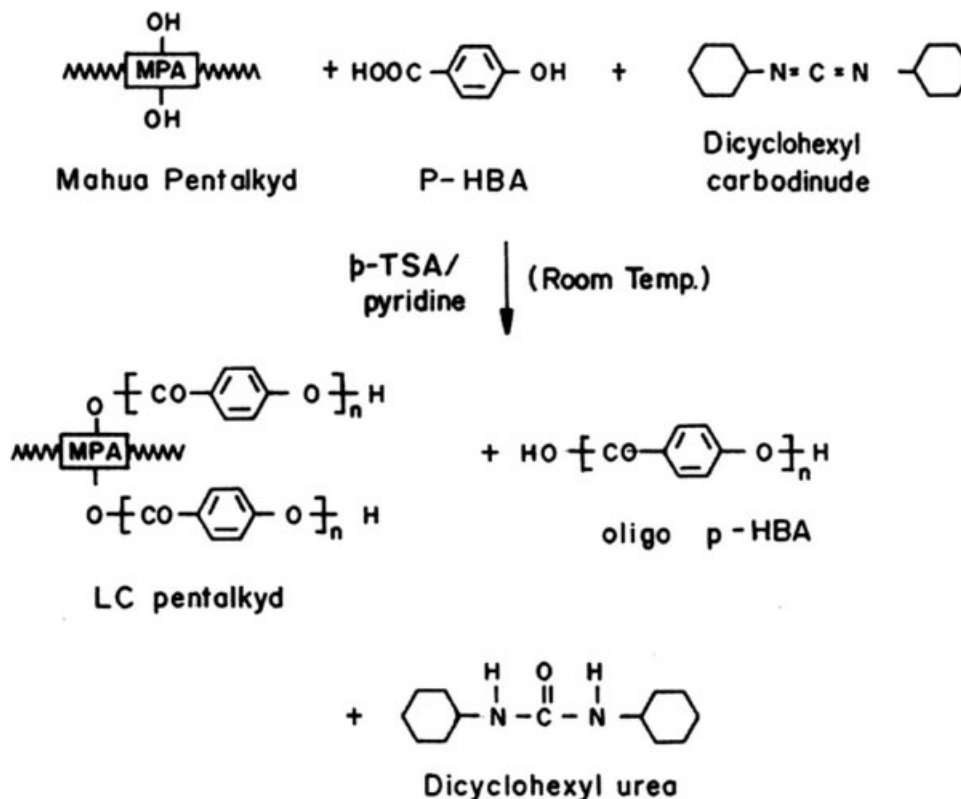


Figure 2 Chemical reactions showing grafting of *p*-HBA to pentalkyds.

TABLE V
Properties of Liquid Crystalline Pentalkyds

S.No.	Property	Observed values		
		LC1	LC2	LC3
1	Graft Efficiency (%)	95.2	89.6	72.57
2	Intrinsic viscosity (η)	0.31	0.35	0.38
3	M.P. ($^{\circ}\text{C}$) by capillary method	198	219	225
4	Tg ($^{\circ}\text{C}$) by DSC	6	7	10
5	Tm ($^{\circ}\text{C}$) by DSC	195	210	220

Comparative IR analysis of amorphous and crystalline resins

The infra red spectra of Mahua oil, Mahua fatty acid, Mahua alkyd (pentaerythritol) (MPAL), and *p*-HBA grafted MPAL are illustrated in Figure 4. A comparison of these spectra indicates the occurrence of grafting in *p*-HBA grafted MPAL as spectra shows distinctive peaks at 1510 and 1610 cm^{-1} assigned to C=C stretching of para disubstituted aromatic ring.²⁰

Properties of LC alkyd resins

The LC pentalkyds had poor solubility in many organic solvents like diethyl ether, DMSO (dimethyl sulfoxide), were partly soluble in DMF dimethyl formamide), and were sufficiently soluble in 60 : 40 mixture of trichloroacetic acid and methylene chloride. The poor solubility could be attributed to the presence of mesogens and also to high MPs of these polymers.²¹ Their solubility is indicative of reaction of *p*-HBA with amorphous alkyds to form ternary copolyesters because *p*-HBA as such is insoluble in these organic solvents.²² The viscosity of resins showed an increase with increasing *p*-HBA content (Table V). On comparing the viscosity of LC resins with their amorphous counterpart, LC resins showed a lower viscosity (indicative of low molecular weight

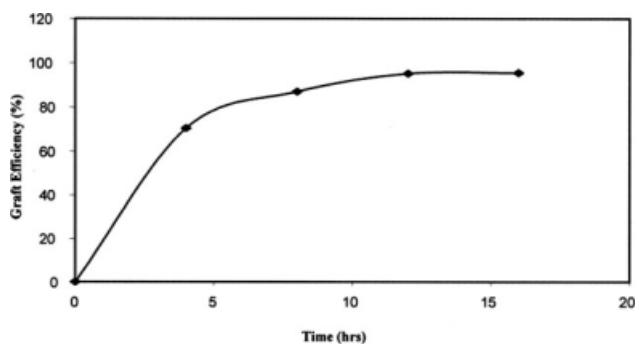


Figure 3 Variation of graft efficiency with time of addition of *p*-HBA.

