

Synthesis, Characterization, and Rheological Studies of Methacrylic Acid–Ethyl Acrylate–Diallyl Phthalate Copolymers

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ABSTRACT: Copolymerization of methacrylic acid (MAA) and ethyl acrylate (EA) was performed by the emulsion polymerization technique in the presence of a mixture of ionic and nonionic emulsifiers, at 85°C, using potassium persulfate as initiator (0.16 wt % of monomer). The molar ratio of MAA : EA varied between 44 : 56 and 54 : 46 in the monomer feed. Copolymers of MAA and EA were synthesized by incorporating diallyl phthalate (DAP) with varying concentrations (0–1.7 mol % of total monomer) in the feed. A copolymer latex of MAA, EA, and DAP was also prepared by the variable feed process. The intrinsic viscosity and gel content were determined. Copolymers were characterized by IR and NMR spectroscopic techniques. The composition

of copolymers was determined by ¹H-NMR spectra and sequential distribution from ¹³C{¹H}-NMR spectra. The pH of the copolymer emulsion varied between 3 and 10 by addition of aqueous ammonia (23% w/w) and its effect on Brookfield viscosity was studied. The effects of copolymer composition, crosslinking agent concentration in the feed, monomer feed process, polymer solid contents, and shear rate on Brookfield viscosity were studied at pH ~ 8. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 1430–1441, 2003

Key words: methacrylic acid–ethyl acrylate–diallyl phthalate copolymers; differential feed; NMR; sequence distribution; rheology

INTRODUCTION

Carboxylic acid–containing emulsions have been used in a variety of applications, for example, in paints, adhesives, binders, and thickeners. Investigations on emulsion polymerization of carboxylic acid–containing polymers by various researchers^{1–5} revealed that properties of the final products are significantly affected by the concentration, polarity, and partition of acid monomer in the aqueous and organic phases. Bajaj et al.⁶ studied the emulsion stability of carboxyl acid–containing polymer latex as a function of the concentration and the nature of emulsifiers. They concluded that a mixture of anionic and nonionic emulsifiers improves the emulsion stability. They also derived the reactivity ratios of methacrylic acid (MAA) and ethyl acrylate (EA) pairs by use of the method of nonlinear least-square error in variable. The reactivity ratios of MAA and EA are reported to be 2.58 and 0.157, respectively; thus, both MAA and EA units prefer the proximity of added MAA units. Both the mechanism and kinetics of polymerization involving hydrophilic monomers such as methacrylic acid, acrylic acid (AA), and itaconic acid (IA) with hydrophobic monomers such as EA, butyl acrylate (BA), and

styrene (St) were previously studied by Poehlein et al.⁷ They suggested that the primary reaction locus in the AA–St system shifts from particles to the aqueous phase after the hydrophobic monomer has been consumed.

Semicontinuous emulsion polymerization is the most common method of latex synthesis and it is reported that any modification in the feed process can affect the characteristics of the polymer.^{8–11}

Fordyce et al.^{12,13} reported the marked increase in the viscosity of MAA-containing copolymer upon addition of a base. The viscosity versus pH relationship for a large number of MAA-containing emulsion polymers was studied by Verbrugge.^{14,15} The alkali solubility of copolymers of MAA and AA with different comonomers such as EA, ethyl methacrylate (EMA), methyl methacrylate (MMA), and St was studied by Muroi et al.^{16,17} Alkali solubility was found to be dependent on the concentration of the acid component in the copolymer, water solubility of the nonacidic component, degree of polymerization, glass-transition temperature (T_g), chain configuration, and dissolution temperature. They reported that the dissolution behavior of MAA copolymers is better than that of AA copolymers and concluded that MAA units distributed more uniformly than AA in the polymer particles.

Jenkins et al.¹⁸ studied the effect of carboxylic acid monomer concentration, polymer T_g , and water solubility of the polymer chain on aqueous solution rheo-

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TABLE I
Polymerization Recipe^a

Compound	Weight (g)
Methacrylic acid (MAA)	124–155 (44–54 mol %)
Ethyl acrylate (EA)	155–186 (46–56 mol %)
Diallyl phthalate	0–2 (0–1.7 mol % of MAA and EA)
Sodium lauryl sulfate	2 (0.65% of monomer)
Spectra S 301	2 (0.65% of monomer)
Alfox 200	2 (0.65% of monomer)
Potassium persulfate	0.5 (0.16% of monomer)
Deionized water	745 (water:monomer = 71:29)

^a Conditions: time, 4.5 h; temperature, 85°C; atmosphere, air.

logy of alkali swellable emulsion polymers. They used EA, BA, MMA, or St as comonomer (30–60 wt %) with MAA, and found that, among those monomers in order of increasing water solubility and decreasing T_g of the polymer-promoting thickening power, EA is the most suitable for combination with MAA.

In the current study, the polymerization of MAA-EA-DAP, suitable for printing thickeners in textiles, using the semicontinuous emulsion polymerization technique in the presence of anionic and nonionic emulsifiers, is reported. Copolymers obtained at high conversions were characterized by viscometry and both IR and NMR (^1H and $^{13}\text{C}\{^1\text{H}\}$) spectroscopy techniques; thermal studies were done by DSC and TGA to understand the microstructure of the copolymers. The effect of the monomer feed process on Brookfield viscosity was also studied.

EXPERIMENTAL

Materials

Methacrylic acid (MAA), ethyl acrylate (EA), and diallyl phthalate (DAP) of LR grade were used. Sodium lauryl sulfate (SLS; Spectra S301, Glaxo India Ltd.), an ammonium salt of polyoxyethylene sulfonic acid (Spectra Chem Ltd., India), and Alfox 200 (Indian Glycol Ltd.), a nonyl phenyl ethylene oxide condensate, were used as emulsifiers. Potassium persulfate (KPS, AR grade; BDH Chemicals, Poole, UK) was used as a free-radical initiator. Ammonium hydroxide (23 wt %) was used for pH adjustment of the polymer emulsion.

Polymerization

The emulsion polymers were prepared in a 2-L four-neck glass reactor equipped with a stirrer, a reflux condenser, a thermometer, and two dropping funnels through a Y-shaped connector. MAA-EA-DAP copolymers of varying compositions (MAA, 44–54 mol %; EA, 46–56 mol %; and DAP, 0–1.7 mol %) were synthesized by the semicontinuous emulsion polymerization technique. The recipe of a single batch is given in

Table I. The monomer emulsion was prepared by high-speed stirring of the monomer mixture with 120 g water, 2 g anionic Spectra S301, and 2 g nonionic Alfox 200 emulsifiers. The initiator solution was prepared with 0.5 g KPS in 80 g water. The remaining quantity of water (545 g) and emulsifiers (SLS, 2 g; Spectra S301, 2 g) was charged into the reactor and the temperature was increased to 85°C, after which 10 mL of initiator solution was fed in a single shot. After 1 min, the monomer emulsion was fed dropwise (120 mL in 60 min) in parallel with initiator solution (20 mL in 60 min). After a 20-min polymerization time at $85 \pm 2^\circ\text{C}$, 10 mL of initiator solution was added in a single shot, and the remaining monomer emulsion was fed in a period of 90 min. Subsequently, 10 mL of initiator solution was added in single shots at 30-min intervals until the monomer feeding was completed. At 10 min after the completion of monomer feed, the rest of the initiator solution was slowly added. The polymerization was continued for another 60 min at the same temperature. The course of feeding the monomer emulsion and initiator solution is given in Figure 1. The polymer emulsion was then cooled to room temperature and filtered through cheesecloth. The coagulum was negligible. Compositions of the copolymers with codes are given in Table II.

