

Synthesis and Characterization of Poly[methyl methacrylate-*co*-2-ethylhexyl acrylate-*co*-poly(propylene glycol diacrylate)] Latices

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ABSTRACT: The emulsion polymerization of the monomers methyl methacrylate (MMA) and 2-ethylhexyl acrylate (EHA) was studied to investigate the effect of the crosslinkable monomer poly(propylene glycol diacrylate) (PPGDA). IR spectroscopy, NMR, differential scanning calorimetry, gel permeation chromatography, and scanning electron microscopy were used to characterize the synthesized polymers. These polymers were coated on glass panels and cured at appropriate temperatures to study the physical properties, swelling behavior, surface tension, and contact angle of these polymer latices. The results show that as the concentration of EHA monomer increased, the surface tension of the latices decreased. The

copolymers were characterized by ¹H-NMR spectroscopy to ensure the absence of unreacted monomer, and the results confirm the incorporation of EHA units in the copolymer. The contact angle of the latices on the glass substrate was smaller than that on the metal. The swelling mechanism of the film showed that the Fickian diffusion coefficient with 10 wt % PPGDA was at a minimum value and was the most highly crosslinked polymer among the samples. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 676–684, 2011

Key words: coatings; crosslinking; emulsion polymerization; glass transition; swelling

INTRODUCTION

Polyacrylates, especially poly(methyl methacrylate) (PMMA), have been widely used as emulsion coatings for the last few decades because of their good film-forming properties, gloss, clear transparency, surface brilliance, and mechanical strength. The performance of PMMA in coatings can be improved by the copolymerization of methyl methacrylate (MMA) with other acrylates, diacrylates, and dimethacrylates. These may provide a means for tailoring the properties, including low surface tension, good water repellence and weather resistance, and low glass-transition temperature (T_g), depending on the structures of the comonomers used. A number of investigators have worked on modifying the properties of polyacrylates through copolymerization. This includes the synthesis and characterization of crosslinked polymers of MMA with various monomers, such as divinylbenzene, diol dimethacrylates, or trimethylolpropane trimethacrylate.^{1–8}

Loshaek and Fox⁶ studied the crosslinking of MMA with diol dimethacrylate and found that the efficiency of crosslinking increased with increasing

chain length of the dimethacrylate molecule and decreased with increasing concentration of dimethacrylate in the reaction mixture. Crosslinked polymers exhibit unique properties, which depend on their degree of crosslinking. In general, the crosslinking affects the swelling behavior, pore size, thermal stability, and mechanical strength of the network.^{7,9}

The studies related to crosslinking during polymerization, and many workers in the field^{10–12} have reported the copolymerization of vinyl monomers. Guo et al.¹³ prepared self-crosslinking poly(methylmethacrylate-*co*-*n*-butyl acrylate-*co*-styrene-*co*-vinyltriethoxysilane) latices by emulsion polymerization. They found that the mechanical properties and water resistance of the copolymer films could be improved through the introduction of vinyltriethoxysilane in the system.

Duarte et al.¹⁴ studied the equilibrium solubility of carbon dioxide in poly(methyl methacrylate-*co*-2-ethylhexyl acrylate-*co*-ethylene glycol dimethacrylate) by a gravimetric method at different temperatures and pressures. The crosslinked copolymer showed Fickian behavior, and Fick's diffusion model was applied to determine the amount of carbon dioxide and the diffusion coefficients (D 's).

In emulsion polymerization, it is important to optimize the emulsifier, initiator concentrations, and monomer feed ratio because these parameters affect the composition of the polymer, which plays a

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significant role in the film properties, such as wettability, adhesion, and swelling. Yu et al.¹⁵ reported the emulsion polymerization of MMA, butyl acrylate (BA), and dimethylaminoethyl methacrylate with a combination of emulsifiers and found that the particle size and surface tension of the latices decreased with increasing emulsifier concentration. Sundardi and Zubir¹⁶ prepared emulsions with monomers having epoxy and carboxyl groups using radiation emulsion polymerization and investigated the influence of the irradiation dose rate and emulsifiers. Xu et al.¹⁷ prepared emulsions with similar monomers by the seeded emulsion polymerization technique. These copolymer emulsions possessed self-crosslinking properties. Glycidyl methacrylate copolymer emulsions without carboxyl groups were prepared by Zurkova et al.¹⁸ and Okubo et al.¹⁹

The aim of this study was to polymerize MMA with 2-ethylhexyl acrylate (EHA) in the presence of the crosslinking monomer poly(propylene glycol diacrylate) (PPGDA) with the emulsion polymerization technique and to study the film characteristics by determination of the physical properties, surface tension, contact angle, and swelling behavior. The polymers were characterized by Fourier transform infrared (FTIR) spectroscopy, differential scanning calorimetry (DSC), and scanning electron microscopy (SEM).