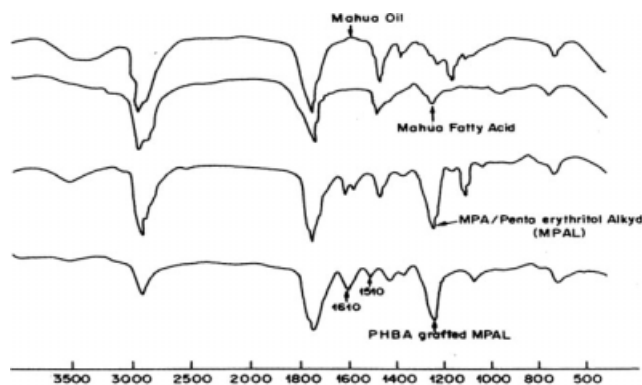


Figure 4 Comparative IR graphs for amorphous and LC pentalkyds.

resin), which in fact is desirable for coating applications. Generally, polymers with high molecular weights have high solution viscosities and offer better film properties. As more solvent is needed to bring down their undesirably high viscosity²³ for coating applications, the high molecular weight polymer coatings are more polluting.

Thermal properties of LC resins

As seen in the DSC plots of Figure 5, glass transition temperature (Tg) of the LC alkyds was higher than the amorphous ones. The presence of rigid segments of mesogens (*p*-HBA) in LC resins, which restricts the segmental motion of the main chains,²⁴ explains the higher Tg of LC alkyds.

The crystalline nature of alkyds was evident by their sharp melting points (MPs), obtained by capillary method, which was absent in case of amorphous resins (Table V). It was further investigated to ascertain whether the MP observed by capillary method is melting or clearing point. Therefore, the crystallinity in LC resins was subjected to

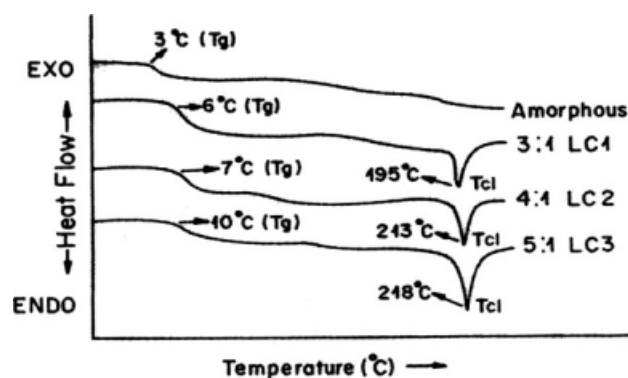


Figure 5 DSC thermograms of amorphous and LC pentalkyds.