Polymerization with modification of monomer emulsion and feed

P(MAA-EA-DAP) copolymer (MAA : EA : DAP :: 48.4 : 50.9 : 0.7 mol %) was prepared with slight variation of the monomer feed process. Two sets of monomer emulsions were prepared: (1) monomer emulsion 1 (ME1), with a greater amount of EA comonomer (MAA : EA : DAP :: 43.5 : 55.8 : 0.7 mol %); (2) monomer emulsion 2 (ME2), with a greater amount of MAA comonomer (MAA : EA : DAP :: 53.4 : 45.9 : 0.7 mol %). Polymerization was carried out at $85 \pm 2^\circ\text{C}$ by feeding ME1 followed by ME2 in the same manner as given in the previous section. This polymer was coded as P15 (Table II).

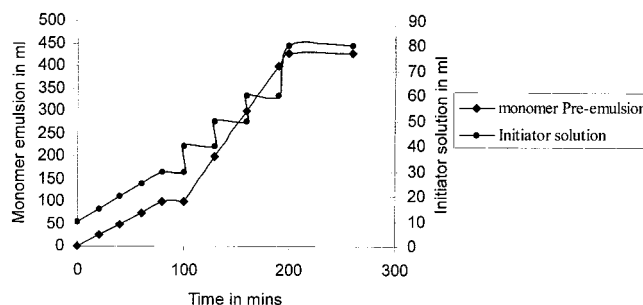


Figure 1 Plot of feeding process of monomer emulsion and initiator solution with time.

TABLE II
Composition and Brookfield Viscosity of Copolymers

Polymer code	Monomer ratio						Brookfield viscosity (cps)
	MAA		EA		DAP		
	wt %	mol %	wt %	mol %	wt %	mol %	
P1	40	44	60	56	0	0	570
P2	39.6	43.3	59.4	55.8	1	0.9	23,000
P3	39.2	42.9	58.8	55.3	2	1.7	11,800
P4	45	48.7	55	51.3	0	0	720
P5	44.5	48.3	54.4	50.7	1	0.9	25,200
P6	44.1	47.9	53.9	50.3	2	1.7	10,400
P7	50	53.7	50	46.3	0	0	520
P8	49.5	53.3	49.5	45.8	1	0.9	22,000
P9	49	52.8	49	45.4	2	1.7	7,800
P10	44.7	48.5	54.7	51.1	0.6	0.5	15,000
P11	44.6	48.4	54.5	50.9	0.8	0.7	26,600
P12	44.4	48.3	54.3	50.7	1.2	1	23,700
P15 ^a	44.6	48.4	54.5	50.9	0.8	0.7	31,500

^a Polymer synthesized by modified feed process.

Polymer characterization

Polymer emulsions were broken by the addition of a 15% NaCl solution. The polymers obtained were washed several times with distilled water and dried at 70°C for 24 h, after which characterization of these polymers was carried out.

Intrinsic viscosity

The intrinsic viscosity of the uncrosslinked MAA-EA copolymers was measured in *N,N'*-dimethyl formamide (DMF) by Ubbelohde viscometer in a thermostat at $30 \pm 1^\circ\text{C}$.

Acidimetric titration

The MAA concentration of the uncrosslinked copolymers was determined by acidimetric titration of 0.5% polymer solution in methanol against a standard NaOH solution, with phenolphthalein as indicator.

Gel content determination

The gel content of the crosslinked polymers was measured gravimetrically.¹⁹ Nearly 5 g of the solid polymer was mixed with 100 mL of methanol and kept at 40°C. After 48 h, the mixture was centrifuged at 7500

rpm at room temperature using an Eltek Research centrifuge (Model TC 81008). The swollen gel was washed with fresh methanol two to three times to remove the sol and centrifuged again. The gel was then dried in a vacuum oven at 60°C for 24 h and weighed to calculate the gel content.

FTIR studies

The FTIR spectra of MAA-EA copolymers were recorded on a Jasco Micro Jansen FTIR 200 (Tokyo, Japan). Pellets were prepared by grinding 5 mg of sample with 50 mg of moisture-free KBr in a mortar and then compressed to obtain a pellet.

NMR studies

The ¹H- and ¹³C{¹H}-NMR spectra of uncrosslinked MAA-EA copolymers were recorded on a Bruker DPX300-MHz spectrophotometer (Bruker Instruments, Billerica, MA) operating at 300 and 75 MHz, respectively. All the samples were recorded at 80°C using DMSO-*d*₆ as solvent. Tetramethylsilane was used as an internal standard. Calculation of the fractional peak area was made using a Lorentzian-shape curve-fitting computer program.

TABLE III
Polymer Characterization Data

Polymer code	Feed concentration MAA (mol %)	Copolymer composition MAA (mol %)		Intrinsic viscosity (dL/g)
		¹ H-NMR studies	Acidimetric titration	
P1	44.0	39.7	36.3	5.3
P4	48.7	51.0	44.9	4.3
P7	53.3	56.3	49.5	3.7

TABLE IV
Gel Content and Brookfield Viscosity of Copolymers with Varying Diallyl Phthalate (DAP) Concentrations

Polymer code	DAP in feed (wt %)	Gel content (wt %)	Brookfield viscosity (cps)
P4	0	—	720
P10	0.6	38	15,000
P11	0.8	63	25,200
P5	1.0	41	25,200
P12	1.2	42	23,700
P6	2.0	33	10,400
P15	0.8	62	31,500

Thermal studies

TGA and DSC studies of MAA-EA copolymers were carried out on DSC 7 and TGA 7 module of a Perkin-Elmer Delta series thermal analyzer (Perkin Elmer Cetus Instruments, Norwalk, CT). The measurements were carried out in an oxygen-free nitrogen atmosphere at a heating rate 10°C/min. The sample size was kept at 4–5 mg in all the experiments.

Rheological studies: Brookfield viscosity studies

Brookfield viscosity of the neutralized solution of polymers was measured by a Brookfield RVDT digital viscometer. The effects of pH, copolymer composition, gel content, monomer feed process, polymer solid contents, and shear rate on Brookfield viscosity were studied.

RESULTS AND DISCUSSION

Polymer characterization

Acidimetric titration

The MAA content of these copolymers was determined by acidimetric titration of solutions of these uncrosslinked copolymers in methanol with standard aqueous NaOH solution. In spite of high reactivity of MAA, the MAA content was much lower than the amount of MAA incorporated in the feed (Table III). The conversion in this polymerization was also $\geq 95\%$. In this direct titration technique, neutralization or endpoint appearance is quite rapid. Under these test conditions, it is probable that not all carboxylic groups are available for neutralization.² If the samples are kept for some time to ensure neutralization of all carboxylic groups, the simultaneous hydrolysis of the ester groups (of EA units) may also occur during that period to give a higher acid value.

