

Binders for Higher-Solids Coatings. IV. Liquid-Crystalline Acrylic Lacquers

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Synopsis

A previously reported synthetic procedure was used to graft oligo-*p*-hydroxybenzoic acid (oligo-PHBA) to COOH-functional acrylic copolymers. Most of the products were side-chain LC copolymers. Length of the mesogenic oligo-PHBA groups averaged up to five aromatic rings per group. Because these long mesogenic groups have a strong tendency to form LC domains, it was possible to prepare LC side-chain copolymers having as little as 5 mol % of mesogenic monomer. Thus this synthetic procedure provides a versatile route for exploration of the properties of LC copolymers having relatively few but especially effective mesogenic groups. The potential utility of such LC copolymers as binders for nonbake coatings was assessed. Variables studied were molecular weight and T_g of the acrylic copolymer backbone, number and average length of oligo-PHBA segments, and the presence or absence of a flexible spacer between the acrylic backbone and the PHBA segments. Optimum LC copolymers have moderate (15,000–30,000) M_n , low (-10°C) backbone T_g , and low (5–7.5 mol %) population of long (5 PHBA units) oligo-PHBA units. Such copolymers have two major advantages as coatings binders: They form concentrated, stable, low-viscosity dispersions in common solvents, a very desirable characteristic for application. Coating films have excellent adhesion to metal, and they have an extraordinary combination of hardness (H-2H) and impact resistance (> 80 in. lb). These properties are key indicators of coating performance and indicate that LC copolymers have excellent potential for use as binders for nonbake coatings. Other properties remain to be investigated.

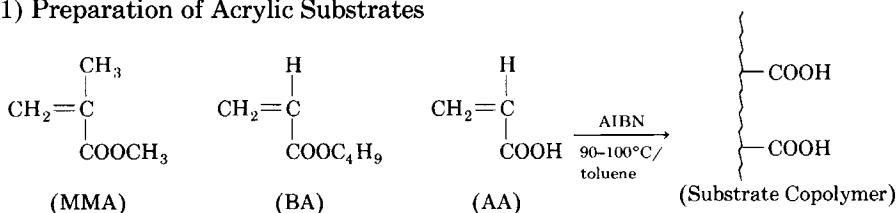
INTRODUCTION

An unmet need in the field of organic coatings is for tough, weatherable coatings that can be formulated as stable, one-package, nontoxic liquids and can be applied without baking and without use of large amounts of organic solvent. We have been investigating various approaches to this objective. This paper is the fourth in a series describing our findings.

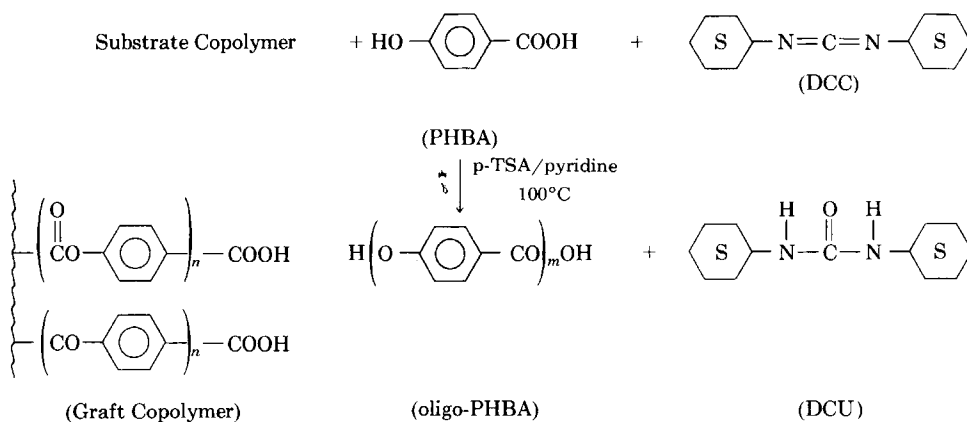
In Part III we reported synthesis of alkyd resins modified with liquid crystalline (LC) structures.¹ We found that liquid crystallinity provides at least three important benefits: Solution viscosity is reduced by formation of nonaqueous dispersions, dry times are sharply reduced, and films are both hardened and toughened. A probable drawback of this approach is that alkyd coatings have limited service lives; their weatherability is inferior to that of acrylic coatings, and they tend to embrittle with age. There is no reason to think that LC alkyds will be improved in these respects.

In this paper we report use of LC structures to modify acrylic copolymers. The objective is to achieve the benefits of LC alkyds in a binder that is capable of excellent long term weatherability. The experimental approach was to prepare several series of —COOH functional acrylic copolymers in which

(1) Preparation of Acrylic Substrates



(2) Grafting with PHBA



Scheme 1. Synthesis of GA series acrylic copolymers

molecular weight, T_g , and functionality were varied and then to graft oligo-*p*-hydroxybenzoic acid (oligo-PHBA) to the $-\text{COOH}$ groups. The grafting method was described previously, and it was shown that oligo-PHBA units can form LC domains in the polymer.²

Two types of LC acrylic copolymers were synthesized. In type A the oligo-PHBA was grafted to $-\text{COOH}$ groups attached directly to MMA/BA/(M)AA acrylic copolymer backbones (Scheme 1). In type B an eight-unit flexible spacer was placed between the copolymer backbone and the oligo-PHBA (Scheme 2). The behavior of these copolymers as film formers was investigated.

Here it will be shown that LC acrylic copolymers have excellent potential as coatings binders. They can be applied without baking to form tough, LC-reinforced films. Their lyotropic nature indicates potential for low-solvent formulations. Thus it appears that with further refinement LC acrylic lacquers could be developed to meet all the needs cited above.

EXPERIMENTAL

Materials

Monomers were distilled before use. Pyridine was distilled and then dried by stirring with anhydrous Na_2SO_4 . All other reagents (Aldrich) were used as received.

Preparation of COOH-Functional Acrylic Polymers

COOH-functional acrylic polymers were prepared as substrates for grafting by radical copolymerization in toluene at 90–100°C under monomer starved conditions³ using azobisisobutyronitrile (AIBN) as initiator. Substrates for type A copolymers (Scheme 1) were composed of methyl methacrylate (MMA), butyl acrylate (BA), and acrylic acid (AA) or methacrylic acid (MAA). Substrates for type B copolymers (Scheme 2) were composed of MMA, BA, and 2-hydroxyethyl methacrylate (HEMA); they were modified to become COOH-functional by treatment with stoichiometrically equivalent amount of succinic anhydride in pyridine at 80°C.

Example. Preparation of a COOH-functional acrylic polymer of type B:

(a) *Polymerization:* Toluene (57 g) was placed in a 250-mL, three-neck flask, heated in an oil bath and stirred mechanically. A solution of 32.68 g (0.255 mol) of BA, 22.03 g (0.22 mol) of MMA, 3.25 g (0.025 mol) of HEMA, and 0.57 g of AIBN was added dropwise for 3 h with continuous stirring. Temperature was maintained at 95–100°C during addition and for 2 h thereafter. A solution of 0.2 g of AIBN in 10 g of toluene was added for 10 min, and the temperature was maintained for 1 h. The solution was concentrated on a rotary evaporator and was vacuum-dried at 80°C. The residue (polymer B6) had 5 mol % OH functionality (calcd), a T_g of 10°C (calcd), and M_n of 15,400 (measured by GPC). Acrylic copolymers of type A were prepared similarly.

(b) *Modification with succinic anhydride:* A solution of 11.45 g (0.005 eq OH) of the above polymer and 0.50 g (0.005 mol) of succinic anhydride in 50 g of pyridine was stirred and heated at 80°C for 12 h. The solution was concentrated; the residue was dissolved in CH_2Cl_2 and washed with 10% aq HCl. The CH_2Cl_2 layer was concentrated, and the residue was vacuum-dried at 80°C. The yield was 92%, and the acid number was 24 mg KOH/g.

