

Liquid Crystalline Acrylic Copolymers for High-Solids Enamel Coatings

DER-SHYANG CHEN and FRANK N. JONES, *Polymers and Coatings Department, North Dakota State University, Fargo, North Dakota 58105*

Synopsis

Carboxyl functional liquid crystalline (LC) acrylic copolymers were synthesized and were compared with carboxyl functional control copolymers of \bar{M}_n about 5000–15,000. Both types were crosslinked with a hexakismethoxymethyl melamine (HMMM) resin at 150°C, a temperature below the clearing points of the LC copolymers. Birefringent phases were visible in the crosslinked films made from LC polymers. FT-IR indicated the presence of unreacted COOH in all crosslinked materials. Unreacted COOH groups in crosslinked LC copolymers appeared only slightly higher than those in crosslinked amorphous copolymers. The potential utility of these LC copolymers as binders for thermosetting coatings was assessed. Variables studied were HMMM content, the length of PHBA grafts, T_g and \bar{M}_n of the acrylic copolymer backbone, and functionality. Optimum LC copolymers have low backbone T_g ($< 0^\circ\text{C}$) and low functionality (< 7.5 mol %). Cured films of such copolymers have both high hardness (> 35 KHN), high impact resistance (> 80 in. lb), excellent adhesion, and good solvent resistance.

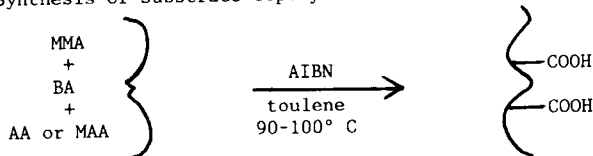
INTRODUCTION

Melamine resin crosslinked acrylic high solids coatings are widely used when hard, weatherable films are required.¹ However, hard films of such coatings tend to be brittle. A combination of high hardness and good toughness cannot be achieved by adjusting the usual structural parameters such as \bar{M}_n , functionality, T_g , and content of melamine resin.² This article concerns a new approach toward this desirable combination of properties.

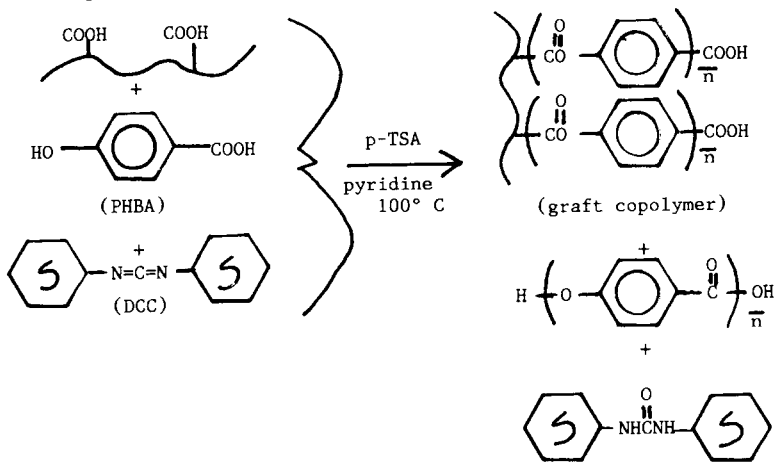
In a previous article³ we reported a convenient method for grafting *p*-hydroxybenzoic acid (PHBA) segments to COOH-functional oligomers or polymers (Scheme I). Oligomers or polymers grafted with oligo-PHBA segments usually have thermotropic, liquid crystalline phases, although a few are crystalline.

In another article⁴ we reported that liquid crystallinity in alkyd resins provides at least three important practical benefits: solution viscosity is reduced by formation of nonaqueous dispersions, dry times are sharply reduced, and films are both hardened and toughened. We also reported⁵ that liquid crystalline acrylic lacquers have two major advantages as binders for higher-solids nonbake coatings: (1) They form concentrated, stable, low viscosity dispersions in common solvents, a very desirable characteristic for application. (2) Coating films have an extraordinary combination of high hardness and high impact resistance. In recent articles Wang and Jones⁶ and Dimian and Jones⁷ showed that LC oligoesters can be crosslinked with hexakismethoxymethyl melamine (HMMM) to give hard, impact-resistance coatings.

(1) Synthesis of substrate copolymers:



(2) Grafting with PHBA (substrate copolymers):



Scheme I. Synthesis of LC acrylic copolymers

Here we report the use of melamine resins to crosslink LC acrylic copolymers to give coating films that are both hard and tough. In this study COOH-functional low molecular weight LC acrylic copolymers were synthesized as described.⁵ These copolymers were crosslinked with HMMM at 150°C, a temperature below the clearing points of their LC phases. It will be shown that LC acrylic copolymers have excellent potential as binders for thermosetting coatings. The best melamine crosslinked films are extraordinarily hard; yet they have good impact resistance. Control enamels made from conventional amorphous acrylic copolymers were inferior in both respects.

EXPERIMENTAL

Materials

Monomers were distilled before use. Pyridine was distilled and then dried by stirring with anhydrous Na_2SO_4 . HMMM was Monsanto Resimene 746. All other reagents (Aldrich) were used as received.

Preparation of COOH-Functional Acrylic Copolymers; Grafting with *p*-Hydroxybenzoic Acid (PHBA)

COOH-functional acrylic copolymers were prepared as described⁵ by free radical copolymerization in toluene at 90–100°C under monomer starved conditions⁸ using methyl methacrylate (MMA), butyl acrylate (BA), and acrylic acid (AA) as monomers and 2,2'-azobis(2-methylpropanitrile) (AIBN) as initiator. These copolymers were used as substrates for grafting with

p-hydroxybenzoic acid (PHBA) by the DCC/*p*-TSA/pyridine process to give LC copolymers as described previously.³ Ratios of mol of PHBA to equiv of COOH ("equivalent ratio") were varied from 3.5, 5.5, and 7.0 in order to vary the length of the grafted oligo-PHBA segments to 3 + 0.2, 4 + 0.2, and 5 + 0.3 units of aromatic rings. Scheme I shows the preparation of COOH-functional acrylic copolymers and grafting with PHBA.

