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Copolymerization of 4-Maleimidobenzoic Acid with Alkyl Acrylates. Kinetic Penultimate Unit Effect and Copolymer Characteristics[†]

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ABSTRACT: 4-Maleimidobenzoic acid (MBA) was copolymerized with methyl methacrylate (MMA) and *n*-butyl acrylate (BuA) to derive pendant carboxylic acid-bearing acrylic polymers. The copolymerization kinetics revealed the existence of a marked penultimate unit effect in both cases with respect to the radicals terminated with the acrylate monomer. The effect was so pronounced in the case of MMA that the MMA-terminated radicals showed a nearly 2-fold preference to add to its own monomer when neighbored by an MBA group than when neighbored by its own molecule. The penultimate reactivity ratios were determined by both linear and nonlinear methods. The values are respectively $r_1 = 0.01$, $r_1' = 0.04$, $r_2 = 1.19$, $r_2' = 2.09$ for MBA-MMA and for MBA-BuA; the corresponding values are $r_1 = 0.41$, $r_1' = 0.43$ and $r_2 = 1.00$, $r_2' = 1.22$. Although in the case of BuA, both the terminal and penultimate models could explain the composition curves, for MMA the latter model was the only choice. The variations in the apparent copolymerization rate and copolymer molecular weights with the feed composition were in agreement with the observed trends in reactivity ratios and the models proposed. The copolymers exhibited high T_gs and superior thermal stabilities vis-à-vis the acrylate homopolymers.

Introduction

Pendant carboxylic acid functional polymers are very much desired in several applications wherein the special features of the carboxylic acid functions can be taken advantage of. Such prepolymers can be conveniently converted to other desired pendant functional polymers through appropriate modification of the carboxylic acid groups by esterification, amidification, etc. The prepolymers themselves can serve as useful precursors such as curing agents for epoxies through the carboxy-epoxy reaction and cross-linking agents for polyesters, polyamides, imides, etc. In our intention to derive pendant photofunctional acrylic polymers, we had a special interest in these types of prepolymers. The carboxyl groups were envisaged as being transformed to the required photosensitive groups by suitable chemical modification. Photosensitive polymers are of great importance in imaging technology in the domain of printed circuit boards and integrated circuits. The acrylate polymers stand a good chance of being utilized as photoresists except for their inherent drawbacks, such as poor thermal stability, low glass transition temperature, and poor resistance to solvents.[1] Our goal was to derive photosensitive acrylate-based polymers for use as photoresists which avoid the usual problems. The pendant carboxylic acid groups were to be introduced through copolymerization of the acrylic monomers with a suitable functional comonomer such as maleimidobenzoic acid (MBA) since the functional groups will be spaced at regular intervals and the resultant copolymer will be thermally stable.[2,3]

This paper deals with the syntheses of pendant COOH-containing polymers through copolymerization of MBA with typical acrylate monomers, viz., MMA and BuA. The prediction of the distribution of the COOH function in the polymer, introduced through copolymerization, necessitates a knowledge of the reactivity ratios of the comonomers. Detailed kinetic studies related to the copolymerization are described based on different methods and two models. The molecular weights and physical and thermal properties of the copolymers are discussed.

Experimental Part

Materials. *p*-Aminobenzoic acid (Aldrich) was used as received. Maleic anhydride was recrystallized from acetic anhydride. Methyl methacrylate (MMA), *n*-butyl acrylate (BuA), and dimethylformamide (DMF) were purified by vacuum distillation. Tetrahydrofuran (THF), acetic anhydride, etc., were purified by distillation.

Instruments. Molecular weights were determined by a Waters GPC Model Delta Prep. 3000, using THF as eluent. Polystyrene standards were used for calibration. Thermogravimetric analyses were performed on a Mettler 3000 thermobalance under a N_2 atmosphere, at a heating rate of 10 °C/min. DSC experiments were run on a Mettler TA 3000 comprised of a TC-10A TA processor coupled with a DSC-20 standard.

Synthesis of 4-Maleimidobenzoic acid (MBA). *p*-Aminobenzoic acid (0.1 mol) was dissolved in 200 mL of dry THF. Maleic anhydride (0.105 mol) dissolved in 50 mL of THF was added dropwise over a period of 1 h at room temperature under stirring. The yellow precipitate was continually stirred for 3 h. The bath temperature was raised to 60 °C, and then anhydrous sodium acetate (2 g) was added followed by the addition of acetic anhydride (0.12 mol) dropwise. A brown solution resulted, which was stirred for 4 h at this temperature. MBA was recovered by precipitation into ice-cold water. It was filtered and dried at 50 °C under vacuum. Recrystallization was done from an ethanol-THF mixture (10:1). Yield: 43%.

Characterizations. Anal. Calcd: C, 60.8; H, 3.2; N, 6.5. Obsd: C, 60.5; H, 3.8; N, 6.6.