Grafting with *p*-Hydroxybenzoic Acid (PHBA)

Both types of COOH-functional acrylic copolymers were grafted with PHBA in pyridine at 100°C for 36 h by the DCC-*p*-TSA process.² Ratios of mol of PHBA to equiv of —COOH (“equivalent ratios”) were 3.5, 5.5, and 7.0 in order to vary the length of the grafted oligo-PHBA segments. The PHBA-grafted products of types A and B were designated GA and GB, respectively. The procedure is exemplified by the grafting of succinic anhydride-modified polymer B6 from example II(b) at equivalent ratio of 7.0.

A solution of 11.80 g (0.005 eq COOH) of polymer B6, 4.84 g (0.035 mol) of PHBA, 7.94 g (0.0385 mol) of dicyclohexycarbodiimide (DCC), and 0.40 g of *p*-toluenesulfonic acid (*p*-TSA) in 150 g of pyridine was stirred at 100°C for 36 h. The mixture was filtered to remove urea of DCC (DCU) and PHBA oligomers. The filtrate was concentrated, dissolved in CH_2Cl_2 , washed with 10% aq HCl, and concentrated. Traces of crystalline contaminants were removed by dissolving the residue in 1:1 pentane–ethyl acetate, cooling in a freezer, filtering, reconcentrating, and vacuum drying at 80°C. The yield was 85%. The combined crystalline byproducts weighed 9.40 g after vacuum drying at 80°C to constant weight. Grafting efficiency (GE%) was estimated as described previously² to be 70%, indicating an average length of oligo-PHBA grafts (# PHBA/COOH) of 4.9 PHBA units.

Structure Characterization

¹H-NMR spectra, IR spectra, differential scanning calorimetry (DSC), optical textures under polarizing microscope, M_n , M_w , polydispersity index, and average #PHBA/COOH ratio were determined as described previously.² The term “#PHBA/COOH ratio” refers to the number average degree of polymerization of oligo-PHBA graft segments actually incorporated in the graft copolymer.

X-ray spectra were recorded with a Philip wide angle diffractometer at 25°C. Samples for X-ray diffraction studies were dissolved or dispersed in acetone, cast on glass slides, and vacuum-dried at 80°C for 12 h.

Measurement of Viscosity

Viscosity was measured using an ICI cone and plate viscometer (shear rate 10^4 s^{-1}) at 25°C. Samples were dissolved or thoroughly dispersed in methylisobutylketone (MIBK) before measuring.

Observation of Solution Appearance

Samples were dissolved or dispersed thoroughly in MIBK and then put in test tubes. The appearance was observed when the test tubes were immersed in an oil bath and equilibrated at different temperatures. Optical textures of some LC polymer dispersions were examined under polarizing microscope at 25°C.

Tests of Film Properties

Samples were dissolved or dispersed in MIBK and cast on untreated cold rolled steel panels by a casting bar to give the dry film thickness of about 25 μm . Reverse impact strength and pencil hardness were measured according to ASTM D2794 and D3363, respectively.

RESULTS AND DISCUSSION

Preparation of Grafting of Model Acrylic Copolymers

In a previous study we showed that oligo-PHBA can be grafted to COOH-functional polymers using the highly reactive esterification reagent dicyclohexylcarbodiimide (DCC) as outlined in Schemes 1 and 2. Structures of the products were established spectroscopically, and a gravimetric method for estimating grafting efficiency and average #PHBA/COOH ratio was demonstrated. The presence of liquid crystalline (LC) domains in the products was demonstrated by DSC and by polarizing microscopy, establishing that the oligo-PHBA units are the mesogenic groups.⁴

In the present study this synthetic method was used to prepare a wider range of LC copolymers, and it was extended to preparation of side-chain LC copolymers containing up to five aromatic units per mesogenic group.

COOH-functional acrylic copolymers served as substrates for the grafting reaction. They were prepared by a standard method using monomer-starved conditions. Monomer ratios were adjusted so that calculated T_g 's varied from -10 to $+10^\circ\text{C}$ and the mole ratio of functional groups varied from 5% to 10%.

T_g 's were calculated by the Fox equation⁵ and were not corrected for molecular weight. M_n (measured by GPC) was varied from about 5000 to about 30,000 by adjusting initiator (AIBN) level. Substrates of type A were copolymers of methyl methacrylate (MMA), butyl acrylate (BA) and either acrylic acid (AA) or methacrylic acid (MAA) (Scheme 1). Substrates of type B were copolymers of MMA, BA, and 2-hydroxyethylmethacrylate (HEMA), which were further modified by post-reaction with succinic anhydride (Scheme 2).

Grafting was effected as described previously² to give LC copolymers of types GA and GB. These types differ primarily in that the mesogenic PHBA grafts are attached directly to the polymer backbone of type GA copolymers while type GB copolymers have eight-atom flexible spacers between the polymer backbone and the mesogenic grafts. Individual copolymers were numbered as shown in Tables I and II. Grafting efficiency (GE%) was determined gravimetrically.² It ranged from about 85% to about 70%. As expected, GE% decreased as the COOH equivalent ratio of PHBA/acrylic increased.

Averaged #PHBA/COOH ratios were calculated from GE%. In order to achieve #PHBA/COOH ratios of 3 ± 0.2 , 4 ± 0.2 , and 5 ± 0.3 , it proved necessary to feed PHBA monomer in the ratio of 3.5, 5.5, and 7.0 mol, respectively, to the grafting reaction.

The mesogenic groups of most previously reported side-chain LC copolymers contain only two aromatic units.^{6,7} The limiting factor is probably the intractibility of monomers containing more than two aromatic units linked in semirigid rods. The synthetic method used here circumvents this limitation by grafting the aromatic units one at a time to dissolved or suspended polymer. Thus mesogenic groups containing three to five aromatic units are readily formed, and there is no apparent limit to the length of mesogenic groups that could be formed by this process.

The ability of this procedure to form long mesogenic groups has a potentially important benefit. It makes it possible to form LC side-chain copolymers having a low mole fraction of mesogenic monomer. Previously reported LC acrylic copolymers contain at least 20 mol % of mesogenic monomer,⁶ but in this study copolymers containing 5 mol % of mesogenic monomer were shown to be liquid crystalline. This benefit can be realized because the ability of mesogenic groups to form LC phases increases with the axial ratio (the ratio of length parallel and transverse the molecular axis) of the mesogenic group.⁸ It will be interesting to explore the properties of LC side-chain copolymers having very low mole fractions of mesogenic groups having very high axial ratios.

A shortcoming of the synthetic method used in this study is that it cannot be expected to produce mesogenic groups of uniform length. It is not known whether this is a serious drawback; for many practical purposes it may not be.

Characterization of Polymer Structures

Assignment of the graft copolymer structures shown in Schemes 1 and 2 were supported by IR, ¹H-NMR, the increase in T_g , and the presence of endothermal peaks in the DSC thermograms.²

The IR spectra of the oligo-PHBA grafted acrylics have sharp peaks at 1610 and 1510 cm^{-1} assignable to the para aromatic C—H stretching. These two peaks are characteristic of oligo-PHBA grafted copolymers. They are absent in the ungrafted acrylics.

$^1\text{H-NMR}$ spectra of the PHBA-grafted acrylics show multiple peaks in the range of 7.0–7.3 and 8.0–8.3 ppm, assignable to the aromatic protons ortho to the OH group and to the COOH group, respectively. They are absent in the ungrafted acrylics.

In the previous study,² it was established that PHBA segments are covalently grafted to the acrylic backbones, not physically blended. Ungrafted oligo-PHBA is insoluble and is readily removed.

Characterization of Microstructure

Physical behavior of type GA series copolymers in which the grafting site was a methacrylic acid residue and the average functionality was 10 mol % (GA21a–c as shown in Table I) was quite different from behavior of all other copolymers synthesized in this study. These materials were soluble in hot mixtures of acetone and H_2O (10 : 1); upon cooling, the polymers appeared to crystallize, and solid material separated. All other polymers made in this study formed stable dispersions under these conditions. This was true even of polymers GA22a–c and GA23a–c, in which the graft sites were methacrylic acid residues but functionalities were 7.5 and 5 mol %, respectively. This behavior indicated that the 10 mol %, MAA-based type A copolymers had crystalline microstructures and all others were liquid crystalline. The tendency to crystallize seemed independent of the acrylic backbone M_n in the range of 5000–30,000.

