Copolymerization of 4-Chlorophenyl Acrylate with Methyl Acrylate: Synthesis, Characterization, Reactivity Ratios, and Their Applications in the Leather Industry

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ABSTRACT: 4-Chlorophenyl acrylate (CPA) was prepared by reacting 4-chlorophenol and acryloyl chloride in the presence of triethylamine in ethyl acetate solution. Poly(4chlorophenyl acrylate) and copoly(4-chlorophenyl acrylate–methyl acrylate) were synthesized by the free radical polymerization in ethyl acetate at 70°C. All the polymers were characterized by infrared (IR) and nuclear magnetic resonance (NMR) spectroscopic techniques. The composition of the copolymers was determined by the ¹H-NMR spectroscopic technique, that is, by integrating the aromatic peaks corresponding to the 4-chlorophenyl acrylate unit against the carbomethoxy group in the methyl acrylate unit. The reactivity ratios were calculated by Fineman–Ross, Kelen–Tudos (K–T), and the extended Kelen–Tudos methods. The values of r_1 and r_2 obtained by these methods were in close agreement with each other; that is, $r_1(CPA) = 0.64$ and $r_2(MA) = 0.13$ by the K–T method. The number-average molecular weight ($M_n = 1.55 \times 10^3$), the weight-average molecular weight (M_w = 8.39 imes 10³), and the polydispersity index $(\bar{M}_w/\bar{M}_n = 5.42)$ of poly(CPA) were determined by gel permeation chromatography (GPC). Thermal properties of the polymers were studied in a nitrogen atmosphere using thermogravimetric analysis (TGA). As the CPA increases in the copolymer, thermal stability of the copolymer increases (e.g., 90% weight loss occurs at 480°C for 20 mol % CPA, whereas the same weight loss occurs at 571°C for 80 mol % CPA). Acrylic binders, based on the CPA-MA-BA terpolymer, of different glass transition temperatures were prepared for applications in leather industry as top coat and base coat materials. These acrylic emulsions were cast into thin films, and their characteristics were tested for physical properties. These acrylic emulsions were applied as a base coat on leather, and the compositions having T_{σ} values of 1.08 and 9.25°C were found to have excellent properties as base coats for leather when compared with commercial samples. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 1153-1160, 1999

INTRODUCTION

Acrylic polymers are a class of reactive polymers that finds extensive applications due to the pres-

Journal of Applied Polymer Science, Vol. 73, 1153–1160 (1999) © 1999 John Wiley & Sons, Inc. CCC 0021-8995/99/071153-08 ence of electron abstracting groups in the aromatic ring.¹⁻⁴ These activated acrylate polymers find applications in pharmacological drugs as polymer supports, which are easily degradable, and in the binding of drugs into existing natural and synthetic polymers.⁵⁻⁷ Halogen-substituted phenyl acrylates are a class of activated monomers whose incorporation into the aromatic ring provide the facility for further modification with a

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 $\label{eq:Figure 1} \ \ ^1\text{H-NMR spectrum of poly(CPA-co-MA)}.$



Figure 2 ¹³C-NMR spectrum of poly(CPA-co-MA).



Scheme 1

wide range of nucleophilic reagents.^{8,9} Halogenated copolymer acrylates were employed for synthesizing electroactive polymers for the preparation of polymeric reagents carrying piperazine and isonitrile functionalities.^{10,11} Phenyl acrylates were used as polymer supports for various chemical reactions.¹²

The chemical composition of a few acrylate binders were determined by chromatography. Acrylic emulsion polymers, which are compatible with aqueous medium compared to the lacquer system where organic solvents are involved, are used in the modern finishing.¹³

The present work was under taken with an idea to develop a novel aqueous top coat and base coat emulsions for leather based on 4-chlorophenyl acrylate. These emulsions also serve as basically heat-resistant coatings. This work describes the synthesis of 4-chlorophenyl acrylate monomer, polymer, and their copolymers with methyl acrylate. These polymers were characterized, the reactivity ratios of copoly(CPA–MA) were determined, and the thermal stability of the polymers were studied. Further, terpolymers based on CPA–MA–BA were prepared. Terpolymer emulsions were applied as base coat materials in leather industry.

EXPERIMENTAL

Methyl acrylate (MA) (Fluka) and butyl acrylate (BA) (Aldrich) were freed from the initiator by washing successively with NaOH (5% w/v) solution and distilled water, dried over anhydrous sodium sulphate, and distilled under reduced pressure. Benzoyl peroxide (BPO) (Fluka) was purified by recrystallization in a 1 : 1 mixture of chloroform and methanol. Triethylamine (Fluka) was allowed to stand over sodium hydroxide for 12 h and distilled in the presence of 2% (w/v)

naphthyl isocyanate. The fraction boiling between 86–89°C was collected and used. Acryloyl chloride was prepared by distilling a mixture of acrylic acid and benzoyl chloride.¹⁴ Chloroform was shaken with half its volume of water and dried over anhydrous calcium chloride for 24 h; then it is distilled, and the fraction boiling at 61°C was collected and used. Methanol and all other materials were used as received.