Intrinsic viscosity

The intrinsic viscosity values $[\eta]$ of MAA-EA copolymers P7, P4, and P1 synthesized under similar condi-

tions increased from 3.7 dL/g for P7 to 5.4 dL/g for P1. As the EA content in the feed increased from 46.2 mol % in P7 to 56.4 mol % in P1, the intrinsic viscosity value of copolymers increased (Table III). Intrinsic viscosity is a measure of the molecular and hydrodynamic volume of the polymer. Hydrodynamic volume depends on the size, tacticity, and density of polymer coils in the solution. The observed increase in the intrinsic viscosity of EA-rich polymers may be attributed to the increases in both the molecular weight and the size of the side groups (i.e., attributed to ester groups in EA compared to carboxylic acid groups of MAA). This would lead to an increase in the overall dimensions of polymeric coils, resulting in higher hydrodynamic volume.²²

Gel content

The gel content of the copolymer increased with an increase in DAP concentration (up to 0.7 mol %) in the feed, and then decreased with a further increase in DAP concentration (Table IV). The gel content values of 63 and 62% were obtained for P11 and P15, respectively. Copolymers P11 and P15 are copolymers synthesized with the same MAA-EA-DAP (48.4 : 50.9 : 0.7 mol %) composition in the feed but were synthesized with different feed processes of monomers. This indicates that the modification of the feed process does not alter the crosslink density of the copolymer.

When the crosslinking agent is present as one of the comonomers, two types of reactions are in competition with each other:

1. *Intramolecular crosslinking*, in which a pendent double bond of growing polymer radicals cyclizes with its own chain.
2. *Intermolecular crosslinking*, which takes place between a growing radical and the polymer chain that has unreacted pendent double bonds.

TABLE V
Characteristic IR Frequencies of Methacrylic Acid-Ethyl Acrylate Copolymers

Peak position		Assignment
(cm ⁻¹)	Intensity	
3462–3205	Broad	ν_{OH}
2991	Strong	$\nu_{\text{ac-H}}$
1736	Strong	$\nu_{\text{C=O}}$ (Ester)
1702	Strong	$\nu_{\text{C=O}}$ (Acid)
1485	Strong	$\delta (\text{CH}_2) + \delta \text{a}(\alpha - \text{CH}_3)$
1448	Strong	$\delta \text{s}(\text{CH}_3-\text{O})$
1385	Medium	$\delta (\alpha - \text{CH}_3)$
1258–1179	Broad	$\nu_{\text{C-O}}$
1022	Weak	$\nu_{\text{C-O-C}}$
980	Weak	$\gamma_{\text{r}} (\text{CH}_3-\text{O})$

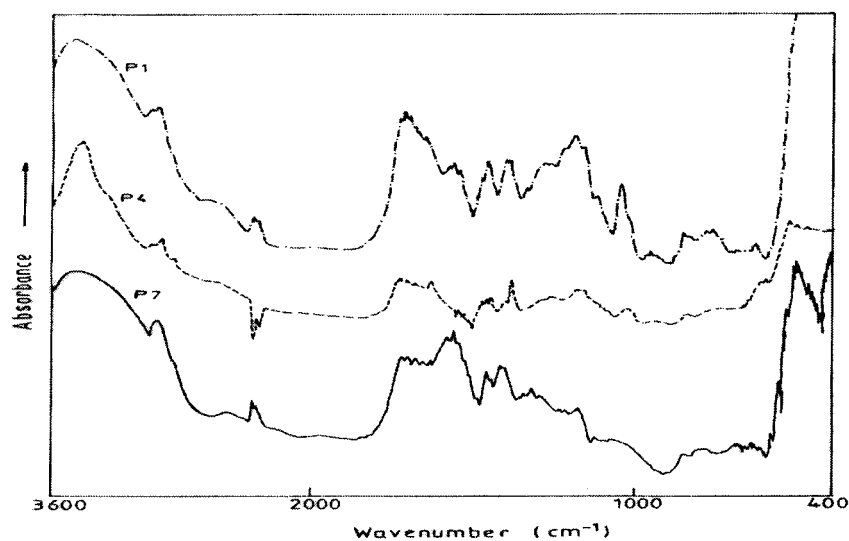


Figure 2 FTIR spectra of MAA : EA copolymers: P1, 44 : 56; P4, 48.3 : 51.7; P7, 53.7 : 46.3.

With an increase in the amount of crosslinking agent, the intramolecular crosslinking reaction increases and thus there is a decrease in the gel content of the copolymer. The effect of crosslinking agent feed concentration on the gel content has been studied in detail with different crosslinking agents¹⁹ and a similar trend is reported.

FTIR studies

The IR absorption bands attributed to carbonyl stretching of the acid and ester units appeared as a broad shoulder in the 1700 to 1740 cm^{-1} range (Table V). There was no shift in the position of absorption bands with a change in the MAA : EA ratio. However, the relative peak intensities attributed to carbonyl

stretching of MAA (1702 cm^{-1}) and of EA (1740 cm^{-1}) showed distinct variation with the copolymer composition (Fig. 2). The peak intensity at 1702 cm^{-1} , corresponding to carboxylic acid C=O stretching, increased with increases in the MAA content in the copolymers from P1 to P7. A similar variation with crosslinking agent (DAP) concentration was not observed with the same copolymer composition (Fig. 3), which may be a consequence of the very low concentration of crosslinking agent concentration in the feed.

NMR studies

¹H-NMR studies. The main chain carbon atoms of MAA-EA copolymers may be represented by the structural units given in Scheme 1.

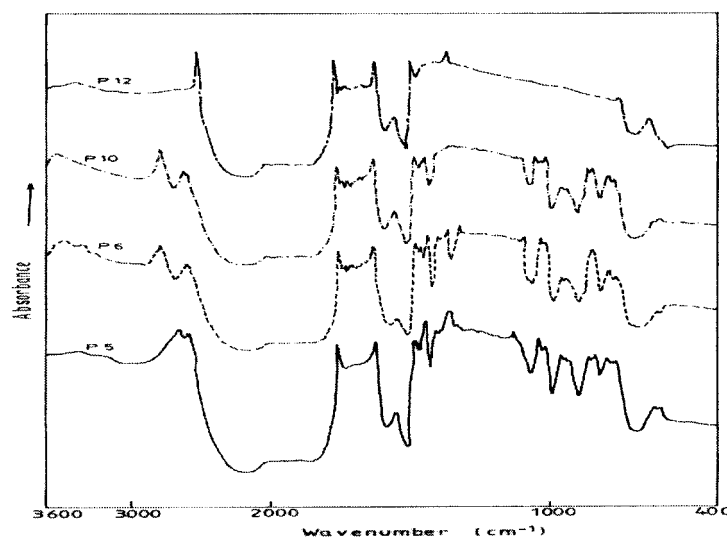
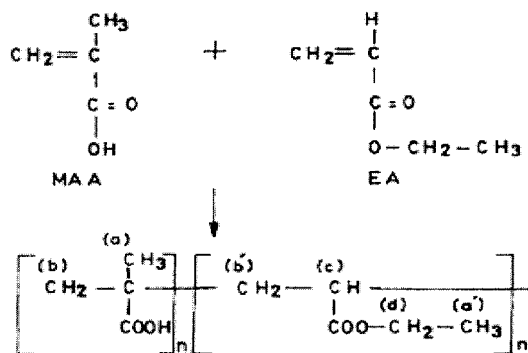


Figure 3 FTIR spectra of MAA : EA copolymers with varying DAP concentration in mol % of total monomer: P5, 0.9; P6, 1.7; P10, 0.5; P12, 1.0.