EXPERIMENTAL

Materials

The monomers MMA and EHA (Aldrich) were purified before use by the alkali wash method. PPGDA was synthesized as per the method reported by Priola et al.²⁰ The chemicals poly(propylene glycol) (PPG; molecular weight = 400; Fluka, Mumbai, India), acrylic acid (Thomas Baker), and benzene (Merck, New Delhi, India); the free-radical initiator potassium persulfate; and the emulsifier sodium lauryl sulfate (Thomas Baker) were used as received. Deionized water was used throughout the experimental work.

Polymerization

The polymerization reactions were carried out in a 500-mL, three-necked, round-bottom flask equipped with a reflux condenser, stirrer, dropping funnel, and thermometer. We prepared pre-emulsions of the monomers by taking MMA and EHA at molar ratios varying in the range of 10 : 0 to 5 : 5 and PPGDA in the weight percentage of 0–20 of the total monomers (Table I). The synthesis of the latex was done by the method described in detail in a previous article.²¹

TABLE I
Feed Composition of the Monomers Used During the Synthesis

Polymer code	Molar ratio of the monomers		Weight percentage of the monomers		
	MMA	EHA	MMA	EHA	PPGDA
SE ₁	9	1	90	10	0
SE ₂	8	2	80	20	0
SE ₃	7	3	70	30	0
SE ₄	6	4	60	40	0
SE ₅	5	5	50	50	0
SE ₃₁	7	3	53.2	41.8	5
SE ₃₂	7	3	50.4	39.6	10
SE ₃₃	7	3	47.5	37.5	15
SE ₃₄	7	3	44.8	35.2	20

Swelling measurements

The synthesized polymers were coated on glass panels (2 × 2 cm²) as per the method given in IS101.²² The films were dried in an oven at 80 ± 1°C for 1 h, and the weight and thickness of the films were taken after cooling. The glass panels were completely immersed in deionized water at room temperature, and their swelling behavior was observed at different time intervals until the equilibrium value was found.

The degree of swelling (Q) was measured by gravimetric measurements. The swelling ratio (Φ) was calculated from eq. (1):

$$\Phi = W_s/W_d \quad (1)$$

Q (%) was calculated from eq. (2):

$$Q = [(W_s - W_d)/W_d] \times 100 \quad (2)$$

where W_d and W_s are the weights of the dry and swollen films, respectively.

Data analysis

The amount of water absorbed by the film at a particular time t is designated by M_t , and M_∞ is the weight of the film after equilibrium is achieved. The following relation²³ between M_t/M_∞ and t was used to calculate the swelling characteristic constant (K) and n :

$$M_t/M_\infty = Kt^n \quad (3)$$

According to Fickian law, the swelling process is considered diffusion-controlled and is termed *Fickian* when $n = 0.5$, and it is termed as *relaxation-controlled* when $n = 1$. When n is between 0.50 and 1.0, the transport phenomenon is considered *anomalous* or *non-Fickian sorption*. The rate of approach to equilibrium

can be characterized by D . This can be calculated according to the following relationship²⁴:

$$M_t/M_\infty = (4/\pi^n)(Dt/L_0^2)^n \quad (4)$$

where t is the swelling time and L_0 is the thickness of the dried film. The values of n and K were calculated from the slope and intercept of the plot between $\log(M_t/M_\infty)$ and $\log t$, respectively.

Characterizations

FTIR spectroscopy

FTIR spectra of various polymers were recorded in the range 400–4000 cm^{-1} with a PerkinElmer RXI spectrophotometer (Germany) with pellets of potassium bromide.

NMR

The composition of the synthesized copolymer was determined by comparison of the intensities of the $-\text{OCH}_3$ and $-\text{OCH}_2$ proton resonances on the ^1H -NMR spectra at 302 K in a deuteriochloroform (CDCl_3) solution with a Bruker WM 250 spectrometer (Johannesburg, South Africa) operating at 400 MHz.

DSC

T_g of the polymers was determined with a TA Instruments (California, USA) TA Q20 at $10^\circ\text{C}/\text{min}$ under a nitrogen atmosphere.

Viscosity

The viscosity was determined in accordance with ASTM D 789 with a Brookfield viscometer (model RVT 104,027) (Germany) at 20 rpm at 25°C .

Gel content

The gel content of the samples was determined with chloroform as an extraction solvent. A known weight (50–100 mg) of the polymer was added to about 50 mL of chloroform and kept under stirring for 48 h. Then, the mixture was filtered with 2- μm filter paper, which was dried at room temperature to obtain a constant weight.

The gel content was calculated as follows:

$$\text{Gel content} = W_2/W_1 \times 100$$

where W_1 and W_2 are the weights of the initial and dried samples, respectively.

