Preparation and Properties of Liquid Crystalline Alkyd Resin with *para*-Hydroxybenzoic Acid Mesogenic Side Chain

WEN-YEN CHIANG* and CHUN-SHYURNG YAN

Department of Chemical Engineering, Tatung Institute of Technology, 40 Chungshan North Road, 3rd Sec., Taipei 10451, Taiwan, Republic of China

SYNOPSIS

Liquid crystalline (LC) alkyd resins with mesogenic side chains are prepared with the following three methods: (a) grafting *p*-hydroxybenzoic acid (PHBA) to hydroxy-terminated alkyd resin, (b) grafting PHBA to carboxyl-terminated alkyd resin, and (c) grafting PHBA to an excess succinic anhydride-modified alkyd resin. Dicyclohexylcarbodiimide (DCC) is employed to react with formed water in promoting esterification of PHBA with alkyd at room temperature. Pyridine is used as a solvent, and the catalytic amounts of *p*-toluene-sulfonic acid (*p*-TSA) is added to suppress side reaction and to promote esterification. Grafting efficiency (% GE) is estimated to range from 70 to 95%. The character of liquid crystallinity is imparted only when at least two or more aromatic units of PHBA are connected to form the rodlike mesogenic side chain. At present, we have found that LC alkyd resins have the following merits: the polymer solution viscosity is reduced; the coating's dry-to-touch time is reduced; and the coating film is both hardened and toughened and has excellent resistance to water and acid. © 1992 John Wiley & Sons, Inc.

INTRODUCTION

In general, there are two methods, the fatty acid method and the oil method, to synthesize alkyd resins.[1-4] The former is more often used than the latter in alkyd manufacture because neither alcoholysis nor acidolysis is needed. In fact, the former enjoys a number of other advantages in alkyd processing.[2] In this study, we substitute pentaerythritol for glycol because prepared alkyd derivatives are characterized by having a higher degree of polymerization, faster drying, and superior water resistance. Ethylene glycol is added to avoid gelation. Two techniques,[4] the fusion (N₂ inlet) and the azeotropic (adding xylene) process, are used to remove water (byproduct).

As liquid crystalline (LC) polymers have been widely studied,[5-8] their application in plastics and fibers are well known. Material such as Kevlar (DuPont), Xydar (Dartco), and Vectra (Hoechst Celanese) utilize the character of LC regions to en-hance physical properties. In general, there are two types of thermotropic polymers: main-chain liquid crystalline polymers[9-11] (M.C.LCPs) and side-chain liquid crystalline polymers[12-16] (S.C.LCPs). In M.C.LCPs, the mesogenic groups form the backbone of the molecular chains, whereas in S.C.LCPs, the mesogenic units link to a polymer backbone as pendants in the side chain. The polymer with mesogenic side chains exhibits LC behavior, which is influenced by the nature of the polymeric backbone and its neighbor to the mesogenic group in the side chain. However, the polymeric backbone must form an LC phase, and in that condition, the mesogenic group in the side chain could exhibit the stable regular arrangement. In most cases, the chemical constitutions of mesogenic units in LCPs usually have at least two linear-substituted cyclic units that may or may not be linked by a short rigid central bridging group. However, the potential of LC materials in coatings appears to have been neglected.

In this study, three methods for synthesizing LC alkyd resins are presented (listed in Scheme I). The esterification method[17] used for grafting is well known and has recently been used in polymer synthesis.[18-20] The method involves the reaction of car-
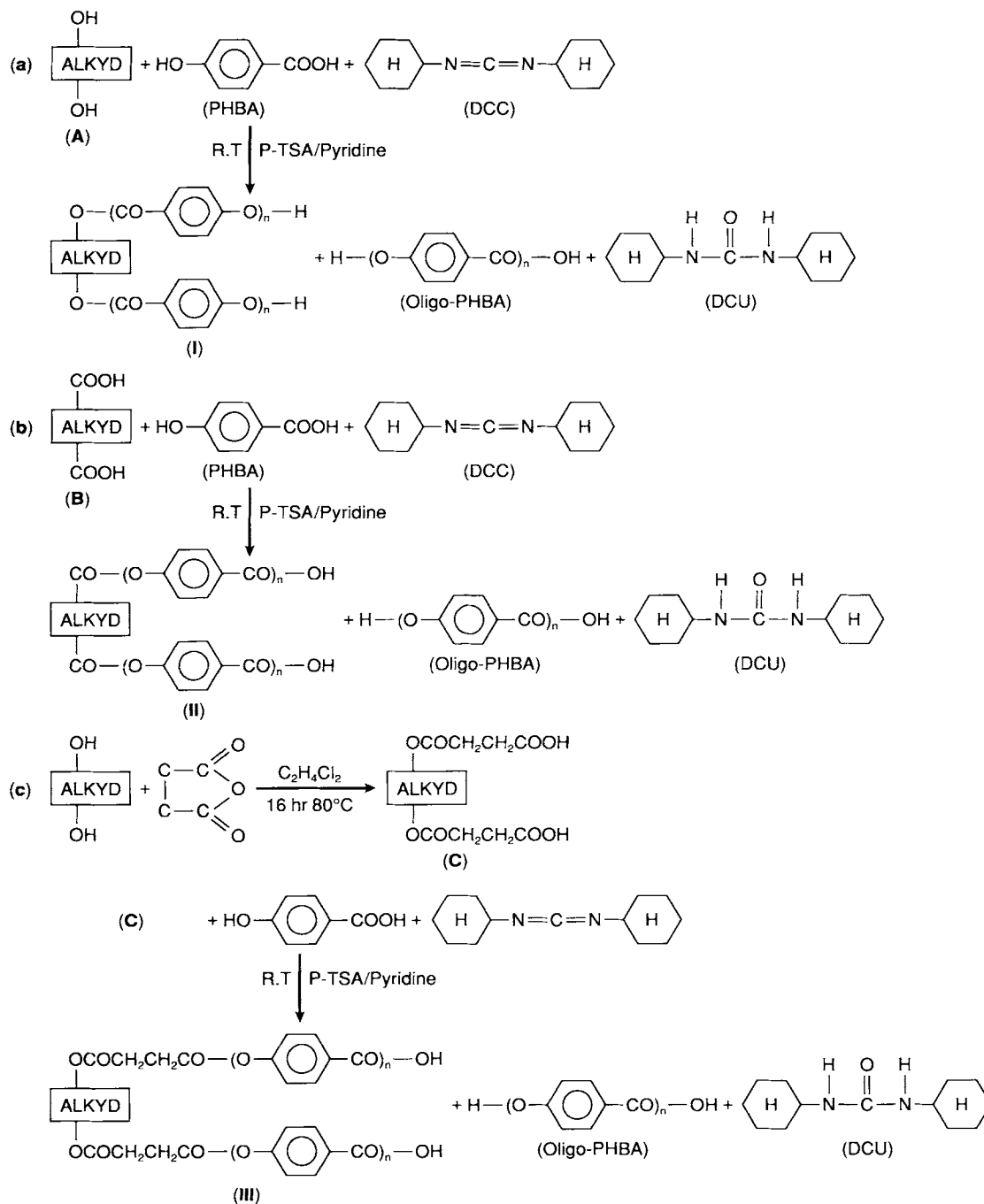
Scheme I LC alkyds with mesogen side chains are prepared by three methods.