Scheme 1 Main-chain carbon atoms of MAA-EA copolymer.

The $^1\text{H-NMR}$ spectra of copolymers (P1, P4, and P7) displayed a multiplet between 0.9 and 1.2 δ (Fig. 4), attributed to the methyl protons of MAA and the methyl protons of alkyl chains of EA. A broad signal between 1.5 and 1.7 was assigned to methylene protons (b + b') of both EA and MAA. Methine protons (c) of the EA unit showed a peak at δ 2.2. The signals at δ 2.7 and δ 3.4 were assigned to the residual protons of $\text{DMSO-}d_6$. The most upfield peak at δ 4.0 is probably attributable to OCH_2 (d) protons of EA.

The composition of the copolymers was calculated⁶ by measuring the intensity (I) of the peak attributed to OCH_2 (d) protons of EA at δ 4.0 and then subtracting the contribution of EA from the multiplet of methyl protons of MAA and EA (a + a'). This value represents the contribution of the methyl protons of MAA units. From this, the concentration of MAA in the copolymer was calculated. The result, thus obtained, was found to be closer to the feed concentration than the results obtained from acidimetric titration (Table III).

TABLE VI
 $^{13}\text{C}/^1\text{H-NMR}$ Data

Chemical shift (ppm)	Assignment
13-14	CH_3 carbon of EA
15.5-19.7	CH_3 carbon of MAA
36.6-41.2	Quaternary carbon of MAA
58.5-59.5	OCH_2 of EA
172-178	Carbonyl carbon ($\text{C}=\text{O}$) of MAA and EA

$$I[(\text{CH}_3)_M] = I[(\text{CH}_3)_M + (\text{CH}_3)_E] - I[(\text{OCH}_2)_E] \times 3/2 \quad (1)$$

$$\% \text{MAA} = I[(\text{CH}_3)_M] \times 100 / I[(\text{CH}_3)_M + (\text{CH}_3)_E] \quad (2)$$

$^{13}\text{C}\{^1\text{H}\}$ -NMR studies. The signals and assignments of $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra of the MAA-EA copolymers (P1, P4, and P7) are given in Table VI. Signals attributed to carbonyl carbon ($\text{C}=\text{O}$) of EA and MAA (172-178 ppm) were used for sequential analysis because of their superior resolution.

Spectra of carbonyl carbon expansion of three copolymers, P1, P4, and P7, are shown in Figure 5. Signals at around 173.3, 174.4, 175, 175.5-176, 177.1, and 178.2-178.7 can be assigned to EEE, EEM, MEM, EME, MME, and MMM triads, respectively. The fraction of M- and E-centered triads was calculated from the relative areas of resonance signals (Table VII). The carbonyl carbon of EA units, which is configurationally insensitive,⁶ appeared as a multiplet in the copolymer at 172.5-174.4 ppm. The splitting may be attributed to the sensitivity to compositional sequences. The carbonyl carbon of MAA units appeared in the range of 174.8-178 ppm, which justifies its sensitivity to-

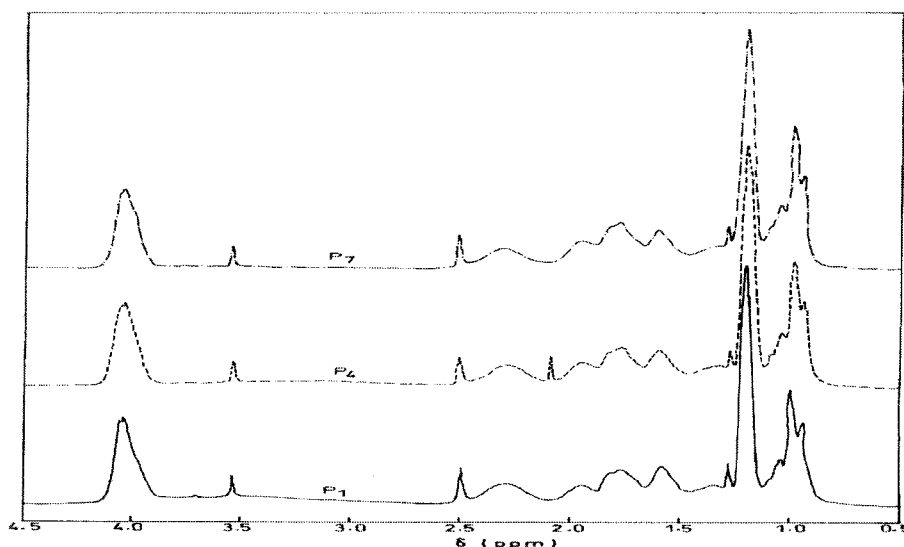


Figure 4 $^1\text{H-NMR}$ spectra of MAA : EA copolymers: P1, 44 : 56; P4, 48.3 : 51.7; P7, 53.7 : 46.3.

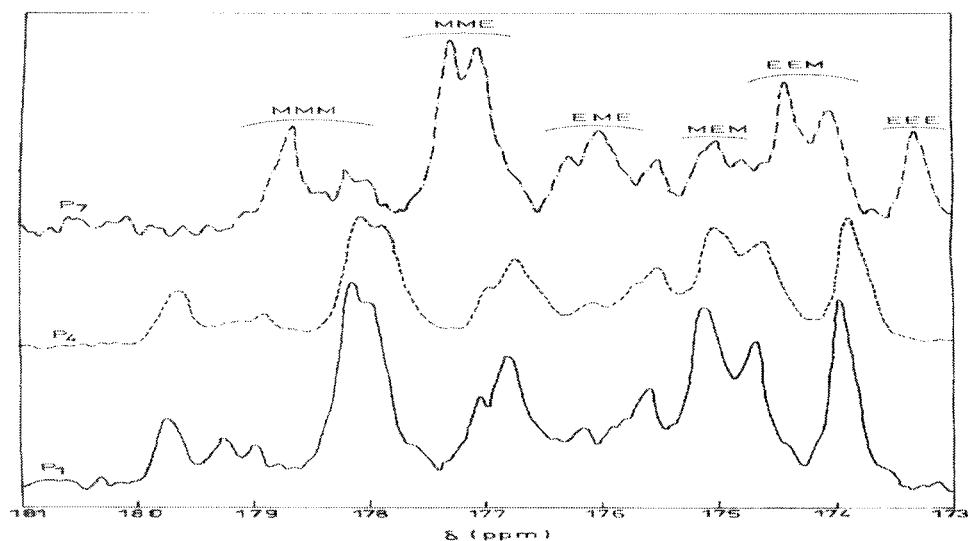


Figure 5 Carbonyl carbon expansion of $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra of MAA:EA copolymers: P1, 44:56; P4, 48.3:51.7; P7, 53.7:46.3.

ward different monomer sequences in the polymer chain.¹²

The concentration of different triads varied with MAA and EA concentration in the polymer. The mole fraction of the MMM triad increased from 0.24 to 0.32 and that of the EEE triad decreased from 0.25 to 0.21 when the concentration of MAA increased from P1 (39.7 mol %) to P7 (56.3 mol %). The mole fraction of MME, EME, and MEM triads increased with an increase in MAA concentration from P1 to P4 and then decreased for P7. However, the mole fraction of the EEM triad decreased with an increase in MAA content from P1 to P4 and then increased for P7 (Table VII). The mole fraction of the EEE triad decreased with an increase in MAA concentration in the polymer.