Molecular weight

The number-average molecular weight (M_n) and polydispersity index (PDI) of the polymers were

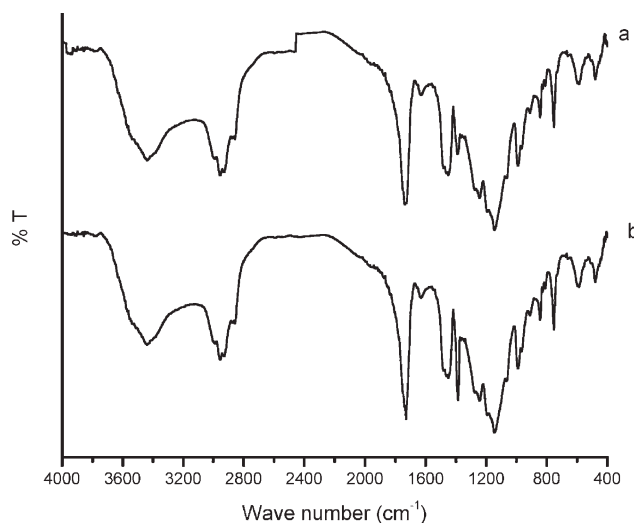


Figure 1 FTIR spectra of the samples with the (a) absence of PPGDA (SE_3) and (b) presence of PPGDA (SE_{32}).

obtained with gel permeation chromatography (Milford, MA). An high-performance liquid chromatography (HPLC) pump (Waters 515) with a refractive index range 1.00 to 1.75 detector and a stainless steel column (Pl-gel 50A, $60 \times 7.5 \text{ mm}^2$) were used with tetrahydrofuran (HPLC grade) as the mobile phase at a flow rate of 1 mL/min. The sample was introduced through a Rheodyne injector with a 20- μL loop. The molecular weights of the copolymers were calculated against polystyrene standards.

SEM

The morphological properties of the films were studied with a scanning electron microscope (JEOL Quanta 200) (Germany).

Contact angle and surface tension

The contact angle and surface tension measurements of the polymer lattices were conducted with a Data-physics DCAT II tensiometer (Germany) at $25 \pm 1^\circ\text{C}$.

RESULTS AND DISCUSSION

FTIR spectroscopy

FTIR spectra of synthesized polymers of MMA and EHA prepared in the absence and presence of PPGDA and designated as SE_3 and SE_{32} are given in Figure 1(a,b), respectively. It was evident from Figure 1 that the peak near 1600 cm^{-1} , representing the terminal methylene group of the monomers, was absent; this indicated that all of the vinyl groups were polymerized.

Figure 1(b) shows a strong absorption peak at 1390 cm^{-1} representing C- CH_2 bond and peaks at 1194 and 1145 cm^{-1} representing the C-O-C stretching

vibration of the PPGDA segment. This indicated that PPGDA was incorporated in to the polymer structure. In addition, the strong peaks at 1175 cm^{-1} of C—O stretching, at 1250 cm^{-1} of C—C—O stretching, and at 1730 cm^{-1} of the ester linkage confirmed the presence of PPGDA in the synthesized polymer. The peaks appearing at 2873 and 2930 cm^{-1} were attributed to the alkyl chain (C—H) stretching vibrations.

NMR

The nonappearance of peaks due to unsaturated protons between 5 and 6 ppm indicated the absence of monomer impurities. It is well known that the integral intensities of peaks due to the comonomers are directly proportional to the copolymer composition.²⁵ The composition of the synthesized copolymers in the absence of crosslinker was determined by a comparison of the intensities of the chemical shifts. The $^1\text{H-NMR}$ spectra of the SE₁, SE₃, and SE₅ copolymers are given in Figure 2(a–c), respectively. The chemical shifts at 3.6 and 3.9 ppm were assigned to the hydrogen of methyl and methylene groups linked to the oxygen of the carboxylated groups of MMA and EHA units, respectively. The area of these peaks was chosen for the determination of the copolymer composition. Thus, we divided the relative areas of these two NMR lines by 3 and 2, respectively, according to the following equation:

$$\% \text{ MMA} = \left(\frac{A_{3.6\text{ ppm}}/3}{A_{3.6\text{ ppm}}/3 + A_{3.9-4.1\text{ ppm}}/2} \right) \times 100$$

The results of the copolymer compositions of the SE₁, SE₃, and SE₅ (90 : 10, 70 : 30, and 50 : 50) copolymer systems obtained by $^1\text{H-NMR}$ analysis were 87 : 13, 68 : 32, and 66 : 34, respectively. The deviation from the initial feed ratio was due to the different reactivity ratios of MMA and EHA.

DSC

The T_g values of the alkyl acrylate and alkyl methacrylate homopolymers were governed by the nature of the alcoholic moiety of the ester. T_g decreased as the number of carbon atoms increased in the monomers. From the DSC thermograms, as shown in Figure 3, the T_g 's of PMMA, poly(2-ethylhexyl acrylate) (PEHA), SE₃, and SE₃₂ were found to be 383, 223, 281.1, and 251.5 K, respectively.

