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Synthesis, characterization and coating applications of liquid crystalline acrylic copolymers

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The synthesis and characterization of the coating properties of liquid crystalline acrylic copolymers containing *p*-hydroxybenzoic acid as mesogenic group are described. The synthetic method involves the grafting of *p*-hydroxybenzoic acid onto acrylic copolymers, confirmed by characterization with IR and ^{1}H NMR techniques. The presence of liquid crystal was assessed by observing optical textures under the polarizing microscope and by DSC and TGA. The coating properties such as flexibility, hardness, adhesion, drying time, viscosity, etc. of acrylic copolymers as well as of liquid crystalline acrylic copolymers were studied. The results showed that LC polymers have potential for coating applications.

1. Introduction

Liquid crystalline (LC) polymers in general have a rigid or semi-flexible molecular chain and hence exhibit distinct physical properties not to be expected in common flexible polymers. There has been much interest in the structural aspect of polymer solids prepared from the liquid crystalline state. They often show specific kinds of supermolecular structure and morphology not to be seen in the majority of conventional synthetic polymers in the solid state. A variety of liquid crystalline polymers have been synthesized and investigated [1–3]. Thermotropic LC polymers belong to a relatively novel class of liquid crystalline compounds and may have mesogenic units in the main chain or in the side chain. In side chain LC polymers the mesogenic units link as pendant in the side chain to a polymer backbone.

LC polymers have been widely studied [4–7], nevertheless there is ample scope for development of liquid crystalline acrylic copolymers in coatings applications. Previously reported work [5–7] on LC polymers focussed only on this synthesis and characterization, but relatively few references [8, 9] are available on the study of coating properties of LC acrylic copolymers. A comprehensive study of the coating properties of LC acrylic copolymers was therefore undertaken.

The present paper reports the synthesis of LC acrylic copolymers by grafting the mesogenic *p*-hydroxybenzoic acid, onto acrylic copolymers. The experimental approach was to prepare carboxyl functional acrylic copolymers and then graft the acid onto the carboxyl groups using an esterification agent and catalyst. The products were characterized by IR, ^{1}H NMR and optical microscopy to demonstrate the presence of liquid crystallinity in the copolymer. The main emphasis of the work was then to study the coating properties of LC acrylic copolymers. Characteristics such as adhesion, flexibility, hardness, chemical resistance as well as drying time and viscosity were studied.

2. Experimental

2.1. *Materials*

Methyl methacrylate (MMA), ethyl acrylate (EA), butyl acrylate (BA) and acrylic acid (AA) of analytical grade were obtained from Fluka and freed from inhibitor by washing initially with 10% sodium hydroxide solution, followed by distilled water and drying over anhydrous calcium chloride. Azo(bisisobutyronitrile) (AIBN) (BDH, India) was purified by recrystallization from chloroform. *p*-Hydroxybenzoic acid (PHBA), dicyclohexylcarbodiimide (DCC), *p*-toluenesulphonic acid (*p*-TSA), dioxane, toluene, methylene chloride and ethyl acetate were of extra pure grade (s.d. Fine Chem Ltd) and were used without further purification.

2.2. *Copolymerizations*

Toluene was placed in a 250 ml three-necked flask equipped with condenser, stirrer and nitrogen gas inlet. Predetermined amounts of methyl methacrylate, acrylate monomer, acrylic acid and AIBN were charged into the reaction flask and held at 80 ± 1°C with constant stirring for 5 h. After the completion of the reaction the resinous

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product was precipitated by addition of petroleum ether to remove any unreacted comonomers and initiator. The monomer compositions are summarized in table 1 and the reaction is outlined in scheme 1.

