

Swelling Behavior of Poly(MMA-co-BA-co-PPGDA) Polymers

Sweta Bajpai, J. S. P. Rai, Indira Nigam

Plastic Technology Department, H. B. Technological Institute, Kanpur 208002, India

Received 17 January 2008; accepted 11 November 2008

DOI 10.1002/app.29717

Published online 17 February 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The kinetics of emulsion polymerization of monomers MMA/BA was studied to investigate the effect of cross-linkable monomer PPGDA. The results showed that by the incorporation of PPGDA, rate constant of reaction decreased. The IR and differential scanning calorimetry were used to characterize the presence of PPGDA in the synthesized polymers. These polymers were coated on glass panels and cured at appropriate temperature. The

results showed that the polymer containing 15 wt % PPGDA had minimum value of Fickian diffusion coefficient, thus showing highest level of cross-linking among all the polymers studied. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 2374–2382, 2009

Key words: emulsion polymerization; cross-linking; swelling; glass transition temperature

INTRODUCTION

Poly(methyl methacrylate) (PMMA) is known as a tough and moderately hard polymer which has little or no tack at room temperature. The properties¹ of the polymers of *n*-alkyl acrylates vary with the number of carbon atoms in the alkyl group and the brittle point of the polymers decreases with increase in chain length of the alkyl group for the first eight members of the series. The polymers² of methyl, ethyl and *n*-butyl acrylate have brittle points of +8, –20, and –40°C, respectively. The incorporation of these acrylates as comonomer in the polymerization of MMA would lead to improvement in the flexibility of film produced. The other properties like adhesion, gloss, hardness, solvent resistance etc., of MMA based polymers are affected by higher acrylates viz. butyl acrylate (BA), butyl methacrylate (BMA), ethylhexyl acrylate (EHA), glycidyl methacrylate (GMA) etc., therefore in the literature numbers of higher acrylate have been reported to be copolymerized with MMA.

Cross-linking provides another means for modifying the properties of acrylate polymers. Cross-linked PMMA is used in variety of commercial applications such as a membranes,³ dental fillings,⁴ dentures,⁴ latex coatings,⁵ computer-to-sensor data transmission links,⁶ composites,⁷ and similar applications where cross-linking plays a vital role in both processing and ultimate properties of the copolymer. Polymer

chains are viscoelastic in nature and the development of appreciable cohesive strength in a latex polymer film is dictated by the ability of the interconnected polymer chains to participate in the interdiffusion process that occurs during film formation. The cross-linking retards the segmental motion of chains thus improves the rigidity of films.

Several researchers have investigated the polymerization kinetics of cross-linked PMMA.^{8–14} Huang and coworkers¹⁴ used differential scanning calorimetry (DSC) to determine monomer conversion, rate of polymerization, reaction rate constants, and reaction order during the copolymerization of ethylene glycol dimethacrylate (EGDMA) and 2-hydroxyethylmethacrylate (HEMA). This detailed research revealed trends in reaction parameters that were dependent on both EGDMA concentration and temperature.

The emulsion polymerization technique has been considered an efficient one for synthesis of polyacrylates, especially for application involving film formation, as it provides an environment friendly procedure and gives high molecular weight product. Various cross-linkers of different chemical background have been incorporated with acrylates for observing their effect on the properties of synthesized polymers. The copolymerization of MMA and multifunctional monomer EGDMA by emulsion polymerization have been reported by Tobita et al.^{15–17} They compared the experimental results with theoretical predictions,¹⁸ and found that the average cross-linking density was high from the very beginning of the polymerization, contrary to what occurred in bulk or solution polymerization, and that the saturation in monomer concentration in the particles decreased with increasing EGDMA concentration. To fit the above theoretical predictions with experimental results, it was found

Correspondence to: I. Nigam (indiranigam@rediffmail.com).

TABLE I
Feed Composition of Monomers Used During the Synthesis

Polymer code	Mole ratio of monomers		Weight percentage of monomers			Amount of MMA (g)	Amount of BA (g)	Amount of PPGDA (g)
	MMA	BA	MMA	BA	PPGDA			
SA ₁	9	1	90	10	0	43.75	6.25	0
SA ₂	8	2	80	20	0	37.9	6.25	0
SA ₃	7	3	70	30	0	32.3	17.1	0
SA ₄	6	4	60	40	0	27.0	23.0	0
SA ₅	5	5	50	50	0	21.9	28.1	0
SA ₃₁	7	3	61.4	33.6	5	30.7	16.8	2.5
SA ₃₂	7	3	58.2	31.8	10	29.1	15.9	5.0
SA ₃₃	7	3	54.8	30.2	15	27.4	15.1	7.5
SA ₃₄	7	3	51.6	28.4	20	25.8	14.2	10