The nature of the thermograms suggested that all of the polymers were amorphous. The T_g values of the copolymers could be related to the structures of the monomers and the feed ratios used in the syntheses. The polymers of *n*-alkyl acrylates had lower T_g 's compared to PMMA because of the restricted rotation of the polymer backbone by the presence of

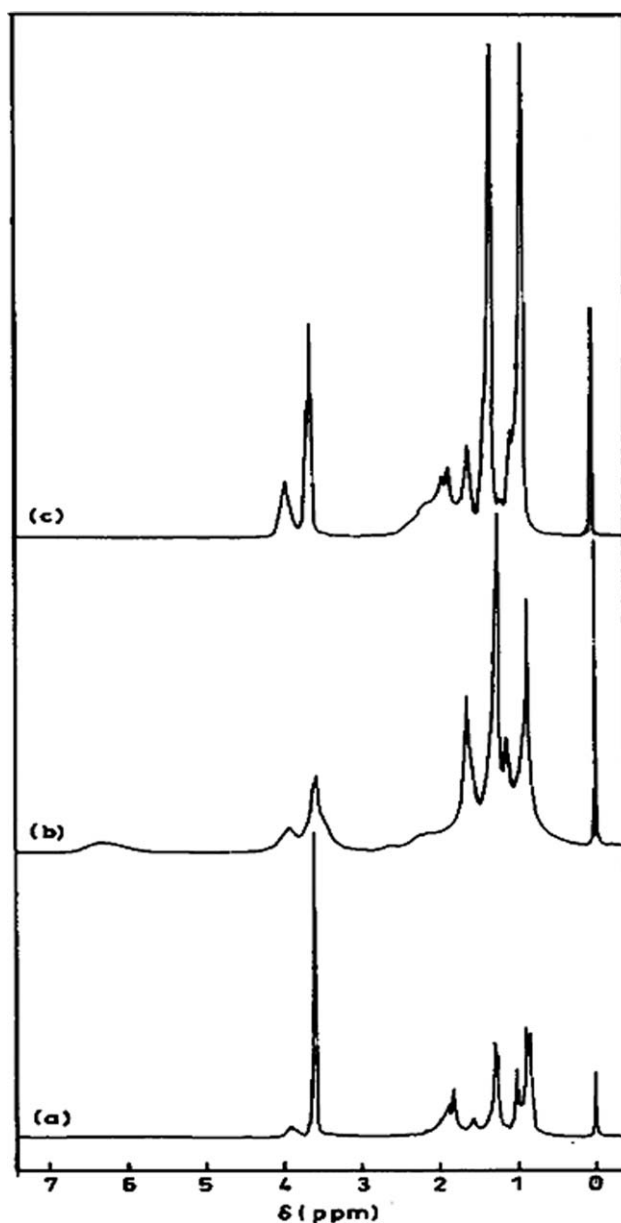


Figure 2 $^1\text{H-NMR}$ spectral scan of poly(methyl methacrylate-co-2-ethylhexyl acrylate)s with different monomer feed ratios: (a) SE₁, (b) SE₃, and (c) SE₅.

the methyl group. The T_g of PEHA was 223 K, whereas that of poly(*n*-hexyl acrylate) was 216 K.²⁶ This was due to an extra alkyl group present in PEHA. From the comparison of the T_g 's of SA₃ and SA₃₂ from thermograms, we determined that T_g of the polymer synthesized with a higher percentage of PPGDA was lower than that of the polymer with a lower concentration. This was due to the presence of alkyl chains in PPGDA, which was responsible for the decrease in T_g of the polymer.

Brookfield viscosity

The viscosity measured by the Brookfield viscometer (spindle number 1 at 20 rpm and 25°C) was

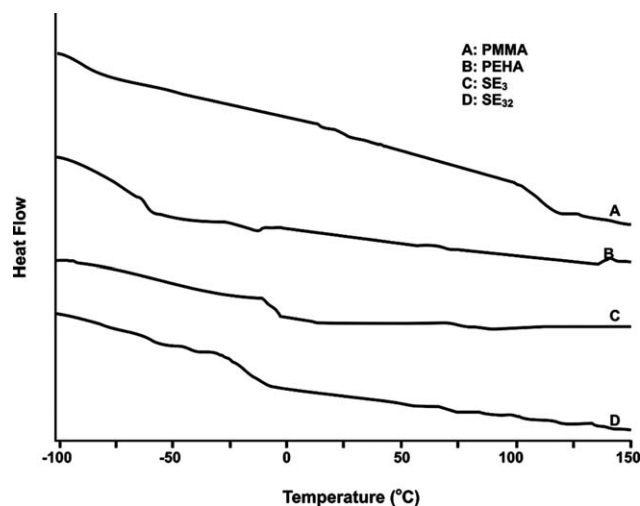


Figure 3 DSC thermograms of PMMA, PEHA, SE₃, and SE₃₂ obtained in flowing nitrogen at a heating rate of 20°C/min.

in the range 38–50 cps (Table II). The Brookfield viscosity was found to be dependent on the feed composition, that is, the MMA : EHA ratio, and it was found to be lowest in sample SE₁, which had highest amount of MMA (MMA : EHA = 90 : 10).