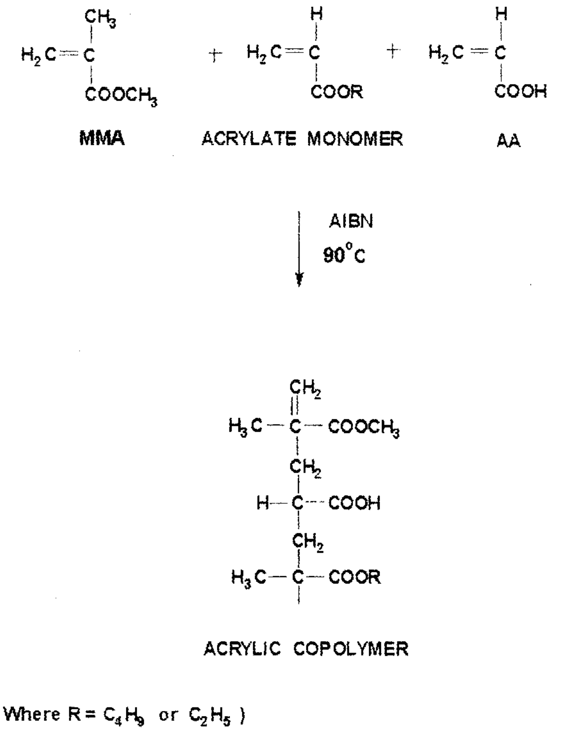
2.3. *Liquid crystalline acrylic copolymers*

A predetermined amount of acrylic copolymer, *p*-hydroxybenzoic acid, dicyclohexylcarbodiimide and *p*-toluenesulphonic acid in dioxan were charged into a three-necked reaction flask equipped with condenser and stirrer. The flask was held at 90 ± 1°C with constant stirring. A precipitate of dicyclohexyl urea (DCU) and *p*-hydroxybenzoic acid oligomer (PHBA oligomer) was obtained after about 5 min. The heating was continued for 30 h and the reaction mixture was then filtered to remove precipitates of DCU and PHBA oligomers. The filtrate was concentrated and redissolved in methylene chloride. This solution was washed with aqueous HCl to remove impurities, and then with water. The solution was further treated with ethyl acetate, cooled overnight and filtered to ensure the complete removal of DCU, if any. It was then cooled in a freezer overnight and filtered. The filtrate was vacuum dried at 85°C to yield a yellow resinous product. The experimental compositions are summarized in table 2 and the reaction is outlined in scheme 2.

Table 1. Compositions of the acrylic copolymers.

Copolymer code	Mole fraction	T_g/°C, calcd
MMA-BA-AA-series[a]		
MBA1	0.36/0.59/0.05	−5
MBA2	0.32/0.63/0.05	−10
MBA3	0.40/0.55/0.05	0
MBA4	0.46/0.525/0.05	5
MBA5	0.47/0.48/0.05	10
MMA-EA-AA series[b]		
MEA6	0.14/0.81/0.05	−5
MEA7	0.10/0.86/0.05	−10
MEA8	0.20/0.75/0.05	0
MEA9	0.25/0.70/0.05	5
MEA10	0.30/0.65/0.05	10

[a] Methyl methacrylate–butyl acrylate–acrylic acid.
[b] Methyl methacrylate–ethyl acrylate–acrylic acid.



Scheme 1. Synthesis of acrylic copolymer.

2.4. *Characterization of copolymers and liquid crystalline copolymers*

IR spectra of acrylic copolymers and LC acrylic copolymers were recorded on a Shimadzu FTIR 4200 spectrophotometer; the samples were dissolved in chloroform and a thin film of polymer was cast on a NaCl pellet. ^{1}H NMR spectra of acrylic copolymers and LC acrylic copolymers were recorded using a Varian 60 MHz ^{1}H NMR spectrophotometer. Samples were in the form of solutions in carbon tetrachloride (spectroscopic grade) at ambient temperature. Tetramethylsilane (TMS) was used as internal standard.