The acid value is as follows. Calcd: 258 mg of KOH/g. Observed: 256 mg of KOH/g.

Polymerizations. All polymerizations were performed in glass ampules sealed under vacuum with stopcocks. The monomer and initiator concentrations are given in Table I. In a typical experiment, MBA (2.0 g) and BuA (3 mL) along with AIBN (5 mg, 0.0305 mmol) were dissolved in 5 mL of DMF in glass ampules and the tubes were sealed after evacuation. The tubes were polymerized in a thermostat at 70 °C. The polymer was isolated

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[†] This paper is dedicated to the fond memory of Mr. K. Sajush, M. Sc. project trainee from M. G. University, Kerala, who was partly associated with this work and is since deceased on July 8, 1992.

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Table I
Copolymerization Conditions and Copolymer Characteristics

system	total monomer conc (mol/L)	[AIBN] × 10^3 (mol/L)	mole fraction of MBA in the feed (F_1)	convn (%)	polymn time (min)	convn rate (mol %/min)	mole fraction of MBA in the copolym (f_1) ex: acid value	ex: N %	$M_n \times 10^{-4}$	I
MBA–MMA	4.511	6.165	0.056	13.25	45	0.30	0.043	0.045	10.33	1.53
	4.321	6.266	0.110	10.96	30	0.37	0.088	0.104	10.90	1.34
	4.134	6.351	0.175	11.51	30	0.40	0.123	0.132	10.40	1.30
	3.964	6.418	0.248	*a*	30		0.167	0.193	9.57	1.35
	3.724	6.503	0.330	*a*	30		0.208	0.214	9.88	1.30
	3.523	6.557	0.429	9.51	25	0.38	0.257	0.261		
MBA–BuA	3.424	6.184	0.070	38.0	16	2.65	0.064	0.097		
	3.348	6.260	0.145	19.1	17	1.13	0.132	0.152	5.72	1.67
	3.267	6.348	0.215	9.8	23	0.44	0.199	0.222	5.30	1.47
	3.179	6.422	0.309	18.7	181	0.09	0.273	0.298	4.03	2.0
	3.093	6.500	0.402	26.7	457	0.06	0.324	0.368	2.60	1.95
	3.005	6.578	0.502	15.4	757	0.02	0.404	0.443	2.22	1.93

[a] Loss during recuperation.

by precipitation to methanol containing 5–10 vol % water. It was dissolved in THF and reprecipitated the same way. The collected polymer was dried at 60–70 °C under vacuum. The same procedure was followed in all cases. For reliable composition data the conversions were kept below 20%.

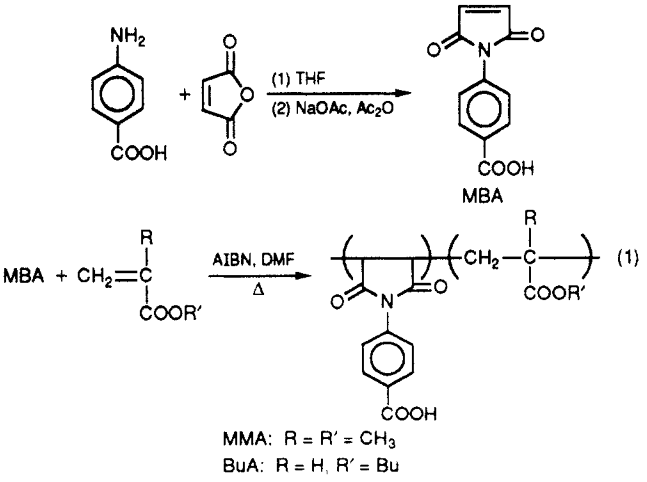
Homopolymerizations of MBA, MMA, and BuA. MBA was homopolymerized in DMF (2 g in 5 mL) using AIBN (10 mg) as initiator at 80 °C for 16 h. Precipitation was done in methanol containing 10 vol % water. Yield: 100 mg (5%).

MMA and BuA were homopolymerized under the same conditions as the copolymerization.

Determination of Copolymer Compositions. Copolymer compositions were determined from the N content of the copolymers obtained by elemental analyses. Compositions were also determined from acid values as measured by titration of the copolymers in DMSO against standard alcoholic KOH using cresol red as the indicator.

Results and Discussion

Pendant carboxylic acid-bearing acrylic polymers of varying compositions were synthesized by the radical copolymerization of MBA with MMA or BuA. MBA was prepared and copolymerized according to the following reaction scheme.



Several studies have been devoted to the radical copolymerization of *N*-phenylmaleimides and their derivatives with various comonomers.[4-10] Most of them are confined to the determination of reactivity ratios by the terminal model. The syntheses of copolymers of MBA with acrylamide have recently been reported.[11] However, no details of the kinetics have been given. With the goal to determine the reactivity ratios of the pairs MBA (M_1)–MMA (M_2) and MBA (M_1)–BuA (M_2), several copolymers of these systems from different feed compositions were prepared and analyzed for their composition. The details are compiled in Table I.