boxylic acid and alcohols with dicyclohexylcarbo-diimide (DCC) in the presence of pyridine. DCC participates in esterformation and takes up water, forming dicyclohexyl urea (DCU). Side reactions may occur under certain conditions, but they can be suppressed by using pyridine as a solvent and by adding a catalytic amount of p-toulenesulfonic acid.[19,20]

EXPERIMENTAL

Materials

Pyridine (Aldrich) was distilled and dried with anhydrous Na_2SO_4. Phthalic anhydride (PA), ethylene glycol (EG), pentaerythritol (PE), terephthalic acid (TPA), p-hydroxybenzoic acid (PHBA), p-tolu-

enesuldonic acid (p-TSA), dicyclohexylcarbodiimide (DCC), succinic anhydride (SA), and xylene were of extrapure grade and were used without further purification. Linseed fatty acid was made up of 17% linoleic acid and 51% linolenic acid, 22% oleic acid, 6% palmitic acid, and 4% stearic acid.

Syntheses

(1) Preparation of Hydroxy-Terminated Alkyd Resins

Alkyds were prepared according to the following procedure as shown in Table I, OH-1: 59%-oil length, 18% OH-terminated alkyd resin prepared from linseed fatty acid (60 g, 0.214 mol), PA (40 g, 0.214 mol), EG (9 g, 0.145 mol), PE (17.9 g, 0.132 mol), and xylene (7 g, 5 wt % based on all weights) were placed in a 500 mL four-neck round-bottom flask equipped with a Dean–Stark trap, a cold-water condenser, a heating mantle, a thermometer, a nitrogen inlet, and a mechanical stirrer. The mixture was heated under nitrogen flow (approximately 5 mL/min) to 170°C for about 1 h and then was heated to 220°C for 5–8 h. The temperature was maintained, xylene was refluxed, and water was removed until an acid number lower than 5 was attained. The solvent was evaporated in vacuo at 80°C and the obtained resin (A) was stored under nitrogen. The OH value was 61.7 determined by the acetic anhydride/pyridine method.[21]

(2) Preparation of Carboxyl-Terminated Alkyd Resins

Synthese of HOOC-terminated alkyd resins were the same as method (1). A solution of 52% oil length, 15% OH-terminated alkyd resin was prepared from linseed fatty acid (90 g, 0.32 mol), PA (63 g, 0.43 mol), EG (15.5 g, 0.5 mol), and PE (22.67 g, 0.51 mol). The reaction temperature was maintained at 220°C until the acid number of the reaction mixture reached a constant. The acid number of obtained resin (B) was 54.7 determined by titrating alkyd with alcoholic KOH.

(3) Preparation of Succinic Anhydride-Modified Alkyd Resin

Hydroxy-terminated alkyd resin (A) was heated with SA (1 mol per equiv OH group) in ethylene

Table I   Conventional Alkyds Formulated at Fixed 53% Oil Length and Variable Excess OH Level (Nos. in Parentheses in Moles; Other Nos. in Grams)

	OH-1	OH-2	OH-3	OH-4	OH-5
Linseed	60.0	64.0	58.7	65.0	65.9
fatty acid	(0.214)	(0.229)	(0.210)	(0.232)	(0.235)
PA	40.0	40.0	37.0	40.0	40.0
	(0.270)	(0.270)	(0.264)	(0.270)	(0.270)
EG	9.0	9.6	8.7	10.4	10.7
	(0.145)	(0.155)	(0.140)	(0.168)	(0.173)
PE	17.9	19.3	19.0	20.8	21.4
	(0.132)	(0.142)	(0.140)	(0.153)	(0.157)
Excess OH %[a]	8	14	18	23	26
Fav[b]	1.98	1.93	1.92	1.88	1.86
Acid number	4.1	4.2	3.2	3.9	4.0
Conversion (%)	98.3	98.5	99.2	98.9	99.0
M_n	3430	3210	2920	2640	2410
Viscosity (poise)	3.45	2.85	2.40	2.00	1.75
Dry time (days)	1	1.5	2	2	2.5
Hardness	H	HB	HB	HB	6B
Adhesion (%)	100	100	100	100	100
Reverse impact (500 g cm)	30	20	10	10	10
Resistance to water	Ex[c]	Ex	Ex	Ex	Good
Resistance to HCl	Ex	Ex	Good	Good	Good
Resistance to NaOH	Good	Fair	Fair	Poor	Poor

[a] Excess OH % = (NC∗2 + ND∗4) − (NA∗1 + NB∗2)/(NA∗1 + NB∗2). NA: The mole of the fatty acid; NB; the mole of the phthalic anhydride; NC: the mole of the ethylene glycol; ND: the mole of the pentaerythritol.

[b] Fav = 2(NA∗1 + NB∗2)/NA + NB + NC + ND.

[c] Ex, no spotting; good, slight spotting; fair, spot/soften; poor, dissolve film.

dichloride at 80°C for 16 h. The solvent was evaporated *in vacuo* and resin (C) obtained with acid number of 71.2.