Polarizing microscopy, differential scanning calorimetry (DSC), and wide angle X-ray diffraction (WAXS) were used to further characterize the microstructures of the graft copolymers in the bulk phase. Results (Tables I and II) were consistent with assignment of LC microstructure to all polymers except GA21a–c.

Examples of polarizing microphotographs taken at 25°C are shown in Figure 1. The 10 mol %, methacrylate-based type A copolymers displayed large particles of variable size [Fig. 1(a)]; they were judged to be crystalline. All other materials had small, grainy or batonnetlike optical textures of uniform size [Figs. 1(b) and 1(c)]. Appearance of these textures supported the assignment of LC microstructures and suggested that the LC domains exist in smectic states.^{9,10} However, the smectic structure was not definitely confirmed by WAXS studies (see below).

Typical DSC thermograms of the crystalline and the LC copolymers are shown in Figures 2 and 3. Thermograms of copolymers GA21a–c series had large, broad endothermic peaks attributable to melting of the crystalline phases. Thermograms of all the other copolymers had much smaller endothermic peaks at the temperatures indicated in Tables I and II. These endotherms are attributable to clearing (T_{cl}) of the LC phases, further supporting the assignment of liquid crystallinity to these materials. T_{cl} increased 10–15°C as the #PHBA/COOH ratio increased from 3 to 5.

TABLE I
Compositions of Type A Acrylic Substrates and Type A PHBA-Grafted Acrylic Copolymers

(a) Type A acrylic substrates:						
No.	Mol fraction	T_g (°C, calcd)			M_n	
(a1) The -MMA-BA-AA- series						
A11	0.274/0.676/0.05	- 10			15,700	
A12	0.355/0.595/0.05	0			28,400	
A13	0.274/0.676/0.05	- 10			4870	
A14	0.274/0.676/0.05	- 10			9945	
A15	0.274/0.676/0.05	- 10			14,865	
A16	0.274/0.676/0.05	- 10			28,500	
A17	0.355/0.595/0.05	0			4750	
A18	0.332/0.593/0.075	0			4810	
A19	0.309/0.591/0.10	0			5100	
A20	0.355/0.595/0.05	0			15,630	
(a2) The -MMA-BA-MAA- series						
A21	0.351/0.549/0.10	10			4910	
A22	0.383/0.542/0.075	10			5130	
A23	0.415/0.535/0.05	10			5490	
(b) Type GA PHBA-grafted acrylic copolymers:						
No.	# PHBA/COOH	PHBA content (wt %)	T_g (°C, measured)	T_{cl}	Phase ^a	
(b1) Series from -MMA-BA-AA-						
GA11	4.9	20.0	-2	173	Smectic	
GA12	5.1	21.0	-4	175	Smectic	
GA13	5.2	21.0	-2	174	Smectic	
GA14	5.0	20.3	-3	174	Smectic	
GA15	4.9	20.0	-2	173	Smectic	
GA16	5.1	20.7	-4	174	Smectic	
GA17	4.9	20.3	7	173	Smectic	
GA18	5.2	29.0	9	174	Smectic	
GA19	4.8	33.6	14	181	Smectic	
GA20	4.8	19.8	4	175	Smectic	
(b2) Series from -MMA-BA-MAA-						
GA21a	3.2	25.2	16	147	—	Crystal
GA21b	4.1	30.1	22	186	—	Crystal
GA21c	4.9	34.0	25	210	—	Crystal
GA22a	3.0	20.3	15	—	165	Smectic
GA22b	3.8	23.2	18	—	175	Smectic
GA22c	4.8	27.6	20	—	184	Smectic
GA23a	3.1	14.0	14	—	162	Smectic
GA23b	4.0	17.4	15	—	173	Smectic
GA23c	5.1	21.1	17	—	178	Smectic

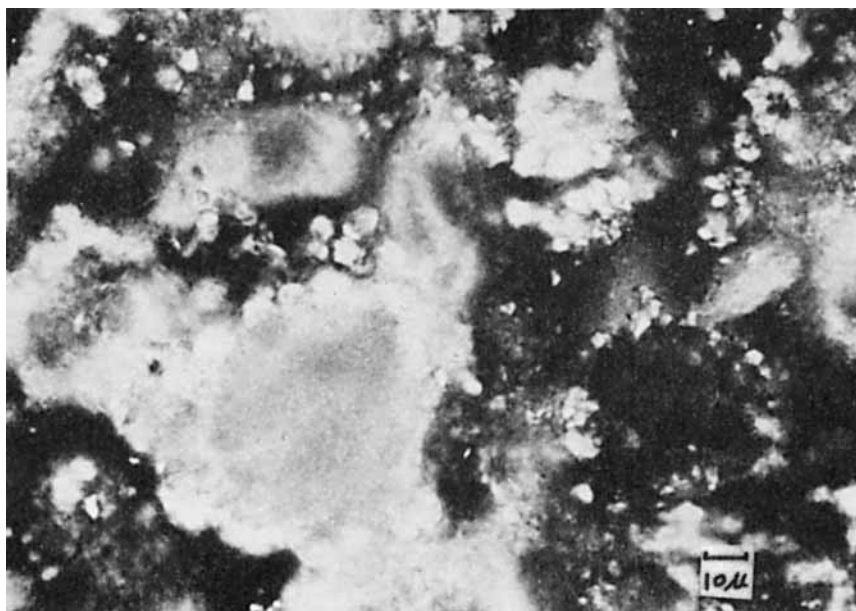
^aAccording to Optical texture; (b1) LC phase.

TABLE II
Compositions of Type B Acrylic Substrates and Type GB PHBA-Grafted Acrylic Copolymers

(a) Type B acrylic substrates:						
No.	Mol fraction (MMA/BA/HEMA)		T_g (°C, calcd)		M_n	
B1	0.282/0.668/0.05		-10			14,500
B2	0.364/0.586/0.05		0			15,130
B3	0.364/0.586/0.05		0			5050
B4	0.364/0.586/0.05		0			10,000
B5	0.364/0.586/0.05		0			28,200
B6	0.44/0.51/0.05		10			15,420

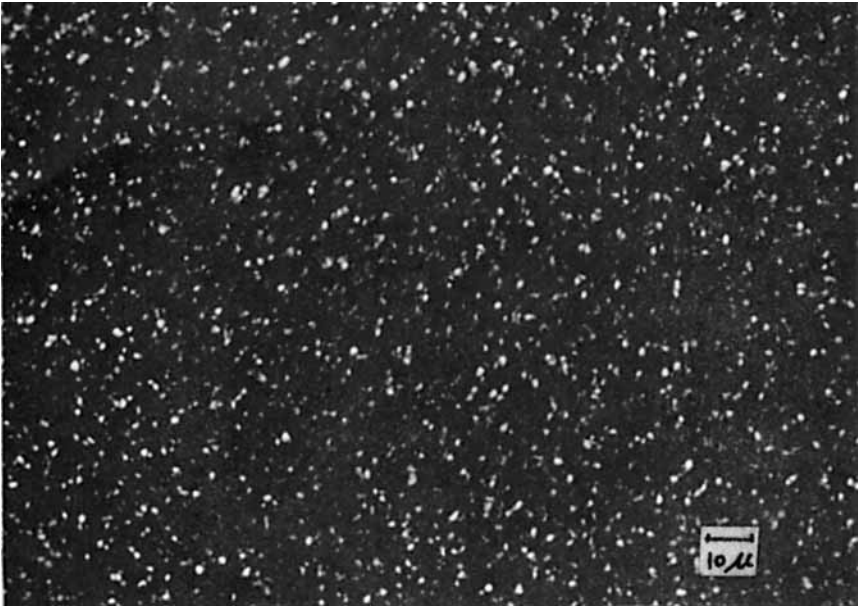
(b) Type GB PHBA-grafted acrylic copolymers						
No.	# PHBA/COOH	PHBA content (wt %)	T_g (°C, measured)	T_{cl}	LC phase ¹	
GB1	5.0	19.3	-5	171	Smectic	
GB2a	4.8	19.0	4	174	Smectic	
GB2b	3.2	13.5	3	159	Smectic	
GB2c	4.1	16.7	3	164	Smectic	
GB3	5.1	19.9	4	175	Smectic	
GB4	4.9	19.3	5	174	Smectic	
GB5	5.2	20.2	5	174	Smectic	
GB6	4.9	19.6	14	177	Smectic	

^aAccording to optical texture.