Structure Characterization of Copolymers

¹H-NMR Spectra, IR spectra, differential scanning calorimetry (DSC), optical textures under polarizing microscope, \bar{M}_n , \bar{M}_w , polydispersity index, and average PHBA/COOH ratio of uncured acrylic copolymers were determined as described previously.⁵ T_g 's were calculated by the Fox equation⁹ without molecular weight correction.

The term "PHBA/COOH ratio" refers to the number of average degree of polymerization of oligo-PHBA graft segments actually incorporated in the graft copolymer.

Crosslinking and Characterization of Coating Films

Amorphous acrylic copolymers and LC acrylic copolymers were dissolved or dispersed in MIBK. HMMM and *p*-TSA (catalyst) were added and mixed by ultrasonic energy. The total solid content was 70 wt%. The weight ratio of HMMM to copolymer was 28.6:71.4 in most cases, but this ratio was varied from 16.7:83.3 to 44.4:55.6 in a study of effects of HMMM level on film properties. The concentration of *p*-TSA was at 1 wt % of the acrylic copolymer.

These MIBK solutions or dispersions were cast on untreated cold rolled steel panels using a casting bar. Three minutes after casting, the panels were placed in a forced air oven and heated at 150°C for 30 min. Dry film thickness was about 1 mil.

Samples for FT-IR were prepared by mixing LC acrylic copolymers with HMMM, *p*-TSA, and CH₂Cl₂, casting on NaCl plates, and heating in a forced air oven at 150°C for 30 min to form relatively thin films. FT-IR spectra were recorded with a Mattson Model Cygnus 25 spectrophotometer. Absorbance at 3445 cm⁻¹ (A_{3445} , absorbance of OH in COOH) and 1735 cm⁻¹ (A_{1735} , absorbance of C=O in esters) were measured. Ratios of A_{3445}/A_{1735} were used as approximate indexes of reaction extents of COOH groups with HMMM.

Samples of crosslinked films were prepared similarly for microscopy except they were cast on glass plates. Optical textures were examined with a polarizing microscope 7 days after crosslinking.

Tests of Coatings

Film properties of enamels made from LC acrylic copolymers and from amorphous copolymers were measured 7 days after crosslinking. Reverse impact strength, Knoop hardness (KHN), resistance to acetone, and crosshatch adhesion were measured according to ASTM D2794, D1474, D2792, and D3359, respectively. The conical mandrel bend test was graded "pass" when there was no cracking, and graded "fail" when cracking occurred.

TABLE I
 Composition and \bar{M}_n of Amorphous Acrylic Copolymers

Copolymer code	Mol ratio (MMA/BA/AA)	T_g ($^{\circ}\text{C}$, calcd)	\bar{M}_n ($\times 10^{-3}$)
R1	0.164/0.761/0.075	-30	4.7
R2	0.35/0.60/0.05	-10	4.5
R3	0.443/0.457/0.10	10	4.8
R4	0.14/0.76/0.10	-30	4.5
R5	0.30/0.60/0.10	-10	4.9
R6	0.506/0.394/0.10	20	4.7
R7	0.646/0.254/0.10	45	4.8
R8	0.35/0.60/0.05	-10	15.1
R9	0.423/0.527/0.05	0	14.3
R10	0.49/0.46/0.05	10	13.7
R11	0.35/0.60/0.05	-10	13.1
R12	0.35/0.60/0.05	-10	28.5
R13	0.423/0.527/0.05	0	4.8
R14	0.400/0.525/0.075	0	4.6
R15	0.376/0.524/0.10	0	4.6
R16	0.188/0.762/0.05	-30	5.0

RESULTS AND DISCUSSION

Preparation and Characterization of LC Acrylic Copolymers

Procedures for preparation of acrylic copolymers, grafting with PHBA to form LC acrylic copolymers, structural characterization of graft copolymers, and characterization of LC phases in the graft copolymers were essentially as described previously.³⁻⁵

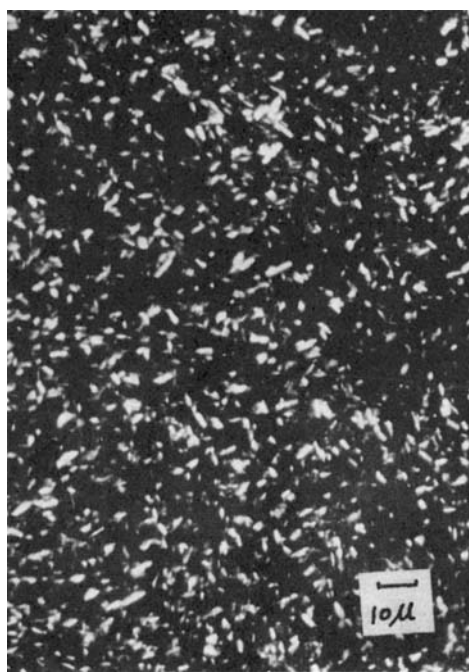
Amorphous acrylic copolymers composed of methyl methacrylate (MMA), butyl acrylate (BA), and acrylic acid (AA) were synthesized. These compositions are shown in Table I. These copolymers were used both as controls and as substrates for grafting. The difference in acrylic substances between this study and the previous study is the molecular weight of the substrate copolymer. In the previous study, optimum \bar{M}_n 's for uncrosslinked coatings were above 15,000. In this study \bar{M}_n 's were 4500-5000 except for one series in which higher \bar{M}_n 's were studied. Calculated (Fox equation) T_g 's were varied from -30 to 45 $^{\circ}\text{C}$ average. Functionality was varied from 5 to 10 mol %.