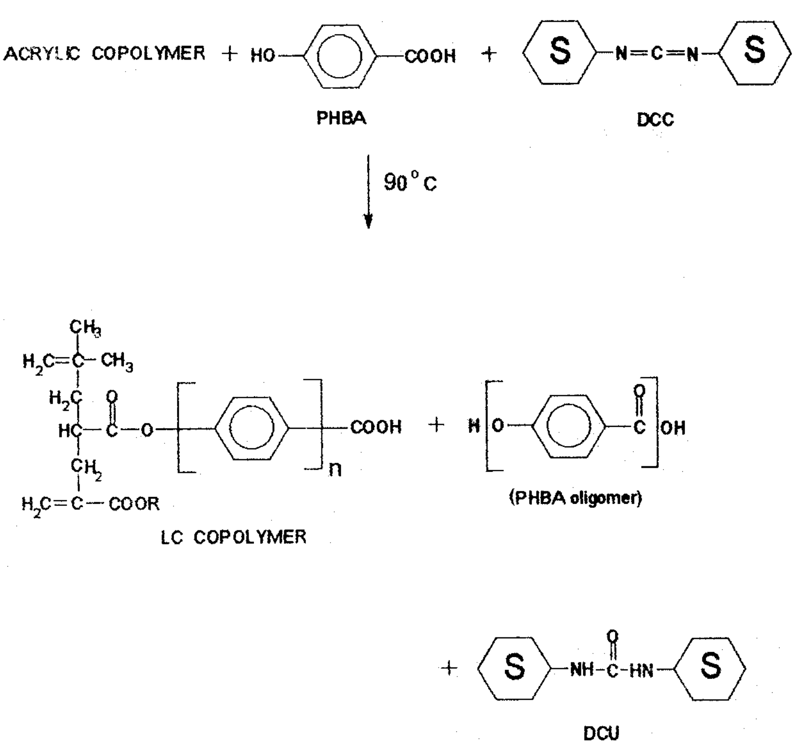
Optical textures were observed under a polarizing microscope by Carl Zeiss MC-63, Germany. A small amount of sample was placed between two glass slides and was moved back and forth until the texture was observed.

Differential scanning calorimetry (DSC) was performed on a Mettler TA 4000 DSC-30 instrument, at a heating rate of 10°C min^{-1}, between − 50°C and 100°C

Table 2. Compositions of liquid crystalline acrylic copolymers.

LC code[b]	Copolymer /mol	PHBA /mol	DCC /mol	*p*-TSA /wt %[a]
GMBA1	0.008	0.016	0.016	1
GMBA2	0.008	0.016	0.016	1
GMBA3	0.007	0.014	0.014	1
GMBA4	0.007	0.014	0.014	1
GMBA5	0.007	0.014	0.014	1
GMEA6	0.006	0.012	0.012	1
GMEA7	0.006	0.012	0.012	1
GMEA8	0.008	0.016	0.016	1
GMEA9	0.008	0.016	0.016	1
GMEA10	0.008	0.016	0.016	1

[a] wt % of the total amount of copolymer and PHBA.
[b] Graft copolymer of MBA1 to MBA5 (methyl methacrylate–butyl acrylate–acrylic acid) and MEA6 to MEA10 (methyl methacrylate–ethyl acrylate–acrylic acid).



Scheme 2. Synthesis of liquid crystalline (LC) acrylic copolymer.

(R = C_4H_9 OR C_2H_5)

under nitrogen. Thermogravimetric analysis (TGA) was performed on a Mettler TA 4000 TG-50 instrument, in the temperature range 35 to 450°C with a heating rate of 10°C min^{-1}, under nitrogen. The viscosities of polymer samples were measured on a Brookfield viscometer (Model LVTD DV II). The viscosity of each polymer sample was measured using a small sample holder at 30°C.

2.5. *Measurement of coating properties*

The acrylic copolymers and LC acrylic copolymers were cast on steel panels by a casting bar. The mechanical properties of the film such as flexibility, pencil hardness, cross-cut adhesion and drying time were tested according to ASTM-D-522, ASTM-D-3363, ASTM-D-3359, ASTM-D-1640, respectively. The chemical resistance properties of the films, were studied by immersing the coated glass panels in 0.1N HCl, 0.1N NaOH or water for 24 h and examining for any changes.