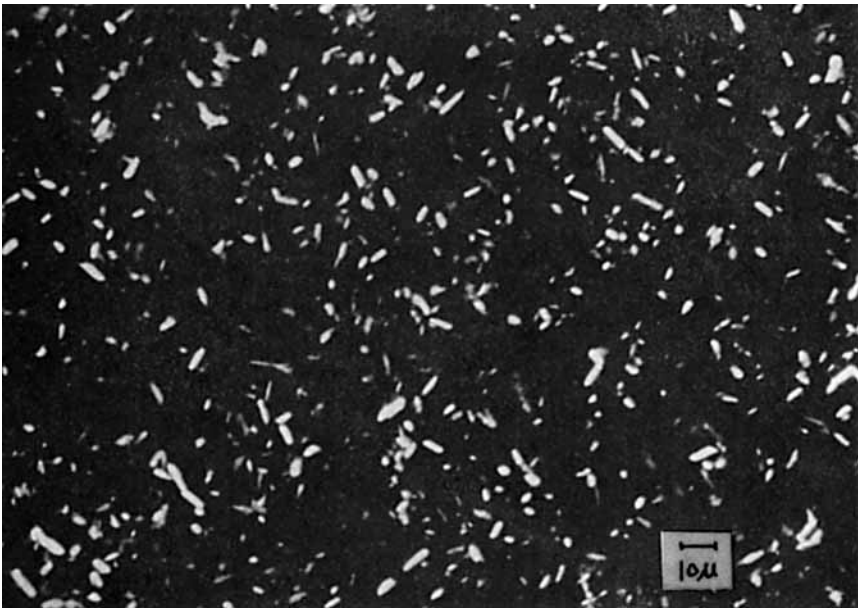


(a)

Fig. 1. Polarizing micrographs of PHBA-grafted acrylic copolymers: (a) crystalline copolymer GA21b; (b) LC copolymer GB1; (3) LC copolymer GA13.



(b)



(c)

Fig. 1. (Continued from the previous page.)

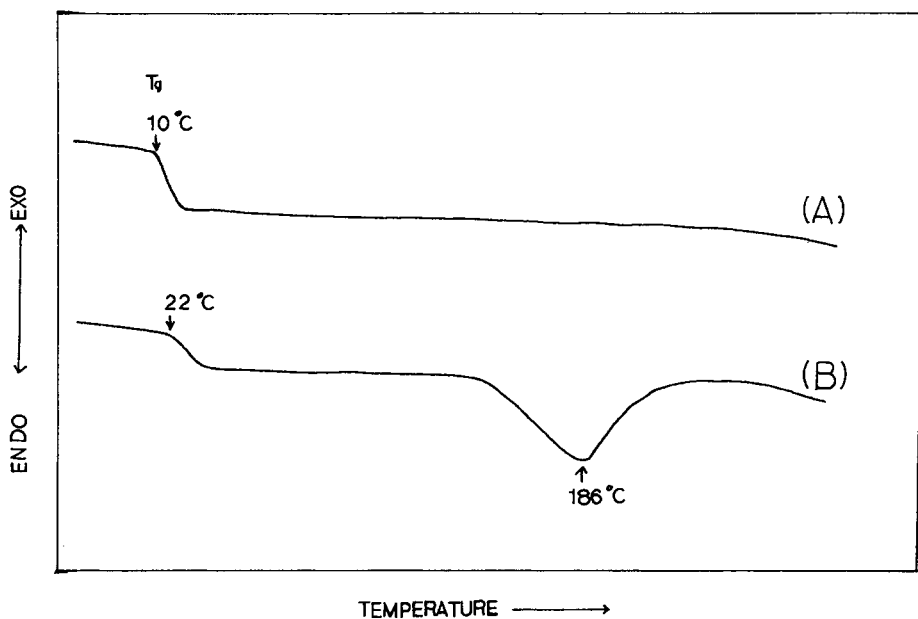


Fig. 2. DSC thermograms of amorphous acrylic copolymer A21 (A) and crystalline copolymer GA21b (B).

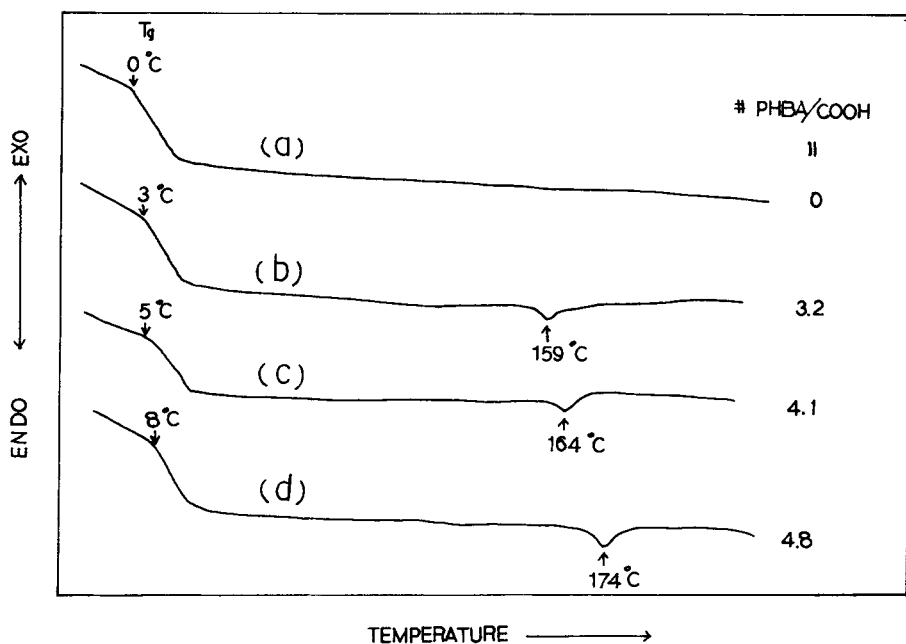


Fig. 3. DSC thermograms of (a) amorphous acrylic copolymer BC, (b) LC acrylic copolymer GB2b, (c) LC acrylic copolymer GB2c, and (d) LC acrylic copolymer GB2a.

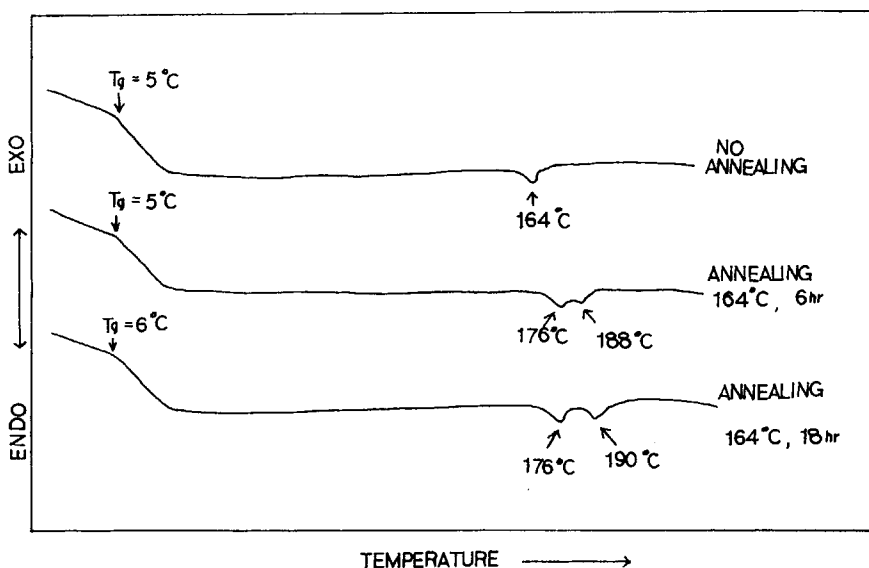


Fig. 4. DSC thermograms of LC acrylic copolymer GB2b: (a) without annealing; (b) annealed at 164°C for 6 h; (c) annealed at 164°C for 18 h.