Gel content

We measured the gel content of the latices by stirring a known weight of dried polymer with chloroform continuously for 48 h and then taking the weight of the dried residue. Higher gel contents were observed in samples SE₃₁, SE₃₂, and SE₃₃, as

TABLE II
Properties of the Polymers

Polymer	M_n	M_w	PDI	Gel content (%)	Viscosity (cps)
SE ₁	178,108	314,266	1.76	0.0	38.9
SE ₂	255,275	560,948	2.19	0.0	42.6
SE ₃	149,158	377,490	2.53	0.58	44.8
SE ₄	168,750	326,753	1.94	1.1	45
SE ₅	250,536	522,791	2.09	5.1	46.6
SE ₃₁	—	—	—	69.8	48.5
SE ₃₂	—	—	—	88.6	50
SE ₃₃	—	—	—	84.8	48

given in Table II. The major contributor to the gel content in this system was likely to be the PPGDA monomer because of its crosslinkable properties. The PPGDA content led to back-biting or chain transfer to the polymer; this resulted in the formation of double bonds, which could further polymerize and form branches. However, no definite trend was observed as a function of the monomer composition.

Molecular weight

The relative molecular weights [M_n , weight-average molecular weight (M_w)] and molecular weight distribution (MWD), as determined by gel permeation chromatography with polystyrene standards, are summarized in Table II. In all of the copolymer samples, MWD with PDI was lower and ranged from 1.76–2.53. In the copolymers, branching may not have been significant, so a relatively narrow MWD was obtained. There was no definite trend of

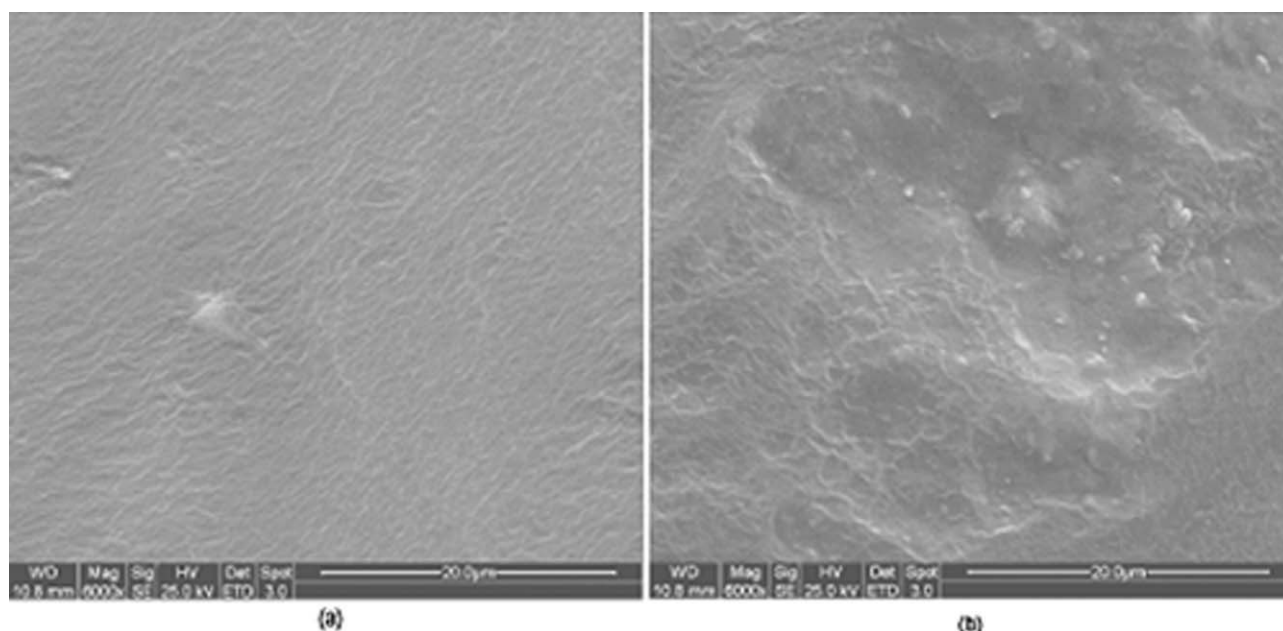


Figure 4 Scanning electron micrographs of the polymer films: (a) SE₃ and (b) SE₃₂.