that the reactivity of the pendant double bonds decreased as the cross-linker concentration increased. The cross-linking reactions of MMA and butyl acrylate (BA) with methacrylic acid (MAA) or Hydroxyethylmethacrylate (HEMA) using a cycloaliphatic diepoxide¹⁹ were monitored using DSC, infrared spectroscopy, and dynamic mechanical thermal analysis (DMTA) along with the morphology. The spectroscopic and rheological data showed that the cycloaliphatic diepoxide effectively cross-linked both the hydroxyl and carboxyl functional latices. The water resistance, solvent resistance, gel content, pencil hardness and pull-off-adhesion improved with the cross-linking temperature, time, and the amount of the cross-linker. Yu et al.²⁰ reported the emulsion polymerization of MMA/BA/dimethylaminoethyl methacrylate (DMAEMA) using combination of emulsifiers and found that the particle size and surface tension of the lattices decreased with increase in emulsifier concentration.

In this work, we report the emulsion copolymerization of MMA with BA in presence of different concentrations of a cross-linkable monomer polypropylene glycol diacrylate (PPGDA). The kinetics of the reaction has been studied by varying the ratios of monomers in the feed, concentration of initiator, and emulsifier. The synthesized copolymers have been characterized by FT-IR and DSC. The polymers coated on glass panels have been used to study their swelling behavior in aqueous medium.

EXPERIMENTAL

Materials

MMA and BA monomers (Aldrich) were purified by treating with 5% sodium hydroxide solution followed by washing with deionized water. PPGDA was synthesized as per the method reported by Priola and coworkers.²¹ Polypropylene glycol (PPG

Mol.wt. 400; Fluka), acrylic acid (AA; Thomas baker), and benzene (Merck).

Potassium persulfate (KPS) and emulsifier sodium lauryl sulfate (SLS; Thomas baker) were used as received. Deionized water was used throughout the course of reaction.

Polymerization

The polymerization reactions were performed in a 500 mL three-necked flask fitted with reflux condenser, stirrer, sampling device and thermometer. Pre-emulsion solution was prepared by adding two third of emulsifier SLS, water (250 g) and monomers (MMA, BA, PPGDA) as per requirement based on the molar ratio (Table I) to a beaker which was agitated for 30 min and then kept for 10 min to check the stability of the emulsion. The codes for the synthesized polymers are as given in Table I.

One third of emulsifier was dissolved in water (200 g) and taken in the three-necked flask at $70 \pm 1^\circ\text{C}$ under nitrogen atmosphere. The pre-emulsion and the initiator solution (prepared separately by dissolving KPS in 150 g water) were added to the flask in a period of about 30 min under constant stirring. The polymerization was performed for 3 h.

During the polymerization, the monomer conversion was determined gravimetrically, by withdrawing the sample at different time intervals. The data of monomer conversion was interpreted in terms of rate constant by determining the weight of polymer formed at different time intervals and by plotting a graph between percentage conversions and time.

FTIR analysis

The Fourier transform infrared (FTIR) spectra of polymers were recorded on a Perkin-Elmer RXI spectrometer.

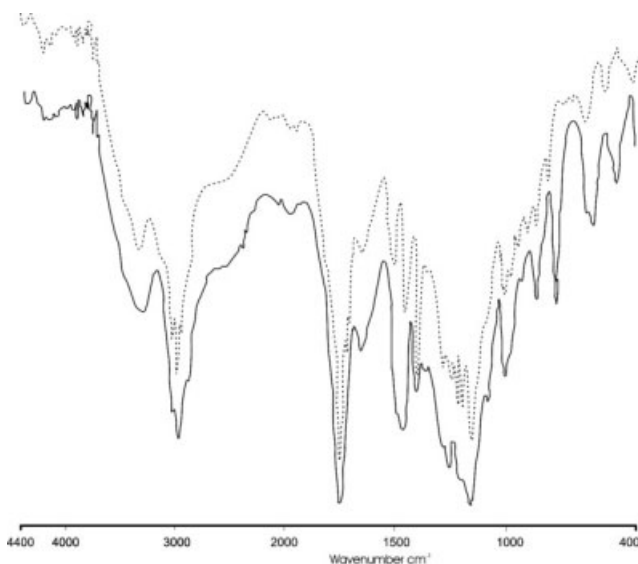


Figure 1 FTIR spectra (a) (—) absence of PPGDA (SA3); (b) (---) presence of PPGDA (SA33).

DSC analysis

The glass transition temperature (T_g) of polymers was determined using TA instruments, TA Q20 at a heating rate of 10°C/min under nitrogen atmosphere.

Swelling measurements

The swelling behavior of the synthesized polymers were performed by first preparing the films (2 × 2 cm) on glass panels as per IS101 method and drying the panels in an oven at 90°C for 1 h. The thickness and weight of the dried films were taken before the panels were immersed in water at room temperature. The water uptake of the films was determined by measuring the weight gain at definite time intervals.