(4) Grafting PHBA to Hydroxy-Terminated Alkyd Resin

Grafting PHBA to OH-terminated alkyd resins is outlined in Scheme I, method (a). The grafting reaction used hydroxy equivalent ratios of PHBA monomer to alkyd resins of 1-5. For example, the reaction with a ratio of 4 is described: A solution of 10.0 g (0.0107 equiv) of alkyd (A), 9.008 g (0.0437 mol, 0.2% excess) of solid DCC, and 0.45 g (5 mol % based on DCC) of p-TSA in 100 mL of pyridine was stirred before 5.912 g (0.0428 mol) of PHBA was added slowly to dissolved in 50 mL of pyridine by using a pressure-equalizing dropping at 25°C for 24 h. A precipate (identified ás DCU by mp and IR) began forming in about 1 min. After 24 h, the by-product (DCU and oligo-PHBA) was filtered, and the solution was concentrated. Then, 50 mL of CH_2Cl_2 was added to the concentrate filtrate, which was later washed with three 200 mL portions of 1 M HCl and with water. The CH_2Cl_2 solution was dried by $MgSO_4$, then filtered and evaporated *in vacuo*. The resinous residue was dissolved in a pentane and

ethyl acetate-mixed solvent. The solution was cooled to −5°C overnight and filtered to remove traces of precipitated DCU. Filtrate was evaporated *in vacuo* using a rotary evaporator to yield 13.5 g (85.0% yield) of light yellow resin (I).

(5) Grafting PHBA to Carboxyl-Terminated Alkyd Resin

Grafting PHBA to HOOC-terminated alkyd resins (B) is outlined in Scheme I, method (b). The grafting reaction used the ratio of carboxyl (B) and (C) equivalent to PHBA and was prepared in the same way as (4). The resin (II) was obtained in the yield of 88.2%, and (III), in the yield of 87.5%.

Measurement of Various Properties

Acid number, hydroxy value, IR spectra, resin viscosity, molecular weight from GPC, thermal properties (DSC, TGA), and coating properties were measured as described in Ref. 21.

Visual observation of stir-opalescence of the resin was made as follows: A small amount of resin was heated and placed between two cover glasses on a hot plate that was moved back and forth until stir-opalescence was observed. The texture of the phase

Table II Conventional Alkyds Formulated at Variable Oil Length and a Fixed Excess OH Level of 18% (Nos. in Parentheses in Moles; Other Nos. in Grams)

|	OL-59	OL-53	OL-50	OL-48	OL-43
Linseed	59.9	58.7	96.0	57.4	53.4
fatty acid	(0.214)	(0.210)	(0.343)	(0.205)	(0.191)
PA	29.6	37.0	66.2	44.4	50.8
	(0.200)	(0.250)	(0.447)	(0.300)	(0.343)
EG	7.4	8.7	20.0	10.1	10.7
	(0.119)	(0.140)	(0.323)	(0.163)	(0.173)
PE	16.2	19.0	28.0	21.6	23.4
	(0.119)	(0.140)	(0.213)	(0.159)	(0.172)
Oil length (%)	59	53	50	48	43
Fav[a]	1.88	1.92	1.93	1.96	2.00
Acid number	3.45	4.22	3.17	3.82	3.40
Conversion (%)	99.4	99.2	99.2	98.9	99.0
M_n	2740	2920	3140	3360	3580
Viscosity (poise)	1.71	2.40	2.95	3.00	3.65
Dry time (day)	1.5	2	2	2.5	2.5
Hardness	HB	HB	H	H	H
Adhesion (%)	100	100	100	100	100
Reverse impact (500 g cm)	25	20	10	10	10
Resistance to water	Ex[b]	Ex	Ex	Ex	Ex
Resistance to HCl	Good	Ex	Ex	Ex	Ex
Resistance to NaOH	Poor	Fair	Fair	Fair	Fair

[a] See footnote a to Table I.
[b] See footnote b to Table I.
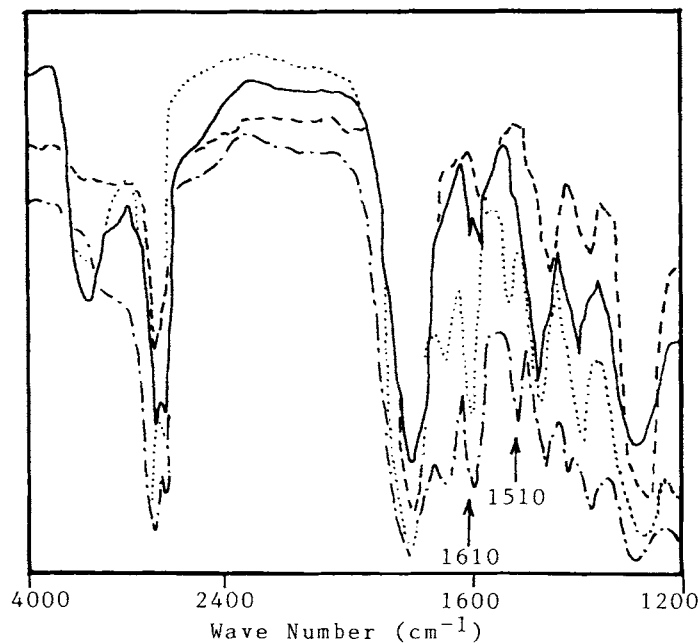
Figure 1   IR spectrum of synthesized alkyds and LC alkyds: (——) method (a) alkyd
(A); (· · · · ·) LC alkyd Id; (- - - - -) method (b) alkyd (B); (- · - · -) LC alkyd IId.
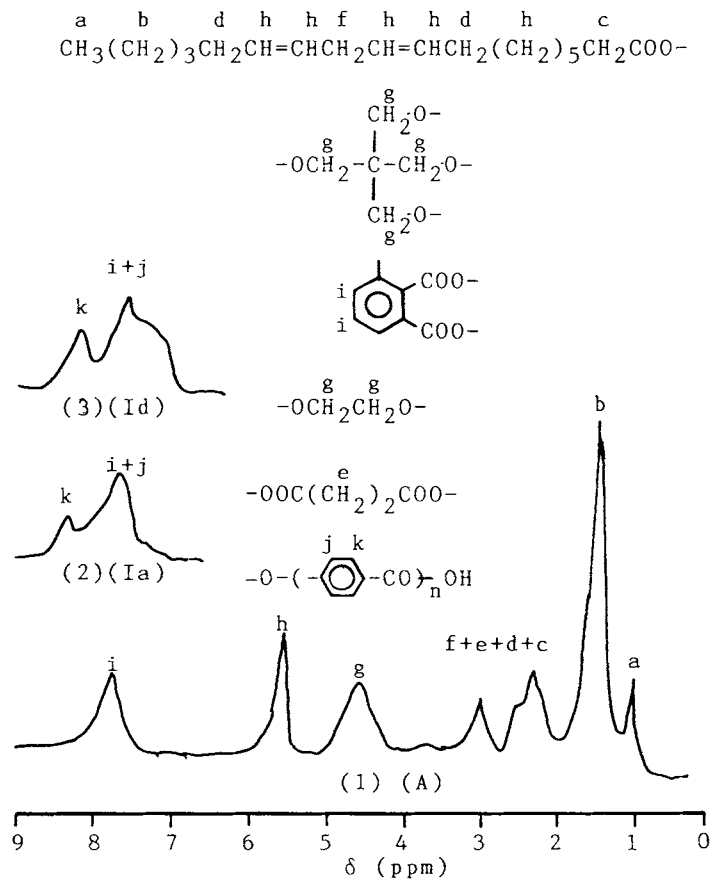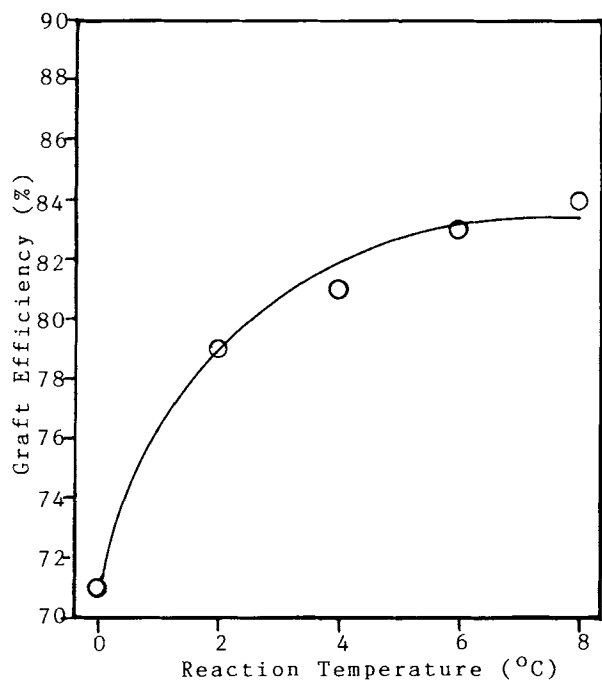