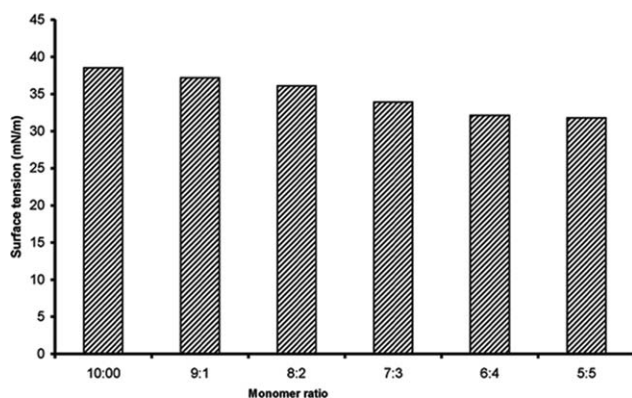


Figure 5 Surface tension of the latices as a function of the monomer ratios.

molecular weight found by variation of the feed composition of MMA to EHA.

SEM of the films

The SEM micrographs of the film surfaces of SE₃ and SE₃₂ are shown in Figure 4(a,b), respectively. It was apparent from Figure 4(a) that the surface of the SE₃ polymer film was smooth and homogeneous and had no phase separation. This behavior may have been due to the good miscibility of MMA with EHA, which was due to uniform distribution of copolymer moieties in the aqueous phase, but when the crosslinker PPGDA was added, the polymer presented some small holes. These holes were due to the incorporation of PPGDA. Increasing the amount of PPGDA in the copolymer resulted in a larger particle size of the dispersed monomers because of the

PPG group in the acrylate ester, which decreased the polarity of the copolymer smoothness of the film surface. Also, SEM showed an irregular pattern, as obvious in Figure 4(b).

Analysis of the surface tension and contact angle of the latices

The surface tension of polymers is an important parameter, which plays a decisive role in determining their wetting characteristics and adhesion. Figure 5 shows the variation of the surface tension of the copolymer latices prepared by the variation of the molar ratios of MMA and EHA. It was apparent from Figure 5 that PMMA had the largest surface tension (38.5 mN/m) followed by SE₁ to SE₅, and PEHA had the lowest (28.1 mN/m). This may have been due to the polar polyester backbone being shielded by the alkyl side chains, which decreased the surface tension of the polymers as the length and size of the substituents increased. The results indicate that as the concentration of EHA increased in the copolymer latices from SE₁ to SE₅, the surface tension decreased because of interparticle complexation between the groups.

Figure 6 shows the contact angles of various synthesized copolymer latices with respect to glass and metal. The contact angle is useful in indicating the extent to which a liquid will spread on a given solid. It was apparent from Figure 6 that when the concentration of PPGDA was increased from 5 to 20%, the contact angle decreased from 57.6° continuously to 48.5° with respect to the glass substrate and from 63.5 to 58.7° with respect to the metal substrate for

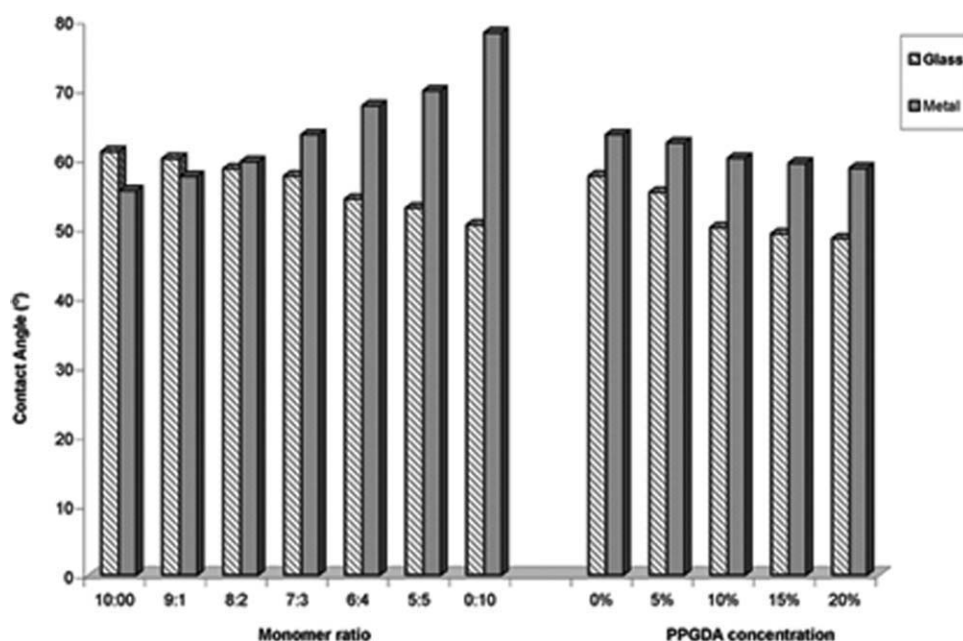


Figure 6 Contact angle of the latices as a function of the monomer ratio and the PPGDA concentration.