Synthesis of the Monomer

4-Chlorophenyl acrylate (CPA) was synthesized by dissolving 4-chlorophenol (20 g) in ethyl acetate (100 mL) and triethylamine (27.6 mL) in a three-necked flask fitted with a condenser, a dropping funnel, and a stirrer. Acrylol chloride (18 mL) was dissolved in ethyl acetate (20 mL), taken in a 100-mL addition funnel, and added dropwise into the flask in such a way that the temperature was maintained around $0-5^{\circ}$ C. The reaction was allowed to proceed for 5 h at 0° C with constant stirring and left overnight at room temperature. The contents were washed with water and the solvent was evaporated to give viscous CPA monomer (19.31 g).

Yield: 68%. Elemental analysis is as follows.

Calcd: %C = 59.19; %H = 3.84. Experimental: %C = 58.87; %H = 3.74.

Synthesis of the Polymers

Homo(co)polymers were synthesized by taking appropriate quantity(ties) of the monomer(s), benzoyl peroxide as a free radical initiator (1% wt of monomers and solvent) and ethyl acetate as a solvent, in a 250-mL polymerization tube. Oxygen-free nitrogen was passed into reaction tube for about 3 min. Monomer(s) were allowed to polymerize at 70°C in a thermostatic bath. After



Structure 1

S1 No	Mole Fraction of CPA in Feed		Mole Fraction of CPA in Copolymer				
	M_{1}	M_2	m_1	m_2	M_1/M_2 X	m_1/m_2 Y	Conversion
1	0.20	0.80	0.283	0.717	0.250	0.394	8.84
2	0.35	0.65	0.290	0.710	0.538	0.408	7.68
3	0.50	0.50	0.416	0.584	1.000	0.712	8.25
4	0.65	0.35	0.481	0.519	1.857	0.926	6.82
5	0.80	0.20	0.635	0.365	4.000	1.739	8.25

Table I Copolymerization Data of CPA and MA

the desired time, the viscous polymer solution was diluted in chloroform and precipitated into excess methanol. The resultant polymer was dried *in vacuo*.

Preparation of the Binder

Monomer mixture comprising of 60 g of BA, 12 g of MA, and 2 g of CPA dissolved in ethyl acetate were taken in a 250-mL addition funnel. Catalyst (0.25 g of potassium persulphate and emulsifier mixture, 1.9 g of sodium lauryl sulphate, and 1.9 g of Noigen XY) dissolved in 50 mL of water were taken in the other addition funnel. These two addition columns were fitted to a RB flask (1 L) in which 0.18 g of sodium bisulphite dissolved in 70 mL of water was already taken. One-fourth of the mixture and equivalent amount of catalyst-emulsifier mixture were added to the reaction flask and stirred for 10 min. The remaining monomer mixture and the catalyst-emulsifier mixture were added dropwise with stirring at 70°C. The resulting emulsion was filtered and neutralized using ammonia solution.

Preparation of a Base Coat for Leather Finishing

75 mL of the binder prepared by the above procedure was mixed with 50 g of pigment, 10 mL of wax emulsion, 15 mL of protein binder, and 5 mL of liquid ammonia. The resulting emulsion was stirred well and made up to 500 mL with water. The emulsion must be stirred well so as to obtain a uniform distribution of binder in aqueous phase.

Characterization

The Fourier transform (FT)-NMR spectra were recorded on Bruker 300 MHz instrument in CDCl₃ for the monomer and the polymers Fourier transform infrared (FTIR) spectra of the samples were recorded on a Nicolet 20 DXB using the KBr pellet technique. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) curves were recorded with a Dupont 2000 microthermoblance. The heating rate for TGA is 10°C/min in the nitrogen atmosphere. Tensile strength and the percentage of elongation of the films were determined using the Instron Tensile Testing Machine 1112. The specimens of even thickness were selected by measuring the thickness of the film. To determine the properties of the emulsions, 10 mL of prepared emulsion was diluted with equal amount of water and poured into a circular glass plate. The emulsion must be spread uniformly, and the plate was adjusted with spirit level so that thickness of the film was