Compositions of PHBA-grafted copolymers with different PHBA/COOH ratios are described in Table II. Evidence for the assigned graft copolymer structures (Scheme I) included IR, $^1\text{H-NMR}$, the modest increase in T_g , and the presence of endothermal peaks in the DSC thermograms as described previously.³ Grafting efficiency (GE%) was estimated gravimetrically.³ Average PHBA/COOH ratios were calculated from GE %. They were 3 + 0.2, 4 + 0.2, and 5 + 0.3 when PHBA monomer in the ratio of 3.5, 5.5, and 7.0 mol, respectively, per equivalent acrylic copolymer was fed to the grafting reaction.

The presence of LC phases in the PHBA-grafted acrylic copolymers was established by polarizing microscopy and differential scanning calorimetry (DSC). Polarizing micrographs [for example, Fig. 1(a)] were taken at 25 $^{\circ}\text{C}$. All the grafted copolymers had small, grainy or batonnet like optical textures of

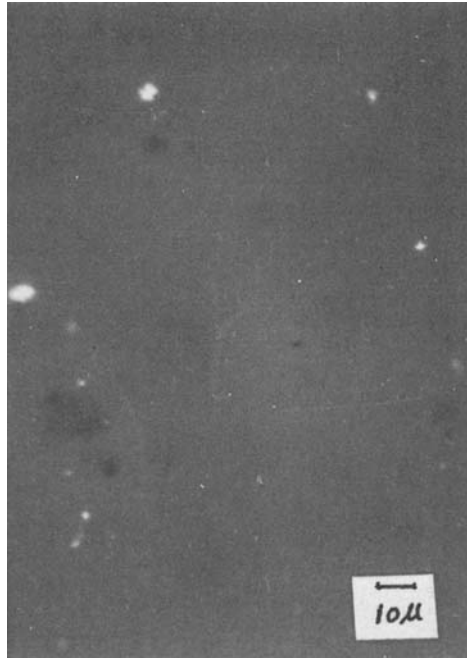
TABLE II
Compositions and Characteristics of PHBA-Grafted Acrylic Copolymers

Copolymer code	PHBA/COOH	PHBA content (wt %)	T_g ($^{\circ}\text{C}$, measured)	T_{cl}	Appearance
GR1a	5.2	28.2	-24	179	Smectic
GR1b	4.1	18.9	-25	168	Smectic
GR2a	3.1	13.9	-7	152	Smectic
GR2b	4.2	18.0	-5	163	Smectic
GR2c	4.9	20.3	-4	174	Smectic
GR3a	3.2	25.9	15	156	Smectic
GR3b	4.0	30.3	17	167	Smectic
GR3c	5.2	36.2	19	180	Smectic
GR4	4.1	30.0	-22	165	Smectic
GR5	3.9	29.1	-3	164	Smectic
GR8	4.8	20.0	-3	163	Smectic
GR9	5.1	21.3	6	177	Smectic
GR10	5.0	21.2	17	179	Smectic
GR11	4.9	20.3	-4	175	Smectic
GR12	4.9	20.3	-3	177	Smectic
GR13	5.2	21.6	7	178	Smectic
GR14	5.1	28.9	10	181	Smectic
GR15	4.8	34.0	12	183	Smectic
GR16	4.0	16.7	-25	167	Smectic

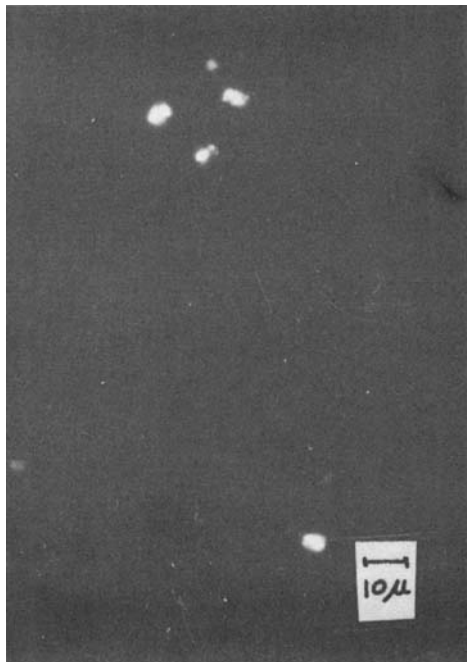


(a)

Fig. 1. Polarizing micrographs LC copolymers of GR1a: (a) before crosslinking; (b) same crosslinker with 16.7 wt % HMMM; (c) crosslinked with 44.4 wt % HMMM.



(b)



(c)

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

uniform size, similar to those observed in the previous study.⁵ Appearance of these textures supported the assignment of LC microstructures and suggested that the LC domains exist in smectic states.^{10,11} The DSC thermograms of the grafted products had inflections attributable to T_g 's and small endothermic peaks at the temperatures attributable to the clearing (T_{cl}) of LC phases. T_g and T_{cl} of each LC acrylic copolymer are indicated in Table II.