The relatively small endotherms of the LC materials suggests that either the volume fraction or the degree of order of the LC phases is much lower than the 3-dimensional order of their crystalline counterparts. Annealing of the LC copolymers does not substantially enlarge the endothermic peaks, but it shifts them to higher temperatures and, in some cases, causes them to divide into two peaks (Fig. 4). The shift to higher temperature indicates that annealing promotes ordering within the mesophases, a common phenomenon for LC copolymers.^{11,12} Splitting of this peak may reflect an inhomogeneous distribution of oligo-PHBA unit lengths.

In addition to endothermic peaks, all DSC traces had inflections attributable to T_g 's of polymers. T_g 's of crystalline polymers GA21a-c series were substantially higher than those of the acrylic backbones from which they were made, but T_g 's of LC copolymers were only slightly higher. As the #PHBA/COOH ratio increased from 3 to 5 units/graft, T_g increased by only 3–5°C when concentration of mesogenic monomer was 5 mol %.

WAXS further supported the assignments of crystalline microstructure to the 10 mol %, methacrylic acid-based type A copolymers. Their spectra had seven sharp peaks with angles ranging from 5° to 32°, indicating 3-dimensional order. A strong peak at 7.6° indicates the molecules might arrange in layer structures with a spacing of 11.6 Å. WAXS of all other copolymers studied were much simpler (Fig. 5). Variation was observed when the copolymers had different #PHBA/COOH ratios. Copolymers with #PHBA/COOH ratios around 3.0 usually only had a large broad curve, those with #PHBA/COOH ratios around 4.0 had a small sharp peak at 19.6° ($d = 4.52$ Å) in addition to a large broad curve, and those with #PHBA/COOH around 5.0 had a strong peak at 19.8° ($d = 4.48$ Å) and two weak peaks at 7.8° ($d = 11.33$ Å) and 23.8° ($d = 3.74$ Å) superimposed on a broad curve.

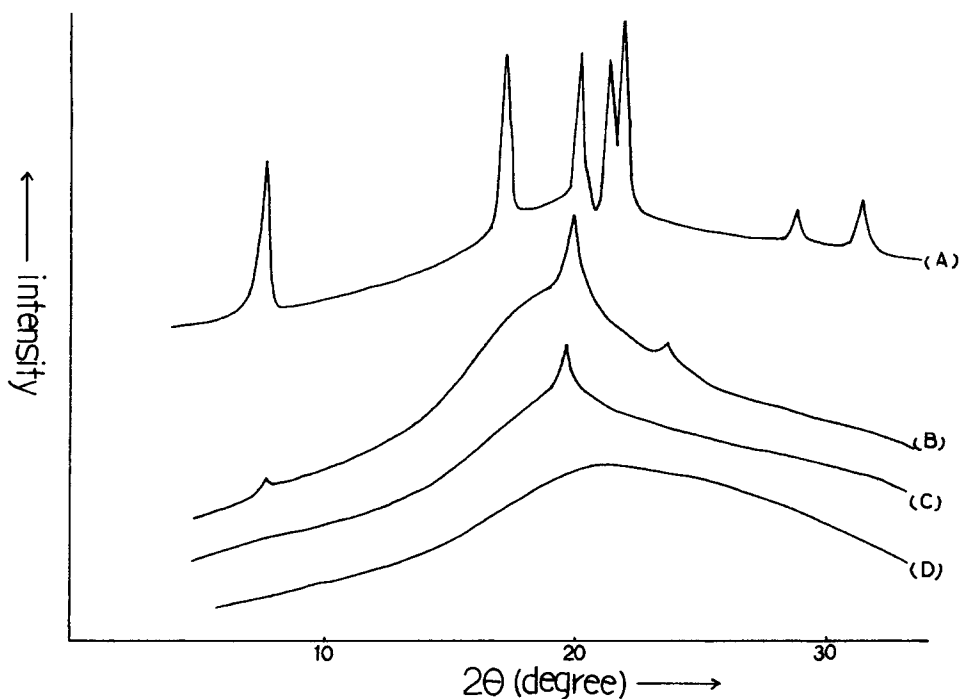


Fig. 5. Wide angle X-ray scattering curves of crystalline copolymer GA21b (A) and LC copolymers GB2a (B), GB2c (C), and GB2b (D).

While these WAXS patterns support the assignment of liquid crystallinity, they are less structured than those reported for smectic LC polymers. Thus they cast doubt on the assignment of smectic structures. There are several possible explanations of the observed lack of structure: (1) The LC domains may not be smectic. (2) Alternatively, the nonuniform length of the mesogenic units may cause WAXS to be atypical. (3) Yet another possibility is that the concentration of mesogenic units may be too low to give typical WAXS patterns. The third possibility is supported by a report by Shibaev and Plate,⁷ who found that strong low angle WAXS peak(s) of LC copolymers become very weak as the content of the mesogenic monomer was decreased to as low as 20 mol %. The LC copolymers studied here contained only 5–10% by mol of the mesogenic monomers, while most of the LC polymers previously studied by WAXS were homopolymers or copolymers containing more than 50% of the mesogenic monomers.

The presence of peak(s) in WAXS of copolymers having #PHBA/COOH ratios of 4 and 5 suggest that higher ratios promote ordering of the mesophase.

Taken together, the above data strongly indicate that most of the type A copolymers and all of the type B copolymers form LC microstructures. The exceptions are 10 mol % type A copolymers in which the mesogenic unit is attached directly to a methacrylic acid residue in the polymer backbone. These materials are clearly crystalline. Presumably the methyl group of the MAA site constrains mobility of the oligo-PHBA graft segments, impeding

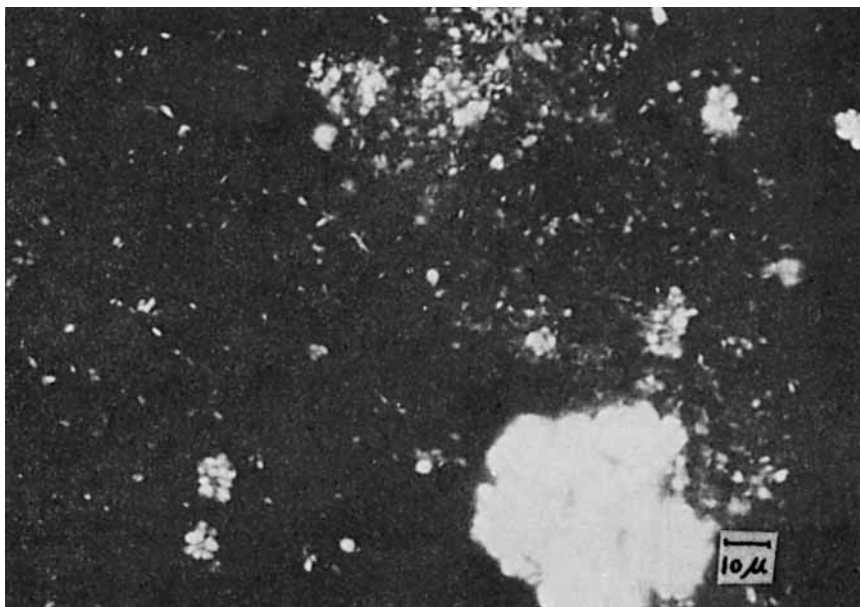


Fig. 6. Polarizing micrograph of LC acrylic copolymer GB2a dispersed in MIBK at concentration of 55 wt %.

formation of LC domains. The assignment of LC microstructures as smectic is considered tentative.