3. Results and discussion

The acrylic copolymers were prepared by a free-radical polymerization technique using a standard method [10]. Monomer ratios were adjusted so that calculated glass transition temperature (T_g) varied from − 10°C to + 10°C (i.e. − 5, − 10, 0, 5 and 10°C). T_g values were calculated by Fox equations [10]. AIBN was used as initiator, since it causes relatively few side reactions and gives superior exterior durability to the films. In previously reported work [8] on the synthesis of LC acrylic copolymers, pyridine was used as solvent; in the present work, dioxan was used, to avoid the hazardous nature of pyridine.

3.1. *Characterization of acrylic copolymers and liquid crystalline acrylic copolymers*

The copolymers and the LC acrylic copolymers were characterized by IR and ^{1}H NMR spectra to confirm the grafting of *p*-hydroxybenzoic acid onto the acrylic copolymers. The IR spectra of the LC acrylic copolymer showed sharp peaks at 1610 and 1510 cm^{-1} attributed to the aromatic C–H stretching of *p*-hydroxybenzoic acid; these peaks were absent in the parent acrylic copolymer. ^{1}H NMR spectra of LC acrylic copolymers showed multiple peaks in the range of δ 7.0–7.3 ppm and δ 8.0–8.3 ppm, assignable to the aromatic hydrogens *ortho* to OH and COO*R* groups respectively. The IR and ^{1}H NMR results confirmed the grafting of *p*-hydroxybenzoic acid onto the acrylic copolymers.

At 25°C the liquid crystal regions in the grafted acrylic copolymers [11] appeared as birefringent rod-shaped domains under the polarizing microscope, as shown in the photograph of figure 1. The birefringence disappeared at the transition of $T = 150°C$ and reappeared upon cooling. Hence the copolymer at room temperature is apparently phase separated into liquid crystalline and non-liquid crystalline domains.

3.2. *DSC*

In the present study the acrylic copolymer compositions were calculated by adjusting T_g by the Fox equation and they were then grafted onto the mesogenic group to form the LC acrylic copolymer. DSC was used to obtain the glass transition temperature of the polymer sample and to compare the calculated T_g of acrylic copolymer with the measured T_g of LC copolymer (mid-point transition temperatures were used). A representative DSC scan of GMBA4 is shown in figure 2; the transition peak is very weak and broad. The glass transition temperature corresponding to the mid-point of the peak is 4.1°C, which is very close to the calculated (Fox equation) T_g (5°C) of copolymer MBA4. The insertion of the mesogenic group marginally lowered the T_g value.

3.3. *TGA*

Every polymer has its characteristic decomposition temperature and thermal stability, thus an assessment of the thermal degradation characteristic of the LC acrylic copolymers was made by thermogravimetric analysis. Figure 3 shows the primary thermogram of GMBA4; thermal decomposition data based on the thermogram is given in table 3. The onset temperature for the major decomposition step was 349.6°C, ranging to 394°C. Most of the polymer sample decomposed by 450°C, which was the maximum temperature of decomposition under the present study, leaving a negligible residue of 0.37%.

Table 3. Thermogravimetric analysis data for GMBA 4[a].

% Weight loss	Specific temp. at wt. loss. (T_p/°C)
10.0	296.3
20.0	349.0
30.0	367.3
50.0	385.1
75.0	400.4

[a] Graft copolymer of MBA4 (methyl methacrylate–butyl acrylate–acrylic acid).