Figure 2 ^{1}H-NMR spectra of (1) alkyd (A), (2) PHBA-grafted LC alkyd (Ia), and (3)
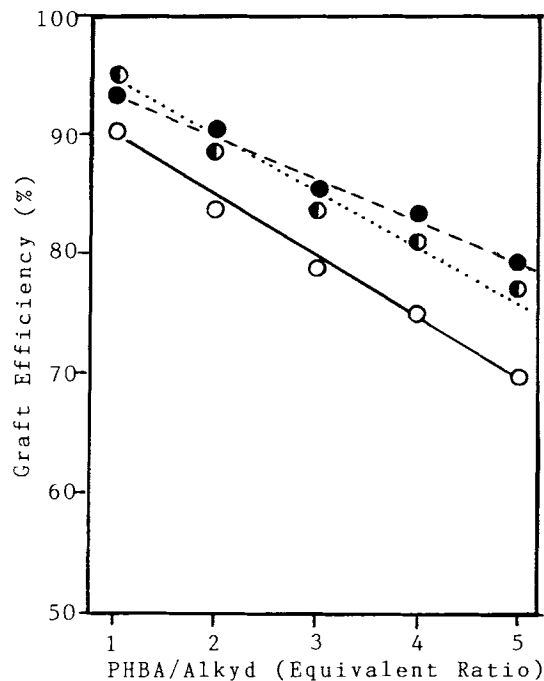PHBA-grafted LC alkyd (Id).
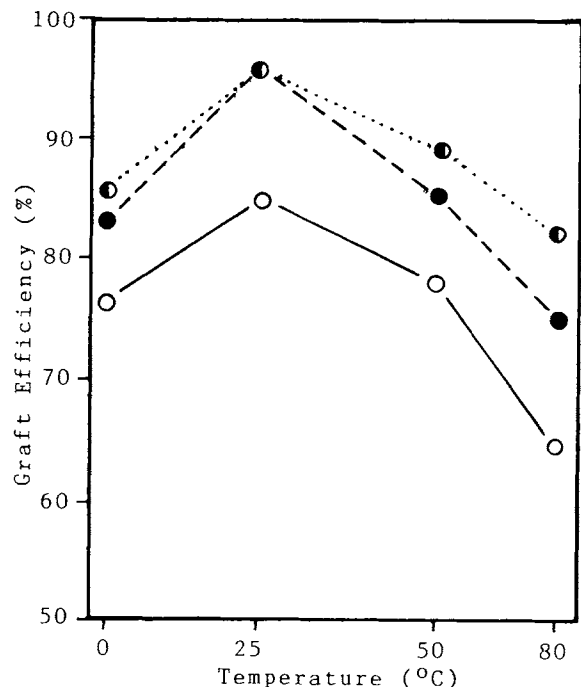
Figure 3 The effect of reaction temperature on graft efficiency: (— O —) method (a); (--●--) method (b); (· · ·◐· · ·) method (c).

was observed between cover slips with a polarizing microscope (Leitz Laborlux 12 poc) equipped with a heating stage (Meter FP8000).

Figure 4 Effect of the time of adding PHBA monomer to alkyd resin on graft efficiency.
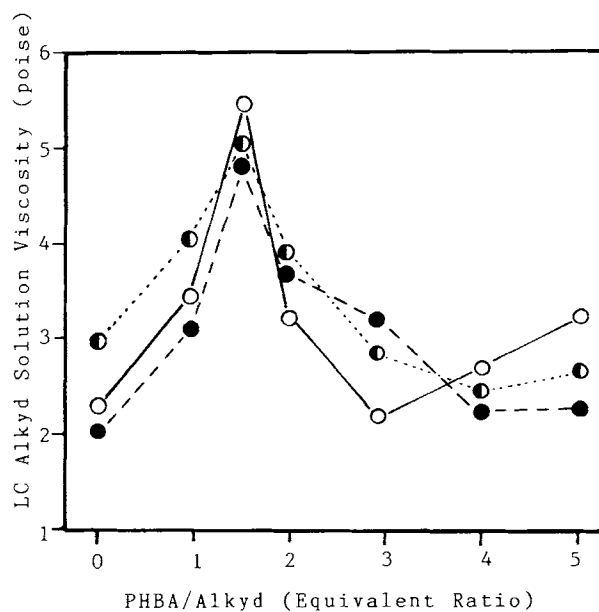

Figure 5 Effect of the equivalent ratio of PHBA monomer to alkyds on graft efficiency: (— O —) method (a); (--●--) method (b); (· · ·◐· · ·) method (c).