The degree of swelling was calculated from eq. (1)

$$\text{Degree of swelling (Q\%)} = [(W_s - W_d) / W_d] \times 100 \quad (1)$$

where W_d is the dry weight of the film and W_s is the swollen weight of the film.

The dynamic swelling behavior of films were studied by determining characteristic swelling constant ' K ' and transport exponent ' n ' using the following equation²²

$$M_t / M_\infty = Kt^n \quad (2)$$

where ' M_t ' is the amount of water absorbed at time ' t ' and ' M_∞ ' is the water absorbed at equilibrium. The eq. (3) is applicable only for $M_t / M_\infty \leq 0.6$.

The diffusion coefficient ' D ', was calculated according to the following relationship²³

$$M_t / M_\infty = (4 / \pi^n) (Dt / L_0^2)^n \quad (3)$$

where ' t ' is the swelling time and ' L_0 ' is the thickness of the dried film. The value of ' n ' and ' K ' were

calculated from the slope and intercept of the plot between ' $\log(M_t / M_\infty)$ ' and ' $\log(t)$ ', respectively.

RESULTS AND DISCUSSION

Characterization

FTIR analysis

FTIR spectra of MMA-co-BA, synthesized in the absence and presence of PPGDA, designated as SA₃ and SA₃₃ are given in Figure 1(a,b), respectively. The spectra of both samples shows absence of C=C band near 1600 cm⁻¹, indicating that the polymers does not contain any monomer. The assignments of the absorption features are as follows^{24,25}: 2930–2990 cm⁻¹ to the C–H stretching of CH₃ and CH₂ groups, 2960 cm⁻¹ to methyl asymmetric deformation of –CH₂ and –CH, 1731 cm⁻¹ to ester linkage C=O, 1453 cm⁻¹ to C–C stretching, and 1342 cm⁻¹ for wagging vibration of CH₂ group of polymers.

On comparing the spectra of copolymers in the Figure 1(a) and 1(b) a large increase in the absorption intensity of C–CH₃ bond at 1396 cm⁻¹ has been observed for copolymer SA₃₃ which may be due to increased C–CH₃ groups present in PPGDA. This indicates that the PPGDA has been incorporated in the polymer SA₃₃. Apart from this it is also apparent from both the spectra that the absorption intensities of peaks at 1176 cm⁻¹ for C–O stretching, 1257 and 1274 cm⁻¹ for C–C–O stretching, 1731 cm⁻¹ for ester linkage have also increased for polymer SA₃₃. This further confirms that in the synthesized polymer SA₃₃ PPGDA is present along with MMA and BA.

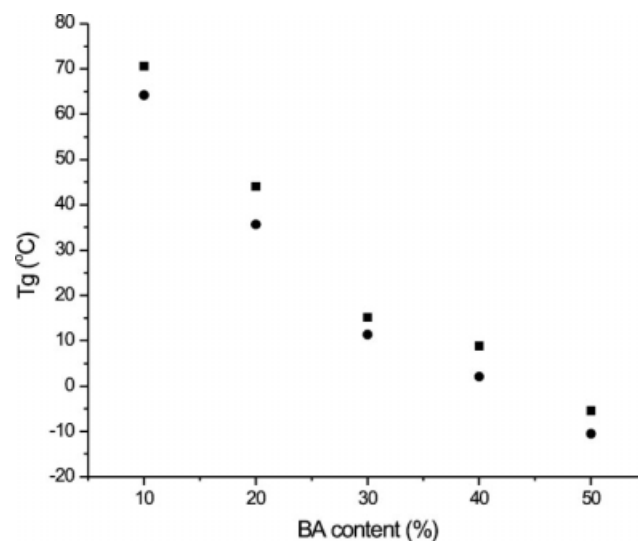


Figure 2 Glass transition temperature (T_g) of MMA-co-BA polymers as a function of concentration of BA in monomer feed.

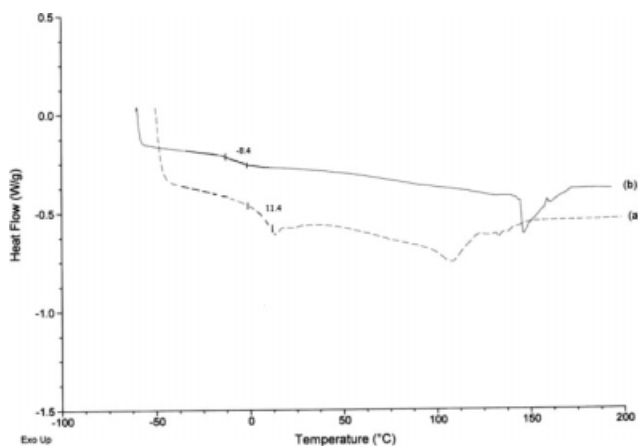


Figure 3 DSC thermogram of polymer synthesized with monomer feed ratio of MMA/BA of 7 : 3 (a) without PPGDA (SA3); (b) with 15 wt % PPGDA (SA33).