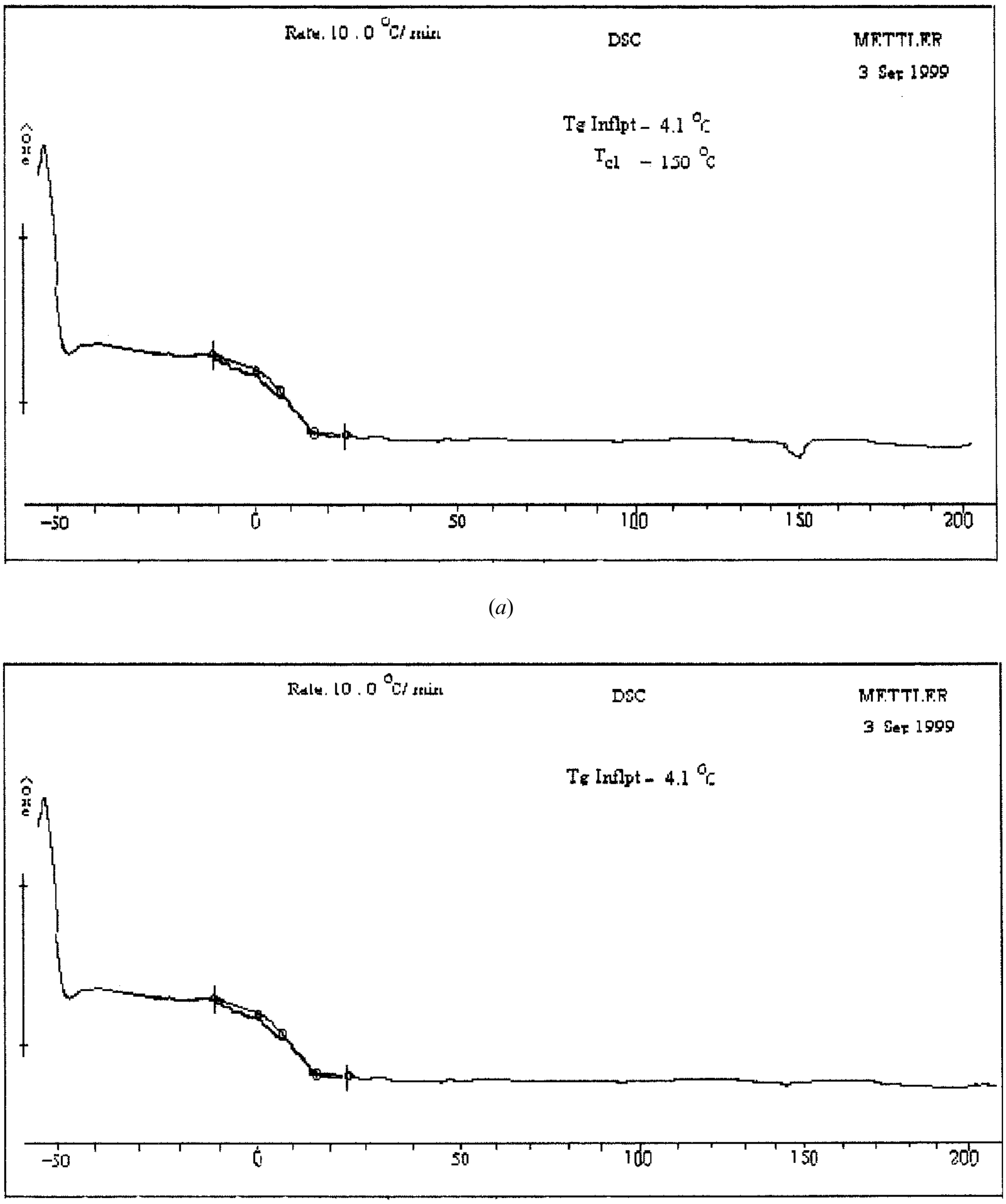
4. Assessment of coating properties

The coating properties of acrylic copolymers and LC acrylic copolymers were studied with respect to adhesion, hardness, drying time, flexibility, viscosity and chemical resistance.

4.1. *Adhesion*

The main purpose of a coating is to protect the substrate from the environment; the coating must adhere to the surface to offer any protection. Without sufficient adhesion, a coating of otherwise excellent properties in terms of chemical resistance and other parameters would be worthless. The adhesion of acrylic copolymer and LC acrylic copolymer was determined by using a cellophane tape cross-cut test (10 lines by 10 lines cut in 1 cm^2). In this method, a piece of cellophane tape was stuck over

Figure 1. Polarizing photomicrograph of liquid crystalline acrylic copolymer GMBA4 at 25°C.