RESULTS AND DISCUSSION

Properties of Alkyd Resins

Alkyds were formulated at fixed 53% oil lengths and variable excess OH levels. Table I shows that the


Figure 6 Solution viscosity vs. PHBA equivalent ratios on alkyds: (— O —) method (a); (--●--) method (b); (· · ·◐· · ·) method (c).

**Table III   Characterization of the Synthesized LC Alkyds**

	PHBA/Alkyd (Ratio)	M_n	Viscosity (Poise)	Yield (%)	T_g (°C)	T_i (°C)	Appearance	Stir-Opalescence
A	0	2920	2.4	—	−14	—	Amorphous	—
Ia	1.0	3080	3.5	92	−1	—	Amorphous	—
Ib	1.5	3150	5.4	88	−6	—	Amorphous	—
Ic	2.0	3220	3.2	88	0	238	Smectic	+
Id	3.0	3420	2.2	85	4	242	Smectic	+
Ie	4.0	3610	2.5	85	6	246	Smectic	+
If	5.0	3800	3.2	82	10	250	Smectic	+
A	0	2450	2.0	—	−16	—	Amorphous	—
IIa	1.0	2630	3.1	95	−10	—	Amorphous	—
IIb	1.5	2710	4.8	92	−5	—	Amorphous	—
IIc	2.0	2780	3.6	90	0	222	Smectic	+
IId	3.0	2980	3.2	90	6	236	Smectic	+
IIe	4.0	3160	2.4	88	10	242	Smectic	+
IIf	5.0	3340	2.4	85	16	248	Smectic	+
C	0	3070	2.9	—	−13	—	Amorphous	—
IIIa	1.0	3250	4.0	94	−10	—	Amorphous	—
IIIb	1.5	3340	5.0	90	−8	—	Amorphous	—
IIIc	2.0	3400	3.8	88	−6	182	Smectic	+
IIId	3.0	3600	2.8	89	−3	186	Smectic	+
IIIe	4.0	3760	2.4	87	0	191	Smectic	+
IIIf	5.0	3960	2.6	85	0	193	Smectic	+

lower OH % has the higher average functionality (fav) value and molecular weight (M_n). As expected, viscosity increased with the increase of M_n. The drying time shortened with the decrease of OH % and with the increase of M_n. These alkyds displayed

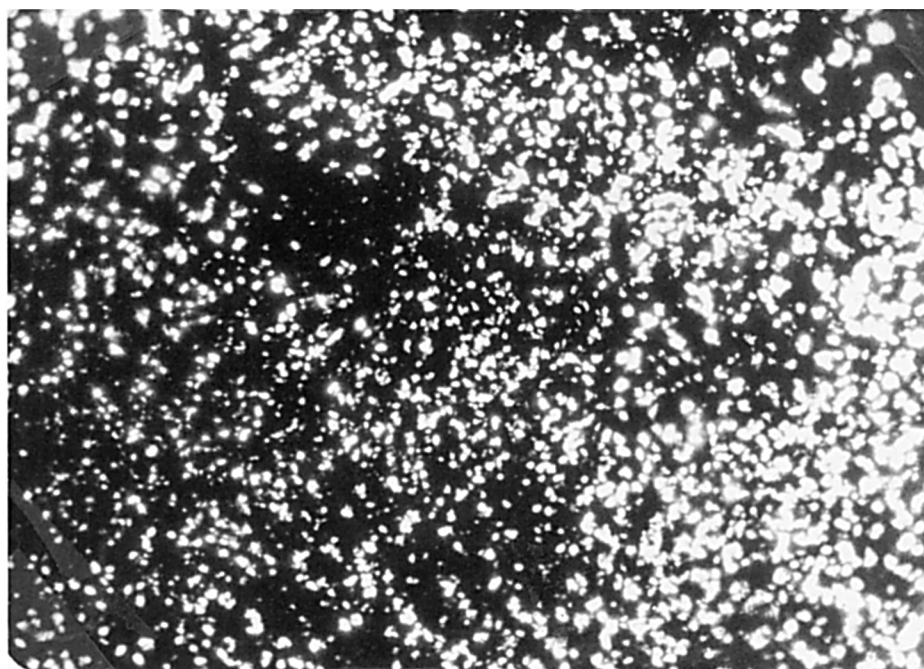good water and acid resistance and excellent adhesion. Generally, alkyds have poor base resistance and, consequently, the high OH % shows inferiority of NaOH resistance to the low OH %. Hardness and
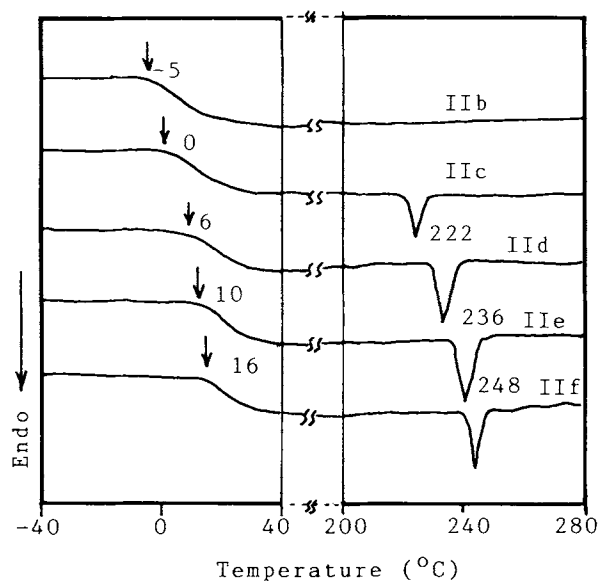
Figure 7   A typical DSC thermogram of alkyd (B) and LC alkyd IIb–IIf.
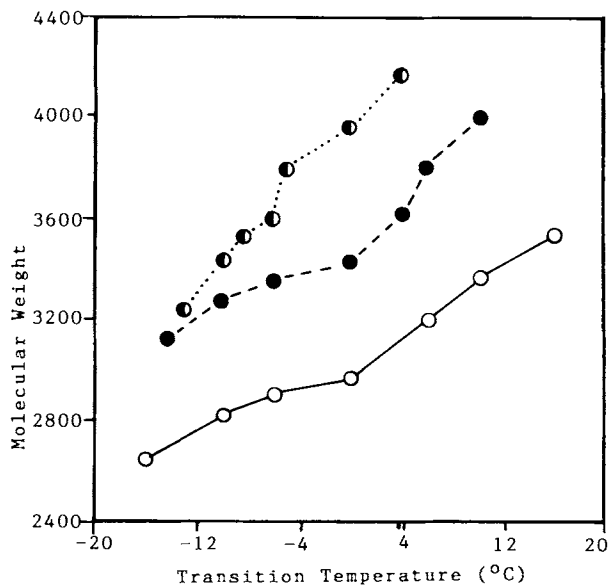
Figure 8   The relationship between T_g and M_n of alkyds: (— O —) method (a); (--●--) method (b); (···◐···) method (c).