DSC analysis

Copolymerization often brings about drastic changes in the mechanical, physical and thermal properties of the polymer. The most important thermal property to be affected is glass transition temperature T_g of the polymer. Fox predicted the changes in the T_g of copolymers according to their composition as per the equation.²⁶

$$\frac{1}{T_g} = \frac{W_A}{T_{gA}} + \frac{W_B}{T_{gB}}$$

where W_A and W_B are the weight fractions of the monomers A and B in the copolymer. T_{gA} and T_{gB} are the respective T_g 's of the homopolymers A and B.

However, this equation is very simple and useful for many systems the observed value of T_g deviate from the theoretical value predicted from this equation. The values of T_g observed by thermograms obtained by DSC analysis of synthesized copolymers and those determined by above equation have been plotted in Figure 2. As shown in this Figure, the theoretical values determined from Fox equation somewhat deviated from the experimental values obtained by DSC. This could be due to the difference between copolymer composition and monomer feed ratios or due to random sequence distribution of monomers in the polymer chain.

The chain flexibility, interaction energy and, forces of attraction between polymer molecules have an important role on T_g . All structural properties which reduce molecular flexibility increase the T_g of the polymer. If a comonomer with low T_g is added, the T_g of the main polymer will decrease. As it can be seen from thermograms that the effect of BA is the reduced T_g of MMA. Figure 3 shows the T_g of polymers (SA₃ and SA₃₃) synthesized in absence and presence of PPGDA. The T_g of SA₃ was found to be 11.4°C whereas that of SA₃₃, -8.5°C indicating that the incorporation of PPGDA decreased the T_g , which could be due to presence of longer alkyl chain in PPGDA monomer.

Kinetics of polymerization and swelling

Effect of emulsifier concentration

The Figures 4 and 5 show the effect of emulsifier concentration on monomer conversion for the emulsion polymerization of MMA and BA in absence and presence of PPGDA, respectively. The concentration

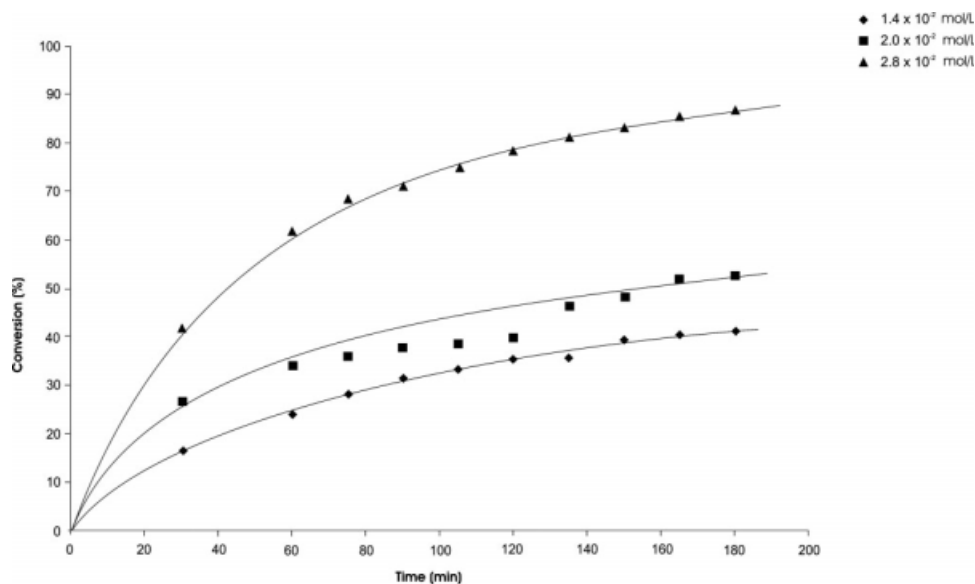


Figure 4 Conversion vs. time at different emulsifier concentrations during the polymerization of MMA/BA.