Reaction Extent of HMMM with COOH Groups Contained in LC Phases

When HMMM is heated with COOH-functional acrylic copolymers at 150°C in the presence of *p*-TSA, it is expected that some fraction of the $-\text{CH}_2\text{OCH}_3$ groups of the HMMM will crosslink with the COOH groups of the copolymer, some fraction will self-condense and some fraction will not react.¹²⁻¹⁵ It was of interest to compare behavior of the COOH groups in amorphous copolymer with those in LC graft copolymer GR1a. Differences might be anticipated because the COOH groups of the LC copolymer are attached directly to the mesogenic units and a substantial fraction of them presumably reside inside LC domains at the start of crosslinking. It was uncertain what fraction will react because the curing temperature (150°C) was below clearing point of GR1a in the absence of HMMM. The ratio of IR absorbances at 3445–1735 cm^{-1} (A_{3445}/A_{1735}) was used as an index of reaction extents of HMMM with COOH groups; 3445 and 1735 cm^{-1} are the characteristic absorption wavenumbers of OH in COOH and C=O in ester respectively. Different weightrratios of HMMM to acrylic were used. Results are shown in Table III.

As can be seen from Table III reaction extents of HMMM with COOH groups were high for both amorphous copolymer R1 and LC copolymer GR1a. However, the extents of reaction of GR1a was slightly lower than those of R1 at all HMMM levels. For example the A_{3445}/A_{1735} ratio of crosslinked film of amorphous polymer R1 was 0.25; it was reduced to about 0.05 in the cured films when $[\text{OCH}_3]/[\text{COOH}]$ ratios were in the range of 3.4–13.5. The A_{3445}/A_{1735} ratio of crosslinked film of LC polymer GR1a was 0.22; it was

TABLE III
IR Absorbance Ratios in Crosslinked Films of R1 and GR1a
with Different Concentration of HMMM

[HMMM] (wt %)	$[\text{OCH}_3]/[\text{COOH}]$	A_{3445}/A_{1735}
R1		
0	0	0.25
16.7	3.37	0.05
37.5	10.11	0.04
44.4	13.48	0.05
GR1a		
0	0	0.22
16.7	3.37	0.06
37.5	10.11	0.07
44.4	13.48	0.06

reduced to about 0.06 in the cured films at the same $[\text{OCH}_3]/[\text{COOH}]$ ratio range. In both cases the extent of reaction of COOH groups with HMMM was virtually unaffected by $[\text{OCH}_3]/[\text{COOH}]$ ratio. To summarize, results in this section suggest that either reactivity of HMMM with COOH groups in PHBA grafts is slightly lower than that of COOH groups in amorphous polymers or that a slightly higher fraction of COOH groups in PHBA grafts is prevented from reacting by spatial constraints.

Optical Textures of Crosslinked Films

Films of uncrosslinked LC acrylic copolymers obtained in this study were translucent or opaque. When examined under the polarizing microscope, they showed grainy or batonnetlike textures suggestive of smectic order. After crosslinking with HMMM, the films were transparent; birefringent domains were still visible under the polarizing microscope, although their population was much reduced. Birefringent domains were visible even in films cured with $[\text{OCH}_3]/[\text{COOH}]$ ratios as high as 13.5. For example, Figures 1(a), 1(b), and 1(c) show the polarizing micrographs of films of LC copolymer GR1a before cure and after crosslinking at $[\text{OCH}_3]/[\text{COOH}]$ ratios of 3.4 and 13.5, respectively.

Comparison of Film Properties between IC Polymers and Amorphous Polymers

A major objective of this study was to assess the potential of LC acrylic copolymers to improve the film physical properties of high-solids baked coatings above the level attainable with amorphous acrylic copolymers. LC acrylic copolymers and their amorphous counterpart polymers were crosslinked with HMMM (acrylic: HMMM wt ratio 71.4:28.6) at the same conditions (150°C, 30 min), and their film properties were measured and compared.

A representative pair of copolymers, amorphous acrylic polymer **R1**, having calcd T_g of -30°C, \bar{M}_n of 4750, and functionality of 7.5 mol%, and its LC counterpart **GR1a** (PHBA/COOH ratio = 5.2) were chosen for study. They were crosslinked with 16.7, 28.6, 37.5, and 44.4 wt% of HMMM.

The empirical indicators of film properties used in this study were Knoop hardness, reverse impact strength, conical mandrel bendability, cross-hatch adhesion, resistance to acetone, and film appearance. The results are summarized in Table IV, where it is seen that properties of films made from LC copolymers were substantially superior to those of their amorphous counterparts. All cured films from both amorphous and LC acrylic polymers were transparent and glossy and had excellent mandrel bendability and excellent adhesion. When concentrations of HMMM were 37.5 wt% or less, all the cured films had excellent impact resistance (> 80 in. lb). However, when concentration of HMMM was 44.4 wt%, films of **GR1a** had poor impact resistance, indicating lack of elasticity. Films of **R1** with 44.4% HMMM had good impact resistance (60 in. lb); this result is not surprising in view of the low T_g of the amorphous copolymer.

The major differences are hardness and solvent resistance. Films made from LC polymer **GR1a** had much higher Knoop hardness and better resistance to acetone than their counterparts made from amorphous copolymer **R1** at each

TABLE IV
Comparison of Film Properties of Coatings made from Amorphous Polymers **R1**
and LC Polymer **GR1a**

HMMM content (wt %)	Knoop hardness (KHN)	Rev. imp. strength (in. lb)	Mandrel bend test	Crosshatch adhesion	Resistance to acetone
(A) Amorphous polymer R1					
16.7	< 4	> 80	Pass	100%	Fair
28.6	< 4	> 80	Pass	100%	Good
37.5	5	> 80	Pass	100%	Good
44.4	12	60	Pass	100%	Good
(B) LC polymer GR1a					
16.7	11	> 80	Pass	100%	Good
28.6	18	> 80	Pass	100%	Good
37.5	32	> 80	Pass	100%	Excellent
44.4	35	< 10	Pass	100%	Excellent

Note: All films appear transparent and glossy.

level of HMMM. For example, when the level of HMMM was 37.5 wt%, films from **GR1a** had a hardness of 32 KHN whereas those of **R1** were only 5 KHN. These results parallel those of air-drying LC acrylic films as described by us previously.⁵ For comparison, typical automotive enamels have hardness of about 12 KHN. Thus the enamel made from LC polymers **GR1a** is extremely hard for an organic coating; yet it retains excellent adhesion, elasticity, and impact resistance.