(*a*)

(*b*)

Figure 2. DSC thermogram of (*a*) liquid crystalline acrylic copolymer GMBA4; (*b*) acrylic copolymer MBA4.

the cross-cut area of the samples; it was then removed by one pull and observed for any removal of the squares. If no squares were removed then the adhesion of film was termed 100%. It can be seen from table 4 that the acrylic copolymers from MBA1 to MBEA10 had 100% adhesion and this was maintained even after modification with the liquid crystalline group (GMBA1 to GMEA10). This was due to presence of the carbonyl group in the acrylic copolymer structure as well as in the LC copolymer structure.

4.2. *Hardness and flexibility*

Black lead pencils of various hardness (6B to 6H) were used for the pencil hardness test. This was done by holding the pencil in a writing position and then pushing it against the sample using a pressure short of breaking the lead. The hardness of the lead pencil which just fails to remove the film was taken as the pencil hardness of the film. From the results given in table 4, the hardness of acrylic copolymers ranged from 2B to HB, whereas the hardness of LC acrylic copolymers ranged from

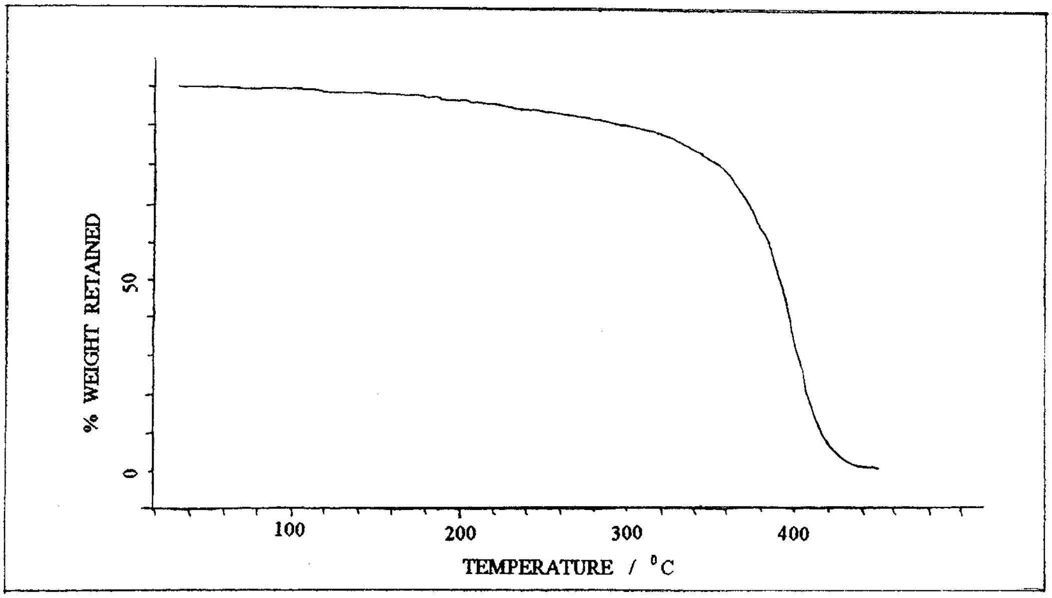


Figure 3. TG curve for liquid crystalline acrylic copolymer (GMBA4).

Table 4. Properties of acrylic copolymers and liquid crystalline acrylic copolymers.