TABLE III
Observed Physical Properties of the Synthesized Latex Films

Polymer	Observed properties of the polymer films			Substrate attachment (adhesion)
PMMA	Hard	Fragile	White	—
PEHA	Soft	Very sticky	Transparent	+
SE ₁	Hard	Elastic	Opaque	—
SE ₂	Hard	Elastic	Opaque	+
SE ₃	Hard	Elastic	Transparent	+
SE ₄	Soft	Sticky	Transparent	+
SE ₅	Soft	Sticky	Transparent	+

SE₃₃ latices. The decreases in the values of the contact angle were due to the presence of hydrophilic PPG molecules in the PPGDA. Also, the contact angles of the latices on the glass substrate were smaller compared to those on the metal substrate because of the lower surface energy of the metal in comparison to glass. This was the reason that the latices spread on the glass substrate easily compared to metal. Interparticle interactions between different functional groups made the surface tension of the latices lower and resulted in smaller contact angles of the latices on the substrates. The results indicate that the incorporation of PPGDA in the system decreased the contact angle, and therefore, the wettability of the lattices increased as per the wettability theory.²⁷

Effect of the monomer concentration on the film properties

The observed physical properties of the films were determined by the variation of the monomer molar ratio and are presented in Table III. The film properties of the latices were affected by the ratio of monomers used during the polymerization. The films of

PMMA were hard and fragile, whereas those of PEHA were soft and very sticky, and therefore, both had limited use in coating applications. It is apparent from the table that as the EHA content increased in the feed composition, the films, which were earlier hard, elastic, and opaque, became more and more soft, sticky, and transparent. Usually, the paint industry requires films that are hard, elastic, and transparent. With these considerations, it could be said that SE₃ was more suitable for such applications than SE₁, SE₂, SE₄, and SE₅.

Figure 7 shows the swelling behavior of samples SE₁, SE₂, SE₃, SE₄, and SE₅. It is clear from Figure 7 that the swelling of the films decreased with increasing concentration of EHA in the feed. The polar nature of ester groups present on the backbone of the polyacrylates produced a fairly hydrophilic surface. As the size of the hydrophobic alkyl substituent on the acrylates increased, the polar nature of their polymer decreased, and it became more hydrophobic. Thus, the presence of long alkyl chains in EHA increased the hydrophobicity of MMA, and the higher the content of EHA in the polymer was, the greater was the hydrophobic nature of the film and

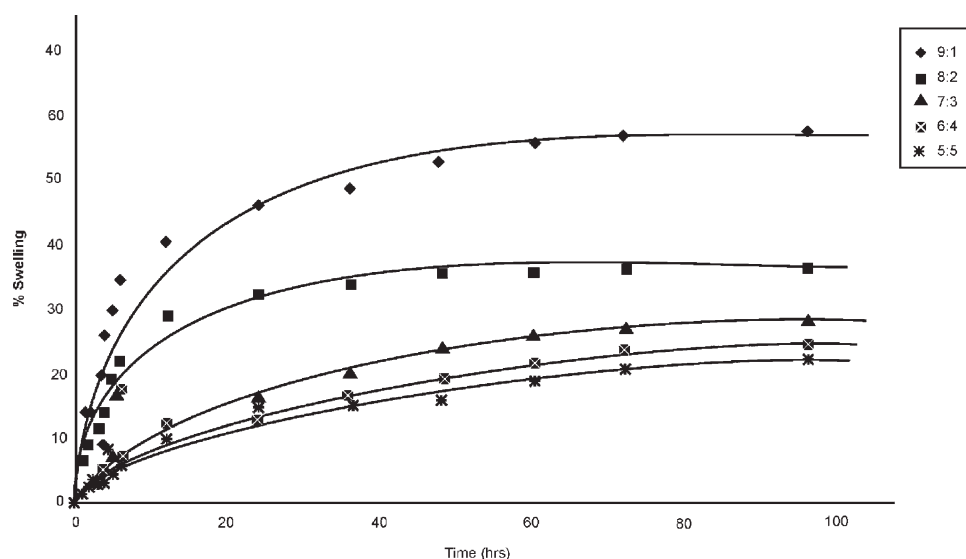


Figure 7 Swelling behavior of the copolymer films as a function of the monomer feed ratios.

TABLE IV
Kinetic Parameters, K , n , and D , for Swelling of Different Polymer Films

Polymer code	$\log K$	Swelling exponent (n)	D
SE ₁	-1.708	0.55	2.35×10^{-6}
SE ₂	-2.075	0.64	1.87×10^{-6}
SE ₃	-2.335	0.59	3.09×10^{-7}
SE ₄	-2.395	0.60	2.86×10^{-7}
SE ₅	-2.359	0.60	2.63×10^{-7}
SE ₃₁	-2.313	0.62	6.43×10^{-7}
SE ₃₂	-2.051	0.51	1.08×10^{-7}
SE ₃₃	-2.293	0.57	1.45×10^{-7}

the lower was the swelling that was observed. The mechanism of swelling was analyzed in terms of n , D , and K . These values were determined from logarithmic plots of the water uptake as a function of time and are shown in Table IV. The diffusion process represents the affinity between the polymer and external solution in which it was swollen. According to the swelling mechanism,²⁸ the latex was of an anomalous type. For all of the samples, SE₁ to SE₅, the values of n as determined were found to be in the range 0.5–1.0.