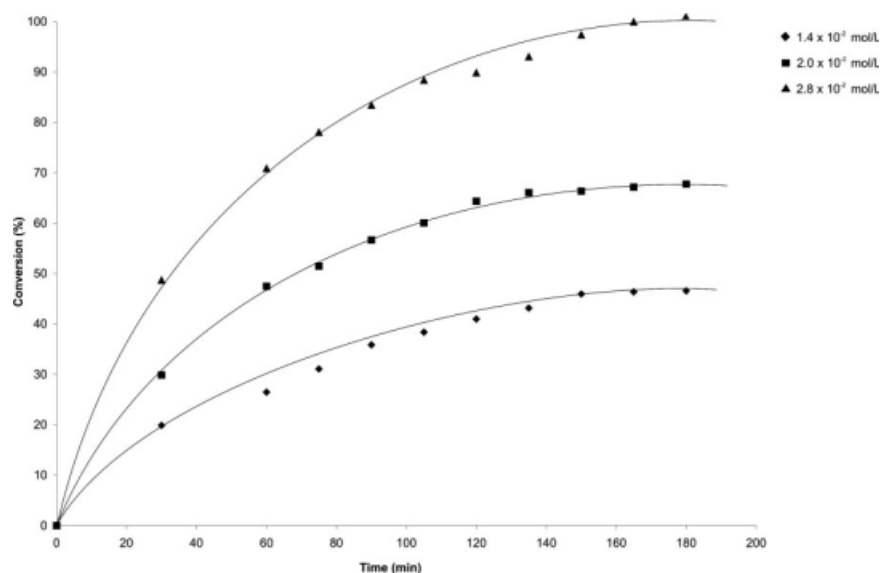


Figure 5 Conversion vs. time at different emulsifier concentrations during the polymerization of MMA/BA/PPGDA.

of the emulsifier SLS was taken above its critical micelle concentration (0.8×10^{-2} mol/L)²⁷ so that nucleation process become micellar,²⁸ resulting in faster generation of polymer particles. It was apparent from both the Figures 4 and 5 that as the concentration of SLS increased from 1.4×10^{-2} to 2.8×10^{-2} mol/L, the conversion of the monomers increased. However, the conversion of the monomers at a particular emulsifier concentration in the absence of PPGDA is less than that in the presence of it. This is probably due to the cross-linking of polymers with PPGDA, and results in an increase in viscosity of polymer and decrease in the termination rate of polymer molecules.

The experiments performed with higher than 2.8×10^{-2} mol/L emulsifier concentration e.g., 3.2×10^{-2} mol/L in the presence of PPGDA it showed that the conversion of monomers decreased (Table II). This indicates that the surface of the growing polymer particles becomes saturated with the soap and therefore no increase in rate occurred at such a high level of emulsifier concentration.

The value of the rate constant (k) for the polymerization reactions in the presence and absence of

PPGDA at different emulsifier concentration is given in Table III. These values were obtained from the slope of plot between $\ln([M_t]/[M_0])$ and time. It is apparent from the data that k increases with the increase in emulsifier concentration and it is higher in the presence of the cross-linking monomer PPGDA at a particular emulsifier concentration.

Effect of monomer concentration

The emulsion polymerization of MMA and BA in varied molar ratio was performed at 70°C and the plots of percentage conversion with time have been shown in Figure 6. It is apparent from the Figure that as the concentration of BA increased in the monomer feed, the percentage conversion also increased. This may be due to the difference of

TABLE III
Rate Constants of Polymerization of Synthesized Polymers

Mole ratio of monomers		Weight % of PPGDA	Emulsifier (SLS) concentration ($\times 10^{-2}$ mol/L)	Rate constant (k) (min^{-1})
MMA	BA			
7	3	0	1.4	3.2×10^{-3}
7	3	0	2.0	4.6×10^{-3}
7	3	0	2.8	1.3×10^{-2}
7	3	10	1.4	4.1×10^{-3}
7	3	10	2.0	7.6×10^{-3}
7	3	10	2.8	2.1×10^{-2}
9	1	0	2.8	7.8×10^{-3}
8	2	0	2.8	9.8×10^{-3}
6	4	0	2.8	1.5×10^{-2}
5	5	0	2.8	1.8×10^{-2}
9	1	5	2.8	1.1×10^{-2}
7	3	5	2.8	1.4×10^{-2}
7	3	10	2.8	5.4×10^{-3}
7	3	15	2.8	3.3×10^{-3}

TABLE II
Percentage Conversion of Monomers With Varied Emulsifier Concentration

Time (min)	Emulsifier concentration	
	2.8×10^{-2} mol/L	3.2×10^{-2} mol/L
30	48.7	47.6
60	70.9	68.1
90	83.5	83.9
120	89.9	87.4
150	97.4	91.5
180	99.9	95.1