Appearance of Solutions and Dispersions

Most amorphous acrylic copolymers form transparent solutions in MIBK, but the behavior of the LC acrylic copolymers in MIBK was more complex. At low concentrations (usually < 10 wt %) LC copolymers formed transparent solutions (the isotropic state). At high concentrations, these materials formed uniform, opaque dispersions, i.e., anisotropic states, when thoroughly dispersed by ultrasonic waves. An example of the optical texture of a typical anisotropic state under a polarizing microscope is shown in Figure 6; the fine particles at the left side indicate the existence of the lyotropic LC phase and the coarse particles on the right side are thought to be particles which had not been dispersed effectively. The anisotropic states did not separate or crystallize when kept for 6 months at 20 – 25°C . At intermediate concentrations (roughly 10 – 50 wt % depending on the particular copolymer), biphasic (two-layer) states were formed: The top layer was transparent while the bottom layer was uniformly anisotropic.

The behavior of LC copolymer/MIBK mixtures depended on temperature, concentration, and #PHBA/COOH ratio. The phase diagrams in Figure 7 are typical. Behavior of two copolymers, GB2b (#PHBA/COOH = 3.2 , dashed line) and GB2a (#PHBA/COOH = 4.8 , solid line) is shown. These graft copolymers are from the same acrylic copolymer substrate; they differ only in the #PHBA/COOH ratio. Both copolymers formed transparent isotropic "solutions" (A) at low concentrations and/or at elevated temperatures. At

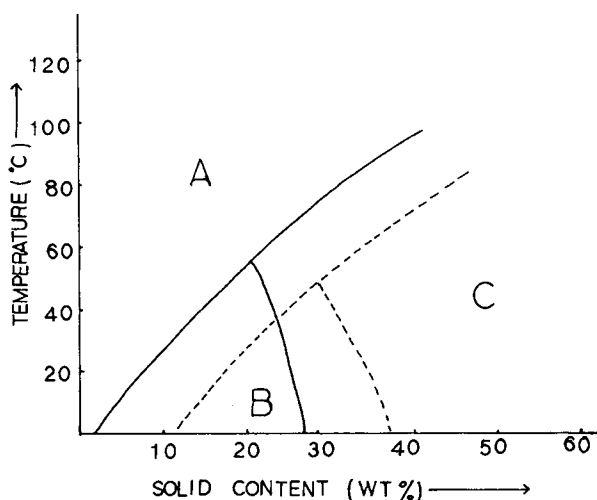


Fig. 7. Phase diagrams of LC acrylic copolymers GB2a (—) and GB2b (---) in MIBK: (A) isotropic state; (B) two-layer state; (C) anisotropic state.

lower temperatures both copolymers formed biphasic states (B) and anisotropic states (C) at high concentrations. This sort of behavior is typical of lyotropic LC polymers.¹³ Increasing the #PHBA/COOH ratio from 3 to 5 decreases solubility, shifting the phase diagram by about 10 wt %, as shown.

The #PHBA/COOH ratio strongly affected the concentrations at phase boundaries. As the #PHBA/COOH ratio increases, the phase boundaries shift to lower concentrations. Temperature also affects the phase boundaries. For example, as shown in Figure 7, both the biphasic state and the anisotropic state become isotropic (i.e., they “clear”) when heated. The clearing temperatures increased as the #PHBA/COOH ratios increased.

Viscosity of Solutions and Dispersions

As discussed above, attempts to prepare concentrated solutions of the LC acrylic copolymers studied here afforded anisotropic dispersions. Because viscosity at high concentration is critical for coatings application, the viscosity of these dispersions was studied briefly.

Figure 8 shows shear viscosities (shear rate 10^4 s^{-1}) of MIBK solutions of three ungrafted acrylic copolymers and of a dispersion of an LC graft copolymer derived from one of them as a function of concentration. The ungrafted copolymers (B1 = III, B2 = II, and B6 = I) differ only in T_g ($-10, 0, +10^\circ\text{C}$, respectively); all three have M_n of about 15,000 and functionality of 5 mol %. LC copolymer GB1 (IV) was prepared by grafting B1 with an average #PHBA/COOH ratio of 5.0. As expected, solution viscosities of ungrafted copolymers increase moderately as T_g increases. However, viscosity of GB1, an anisotropic dispersion throughout most of the concentration range studied, was substantially lower than that of the copolymer from which it was made. The viscosity range 1–2 poise (a viscosity suitable for spray application of coatings) was attained at about 40–45 wt % with the ungrafted polymers and at about 45–50 wt % with LC copolymer GB1.

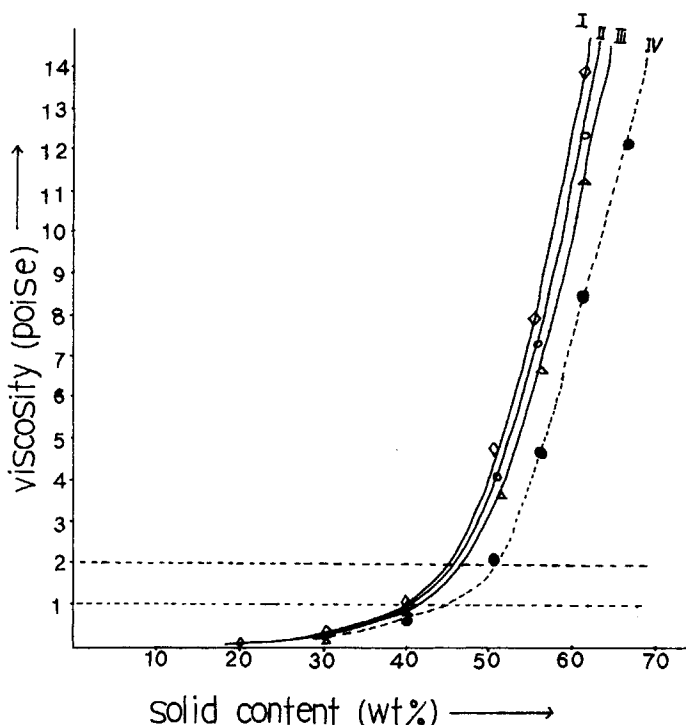


Fig. 8. Shear viscosities of MIBK solutions of amorphous acrylic copolymers B6 (I), B2 (II), and B1 (III), and MIBK dispersions of LC acrylic copolymer GB1 (IV).

The effect of the #PHBA/COOH ratio on viscosity was studied; results are shown in Figure 9. B2 is an ungrafted acrylic copolymer with M_n of about 15,000, T_g of 0°C , and functionality of 5 mol %. GB2a and GB2b are LC graft copolymers prepared from B2 with actual #PHBA/COOH ratios of 4.8 and 3.2, respectively. Again, viscosities of anisotropic dispersions of the grafted copolymers were significantly lower than solutions of the copolymers from which they were made. It appears that increasing the #PHBA/COOH ratio slightly reduces viscosity of the dispersions. The viscosity of dispersions of a third LC copolymer in this series, GB2c, (#PHBA/COOH ratio 4.1) was intermediate between GB2a and GB2b.

The formation of low-viscosity anisotropic dispersions by LC acrylic copolymers is very desirable from the standpoint of coatings application because it may help overcome one of the key shortcomings of soluble acrylic copolymers as coatings binders. Soluble acrylic copolymers whose molecular weights and T_g 's are high enough to provide good film properties without crosslinking (see below) invariably have high viscosities. To apply them as coatings requires a larger proportion of solvent to reduce viscosity to a level suitable for spray application, usually ca. 0.1 Pa s. For example, solution auto lacquers are applied at concentrations of 10–12 vol %.¹⁴ Such formulations are costly, and have been banned from many applications by air pollution regulations.