Effect of the PPGDA concentration on the swelling behavior

The effect of PPGDA, a crosslinker, during the copolymerization of MMA and EHA was studied with SE₃, which showed better physical film properties suitable for the paint industry. The percentage swelling of the SE₃ films with various PPGDA concentrations are given in Figure 8. As observed from Figure 8, the percentage swelling of the films gradually decreased with increasing PPGDA concentra-

tion. This showed that the water resistance of the films improved with the addition of PPGDA. This was probably due to the crosslinking of MMA and EHA by the presence of PPGDA; this caused a decrease in the free space between the polymer chains. The swelling parameter (n), D , and K for all of the films were calculated and are given in Table IV. The swelling exponent (n) of the polymer films of SE₃₂ was 0.51; this was close to that of Fickian swelling behavior, whereas those for SE₃, SE₃₁, and SE₃₃ were 0.60, 0.62, and 0.57, respectively; these corresponded to anomalous or non-Fickian sorption. The latex film of SE₃₄ was peeled off from the substrate in the early stage of the experiment (5 h) so the data of that film could not be calculated. The rate of diffusion of water molecules through the SE₃₂-type film was much lower than that through the SE₃, SE₃₁, and SE₃₃ films. The SE₃₂ film also showed a smaller value of D than the SE₃, SE₃₁, and SE₃₃ films; this indicated more crosslinking. These results indicate that the film of the SE₃₂ latex showed better water resistance in comparison to the other samples.

CONCLUSIONS

From these studies, the following conclusions were drawn:

1. PPGDA was incorporated into the copolymer of MMA and EHA, as evidenced by the appearance of sharp peaks at 1390, 1194, and 1145 cm^{-1} in the FTIR spectra. T_g was also found to decrease with the incorporation of PPGDA into the polymer.
2. The NMR results show the formation of the MMA-EHA copolymer.

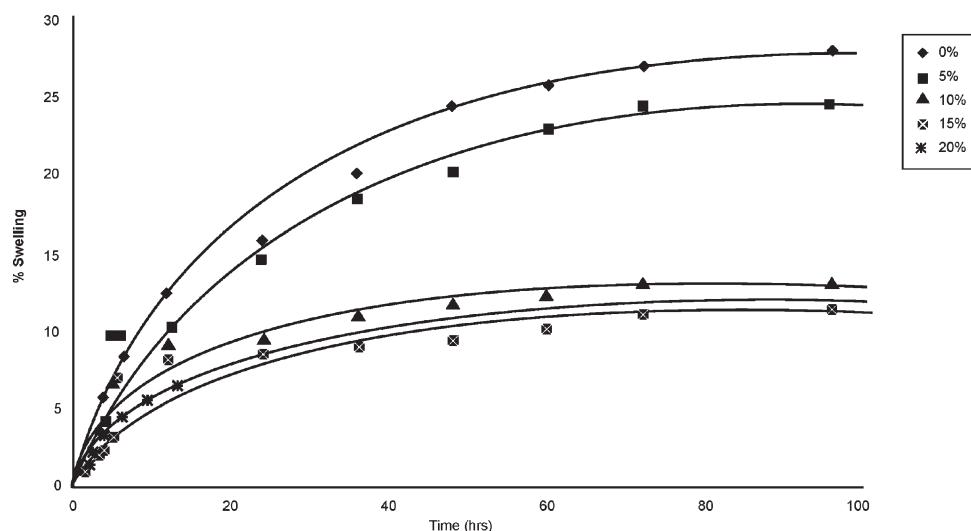


Figure 8 Swelling behavior of the copolymer films as a function of the PPGDA concentration.

3. The surface tension of the latices decreased as the concentration of PPGDA in the feed increased because of the interparticle complexation of groups. The contact angle of the copolymer latices on the glass substrate was smaller than that on the metal substrate.
4. The swelling behavior of the copolymers with various monomer ratios (9 : 1 to 5 : 5) was found to be anomalous, as the value of the swelling exponent was between 0.5 and 1.0. The reason for this may have been the increase in the EHA content in the copolymer, which increased the hydrophobic nature of the polymer.
5. When PPGDA was incorporated into the copolymer, the swelling of the films tended to decrease and show better water resistance. The value of D also decreased with increasing PPGDA; this indicated an increase in the extent of crosslinking.

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