Table II Parameters of Fineman-Ross, Kelen-Tudos, and Extended Kelen-Tudos Plots

S1 No	$\begin{array}{c} X(Y\ -\ 1)/Y\\ G\end{array}$	X^2/Y F	(Y-1)/Z	$Y/Z^2 \ F$	$G/(lpha + F) \ \eta$	$F/(lpha + F) \ \xi$	$G'/(lpha' + F') \ \eta'$	$\frac{F'/(\alpha'+F')}{\xi'}$
1	-0.3833	0.1583	-0.3737	0.1505	-0.2808	0.1159	-0.2687	0.1082
2	-0.5384	0.7097	-0.7901	0.7285	-0.2309	0.3703	-0.4013	0.3700
3	-0.4039	1.4039	-0.4097	1.4451	-0.1650	0.5378	-0.5378	0.5381
4	-0.1468	3.7216	-0.1514	3.9551	-0.0297	0.7552	-0.0291	0.7612
5	1.7007	9.1960	1.7927	10.2191	0.1634	0.8840	0.1564	0.8917



Figure 3 K-T and ext(K-T) plots for poly(CPA-co-MA).

uniform. The films, thus prepared, were assessed visually to determine their transparency. To determine the light fastness of the film, a portion of the film was subjected to ultraviolet (UV) radiation for 24 h, and the change in color was noted. The water repellency of the film was tested by pouring a few drops of water on the film. After 10 min, the film was tested for the presence of any water spots.



Figure 4 Copolymer composition plot for the poly-(CPA-*co*-MA) system.

Table IIIReactivity Ratios of CPA-MACopolymer System Calculatedby Various Methods

Methods	r_1	r_2	$r_{1}r_{2}$
Fineman–Ross Kelen–Tudos Ext(Kelen–Tudos)	$0.600 \\ 0.639 \\ 0.620$	$0.156 \\ 0.125 \\ 0.132$	$0.0936 \\ 0.0798 \\ 0.0818$

RESULTS AND DISCUSSION

Synthesis of 4-chlorophenyl acrylate was prepared according to Scheme 1.

CPA was characterized by microelemental analysis, IR spectroscopy, and ¹H-NMR and ¹³C-NMR spectroscopies.

IR spectrum (cm⁻¹): 3050 (Ar–CH); 1769 (C=O ester group); 1655 (C=O keto group); 1295 (C=C stretching vibration); 830 (bi-substituted ring). ¹H-NMR δ , (ppm): 7.5–7.0 (d, broad, 4 $\underline{\text{H}}$ Ar=H); 2.30–1.40 (m, CC–C $\underline{\text{H}}_2$). ¹³C-NMR (ppm): 127.30 (=CH), 164.00 (C=O), 148.80 (¹C), 122.72 (²C and ⁶C), 129.20 (³C and ⁵C), and 130.90 (⁴C).

Poly(CPA) was prepared using BPO at 70°C. The absence of a characteristic vinyl group absorption in FTIR at 1640 cm⁻¹ representing the C—C in the monomer confirms the formation of CPA polymer. Two doublet signals at 7.4 and 7.2 ppm are due to two types of aromatic protons, and broad signals between 2.30 and 1.40 ppm are due to CH₂ and CH backbone protons.

The resonance signal in the ¹³C-NMR spectrum at 174.2 ppm corresponds to the ester carbonyl and at 150.1 ppm due to the aromatic carbon attached to the ester group. The sharp signals at 131.7, 129.4, and 122.6 ppm are due to the ⁴C, ³C/⁵C, and ²C/⁶C atoms. The backbone methylene and methine carbons appear at 42.4 and 52.3 ppm, respectively. Structure 1 represents the copolymer unit of CPA with MA.

Figures 1 and 2 represent the ¹H- and ¹³C-NMR spectra of copoly(CPA–MA). The signals at 3.63 ppm in the ¹H-NMR spectrum and a triplet at 33.1–36.4 ppm in the ¹³C-NMR is due to —OCH₃ protons, confirming the presence of the MA unit in the copolymer chain.

The mole fraction, m_1 , of CPA in the copolymer chain is determined by adopting a similar method employed by us earlier.¹⁵



Temperature (°C)

Figure 5 TGA Curves of poly(CPA-*co*-MA) in the nitrogen mole fraction of CPA in (a) 0.28, (b) 0.42, and (c) 0.64.

The mole fraction, m_1 , of CPA in the copolymer chain is determined by the following equation:

 $C = \frac{\text{integral intensities of aromatic protons}}{\text{integral intensities of carbomethoxy protons}}$

where
$$m_1 = \frac{3C}{4+3C}$$

Table I represents the copolymerization data of the poly(CPA-co-MA) system and the percentage conversion. The parameters corresponding to the Fineman-Ross,¹⁶ Kelen-Tudos,¹⁷ and Extended Kelen-Tudos^{18,19} methods are presented in Table II; the reactivity ratios CPA (r_1) and MA (r_2) computed by these methods are given in Table III.