(Id)
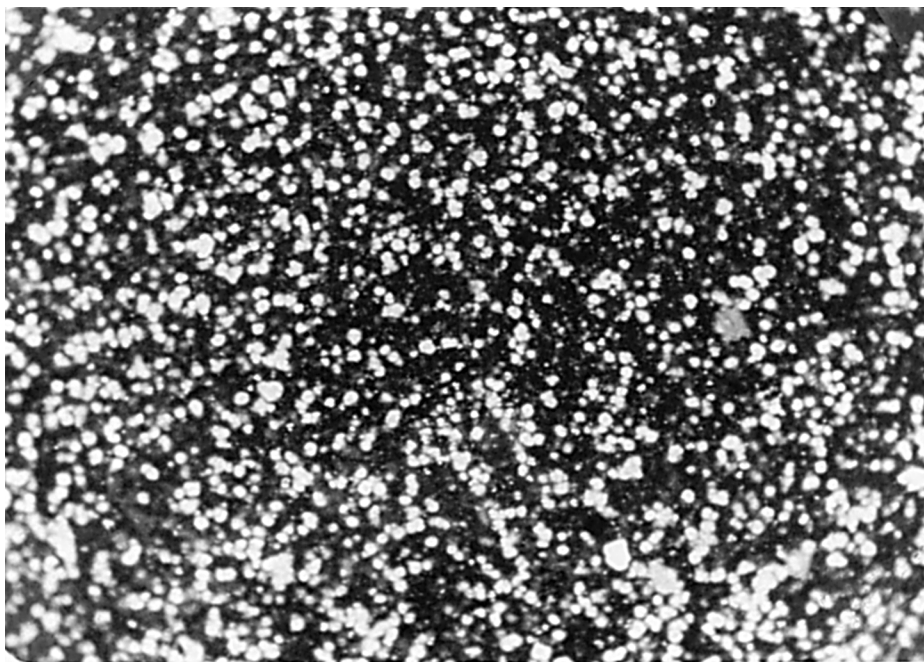
(IId)

Figure 9 Polarizing micrographs of LC alkyds: (1) Id; (2) IId; (3) IIId.

reverse impact increases with the decrease of OH %.

Alkyds at variable oil lengths and with an OH-termination fixed at 18% were formulated as in Table II. It shows that shorter oil lengths have higher fav values and M_n, as well as better base resistance than do the longer oil lengths. The drying time prolonged with the decrease of oil lengths and with the increase of M_n.

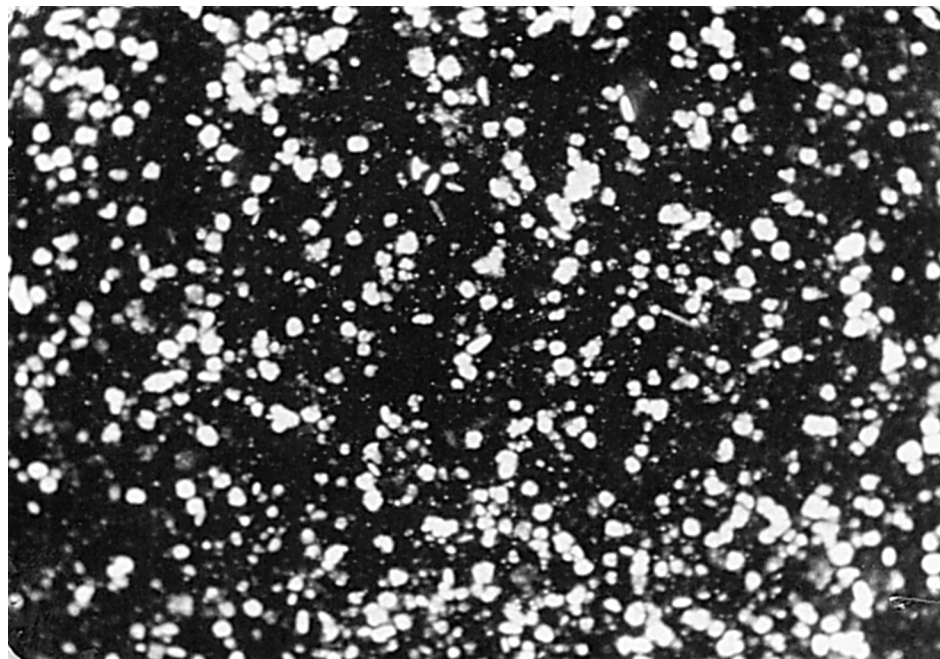**Characterization of Graft Products**

Grafting efficiency (% GE) was calculated by the following formula[22]:

$$\% \text{ GE} = \frac{\text{mol of PHBA grafted}}{\text{mol of PHBA in charge}} 100\%.$$

As long as PHBA oligomerization is not substan-

(IIId)

Figure 9   (Continued from the previous page)

tially faster than grafting, high grafting efficiency (% GE) can be expected. GE does not depend on the relative rates of the two esterification reactions, but on the relative rates of grafting and precipitation of oligo-PHBA.

Oligomeric-PHBA with the degree of polymerization (DP) greater than 5 is reported to be insoluble in all solvents.[23] Thus, oligo-PHBA can be expected to precipitate from pyridine at 25°C when DP reaches 3–5. However, it remains available for grafting as long as it stays in solution. The observed % GE (70–95%) is consistent with theoretical crude analysis.

IR spectra of grafted and ungrafted alkyd resins are shown in Figure 1. The spectra had two sharp absorption peaks at 1510 and 1610 cm^{-1}, which did not appear in ungrafted alkyd resins assigned to $C = C$ stretching on the para-disubstituted aromatic ring. This result is evidence that the grafting has occurred.