Film Properties of LC Acrylic Polymers with Different PHBA / COOH Ratios

In a previous study⁵ we found the PHBA/COOH ratios affected the film properties of air-drying LC acrylic copolymers. Here we investigated whether these ratios similarly affect the properties of crosslinked films of LC acrylic copolymers.

In this part of the present study two amorphous polymers, **R2** and **R3** and their LC derivatives **GR2a**, **GR2b**, **GR2c**, **GR3a**, **GR3b**, and **GR3c** were crosslinked with 28.6 wt % of HMMM at 150°C for 30 min. **R2** and **R3** differ in T_g and in functionality, **R2** being lower in both respects (Table I). The LC derivatives had PHBA/COOH ratios ranging from about 3 to 5 as indicated in Table II.

Film properties are shown in Table V. All the cured films were transparent and glossy, and they had excellent adhesion and good resistance to acetone. However, films from LC copolymers were much harder than their amorphous counterparts. Hardness increased as the PHBA/COOH ratio increased. Impact resistance was greatly affected by T_g and functionality of acrylic backbone for both LC and amorphous copolymers. Films made from LC polymers **GR2a-c**, derived from a low- T_g , low-functionality acrylic backbone, had excellent impact resistance (> 80 in. lb) while films from **GR3a-c**, derived from a higher- T_g , higher functionality acrylic backbone, had poor impact resistance (< 10 in. lb). Effect of PHBA/COOH ratio on impact resistance is not clear from these results.

TABLE V
Effects of PHBA/COOH Ratio on Properties of Films made from LC Acrylic Copolymers

No.	No. PHBA/COOH	Knoop hardness (KHN)	Rev. imp. (in. lb)	Crosshatch adhesion	Mandrel bend test	Resistance to acetone
(A) R2-GR2 series						
R2	0	10	70	100%	Pass	Good
GR2a	3.1	18	> 80	100%	Pass	Good
GR2b	4.2	25	> 80	100%	Pass	Good
GR2c	4.9	30	> 80	100%	Pass	Good
(B) R3-GR3 series						
R3	0	19	15	100%	Pass	Good
GR3a	3.2	32	< 10	100%	Fail	Good
GR3b	4.0	40	< 10	100%	Fail	Good
GR3c	5.2	45	< 10	100%	Fail	Good

Note: All films appeared transparent and glossy.

As shown in Figures 1(b) and 1(c), the cured films made from LC copolymers still have a few visible birefringent domains; their exceptional hardness might be partly due to the presence of visible or submicroscopic LC domains. Another possibility is that the mesogenic PHBA units may harden low- T_g films without forming detectable LC domains; conceivably association of a small number (two or more) of mesogenic units might harden the film without

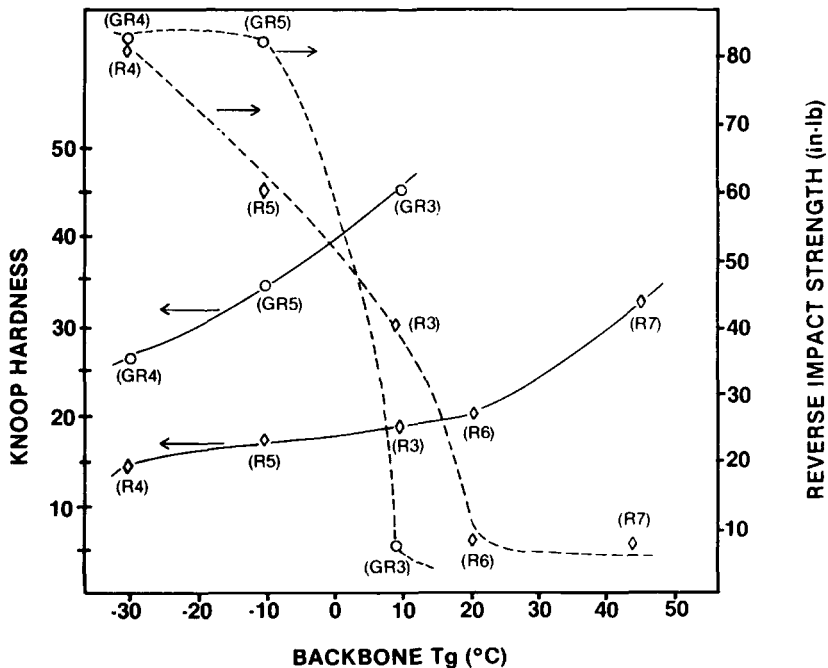


Fig. 2. Effect of backbone T_g on Knoop hardness and reverse impact strength of crosslinked films (I). (—) Knoop hardness; (---) reverse impact strength; (○) LC copolymers; (◇) amorphous copolymers. Acrylic backbone: $\bar{M}_n = 4700 \pm 200$, functionality = 10 mol %, PHBA/COOH ratio = 4 ± 0.2 . Copolymer code is shown in parenthesis.