Code	T_g (calc)/°C	Pencil hardness	Bending test	Cross-cut adhesion	Drying time/h	Viscosity/cps
Acrylic copolymers						
MBA1	− 5	2B	Pass	100%	30	170.3
MBA2	− 10	2B	Pass	100%	27	174.9
MBA3	0	B	Pass	100%	25	177.6
MBA4	5	HB	Pass	100%	23	185.4
MBA5	10	HB	Pass	100%	20	190.0
MEA6	− 5	2B	Pass	100%	31	166.0
MEA7	− 10	2B	Pass	100%	29	174.2
MEA8	0	B	Pass	100%	26	179.9
MEA9	5	HB	Pass	100%	22	188.8
MEA10	10	HB	Pass	100%	19	196.7
Liquid crystalline acrylic copolymers						
GMBA1	− 5	H	Pass	100%	10	80.3
GMBA2	− 10	2H	Pass	100%	9	80.5
GMBA3	0	2H	Pass	100%	7	81.2
GMBA4	5	3H	Pass	100%	6	81.5
GMBA5	10	4H	Pass	100%	6	81.9
GMEA6	− 5	H	Pass	100%	9	80.5
GMEA7	− 10	H	Pass	100%	9	80.7
GMEA8	0	2H	Pass	100%	7	80.9
GMEA9	5	2H	Pass	100%	7	81.0
GMEA10	10	3H	Pass	100%	6	81.3

H to 4H; i.e. the hardness of LC acrylic copolymers improved with respect to the parent acrylic copolymers. This is attributed to presence of the aromatic group in the LC acrylic copolymers, providing added stiffness to the polymer chain.

Flexibility testing was performed on a mandrel-bending tester. The samples were inserted into the test fixture, bent through 180° for about one second, then observed for any cracking of the film detectable by the naked eye. The bend test was graded ‘pass’ when there was no cracking and graded ‘fail’ when cracking occurred. The acrylic copolymer as well as LC acrylic copolymers were graded pass, indicating a flexible polymer (table 4), the flexibility being furnished by the linear molecular chain.

The interesting finding was that even though the hardness of the LC acrylic copolymers increased, the flexibility of the polymer was still retained. This was due to the linear chain of the molecular structure as well as the presence of the aromatic *p*-hydroxybenzoic acid group, giving both flexibility and hardness to the polymers.

4.3. *Drying time*

Drying time was studied at ambient temperature. Although the vast majority of coatings are applied in the fluid state, they are used in dried state. Thus the drying process is important as it can either enhance or detract from the properties of the coating. The results given in table 4 show that the drying times of the LC acrylic copolymers were lower (6–10 h) than those of the acrylic copolymers (19–30 h). The improvement may be attributed to the presence of the liquid crystalline group, providing rapid physical crosslinking through the liquid crystalline phases.

4.4 *Viscosity*

The effect of T_g (calcd) on viscosity is that there is a moderate increase in the viscosity of both acrylic copolymers and LC acrylic copolymers with increasing T_g (table 4). It may be noted that there is a substantial drop in the viscosity of LC acrylic copolymers as compared with the corresponding acrylic copolymers. This drop in viscosity may be due to the presence of liquid crystallinity in the acrylic copolymers: the molecular orientation of the LC phase may reduce the entanglement of the molecules, leading to a lower viscosity than for acrylic copolymers.

4.5. *Chemical resistance*

Glass panels coated with acrylic copolymers and newly synthesized LC copolymers were used for studying their resistance to acid, alkali and water. The coated glass panels were immersed in 0.1N HCl, 0.1NaOH and water for 24 h, then examined for any visual change in appearance of the film. The results are presented in table 5, from which it can be seen that acrylic copolymers MBA1 to MEA10 were slightly affected by acid, alkali and water, i.e. a slight softening of the film was observed; the LC acrylic copolymers GMBA1 to GMEA10 were unaffected by acid, alkali and water.

Table 5. Chemical resistance of acrylic copolymers and liquid crystalline acrylic copolymers.

Code	Water	0.1N HCL	0.1N NaOH
Acrylic copolymer			
MBA1–MBA5	S[a]	S	S
MEA6–MEA10	S	S	S
Liquid crystalline acrylic copolymer			
GMBA1–GMBA5	N[a]	N	N
GMEA6–GMEA10	N	N	N

[a] S = slight effect, N = no effect.

5. Conclusions

From the results of the work it can be concluded that the modification of modifying acrylic copolymers to LC acrylic copolymers by incorporation of a mesogenic group such as *p*-hydroxybenzoic acid has a good potential for coating applications. The resulting films have better adhesion, flexibility, hardness, drying time and chemical resistance, all basic requirements in the coating industry.

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