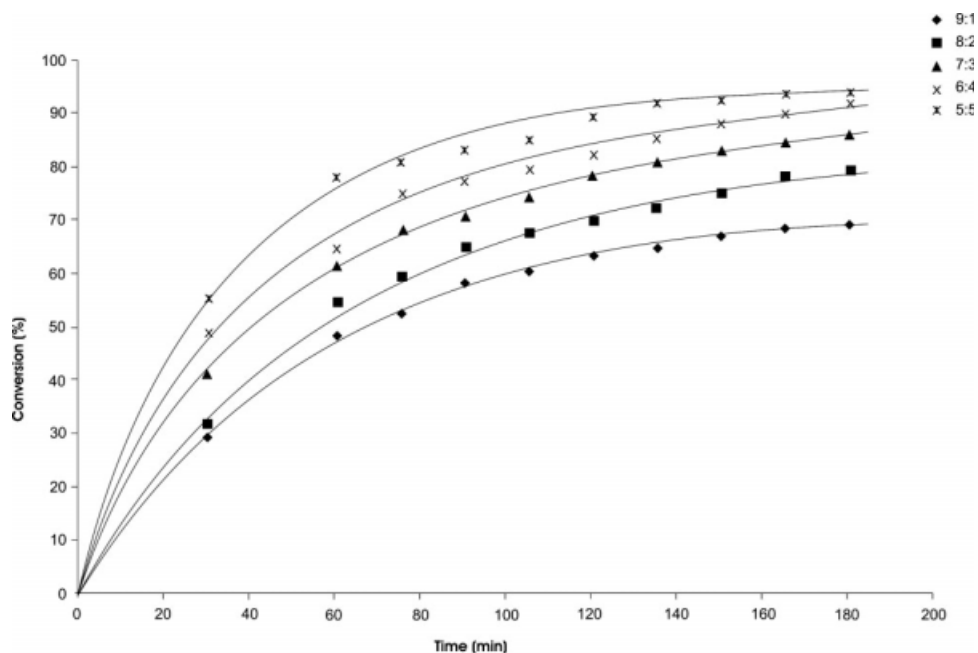


Figure 6 Conversion vs. time with different ratios of MMA to BA.

distribution coefficient of monomers in polymer particle and water phase. The value of distribution coefficient is higher in case of BA than MMA, so once the polymer particles are formed, they absorb monomers faster. The rate constant (k) for the reactions are given in Table III. The values of k were determined by the slope of the plot between $\ln([M_t]/[M_o])$ and time. It is apparent from the data that k increased with the increase in BA concentration.

Figure 7 show the percentage swelling of all the polymers synthesized with varying monomer feed ratio with time. It is clear from the Figure that the swelling decreased with increase in the concentration of BA in the feed. This is due to the fact that the presence of alkyl group in BA leads to an increase in the hydrophobicity of the polymer in comparison to homopolymers of MMA, so higher the content of BA in the polymer more will be the

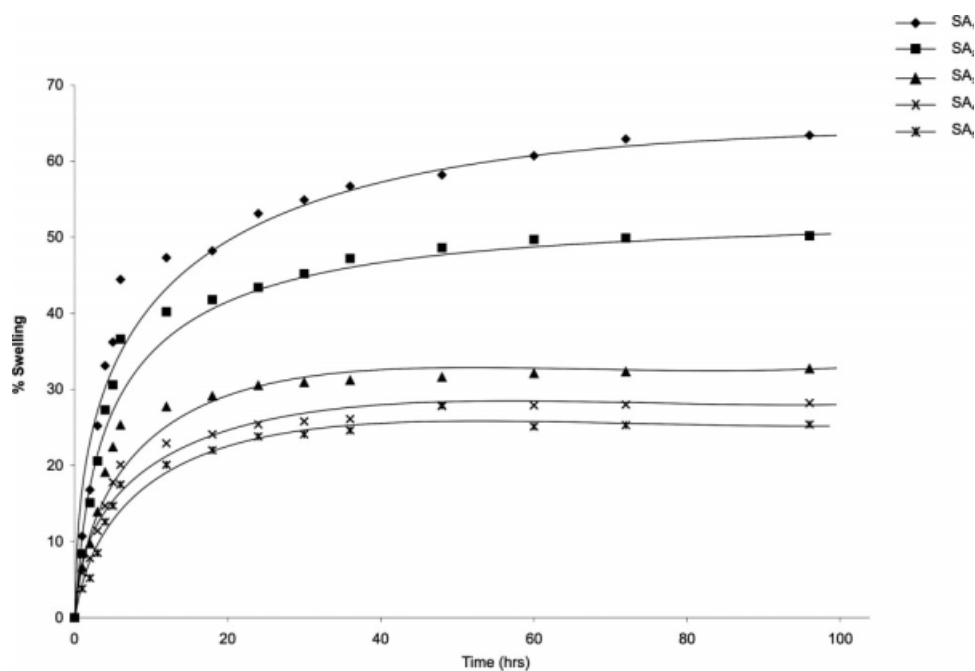


Figure 7 Percentage swelling vs. time of copolymer films with different ratios of MMA to BA.