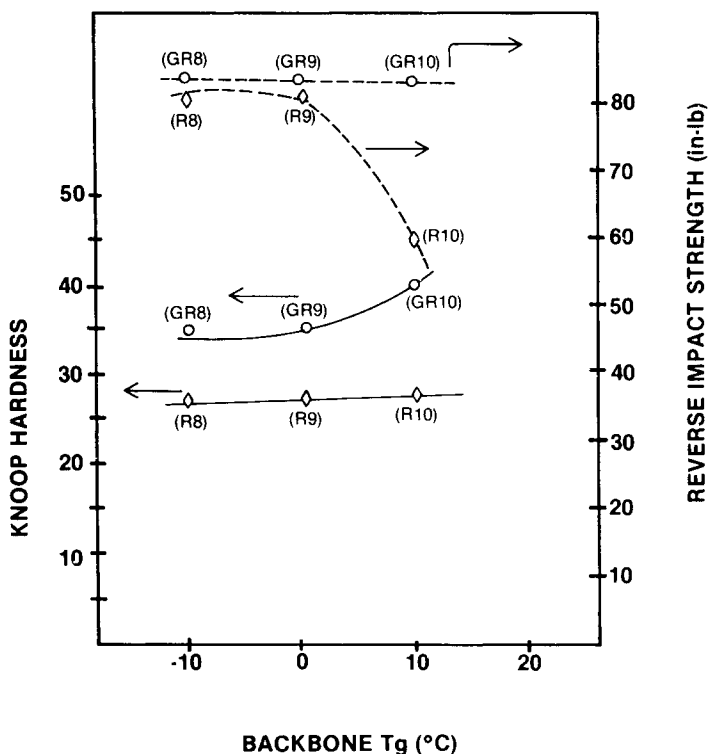


Fig. 3. Effect of backbone T_g on Knoop hardness and reverse impact strength of crosslinked films (II). (—) Knoop hardness; (---) reverse impact strength; (○) LC copolymers; (◇) amorphous copolymers. Acrylic backbone: $\bar{M}_n = 14,000 \pm 1500$, functionality = 5 mol %, PHBA/COOH ratio = 5 ± 0.2 . Copolymer code is shown in parenthesis.

substantially raising T_g . A third, but less likely, possibility is that the observed hardness is attributable to increased T_g of the network; however, this factor appears relatively minor since the LC polymers have T_g 's of only 3–8°C higher than their amorphous counterparts (as shown in Tables I and II), and low T_g films made from LC copolymers are much harder than higher- T_g films made from amorphous copolymers (Figs. 2 and 3).

High impact resistance requires good adhesion and an elastic film. Elasticity results from a proper combination of rigidity and flexibility. In the cured films made from LC copolymers crosslinking and, presumably, mesogenic units impart rigidity. Hardness can be controlled by adjusting the HMMM:copolymer ratio and the concentration and length of PHBA grafts. The present results indicate that, in enamels made from LC copolymers, flexibility depends mainly on the nature of polymer structures between crosslinking sites; flexibility can be controlled by adjusting the structural parameters such as T_g , functionality, and M_n of polymer backbone.

To summarize this section, inclusion of mesogenic units offers a way to escape the dilemma of hardness and elasticity often encountered in designing high solids acrylic enamels. The dilemma is illustrated by comparing films made from amorphous copolymers **R2** and **R3** (Table V). **R2** gives a film that is fairly elastic but is too soft for many purposes; **R3** gives a hard but brittle film. Both films are substantially hardened by grafting mesogenic PHBA units

with little or no sacrifice of other properties. The effect is particularly advantageous when T_g and crosslink density (e.g., **GR2a-c**) are low.

Guidelines for LC Polymer Design

In order to optimize the film properties of LC acrylic polymers it is necessary to study the effects of T_g , \bar{M}_n , and functionality of acrylic backbone. Accordingly, variations of film properties as functions of these parameters were investigated. Knoop hardness and reverse impact strength were the empirical indicators of film properties.

Effect of Backbone T_g

Films from low MW ($\bar{M}_n = 4700 \pm 200$) and high functionality (10 mol %) amorphous polymers **R4**, **R5**, **R3**, **R6**, **R7** and their LC derivatives **GR4**, **GR5**, and **GR3** were tested and compared. Calculated T_g 's of these amorphous polymers ranged from -30 to 45°C as shown in Table I. Results are shown in Figure 2. Both hardness and impact resistance of LC polymers and their amorphous counterparts varied in the same trend: Hardness increased sharply when T_g was above 10°C ; however, reverse impact resistance dropped sharply when T_g was higher than -10°C . With LC copolymers it is possible to obtain both hard (> 30 KHN) and tough (reverse impact > 80 in. lb) films from LC polymers when backbone T_g was optimized. However, all films made from amorphous polymers suffered either from low hardness or poor impact resistance. Such films having impact resistance above 60 in. lb had hardness below 15 KHN, and films having hardness above 25 KHN had impact resistance below 10 in. lb.

Films from high MW ($\bar{M}_n = 14,000 \pm 150$) and low functionality (5 wt%) amorphous polymers **R8**, **R9**, and **R10** and their LC derivatives **GR8**, **GR9**, and **GR10** behaved similarly except that good impact resistance is attainable at higher T_g (Fig. 3). Films from LC polymers had excellent impact resistance (> 80 in. lb) and high hardness (> 33 KHN) when backbone T_g 's were -10 and 0°C , while films from their amorphous counterparts had lower hardness (around 25 KHN) and excellent impact resistance (> 80 in. lb).

The fact that impact resistance improves substantially as backbone T_g decreases has interesting implications. It suggests that motions of mesomorphic groups can to some extent "decouple" from main chain constraints if the backbone T_g is low enough, about -10 – 0°C in the present cases. Thus it is conjectured that flexible spacers may be unnecessary for low- T_g backbones. While this conjecture is unproven, it is consistent with earlier observations.⁵

Effects of Functionality

Films from amorphous polymers **R16**, **R1**, and **R4** and their LC derivatives **GR16**, **GR1b**, and **GR4** were tested and compared. The calculated T_g of acrylic backbone was fixed at -30°C and functionality ranged from 5 to 10 mol%. Results are shown in Figure 4. As expected from the low T_g , both the amorphous and the LC polymers had excellent impact resistance and hardness increased with functionality. However, all the LC polymers were about 10 KHN units harder than their amorphous counterparts.