In the semicontinuous polymerization technique, the monomer is fed slowly over a certain time period. This is done to maintain uniform monomer concentration throughout the reaction. Hence, the variation of triad concentration with MAA-EA molar ratio can be attributed to the reactivity ratios of both monomers. Reactivity ratios¹² of MAA ($r_1 = 2.58$) and EA ($r_2 = 0.157$) suggest that both MAA and EA radicals would prefer the addition of MAA. In the earlier stage

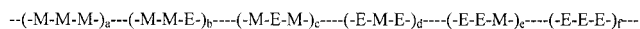
of the polymerization reaction, highly reactive MAA radicals are preferentially incorporated into the growing polymer chain over EA radicals; thus MAA-rich blocks would be formed. In the later stage of reaction when the concentration of MAA is being depleted, EA-rich blocks would be formed in the polymer chain. The increment in MEM and EME triads with an increase in MAA concentration in the feed suggests that MAA also enables EA to be incorporated into the growing polymer chain. Thus, tentative distribution of triads over the polymer chain can be represented as in Scheme 2.

Because of significant differences in reactivity ratios of MAA and EA, they cannot be uniformly distributed in the polymer chain; that is, some portions will be rich in either MAA or EA. If we consider the sum of mole fractions of MEM and EME triads ($c + d$) as the degree of uniform distribution of monomers, then P4 (0.65) is comparatively more uniform than P1 (0.50) and P7 (0.57). This indicates that uniform distribution of monomers depends not only on reactivity ratios but also on the relative concentrations of both monomers available during polymerization. Any modification in

TABLE VII
Concentration of Triads in Mole Fraction from $^{13}\text{C}\{^1\text{H}\}$ -NMR Spectra

Triad	Chemical shift range (ppm)	P1 ^a (MAA, 44 mol %)	P4 ^a (MAA, 49 mol %)	P7 ^a (MAA, 54 mol %)
MMM	178.2–178.7	0.24	0.25	0.32
MME	177–177.5	0.45	0.46	0.40
EME	175.5–176.5	0.31	0.29	0.28
MEM	175–175.5	0.19	0.36	0.29
EEM	174–175	0.56	0.40	0.50
EEE	173–174	0.25	0.24	0.21

^a MAA concentration in monomer feed.



Scheme 2 Tentative triad distribution in MAA-EA copolymer chain.

feeding of monomers can change the sequence distribution.

Thermal studies

Differential scanning calorimetry. All copolymers (P1, P4, and P7) showed a well-pronounced broad endotherm in the temperature range of 160 to 280°C (Fig. 6). This may be attributed to anhydride formation by COOH and COOC₂H₅ groups present in the copolymer, as reported by Bajaj and coworkers.²¹ The difference between peak temperature (T_p) and onset temperature (T_o) is a measure of the rate of reaction (Table VIII). The smaller the difference, the greater the rate of reaction and vice versa.²² In the present system ($T_p - T_o$) values are found to increase from P1 to P4 with an increase in MAA contents from 44 to 48.7 mol %; however, the trend reverses in P7. With a further increase in MAA to 53.3 mol %, the ($T_p - T_o$) value increased from 35.7 to 39.3 for P1 and P4 and then decreased for P7 to 31.7. In other words, the rate of anhydride formation is maximum in P7, which has the highest amount of MAA. The heat of reaction increased from 79.0 to 141.8 J/g for P1 and P4 and then decreased to 127.6 J/g for P7, also following the same trend.

Bajaj et al.²³ reported that the homopolymer of EA does not show any endotherm in the temperature range 160 to 280°C, whereas the homopolymer of MAA undergoes rapid dehydration in the same range; copolymers of MAA-EA showed a similar endotherm in the same range of temperature. They found an

increase in the heat of reaction (ΔH) and a decrease in the rate of dehydration [i.e., a lower ($T_p - T_o$) value] with an increase in EA concentration in the MAA-EA copolymer from 0 to 38.1 mol %, and concluded that EA units presumably participate in the dehydration reaction when present in the copolymer with MAA, thus reducing the rate of reaction and increasing the ΔH . This indicates that the values of ($T_p - T_o$) and ΔH for anhydride formation between two MAA units and between an MAA and an EA unit are different. Hence, the rate and extent of anhydride formation may be correlated to the sequential distribution of MAA and EA units in the copolymer.

From proton NMR and acidimetric titration studies (Table III) it is evident that variation of copolymer composition occurs in accordance with the variation of monomer in the feed. The concentration of M- and E-centered triads varies with copolymer composition (Table VII).

This can be correlated to the triad distribution in the copolymers. The MMM triad may undergo anhydride formation reaction at a faster rate followed by the MME triad. EME, MEM, and EEM triads may undergo anhydride formation at a very slow rate but, because of the participation of EA units in anhydride formation, the ΔH value will be greater than that of the reaction involving MMM triads. EEE triads of the copolymer may not undergo a reaction like that of the homopolymer of EA. Therefore, the EEE triad-rich copolymer P1 has the lowest ΔH value, whereas the MMM triad-rich copolymer P7 has the highest rate of reaction. Copolymer P4 with the highest MEM and EME triad fraction has the lowest rate of anhydride formation, with highest ΔH value among the three copolymers under study.

Thermogravimetric analysis. Analysis of thermogravimetric curves of the copolymers P4, P11, P15 showed

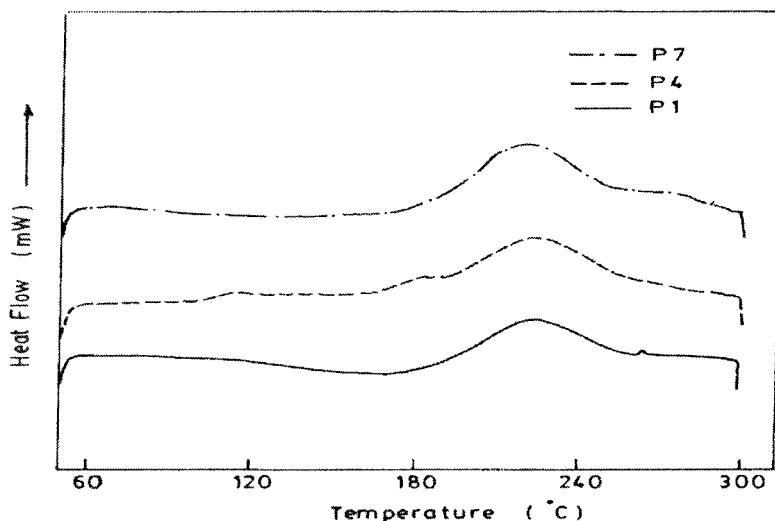


Figure 6 DSC thermograms of MAA : EA copolymers: P1, 44 : 56; P4, 48.3 : 51.7; P7, 53.7 : 46.3.