Gel permeation chromatography data are shown in Table III. M_n increase with the increase of PHBA. ^{1}H-NMR spectra of the PHBA-grafted products of alkyd resins are shown in Figure 2. ^{1}H-NMR spectra indicate that the PHBA-grafted alkyd resin is more complex in the range of 7.5–7.8 ppm in the presence of the ester derivatives of phthalic anhydride in the

range of 7.5–7.8 ppm. Each spectrum has complex signals at about 7.2–7.5 and 8.0–8.3 ppm. This could be due to the influence of hydrogen ortho on the —OH, —COOH, and —COOR groups.

Effects of Grafting Efficiency

The effects of reaction temperatures on % GE were studied by grafting PHBA onto alkyd resins at 25, 50, 80, and 100°C. Figure 3 shows that the optimum reaction temperature is near 50°C, but the coloration of resin begins to set in at this temperature. Lower % GE at reaction temperature below 50°C may be attributed to the lower solubility of PHBA–oligomer leading to earlier precipitation. On the other hand, at a temperature above 50°C, lower % GE occurs, an effect that may result from the occurrence of the homopolymerization of PHBA. Therefore, it is better for the reaction to take place at room temperature to avoid the resin becoming a brown color.

PHBA was dissolved in pyridine by slow addition for the duration of 0, 2, 4, 6, and 8 h by using a pressure-equalizing dropping. Figure 4 shows that longer adding time resulted in higher % GE. Because with the lengthening of adding time, the opportunity for PHBA to collide with each other (homopoly-

merization) will be reduced but the opportunity for PHBA to graft onto alkyds will be increased.

The effects of the carboxyl and hydroxyl equivalent ratio of PHBA on alkyds were studied by treating the alkyd resin with varying amounts of PHBA. As shown in Figure 5, the % GE of PHBA grafted onto the alkyd resin decreases from about 95 to 77% as the equivalent ratio increases from 1 to 5.

The effects of different functional groups of grafting PHBA on alkyds were studied with three synthetic methods. Although PHBA could be grafted onto OH groups or COOH groups, it was established previously that grafting onto COOH groups is more efficient, as shown in Figures 3 and 5.

Solution Viscosity of Alkyd Resins

The relationship between viscosity and PHBA content of 70/30 (w/w) mixture of alkyds in xylene is shown in Figure 6. Viscosity increases with the increase of PHBA content for Ia, Ib, IIa, IIb, and IIIa, IIIb (Table III), but it drops sharply for alkyds Ic,

IIc, and IIIc. The predominant factor of the viscosity drop is due to the presence of liquid crystallinity. The molecular orientation of the LC phase could reduce the entanglement of the moleculars; hence, it has a lower viscosity than that of amorphous alkyds.

Glass Transition Temperature (T_g) and Clearing Temperature (T_i)

T_g and T_i of the alkyd resin are shown in Table III. The DSC scan is drawn in Figure 7. Those materials do not exhibit a crystalline–LC transition because of the amorphous polymers. Thus, the morphology can be described as a frozen liquid crystalline phase below T_g. Figure 8 shows plots of T_g vs. M_n for the alkyds. For each of the synthetic methods of alkyds, T_g increases fairly linearly with M_n. DSCs of alkyd Ic–If, IIc–IIf, and IIIc–IIIf all have sharp endothermic peaks at 190–250°C; these peaks are attributable to the clearing temperature in the LC phases. The longer the average length of PHBA grafts, the higher T_g and T_i.

Table IV   Properties of Coating Film-Synthesized LC Alkyds

Alkyd	Dry-to-Touch Time	Pencil Hardness	Reverse Impact (1/2 500 g cm)	Crosshatch Adhesion (%)	Appearance	Bending Test
A	2 d[a]	HB	25	100	TP[b]	Pass
Ia	1.5 d	HB	20	100	TP	Pass
Ib	1 d	H	20	100	TP	Pass
Ic	2 h	2H	50	100	TL[b]	Pass
Id	1 h	2H	40	100	TL	Pass
Ie	0.5 h	2H	35	100	TL	Pass
If	0.5 h	3H	35	100	TL	Pass
B	3 d	B	30	100	TP	Pass
IIa	1 d	HB	20	100	TP	Pass
IIb	18 h	HB	20	100	TP	Pass
IIc	2 h	2H	45	100	TL	Pass
IId	2 h	3H	50	100	TL	Pass
IIe	1 h	3H	40	100	TL	Pass
IIf	0.5 h	3H	25	100	TL	Pass
C	2 d	HB	25	100	TP	Pass
IIIa	1.5 d	HB	20	100	TP	Pass
IIIb	1 d	H	20	100	TP	Pass
IIIc	4 h	2H	50	100	TL	Pass
IIId	3 h	2H	50	100	TL	Pass
IIIe	1 h	2H	50	100	TL	Pass
IIId	1 h	2H	30	100	TL	Pass

[a] d: day.
[b] TP: transparent, TL: transulcent.

Liquid Crystalline Phenomena of Alkyd Resins

Visual Stir-Opalescence

Thermotropic LC phases have turbidity and anisotropic properties, such as birefringence and light scattering. A particular characteristic is stir-opalescence of these anisotropic melts. Such phenomena are found in Table III, Ic–If, IIc–IIf, and IIIc–IIIf.

DSC Scan

DSC of Ic–If, IIc–IIf, and IIIe–IIIf shows a sharp endothermic peak at 190–250°C. The sharp peak is attributed to the melting of a phase transition, but it could be T_m or T_i. The observation of broadened X-ray diffraction (WAXS) reveals that the sharp peak is T_i not T_m.

Polar Microscopy

A hot-stage and a polarizing microscope are required for the microscopic examination of a thin LC alkyd film at various temperatures. Alkyds Ic–If, IIc–IIf, and IIIc–IIIf have small, grainy, or batonnetlike textures (photographs are shown in Fig. 9), a feature

similar to the smectic materials reported in a book on texture.[26] The specimens became isotropic when heated to about T_i corresponding to the endothermic peaks in the DSCs. As hot specimens were cooled, the "fine-grain" textures reappeared at about T_i.

Coating Properties

Drying Time

As shown in Table IV, all PHBA-grafted alkyds dry faster than do ungrafted alkyds, and drying speed increases with the increase of PHBA content. Dry time of nonback alkyds is governed by the rates of solvent evaporation, and oxidative cross-linking is the determining step. The stiffness of the PHBA monomer raises T_g but reduces drying time. Tables III and IV show that methods (a) and (b) have higher T_g and shorter drying time to touch. LC may improve drying time simply by increasing T_g. Furthermore, dry time could be reduced if quick physical cross-linking through LC phases is provided. Such cross-linking could supply oxidative cross-linking and reduce the number of convalent cross-links to reach a given total density.