Anisotropic dispersions of LC acrylic copolymers offer a potential solution to this problem. For example, dispersions of copolymer GB1 have a viscosity

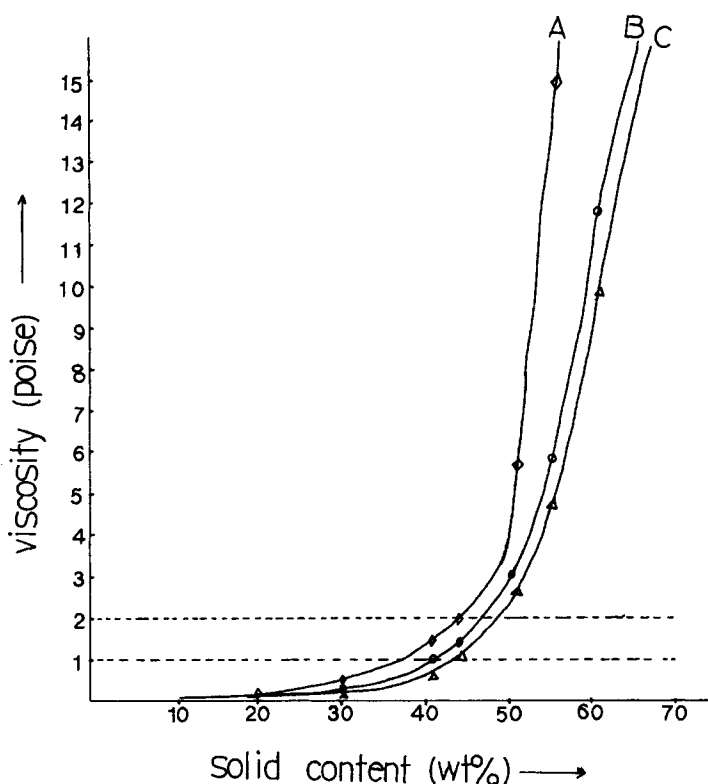


Fig. 9. Shear viscosities of MIBK solutions of amorphous acrylic copolymer B2 (A) and MIBK dispersions of LC acrylic copolymers GB2b (B) and GB2a (C).

of 1–2 poise at about 45–50 wt % in MIBK (Fig. 8). While this solids level is below the range desired for high-solids coatings, it is comparable and often higher than that of many coatings in use today. It is reasonable to think that higher solids could be attained by adjusting the copolymer structure and the solvent solubility parameter.

Capacity of Liquid Crystallinity to Improve Film Properties

A primary objective of this study was to assess the potential of liquid crystallinity to improve the film properties of unbaked coatings. Accordingly, properties of cast films of selected LC acrylic copolymers were compared with those of a series of ungrafted, amorphous acrylic copolymers (A1–A10). Three empirical indicators of film properties were used: crosshatch adhesion, reverse impact resistance, and pencil hardness. Adhesion was good in every case; other results are shown in Table III.

Film properties of the amorphous copolymers were poor. When calculated T_g was below 25°C, the films were very soft, and, when it was higher, they were very brittle. When M_n was below 30,000, impact resistance was negligible regardless of T_g . Copolymer A10 ($M_n = 39,500$ and $T_g = +10^\circ\text{C}$) had the best properties in the series, although films are too soft for practical use.

TABLE III
Comparisons of Film Properties between Amorphous and LC Acrylic Copolymers

No.	M_n (backbone)	T_g (°C) (calcd)	# PHBA/COOH	Rev. imp. (in. lb)	Hardness
<u>Amorphous acrylic copolymers</u>					
A1	5600	30	0	< 10	H-2H
A2	5200	15	0	< 10	2B
A3	11,000	30	0	< 10	H-2H
A4	15,600	30	0	< 10	H-2H
A5	14,800	15	0	< 10	B
A6	15,100	0	0	(sticky)	
A7	28,300	20	0	< 10	2H
A8	29,100	10	0	25	B
A9	28,900	0	0	(slightly sticky)	
A10	39,500	10	0	40	HB
<u>LC acrylic copolymers</u>					
GB1	14,500	-10	5.2	> 80	H
GB2a	15,130	0	5.0	65	2H
GA11	15,700	-10	4.8	70	H
GA12	28,450	-10	5.1	> 80	3H

^a Note: Functionality of all the above polymers is 5% by mol.

These results are typical of those expected for uncrosslinked acrylic lacquers.¹⁴ It was widely thought that lacquers can give useful film properties only if molecular weights are high enough to provide a high population of chain entanglements within the film. The minimum molecular weight for the acrylic polymers to form entanglements was reported around 10,400.¹⁵ Empirical evidence indicates that higher molecular weights are essential for good coating properties. For example, properties of acrylic auto lacquers are unsatisfactory when the acrylic copolymer M_n falls below about 40,000 and M_w is below about 75,000.¹⁴ Thus it is not surprising that of the amorphous copolymers studied only A10 ($M_n = 39,500$) had reasonable impact resistance.

Film properties of representative LC copolymers were substantially better than those of amorphous counterparts (Table III). Reverse impact resistance of 65 to > 80 in. lb is attainable with backbone M_n as low as 15,000, and pencil hardness of H-3H is attainable with T_g as low as -10°C . These properties are well within the acceptable range for many end uses and are, in fact, superior to those of many commercially used nonbake coatings. Appearance of these films is glossy but translucent to opaque. Lack of clarity is a potential drawback in some end uses, but it is thought that with refinement this limitation could be minimized.

It is evident from the above results that films made from LC acrylic copolymers can have substantially better hardness and impact resistance than those made from comparable amorphous copolymers. The ability of liquid crystallinity to enhance both properties simultaneously is a key discovery. With lacquers made from amorphous copolymers, there is a tradeoff between hardness and impact resistance. The generally accepted reason is that impact resistance is governed by film elasticity, among other basic properties; changes that improve elasticity usually soften the film.

The enhanced properties of acrylic copolymers are similar to those we observed previously in Part III of this series with alkyd resins.¹ Alkyds modified with mesogenic oligo-PHBA segments were both tougher and harder than amorphous counterparts. Property enhancement is not surprising in view of the widely reported ability of LC domains to toughen and harden plastics^{16,17} and to increase modulus of fibers.¹⁸

The observed enhancement of properties by introduction of mesogenic groups might be explained in two ways: (1) Mesophases may physically crosslink individual polymer molecules. LC acrylic copolymers of backbone M_n of 15,000–30,000 and functionality of 5–10 mol % would average roughly 7–30 mesogenic units per molecule. When these units form LC domains, a significant fraction would almost certainly form intermolecular crosslinks. The physical crosslinking could logically be expected to increase the population of entanglements of amorphous acrylic backbones of moderate molecular weight, further enhancing properties. The size of the physical crosslinks that are most effective is unknown; quite possibly films contain a large population of submicroscopic LC domains in addition to the domains visible by polarizing microscopy. It is conceivable that associations of a small number (two or more) mesogenic units could affect properties by providing weak physical crosslinks that can break under stress, allowing deformation, and then reform when stress is removed. (2) Alternatively, the presence of LC domains might interrupt crack propagation, improving film toughness, and, perhaps, adhesion. Again the optimum domain size is unknown, but it seems reasonable to think that the larger, visible domains effectively interrupt crack propagation.

Preliminary Guidelines for LC Copolymer Design

Having established that liquid crystallinity can dramatically improve film properties, we addressed a second objective: to develop preliminary guidelines for copolymer design to optimize film properties. Variables studied included M_n , T_g , functionality (number of graft segments), flexible spacer effects, and #PHBA/COOH ratio (length of graft segments). Results are shown in Tables IV–VIII.