TABLE VIII
DSC Data of Uncrosslinked Copolymers of MAA-EA

Polymer code	MAA from ¹ H-NMR (mol %)	Endotherm range (°C)			ΔH (J/g)
		T_o	T_p	$(T_p - T_o)$	
P1	39.7	187	222	35.7	79.0
P4	51.0	183	223	39.30	141.8
P7	56.3	186	218	31.7	127.6

two/three distinct steps of weight loss. The first step occurred in the range of 160–410°C and the second step in the range of 430–560°C (Table IX, Fig. 7). The weight loss in the first step of degradation was higher in uncrosslinked copolymers than in crosslinked copolymers of the same MAA-EA composition.

Weight loss in the range of 160 to 280°C may be attributed to the elimination of side products in the process of anhydride formation, as indicated by an endothermic transition in the DSC scans.²³ Two types of reactions can take place in MAA-EA copolymers involving adjacent MAA units and involving neighboring MAA and EA units (Scheme 3). Theoretically, the maximum weight loss can be calculated, assuming that all the MAA and EA units are participating in the dehydration reaction. Thus, the total weight loss is equal to the total weight of water and ethanol liberated.

In the previous section it was discussed that EA participates in anhydride formation with MAA; thus, the EA units adjacent to MAA units in the blocks can participate in anhydride formation. From TGA data of P4, P11, and P15 copolymers (Table IX) the weight loss in different temperature ranges are given. In the range 170 to 290°C, P4 and P11 have an almost equal weight loss (9.73 and 9.99%, respectively), whereas P15 has a higher weight loss (13.2%). This weight loss may be related to the sequential distribution of MAA and EA units in the polymer chains. Polymers P4 and P11 may have similar distribution of MAA and EA units, leading to a similar weight loss values.

The higher value of weight loss in P15 may be attributed to more ethanol as a side product than that in P4 and P11, given that ethanol has a higher molecular weight than that of water, which is another side product of the anhydride formation reaction. This in-

dicates that a greater number of EA units are present in MAA-EA blocks in P15 than in P4 and P11, although all of these polymers have the same MAA-EA composition in the feed. This suggests that, because of the modification of the monomer feed process, the microstructure of copolymers is altered, which is further supported by ¹³C-NMR analysis discussed earlier.

In the temperature range 290 to 480°C degradation of the polymer backbone occurs. Crosslinked polymers P11 and P15 show slightly lower weight loss (70.51 and 70.02%, respectively) compared to that of the uncrosslinked polymer P4 (74.99%).

Rheological studies: Brookfield viscosity

Effect of pH

Brookfield viscosity was found to increase with an increase in the pH, by addition of ammonia, up to 7.5–8.5. Beyond that, any increase in pH leads to a decrease in viscosity [Fig. 8(a–c)].

On addition of ammonia to the polymer emulsion, some degree of ionization occurs, providing ammonium counter ions and carboxylate ions on the polymer chains. The negatively charged carboxylate ions repel each other electrostatically.^{12,13} Because of this, the polymer chains uncoil and viscosity increases. After complete neutralization, further addition of ammonia results in a buildup of ammonium counter ions, which repress the effective ionization of carboxylate groups. This leads to coiling of the polymer chains and subsequent reduction in viscosity.

Effect of copolymer composition

Brookfield viscosity of uncrosslinked polymers first increased from 570 to 720 cps with an increase in MAA contents from 44 mol % (P1) to 48.7 mol % (P4) and then decreased to 520 cps for 53.7 mol % (P7) (Table II).

The Brookfield viscosity¹⁸ of carboxylated latex on neutralization increases with any of the following three factors:

1. An increase in the carboxylic acid content of the copolymer.
2. A decrease in the T_g of the copolymer.
3. An increase in the gel content of the copolymer.

TABLE IX
Thermal Degradation Data of MAA-EA Copolymers

Polymer code	Copolymer composition (mol %)			Weight loss (%)			
				Temperature range (°C)			
	MAA	EA	DAP	60–170	170–280	280–480	480–600
P4	48.8	51.2	0	2.77	9.73	74.99	12.50
P11	48.41	50.89	0.69	3.20	9.99	70.51	16.21
P15	48.41	50.89	0.69	1.38	13.2	70.02	15.39

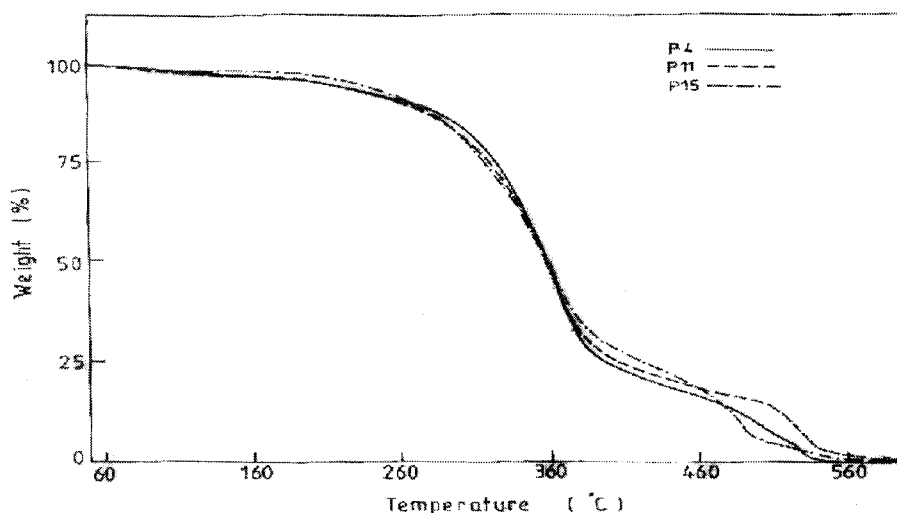
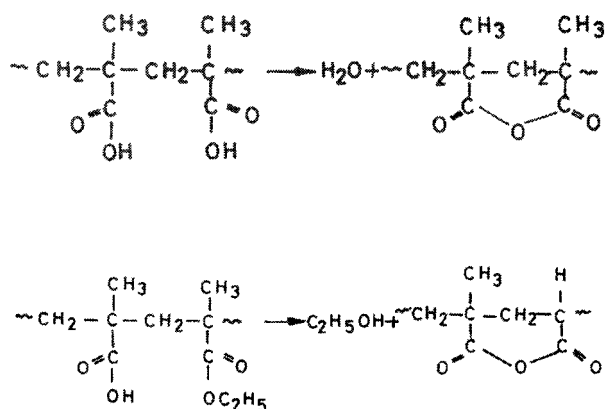


Figure 7 TGA plots of MAA : EA : DAP copolymers: P4, 48.3 : 51.7 : 0; P11, 48.4 : 50.9 : 0.7; P15, 48.4 : 50.9 : 0.7.