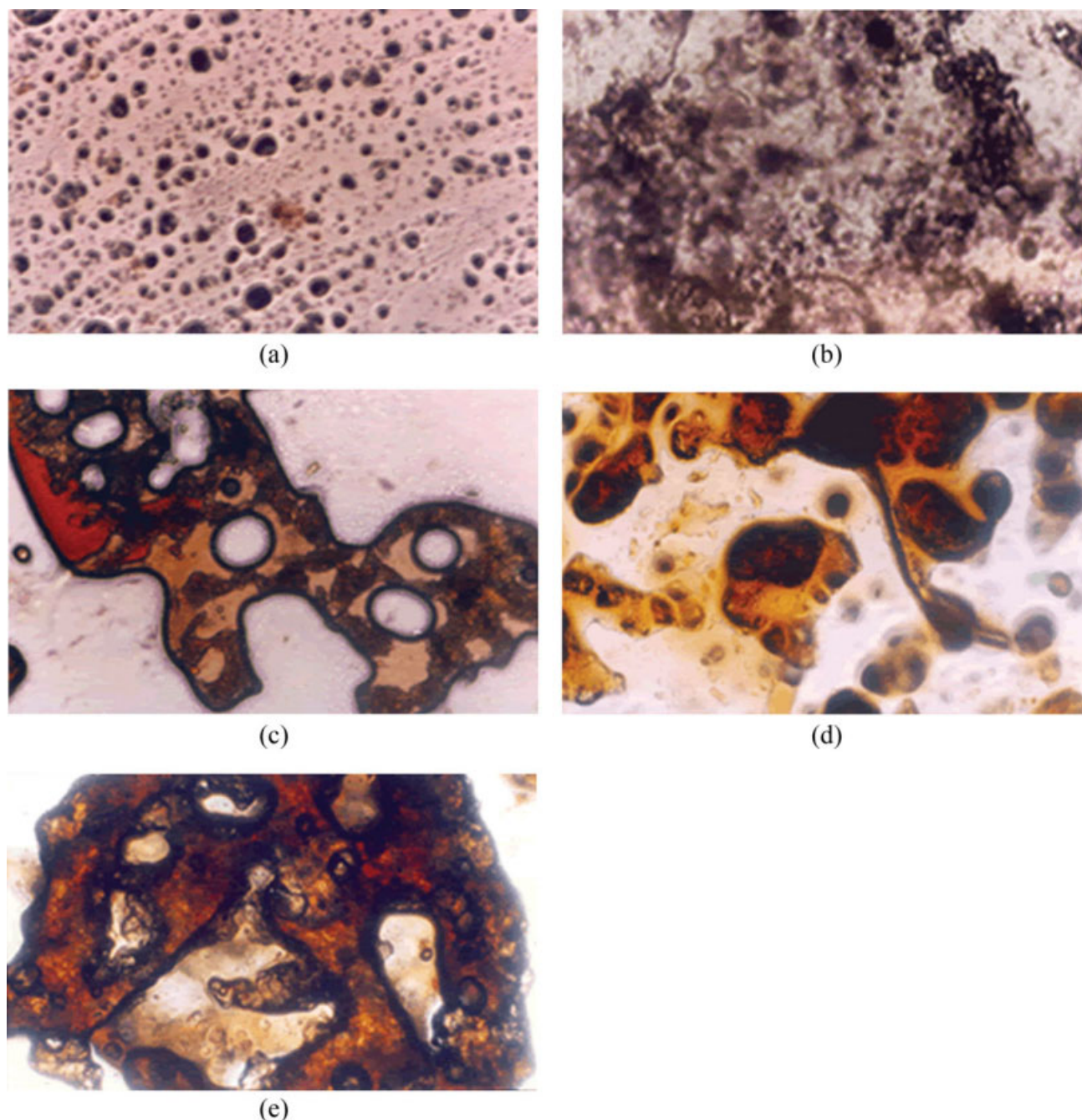


Figure 6 (a) Microstructure of LC pentalkyd at room temperature ($\times 10$). (b) Microstructure of LC pentalkyd at room temperature ($\times 25$). (c) Phase transition in LC pentalkyd (LC1) at 195°C . (d) Phase transition in LC pentalkyd (LC2) at 210°C . (e) Phase transition in LC pentalkyd (LC3) at 220°C . [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

investigation by DSC, as shown in Figure 5. Sharp endothermic peaks were visible in the temperature range of 190 to 210°C , which could be attributed to either melting temperature (T_m) or clearing temperature (T_{cl}). The diffused diffraction peak at $2\theta = 20^{\circ}$ observed in X-ray diffraction pattern of the LC resins indicates²⁵ presence of smectic phase and the endotherms of DSC represent clearing point (T_{cl}),

that is, transition from mesophase to isotropic phase. The endothermic peak was absent in the DSC scan of amorphous resin. Appearance of only one endothermic peak in DSC of LC resins suggests that transition from crystalline to mesophase is absent in these polymers. Therefore, the morphology of these resins below their T_g may relate to frozen liquid crystalline forms.¹²

TABLE VI
Comparative Mechanical Properties of Amorphous and LC Pentalkyds

S.No.	Property	Observed values		
		LC1	LC2	LC3
1	Scratch hardness (kgs)	1.72	1.78	1.82
2	Impact resistance (inches)			
	Direct	13	12	12
	Indirect	15	13	14
3	Adhesion (kg/cm ²)	45	45	40

Morphological study of LC alkyds

A polarizing microscope with a heating stage was used to study the morphological transition in the LC alkyds with temperature. Figure 6(a,b) depicts the polarized micrograph of LC alkyd at room temperature showing fine, grainy, or batonnet-like structure. The texture of the resin was observed to be smectic.^{25,26} When heated to around 190–210°C, the LC resins showed transition from mesophases to isotropic phases [Fig. 6(c–e)]. This temperature corresponds to the endotherms of the DSC scans. On cooling, the smectic structure of the resins was restored.²⁷

Comparative mechanical properties of amorphous alkyds with LC forms

An increase in the equivalents of *p*-HBA content results in an increase in hardness, which may be due to the enforcement effect of rigid mesogenic group and also to their ability to get oriented.²⁸ A decrease in flexibility of LC resins was observed. As flexibility directly relates to impact resistance,²⁹ the decrease in flexibility with increase in *p*-HBA content was expected. Scratch hardness of the LC resins was superior to the amorphous ones (Table VI). The reason may be attributed to the grafting of alkyds by rigid structures of mesogenic groups. A reverse trend was observed for impact resistance. With an increase in *p*-HBA content, the resistance to impact was found to decrease. The increase in glass transition also implied increased hardness and reduced elasticity.

Adhesion property of the amorphous and LC polymers had comparative values (Table V). These observations indicate that introduction of mesogens results in an improvement in toughness and hardness property of the resins for application as coatings.

CONCLUSIONS

Pentalkyds based on Mahua oil were successfully converted from amorphous to liquid crystalline

state, using *p*-HBA as mesogenic groups. Maximum graft efficiency of 95.2% was obtained using equivalent ratio of 3 : 1 of *p*-HBA to alkyd. The drying time of the resins was improved. The liquid crystalline property of the resin was confirmed by DSC and polarized microscopy. The endotherms of DSC corresponded to the transition temperature of mesophase to isotropic phase under crossed polarizers. An improvement was observed in the scratch hardness resistance of the LC resins. Comparatively, the LC resins based on Mahua oil were found to possess better drying time, viscosity, and hardness than their amorphous counterparts.

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