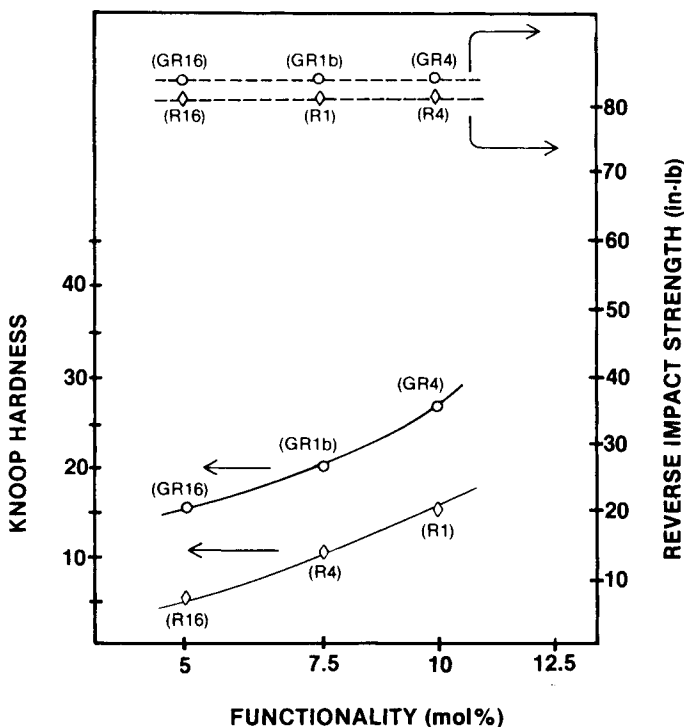


Fig. 4. Effect of functionality on Knoop hardness and reverse impact strength of crosslinked films (I). (—) Knoop hardness; (---) reverse impact strength; (○) LC copolymers; (◇) amorphous copolymers. Acrylic backbone: $\bar{M}_n = 4700 \pm 300$; calcd $T_g = -30^\circ\text{C}$; PHBA/COOH = 4 ± 0.1 . Copolymer code is shown in parenthesis.

To examine variation of film properties as a function of functionality of another series of amorphous polymers R13, R14, and R15 and their LC derivatives GR13, GR14, and GR15 were compound. Results are shown in Figure 5. Calculated T_g was fixed at 0°C , and functionality ranged from 5 to 10 mol%. Again, hardness increased with functionality. In this case LC polymers were about 15 KHN units harder than their amorphous counterparts. Impact resistance dropped sharply at about 7.5 mol% in both series; this drop is attributable to lack of elasticity resulting from the relatively high T_g and high crosslink density.

Effect of Backbone \bar{M}_n

\bar{M}_n 's of acrylic copolymers used for high solids coatings are usually in the range of 2000–5000.¹¹ In this study most of the acrylic substrates had \bar{M}_n around 5000. This \bar{M}_n is below the level (about 10,000) at which chain entanglements substantially affect properties of acrylic copolymers. We previously found that chain entanglements were important in determining the film properties of air-drying uncrosslinked acrylic polymers.⁵ Here we compared the effect of molecular weight on the film properties of crosslinked amorphous and LC polymers. Amorphous polymers R2, R11, and R12 (with calculated T_g of 0°C , functionality of 5 mol %, and \bar{M}_n ranging from about 5000 to about

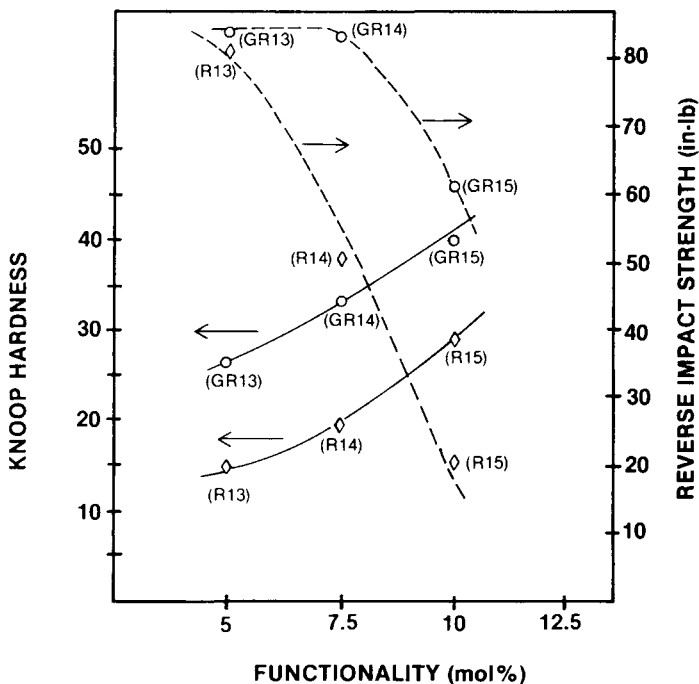


Fig. 5. Effect of functionality on Knoop hardness and reverse impact strength of crosslinked films (II). (—) Knoop hardness; (---) reverse impact strength; (O) LC copolymers; (\diamond) amorphous copolymers. Acrylic backbone: $\bar{M}_n = 4,750 \pm 200$, calcd $T_g = 0^\circ\text{C}$, PHBA/COOH ratio = 5 ± 0.2 . Copolymer code is shown in parenthesis.

30,000) and their LC counterparts **GR2c**, **GR11**, and **GR12** were cured with HMMM and tested. Results are shown in Figure 6. Hardness of both amorphous and LC polymers increased with \bar{M}_n up to about 15,000 and then leveled off. Impact resistance of films from amorphous polymers was high (> 60 in. lb) and increased slightly when \bar{M}_n was above about 15,000. Impact resistance of all films from LC polymers was excellent (> 80 in. lb); the effect \bar{M}_n could not be assessed because all samples were off-scale on our test device. Again, the LC polymers had both higher hardness and higher impact resistance than their amorphous counterparts.