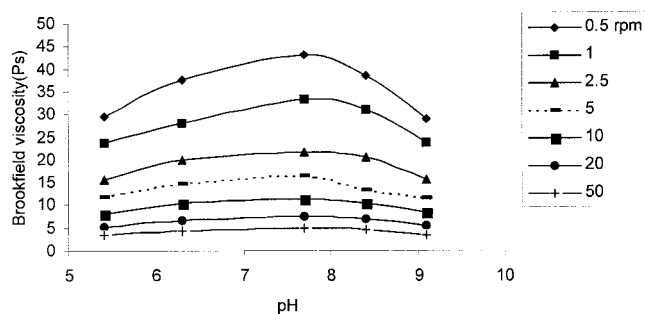
Besides these three factors, the reactivity ratios of comonomers may affect Brookfield viscosity. These copolymers give very high Brookfield viscosity on neutralization. The mechanism of viscosity development is the electrostatic repulsion between carboxylate anions, which leads to uncoiling of the polymer chains. Hence, the hydrodynamic volume increases, which results in an increase in viscosity. Thus, the viscosity will be greater if the carboxyl group-containing monomer (i.e., MAA) is distributed uniformly throughout the polymer chain. The distribution of MAA and EA blocks can be explained by the reactivity ratios¹² of MAA ($r_1 = 2.58$) and EA ($r_2 = 0.157$). In the earlier stage of the polymerization reaction, the highly reactive MAA radicals are preferentially incorporated into the growing polymer chain over EA radicals. In the later stage when MAA is consumed, the remaining EA will form blocks containing EA units only (Scheme 2). This EA tail end may contribute less to Brookfield viscosity and its length will be less if the MAA component in the feed is increased; thus there must be an

optimized ratio of MAA and EA at which uniform distribution of MAA occurs, and this composition will give maximum Brookfield viscosity on neutralization. In the current study, MAA : EA :: 48.7 : 5.1M ratio (P4) appears to be the optimal ratio for uncrosslinked polymers.

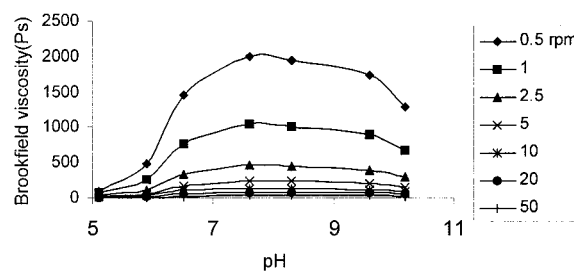
This can be further substantiated from ¹³C-NMR analysis. If we consider the sum of fractions of EME and MEM as the degree of uniform distribution of monomers in a polymer network, then P4 is more



Scheme 3 Anhydride formation reaction in MAA-EA copolymers.

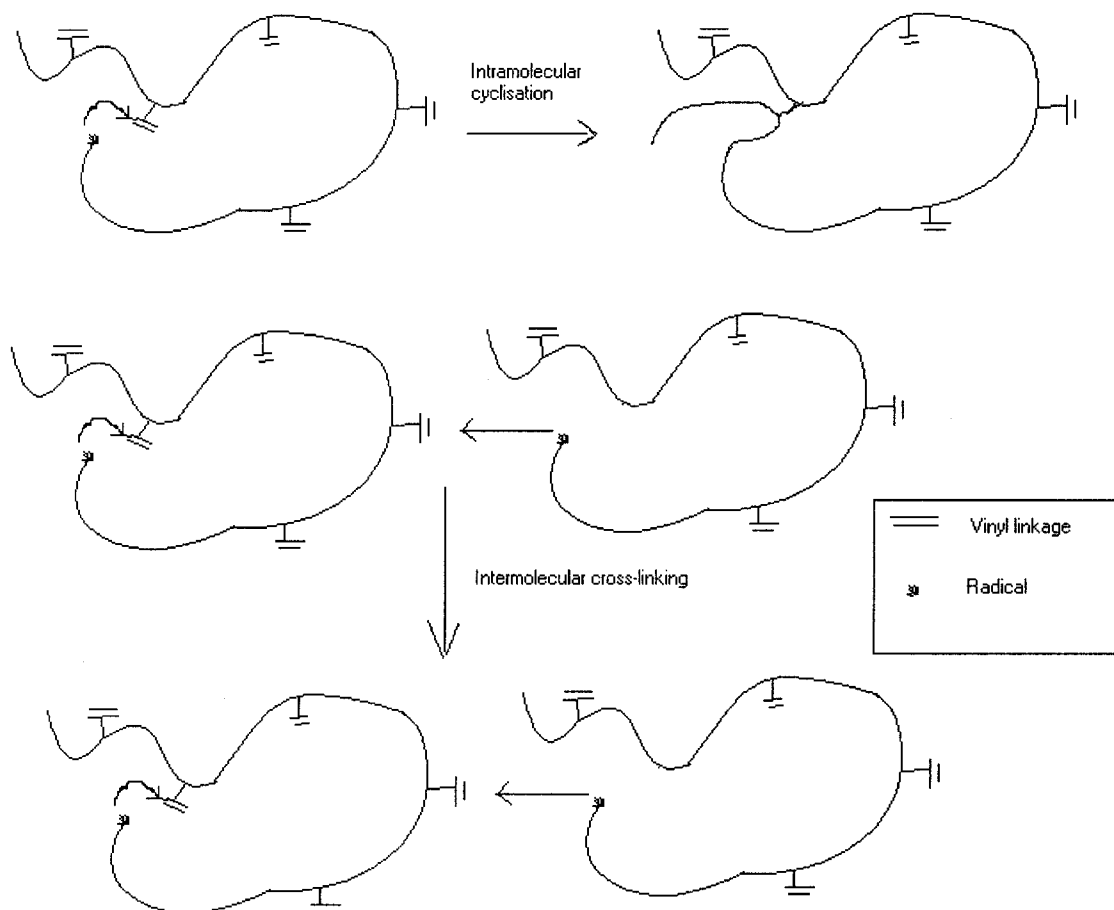


(a)



(b)

Figure 8 Effect of pH on Brookfield viscosity of MAA : EA : DAP copolymers at 2.8% solid contents at different spindle speeds (rpm): (a) P4, 48.7 : 51.3 : 0; (b) P11, 48.4 : 50.9 : 0.7.



Scheme 4 Intramolecular cyclization and intermolecular crosslinking reactions with DAP as crosslinking agent.

uniform than P1 and P7. Therefore, the polymer P4 resulted in higher Brookfield viscosity.