Table V   Chemical Resistance of the Synthesized LC Alkyds

Alkyds	Resistance to			
	Water	Xylene	0.1N HCl	0.1N NaOH
A	Ex[a]	Ex	Good	Fair
Ia	Ex	Ex	Good	Fair
Ib	Ex	Ex	Good	Fair
Ic	Ex	Ex	Ex	Good
Id	Ex	Ex	Ex	Good
Ie	Ex	Ex	Ex	Good
If	Ex	Ex	Ex	Good
A	Ex	Ex	Ex	Poor
IIa	Ex	Ex	Ex	Poor
IIB	Ex	Ex	Ex	Fair
IIC	Ex	Ex	Ex	Fair
IId	Ex	Ex	Ex	Good
IIe	Ex	Ex	Ex	Good
IIf	Ex	Ex	Ex	Good
C	Ex	Ex	Good	Fair
IIIa	Ex	Ex	Ex	Fair
IIIb	Ex	Ex	Ex	Fair
IIIc	Ex	Ex	Ex	Good
IIId	Ex	Ex	Ex	Good
IIIe	Ex	Ex	Ex	Good
IIIf	Ex	Ex	Ex	Good

[a] Ex = excellent.

Toughness and Hardness

An important finding of this study is that both toughness and hardness are improved by grafting LC segments to the alkyd backbone. Table IV shows that the hardness increases but the impact strength decreases with the increase of the PHBA content. However, LC alkyds have a combination of reverse impact resistance and hardness. But the higher PHBA content (Ie, If, IIf, IIIf) has lower impact strength because of the decrease in elasticity. From the theory of the physical properties of polymers, as T_g is increased, hardness is improved but elasticity (reflected by impact resistance) is undermined.[25] Both hardness and toughness are usually antagonistic. The improved hardness and toughness of LC alkyds are not surprising in view of the properties of LC plastics; they are both hard and tough. The enhancement in the above-mentioned properties by grafting LC phases to the alkyd is attributed to the physical cross-linking of the plastic through the association of mesogenic units from different molecules into microscopic LC phases. Materials called "self-reinforcing polymers" are produced by using this principle. LC cross-links are partly solid and partly liquid at the molecular level. Perhaps they can toughen materials by providing a stress relief mechanism along the liquid planes or by impeding crack propagation.

Other coating properties such as adhesion and bending test are excellent in every case and are listed in Table IV. The chemical resistance is listed in Table V. Alkyds display good water, solvent (xylene), and acid resistance. The increase of PHBA-grafted alkyd slightly improves base resistance. The outward appearance of LC alkyd films is glossy but may be translucent or opaque. Lack of clarity is a potential drawback in some end uses. This study shows that film properties of LC alkyds are substantially better than those of their amorphous counter parts.

CONCLUSIONS

In this study, there are three methods for synthesizing side-chain LC alkyd resins, as shown in Scheme I, i.e., grafting PHBA to hydroxy-terminated alkyd resin, grafting PHBA to carboxyl-terminated alkyd resin, and grafting PHBA to succinic anhydride-modified alkyd resin. Such prepared LC alkyd resins appear to have excellent potential utility as a binder for nonbake coatings. They form low-viscosity dispersion in common solvents, a very desirable tendency for application in high solid coating.

Coating film has excellent adhesion to metal and excellent resistance to water, acid, and base. Meanwhile, they also have an extraordinary combination of hardness and impact resistance.

REFERENCES

1. P. Swaraj, *Surface Coating Science and Technology*, Wiley-Interscience, New York, 1985.
2. H. F. Payne, *Organic Coating Technology*, Wiley, New York, 1961.
3. R. R. Myers, *Film-Forming Composition*, Marcel Dekker, New York, 1967.
4. B. J. Lourey, *Surface Coating*, Chapman and Hall, London, 1983.
5. G. Chen and R. W. Lenz, *J. Polym. Sci. Polym. Chem. Ed.*, **22**, 3189 (1984).
6. N. A. Plate, L. B. Stronganov, and O. V. Noah, *Polym. J.*, **19**, 613 (1987).
7. W. J. Jackson and H. F. Fuhfuss, *J. Polym. Sci. Polym. Chem. Ed.*, **14**, 2043 (1976).
8. H. J. Mark, J. I. Jin, and R. W. Lenz, *Polymer*, **26**, 1301 (1985).
9. A. Biswas and J. Blackwell, *Macromolecules*, **21**, 3146 (1988).
10. T. Oryu and J. C. Song, *Polym. J.*, **21**, 977 (1989).
11. G. D. Butzbach and J. H. Wendorff, *Polymer*, **27**, 1337 (1980).
12. S. C. Tai, *Polym. Eng. Sci.*, **26**, 13 (1986).
13. R. Simon and H. J. Coles, *Polymer*, **27**, 811 (1986).
14. A. Blumstein, *Liquid Crystalline Order in Polymer*, Academic Press, Inc., New York, 1978.
15. A. Blumstein, *Polymeric Liquid Crystals*, Plenum Press, New York, 1985.
16. M. Gordon, *Liquid Crystal Polymers I*, Springer-Verlag, Berlin, Heidelberg, 1984.
17. A. Williams and I. A. Ibrahim, *Chem. Rev.*, **81**, 585 (1981).
18. S. Zalipsky, C. Gilon, and A. Zilkha, *J. Makromol. Sci. Chem.*, 839 (1984).
19. C. X. Lu, J. Aixueluel, and C. G. Overberger, *J. Polym. Sci. Polym. Chem. Ed.*, **24**, 269 (1986).
20. K. Holmberg and J. AJohansson, *Org. Coat.*, **6**, 23 (1984).
21. W. Y. Chiang and S. C. Chan, *J. Appl. Polym. Sci.*, **34**, 127 (1987).
22. D. S. Chen and F. N. Jones, *J. Polym. Sci. Part A: Polym. Chem.*, **25**, 1109 (1987).
23. H. R. Kricheldorf and G. Schwarz, *Makromol. Chem.*, **184**, 475 (1983).
24. D. Demus and L. Richter, *Textures of Liquid Crystal*, Verlag Chemie, New York, 1978.
25. L. E. Nielsen, *Mechanical Properties of Polymers and Composities*, Marcel Dekker, New York, 1974.