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

Polymer code	Swelling characteristic constant ($\log K$)	Swelling exponent (n)	Diffusion coefficient (D)
SA ₁	-2.279	0.83	9.96×10^{-6}
SA ₂	-2.293	0.84	1.10×10^{-5}
SA ₃	-2.051	0.75	1.00×10^{-5}
SA ₄	-1.817	0.63	5.05×10^{-6}
SA ₅	-2.390	0.86	1.09×10^{-5}
SA ₃₁	-2.033	0.75	1.04×10^{-5}
SA ₃₂	-1.200	0.33	6.53×10^{-7}
SA ₃₃	-1.090	0.30	5.60×10^{-8}
SA ₃₄	-1.720	0.56	3.67×10^{-6}

hydrophobic character of the polymer and higher will be water resistance.

The swelling mechanism of polymers were analyzed in terms of swelling exponent ' n ', diffusion coefficient ' D ' and swelling exponent ' K ' and the values are given in Table IV. On analyzing the results according to the diffusion controlled mechanism, all the polymers showed anomalous swelling behavior as the value of ' n ' lies in the range of 0.5 to 1.0.

The physical properties viz hardness/softness and opacity were analyzed for all the synthesized acrylic emulsions and the observations are given in Table V. It is seen from the Table that the observed physical properties of the films were affected by the molar ratio of monomers used during their synthesis. PMMA homopolymers forms hard and fragile films, whereas PBA homopolymers form soft and sticky films. As BA content increases in the copolymer, the

TABLE V
Observed Physical Properties of Synthesized Latex Polymer Films

Polymer	Observed	Properties of polymer films	
PMMA	Hard	Fragile	White
PBA	Soft	Sticky	Transparent
SA ₁	Hard	Fragile	White
SA ₂	Hard	Elastic	White
SA ₃	Hard	Elastic	Transparent
SA ₄	Soft	Elastic	Transparent
SA ₅	Soft	Sticky	Opaque

films became more soft, sticky and opaque. When the ratio of monomers was equal, the film became very soft, and peeled out of the glass panel within 6 h of swelling in the water. However, the polymer films made from SA₃ were found to be hard and transparent.

Effect of PPGDA concentration

The effect of variation in concentration of PPGDA on its polymerization with MMA and BA was studied by keeping the molar ratio of monomers MMA and BA at 7 : 3, in the feed. PPGDA concentration was varied from 5 to 20 wt % in the experiments. The Figure 8 shows the percentage conversion with time at different PPGDA concentrations. It is apparent from the plots that the monomer conversion increased when PPGDA concentration was kept at 5 and 10 wt %, where as it was found to decrease when its concentration increased to 20 wt %. The increase in monomer conversion may be ascribed due to cross-linking in presence of PPGDA, which

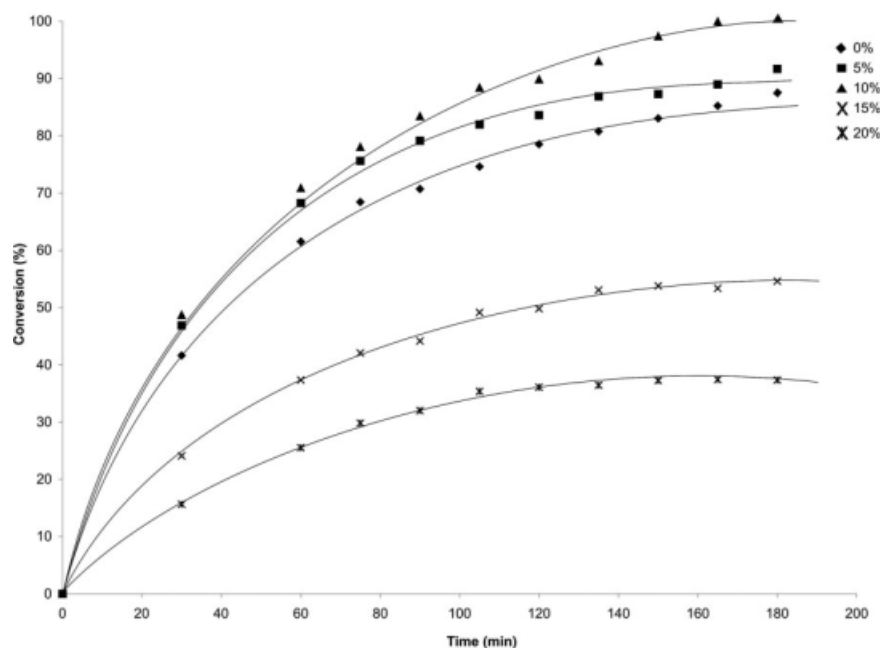


Figure 8 Conversion vs. time at different PPGDA concentrations during the polymerization of MMA/BA/PPGDA.