A significant increment in Brookfield viscosity was observed with the incorporation of DAP as the crosslinking agent. Brookfield viscosity increased from 730 cps (P4) to 25,200 cps (P5) by adding 0.7 mol % of DAP in the feed (Table II). It was also observed that Brookfield viscosity varies with the concentration of crosslinking agent (DAP). With an increase in DAP as crosslinking agent in the feed, the extent of intramolecular cyclization increases. Hence, the intermolecular crosslink formation decreases, which leads to low gel content and low Brookfield viscosity (Scheme 4). In the current study, the optimized concentration of DAP was about 0.7 mol % of total monomer concentration.

Effect of monomer feed process

P15, which has a copolymer composition similar to that of P11 (Table II) and almost the same gel content value (Table V), had more viscosity than that of P11. This indicates that with modification of monomer feed, MAA units are distributed more uniformly throughout the polymer network, which further improves the Brookfield viscosity.

In the modified feed process, ME1 was kept EA rich (55.8 mol %), whereas ME2 was kept MAA rich (53.3 mol %). The reaction was started with feeding of ME1. Because of the higher reactivity ratio of MAA ($r_1 = 2.58$) to that of EA ($r_2 = 0.157$), the concentration of MAA was depleted at a faster rate than that of EA. Hence, during the course of the polymerization reaction, the difference between MAA and EA concentrations increased. When ME2, the MAA-rich feed, was introduced to the reactor, this concentration difference was somewhat offset, thus allowing a more uniform distribution of MAA units throughout the polymer chain, and hence the Brookfield viscosity improved.

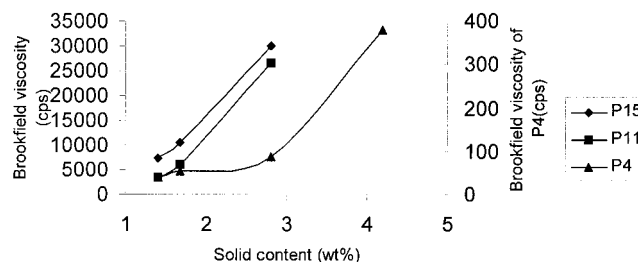


Figure 9 Effect of solid contents on Brookfield viscosity of P4, P11, and P15 MAA : EA : DAP copolymers.

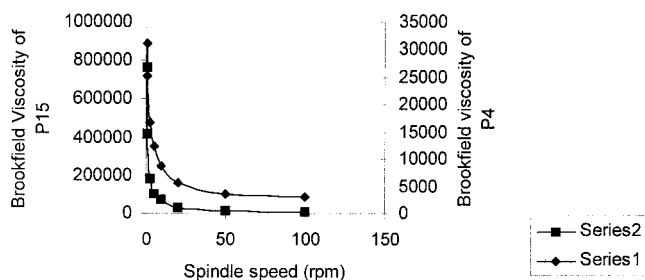


Figure 10 Effect of Brookfield viscosity with shear rate of MAA : EA : DAP copolymers: uncrosslinked P4, 48.3 : 51.7 : 0; crosslinked P15, 48.4 : 50.9 : 0.7.

Effect of polymer solid content

Brookfield viscosity increases with an increase in polymer solid content. According to Vollmert,²⁰ the polymer chains in a solution are completely enveloped by the solvent and there is a critical concentration at which no free solvent remains. Above this polymer concentration, chains are tightly packed, giving rise to a very high viscosity. In the present system, 1.5% solid content appears to be the critical concentration for all the crosslinked polymers. For uncrosslinked polymers this value appears to be at 2.8% solid content (Fig. 9). The Brookfield viscosity of P15 was higher at all solid content percentages, although P11 and P15 had the same copolymer composition. The reason is explained in the previous section.

Effect of shear rate

The effect of shear rate on Brookfield viscosity of four selected copolymers was studied in the range of 0.5–100 rpm (solid content 4.2% for P1 and P4 and 1.7% for P11 and P15) at pH 7.5–8.5. Moreover, all copolymers were found to be pseudoplastic in nature [Fig. 10(a,b)].

CONCLUSIONS

- The sequence distribution of MAA and EA units in the polymer chain is highly dependent on their reactivity ratios and relative concentrations.

- The rate and enthalpy of anhydride formation depend on the sequence distribution of MAA and EA units in the copolymer.
- Brookfield viscosity depends on the MAA concentration and its distribution in the polymer chain.
- With modification of the feed process, the microstructure of the copolymer with uniform distribution of MAA can be achieved, thus producing an increase in Brookfield viscosity.

References

1. Marie-France, L.; Spitz, R.; Christian, P.; Nisida, S. *J Macromol Sci Chem* 1983, A19, 881.
2. Vijayendran, B. R. *J Appl Polym Sci* 1979, 23, 893.
3. Egusa, S.; Makuuchi, K. *J Polym Sci Part A: Polym Chem* 1982, 20, 863.
4. Pichot, C.; Hamoudi, A.; Pham, Q. T.; Guyot, A. *Eur Polym J* 1978, 14, 116.
5. Sundardi, F.; Zubir, A. *J Macromol Sci Chem* 1985, A22, 1647.
6. Bajaj, P.; Goyal, M.; Chavan, R. B. *J Appl Polym Sci* 1994, 53, 1771.
7. Shoaf, G. L.; Poehlein, G. W. *J Appl Polym Sci* 1991, 42, 1213.
8. Amalvy, J. *J Appl Polym Sci* 1996, 59, 339.
9. Arzamendi, G.; Leiza, J. R.; Asua, J. M. *J Polym Sci Part A: Polym Chem* 1991, 29, 1549.
10. Arzamendi, G.; Asua, J. M. *Makromol Chem Macromol Symp* 1990, 35/36, 249.
11. Arzamendi, G.; Asua, J. M. *Ind Eng Chem Res* 1991, 30, 1343.
12. Fordey, D. B.; Drupe, J.; Toy, W. *Off Dig* 1959, 31, 84.
13. Fordey, D. B.; Drupe, J.; Toy, W. *Ind Eng Chem* 1959, 51, 11.
14. Verbrugge, C. J. *J Appl Polym Sci* 1970, 14, 897.
15. Verbrugge, C. J. *J Appl Polym Sci* 1970, 14, 911.
16. Muroi, S. *J Appl Polym Sci* 1966, 1, 713.
17. Muroi, S.; Hosoi, K.; Ishikawa, T. *J Appl Polym Sci* 1967, 11, 1963.
18. Jenkins, R. D.; Mark, L.; Basset, D. R. *Hydrophilic Polymers: Performance with Environmental Acceptance*; Glass, J. E., Ed.; ACS Symposium Series 248; American Chemical Society, Washington, DC, 1996, pp 425–447.
19. Ulbrich, K.; Ilavasky, M.; Dusek, K.; Kopecek, J. *Eur Polym J* 1977, 13, 579.
20. Vollmert, B. *Grundriss Der Makromolekularen Chemie*; Springer-Verlag: Berlin, 1962.
21. Grant, D. H.; Grassie, N. *Polymer* 1960, 1, 125.
22. Elias, H. G. *Macromolecules. 1: Structure and Properties*; Plenum Press: New York/London, 1977; p. 366.
23. Bajaj, P.; Goyal, M.; Chavan, R. B. *J Appl Polym Sci* 1994, 51, 423.