Fineman-Ross method involves the following equation:

$$G = Hr_1 - r_2$$

where G = X(Y - 1)/Y and $H = X^2/Y$ are the functions involving the composition of initial

monomers and copolymer. A plot of *G* versus *H* gave a straight line with a slope equal to r_1 and an intercept equal to $-r_2$.

The Kelen–Tudos and the extended Kelen–Tudos methods involve the following equation:

$$\eta = (r_1 + r_2/\alpha)\xi - r_2/\alpha$$

where η and ξ are the functions involving the composition of initial monomers and copolymer composition. A plot of η and ξ gave a straight line (Fig. 3). The intercept at $\xi = 0$ and the α value gave r_1 , and the intercept at $\xi = 1$ gave r_2 .

The reactivity ratios of CPA and MA determined by various methods were represented in Table III along with the product of reactivity ratios. The nature of the copolymer sequence of CPA-co-MA system appears to be alternating since the product of reactivity ratios (r_1r_2) is closer to zero than unity. Perhaps there is a greater tendency for both the monomeric units to alternate in the polymer chain. The plot between the copolymer composition and the initial monomer composition (Fig. 4) was sigmoidal, and it

	IDT ^b (°C)	Weight Loss (%) at Various Temperature (°C)					
Copolymers ^a		10	25	50	75	90	
a	181.4	311.4	339.9	385.7	394.2	480.2	
b	154.0	257.1	311.4	359.9	379.9	525.0	
с	140.0	245.7	294.2	350.0	379.9	571.4	

 Table IV
 Thermogravimetric Analysis Data of Copolymers

^a The monomer feed compositions (CPA–MA) for the preparation of the copolymer (mole fraction) are as follows: a = 0.2/0.8; b = 0.5/0.5; c = 0.8/0.2.

^b IDT is the initial decomposition temperature.

crossed the ideal line at the point where $m_1 = M_2 = 0.29$, indicating the azeotropic copolymer composition.

From the DSC curves, the glass transition temperatures (T_g) of poly(CPA), poly(MA), and poly(BA) were found to be 63.3, 10.5, and -55° C, respectively.

Figure 5 represents the thermogram curve of poly(CPA-*co*-MA). The percentage of weight loss at various temperatures are represented in Table IV. All the copolymers undergo single stage decomposition, and it is clear that with increase in the mole fraction of MA in the copolymer, the initial decomposition temperature increases and forms a thermally more stable copolymer.

The weight fraction of different monomers present in the copolymer determines the glass transition temperature of the copolymer. T_g was determined by the following equation:

$$1/T_{g(\text{Copolymer})} = w_1/T_{g(\text{CPA})} + w_2/T_{g(\text{MA})} + W_3/T_{g(\text{BA})}$$

where W_1 , W_2 , and W_3 are the weight fractions of the monomers.

Acrylic resin emulsions with a glass transition temperature (T_{σ}) in the range of -5 to 10°C were found to be suitable as a base coat for the manufacture of leather. Terpoly(CPA-MA-BA) emulsion with three different T_g values of 1.80, 5.25, and 9.25°C were prepared. The total solid content in the emulsion was found to be 35 + 1%. These terpolymers were cast into films, as follows: (film 1) 1.80°C; (film 2) 5.25°C; and 9.25°C (film 3). Films 1 and 3 showed good film characteristics. The film produced from these emulsions have excellent properties like transparancy, light fastness, nontacky nature, and water repellancy. The films prepared were assessed visually to determine their transparancy. The light fastness of the film was tested for 2 h under UV radiation, and there was no change in the color. The water repellancy of the film was also tested, and there were no water spots on the film.

The physical characteristics like tensile strength and the percentage of elongation were tested. The tensile strength of films 1 and 3 showed 0.9901 and 0.8406 kg/cm², and their percentage of elongations were found to be 1385 and 656%, respectively. Thermal properties of the films were carried out by TGA. The initial decomposition temperature (IDT) for film 3 is 352°C, which is higher when compared to film 1, whose IDT is 343°C. Both the films undergo single stage decomposition. The decomposition pattern of films with different T_g values almost overlap with each other.

The emulsions (1 and 3) were tested as a base coat for the chrome-tanned goat skin and toping the finish with lacquer emulsion. Finished leather was subjected to dry and wet rub fastness, flexural endurance, and cold crack resistance; and the results were comparable to the leathers finished with a commercially available binder. The leather was found to withstand 50,000 flexes. Both the leather sample and the film did not crack, even after storage at -20° C for 1 h. However, leather sample developed microcracks on prolonged storage at -40° C.

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