The observations in this section suggest the following guidelines for design of LC acrylic copolymers for enamel coatings for applications where both hardness and elasticity are needed:

1. T_g of the acrylic backbone may be low; the optimum may be in the range of -20 – 0°C and possibly lower. The amorphous counterparts of such low T_g usually give soft films. The increase in hardness of LC polymers is attributed to the presence of mesogenic units. The elasticity associated with low T_g is at least partly retained in films from LC polymers. Of course, for high temperature applications higher backbone T_g is probably desirable.

2. When high PHBA/COOH ratios (5 or above) are synthetically feasible, optimum functionality is probably below 7.5 mol%. Lower PHBA/COOH ratios provide shorter mesogenic units and may require higher functionality.

3. While low- \bar{M}_n LC copolymers provide good properties, increasing \bar{M}_n up to about 15,000 will improve both hardness and impact resistance.

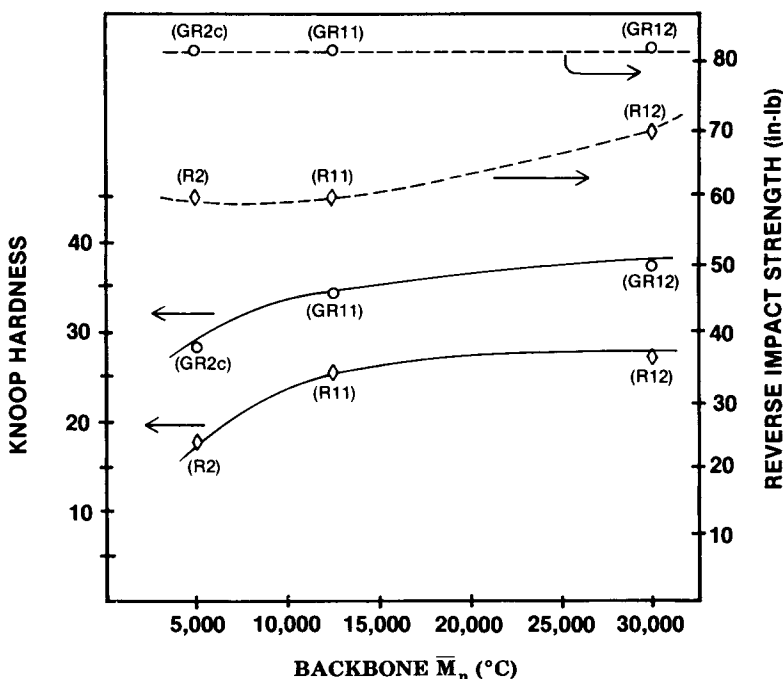


Fig. 6. Effect of backbone \bar{M}_n on Knoop hardness and reverse impact strength of crosslinked films. (—) Knoop hardness; (---) reverse impact strength; (○) LC copolymers; (◇) amorphous copolymers. Acrylic backbone: calcd $T_g = -10^\circ\text{C}$, functionality = 5 mol %, PHBA/COOH ratio = 4.9. Copolymer code is shown in parenthesis.

CONCLUSIONS

Carboxyl-functional liquid crystalline (LC) acrylic copolymers can be obtained by grafting PHBA segments of 3–5 aromatic units to acrylic substrates as shown in Scheme I.

The LC acrylic copolymers with functionality ranging from 5 to 10 mol% can be crosslinked with HMMM at 150°C to form coating films. A low population of birefringent domains is visible in these films.

Coating films derived from LC copolymers have excellent adhesion and solvent resistance, and optimum formulas have an extraordinary combination of hardness (> 35 KHN) and impact resistance (> 80 in. lb). Thus LC copolymers appear to have excellent potential to replace conventional acrylic copolymers in high solids baking coatings.

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References

1. D. H. Solomon, in *The Chemistry of Organic Film Formers*, Krieger, Malabar, FL, 1982, Chap. 10.
2. T. Nakamichi and K. Shibato, *J. Jpn. Soc. Colour Mater.*, **59**, 10 (1986).
3. D. S. Chen and F. N. Jones, *J. Polym. Sci., Polym. Chem. Ed.*, **25**, 1109 (1987).
4. D. S. Chen and F. N. Jones, *J. Coat. Technol.*, **60**(756), (1988), to appear.
5. D. S. Chen and F. N. Jones, *J. Appl. Polym. Sci.*, to appear.

6. D. Z. Wang and F. N. Jones, *Am. Chem. Soc., Div. Polym. Mater. Sci. Eng.*, **56**, 645 (1987).
7. A. Dimian and F. N. Jones, *Am. Chem. Soc., Div. Polym. Mater. Sci. Eng.*, **56**, 640 (1987).
8. R. A. Gray, *J. Coat. Technol.*, **57**(728), 83 (1985).
9. T. G. Fox, *Bull. Am. Phys. Soc.*, **1**, 123 (1956).
10. W. R. Krigbaum and J. Watanabe, *Polymer*, **24**, 1299 (1983).
11. Y. S. Freidzon, A. V. Kharitonov, V. P. Shibaev, and N. A. Plate, *Euro. Polym. J.*, **2**(3), 211 (1985).
12. W. Blank, *J. Coat. Technol.*, **54**(687), 26 (1982).
13. J. O. Santer, *Prog. Org. Coat.*, **12**, 309 (1984).
14. D. R. Bauer, *Prog. Org. Coat.*, **14**, 193 (1986).
15. T. Yamamoto, T. Nakamichi and O. Ohe, *J. Coat. Technol.*, **60** [762], 51 (1988).

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