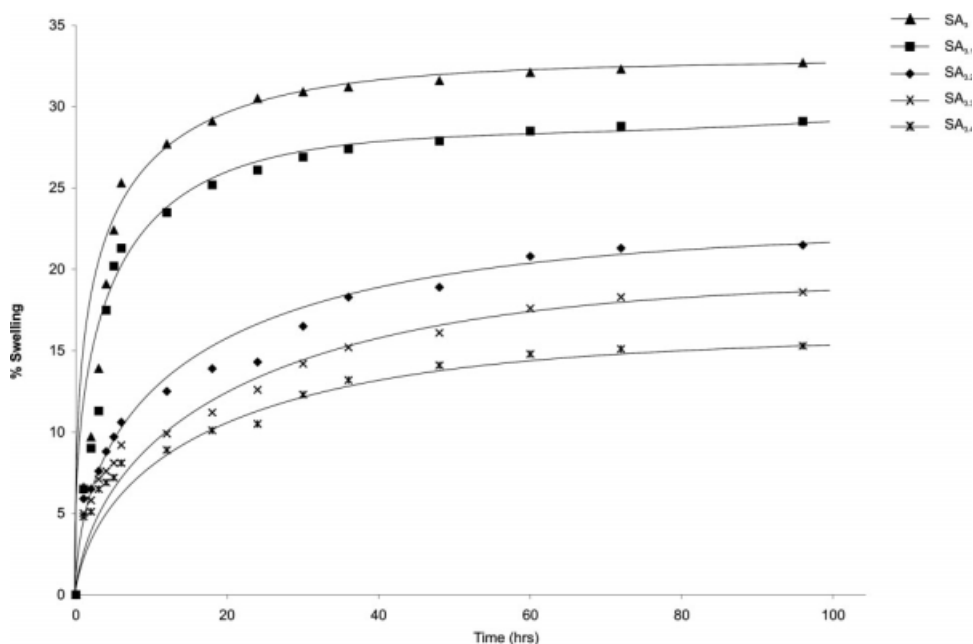


Figure 9 Percentage swelling vs. time of polymer films with different PPGDA concentrations.

might have increased the viscosity of the system reducing the chances of diffusion controlled termination reactions during the course of polymerization. Further increases in PPGDA concentration have resulted in increased cross-linking between the polymer chains to an extent that the free volume reduced and also the monomer conversion. This in turn reduced the polymerization rate of each polymer particle. Except this the lower reactivity of pendant double bonds of PPGDA (Substitution effect), imposes diffusional restrictions on the propagation rate which decreases the initiator efficiency. The value of rate constant k given in Table III all for the ratios reveals the same pattern as was observed in the behavior of monomer conversion.

The percentage swelling of SA_3 polymer film with varying cross-linker concentrations at different time intervals are given in Figure 9. It is clear from the Figure that the percentage swelling of the films gradually decreases with an increase in cross-linker concentration which shows that the water resistance of films is improved by PPGDA. This may be due to increase in cross-link density which causes decrease in free space between the polymer chains and thus diffusion of water to the film.

To get insight into the swelling mechanism of all the polymer films the dynamic swelling parameters ' n ', ' D ', and ' K ' were calculated and are given in Table IV. The swelling exponent ' n ' of the polymer films SA_{32} and SA_{33} are less than 0.5 and thus these films show Fickian behavior where as films of SA_{34} shows minor deviation from the Fickian behavior. From Table IV it is clear that in the values of ' D ' no remarkable variation is observed when PPGDA was varied from 0 to

5 wt % in the monomer feed. The polymer films of copolymer SA_{32} and SA_{33} with 10 and 15 wt % PPGDA had values of D as 6.53×10^{-7} and $5.6 \times 10^{-8} \text{ cm}^2/\text{s}$ respectively, which are smaller than the value of all other synthesized polymers and showed greater cross-linked structure because smaller the value of D greater would be the cross-linking. The similar results were observed by Roman and coworkers.²⁹ by synthesizing polymer films of HEMA with 2, 5, and 10 mol % of triethylene glycol dimethacrylate.

CONCLUSIONS

From the above studies the following conclusions can be drawn

1. The incorporation of PPGDA in the resultant copolymer can be confirmed by the appearance of a sharp peak at 1396 cm^{-1} in the FTIR spectra and decrease in value of T_g observed in DSC thermograms.
2. The MMA/BA polymerized with 5–20 wt % of PPGDA by emulsion polymerization technique the polymer conversion and reaction rate constant increases when PPGDA was taken up to 10 wt % in the monomer feed.
3. The swelling behavior of films of copolymers with varying monomer feed ratios in the range of (9 : 1–5 : 5) was found to be of anomalous behavior, as the values of swelling exponent lies between 0.5 and 1.0. The increase in swelling exponent with increased BA content in the copolymer was due to increased hydrophobic nature of the polymer.

4. When PPGDA was incorporated into the copolymer the swelling of the films decreased and the value of swelling exponent was < 0.5 . The value of diffusion coefficient also decreased with increase in PPGDA which indicated increased cross-linking density of the polymer.

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