Effects of M_n of ungrafted and grafted acrylic copolymer backbones are shown in Table IV. T_g , T_{cl} , and adhesion were essentially independent of M_n regardless of the presence or absence of flexible spacer. However, reverse impact resistance and hardness increased with M_n . LC copolymers with backbone M_n of 15,000 and 28,000 had excellent reverse impact resistance (> 70 in. lb) and good hardness (H–2H) when T_g , functionality, and #PHBA/COOH ratio were optimal.

T_g effects for graft copolymers having a functionality of 5 mol % are shown in Table V. It can be seen that grafting oligo-PHBA has only a slight effect on T_g of the amorphous backbone of the copolymer, increasing it by about 4–5°C. Backbone T_g has only a modest effect on clearing temperatures (T_{cl}) of the mesophases; T_{cl} increased by 6°C as backbone T_g 's increased from –10 to +10°C. However, backbone T_g substantially affected the empirical film properties. Reverse impact resistance ranged from poor (< 10 in. lb) when backbone T_g was 10°C to excellent (> 80 in. lb) when T_g was –10°C. Hardness

TABLE IV
Effects of Acrylic Backbone M_n on the Film Properties of LC Copolymers^a

No.	Backbone M_n	#PHBA/ COOH	T_g (°C measured)	T_{cl}	Rev. imp. (in. lb)	Hardness	Crosshatch adhesion
(a) Copolymers with flexible spacer							
GB3	5050	5.1	4	175	35	2B	100%
BC	5050	0	0	—	< 10	(Sticky)	100%
GB4	10,000	4.9	5	174	60	H	100%
B4	10,800	0	1	—	< 10	(Sticky)	
GB2a	15,130	4.8	4	174	70	2H	100%
B2	15,130	0	0	—	< 10	(Sticky)	100%
GB5	28,200	5.2	5	174	80	2H	100%
B5	28,200	0	2	—	20	2B	100%
(b) Copolymers without flexible spacer							
GA13	4870	5.2	-2	175		(Sticky)	100%
A13	4870	0	-9	—		(Sticky)	100%
GA14	9945	5.0	-3	174	45	HB-H	100%
A14	9945	0	-10	—	< 10	(Sticky)	100%
GA15	14,865	4.9	-2	173	70	H	100%
A15	14,865	0	-9	—	< 10	(Sticky)	100%
GA16	28,500	5.1	-4	174	80	H	100%
A16	28,500	0	-8	—	30	(Sticky)	100%

^aNote: The functionality of all the acrylic polymers is 5% by mol.

increased with backbone T_g .

In Table VI LC copolymers having different functionalities are compared. While the reported data were obtained for LC copolymers with backbone M_n 's of about 5000, similar trends were observed for higher M_n 's. It can be seen that increasing functionality increased T_g and T_{cl} . Increasing functionality increased hardness but had an adverse effect on reverse impact resistance. In general, films with functionality above 7.5 mol % had poor reverse impact resistance.

The effects of the presence of flexible spacer between the acrylic backbone and the oligo-PHBA segments are exemplified in Table VII. The flexible spacer reduces the effect of grafting on T_g . Impact resistance improved when flexible spacer was present. However, the effect of flexible spacer on reverse impact resistance appeared less substantial when the backbone T_g was de-

TABLE V
Effects of the Acrylic Backbone T_g on the Film Properties of the LC Acrylics

No.	T_g (°C)		#PHBA/ COOH	T_{cl} (°C)	Rev. imp. (in. lb)	Hardness	Crosshatch adhesion
	Backbone (calcd)	After grafting (measured)					
GB1	-10	-5	5.2	171	> 80	H-2H	100%
GB2a	0	4	5.0	173	65	2H	100%
GB6	10	14	4.9	177	< 10	2H-3H	100%

TABLE VI
Effects of Functionality on the Film Properties of the LC Acrylic Copolymers^a

No.	Function- ality (mol %)	# PHBA/ COOH	PHBA in polymer (wt %)	Measured		Rev. imp. (in. lb)	Hardness	Crosshatch adhesion
				T_g	T_{cl}			
GA17	5	4.9	19.9	7	173	35	3B	100%
GA18	7.5	5.2	25.6	9	174	20	HB	100%
GA19	10	4.8	32.1	14	181	< 10	H-2H	100%

^a Notes: M_n of acrylic backbones is 4800 ± 300 and calcd T_g is 0°C .

TABLE VII
Effects of Flexible Spacer on the Film Properties of the LC Acrylic Copolymers

No.	T_g ($^\circ\text{C}$)		T_{cl} ($^\circ\text{C}$)	# PHBA/COOH	Rev. imp. (in. lb)	Hardness
	Backbone (calcd)	After grafting (measured)				
GB2a	0	4	173	4.8	70	2H
GA20	0	7	175	4.9	< 10	2H-3H
GB1	-10	-5	171	5.0	80	H
GA11	-10	-2	173	4.9	70	H-2H

creased to about -10°C . Films with flexible spacer were slightly softer than those without one.

Effects of #PHBA/COOH ratio are exemplified in Table VIII. As this ratio increased, T_g (after grafting) increased slightly, T_{cl} of LC phase increased significantly, reverse impact resistance increased greatly, and hardness increased slightly.

Appearance of films were also greatly influenced by the PHBA/COOH ratio. At functionality of 5 mol %, films were translucent when this ratio was about 3, but they were opaque when it was 4 or above.

To summarize the observations in this section, it appears that the following guidelines may be useful in designing LC acrylic copolymers for coatings binders:

1. T_g of the amorphous part of the copolymer may be low; the optimum for a given end use may be in the range of 0 – -10°C or lower. Amorphous

TABLE VIII
Effects of Average #PHBA/COOH on the Film Properties of the LC Acrylics^a

No.	# PHBA/ COOH	T_g	T_{cl}	Rev. imp. (in. lb)	Hardness	Crosshatch adhesion	Appearance
GB2b	3.2	3	159	30	B-HB	100%	Translucent
GB2c	4.1	3	164	45	H	100%	Opaque
GB2a	4.8	4	174	70	2H	100%	Opaque

^aAcrylic backbone: $M_n = 15130$, calcd $T_g = 0^\circ\text{C}$, and functionality = 5% by mol.

copolymers of such low T_g are normally far too soft to be usable as coatings; acrylic lacquers are usually formulated with T_g near or slightly above the highest service temperature. Apparently the presence of LC domains can harden low T_g films, yet the elasticity associated with $\log T_g$ is at least partly retained.

2. The best combination of hardness and elasticity is attained when functionality is low, but the PHBA/COOH ratio is high.

3. Flexible spacer improves impact resistance when backbone T_g is 0°C or higher but has little detectable effect when T_g is -10°C. Introduction of flexible spacer by the method used in this study has the disadvantage of placing relatively unhindered ester groups between the acrylic backbone and the mesogenic group; these ester groups are relatively vulnerable to hydrolysis in water and weather. Other potential routes for introducing flexible spacers are costly. Thus for practical purposes it may be preferable to use low T_g backbones and dispense with flexible spacer.

CONCLUSIONS

The synthetic procedure used here to graft oligo-PHBA to COOH-functional acrylic copolymers is capable of synthesizing side-chain LC copolymers having mesogenic groups whose length averages up to five aromatic rings per mesogenic group. Other synthetic methods are limited to two or, at most, three aromatic rings per mesogenic group. Long mesogenic groups have a strong tendency to form LC domains.

Thus this synthetic procedure makes it possible to prepare LC side-chain copolymers having as little as 5 mol % of mesogenic monomer. It provides a versatile route for exploration of the properties of LC copolymers having relatively few but especially effective mesogenic groups.

Such LC copolymers appear to have excellent potential utility as binders for nonbake coatings. They form concentrated, stable, low-viscosity dispersions in common solvents, a very desirable tendency for application. Coating films have excellent adhesion to metal, and they have an extraordinary combination of hardness (H-2H) and impact resistance (> 80 in. lb). These properties are key indicators of coating performance. Other properties remain to be investigated.

Thus LC acrylic copolymers offer a new technological approach to nonbake coatings having low VOC, excellent film properties, and presumably low toxicity.

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