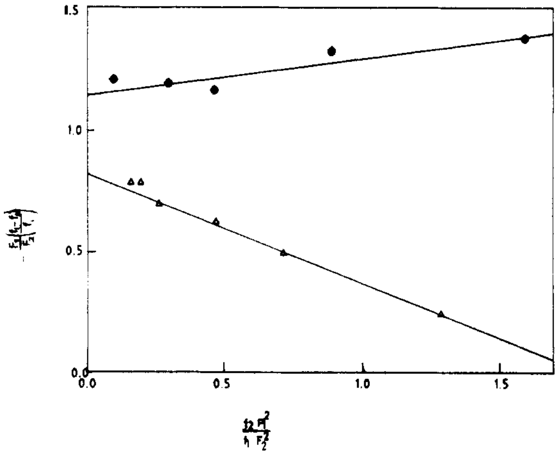


Figure 1. Finemann–Ross plot for the determination of reactivity ratios (elemental analysis): (●) MBA–MMA; (▵) MBA–BuA.

The versatile equation relating the feed and copolymer composition is given as

$$f_1 = \frac{r_1F_1^2 + F_1F_2}{r_1F_1^2 + 2F_1F_2 + r_2F_2^2} \tag{2}$$

where the f and F stand for the mole fractions of the monomer in the polymer and in the feed, respectively, r_1 and r_2 being the respective reactivity ratios.

The above equation has been conveniently transformed to a linear form by Finemann and (FR) Ross as follows:[12]

$$\frac{F_1(f_1 - f_2)}{F_2f_1} = \frac{f_2F_1^2r_1}{f_1F_2^2} - r_2 \tag{3}$$

A plot of the left-hand side versus $f_2F_1^2/f_1F_2^2$ gives r_1 and r_2 as the slope and the intercept, respectively. A typical plot is seen in Figure 1. The Kelen–Tüdo's (KT) method uses a modified form of the Mayo–Lewis (ML) equation[13]

$$\eta = r_1\xi - r_2/\alpha \tag{4}$$

where η and ξ are functions of f and F and α is an arbitrary parameter. We used both the FR and the KT methods for the analyses of the data. A typical KT plot is shown in Figure 2. The reactivity ratios so obtained are given in Table II. Separate reactivity ratios have been calculated

Table II
Terminal Model Reactivity Ratios

	Kelen–Tüdos				Finemann–Ross			
	acid value		elem anal.		acid value		elem anal.	
system	r_1	r_2	r_1	r_2	r_1	r_2	r_1	r_2
MBA–MMA	−0.322	1.105	−0.112	1.120	−0.138	1.221	−0.160	1.117
MBA–BuA	0.396	1.025	0.448	0.839	0.340	1.000	0.447	0.823

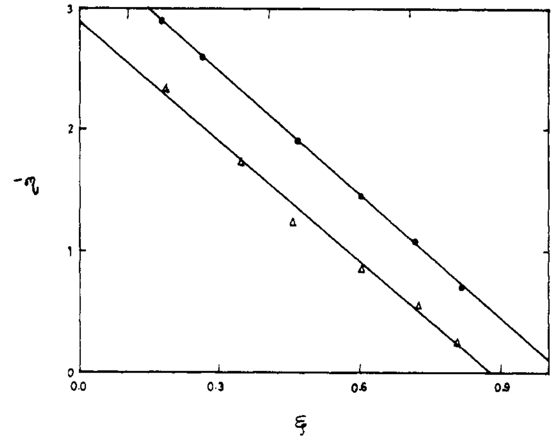


Figure 2. Kelen–Tüdos plot based on acid values: (●) MBA–MMA, $\alpha = 0.336$; (△) MBA–BuA, $\alpha = 0.353$.

for the different analytical techniques used. The values vary slightly depending on the method of composition determination and of data treatment. The trend is however not altered. A look at the reactivity ratios for the system MBA–MMA reveals an apparent negative r_1 value. This is absurd since the minimum value theoretically possible for the reactivity ratio is zero. Both FR and KT methods gave negative values with excellent fits for the linear plots (Figures 1 and 2). Repetition of the experiment for this system gave similar results, ruling out an experimental artifact. This points to the existence of the penultimate effect (second-order Markov's effect) in the polymerization system and that the above terminal model is inadequate to describe the copolymerization behavior. Negative reactivity ratios for other maleimides have already been reported in the literature without a critical analysis of the results.[8,9]

Penultimate Model. The reactivity of a polymer radical with a given monomer can be affected by its penultimate group, especially when the group is highly polar or bulky. Such effects have been observed in the copolymerization of styrene–acrylonitrile,[14] styrene–acrylate,[15] and several other pairs. Although the polymer composition of many systems might appear to be explained by the terminal model, an analysis of their sequence distribution or molecular weight variations reveals the inadequacies of such a model. An excellent fit in the KT or FR plot is no indication of the validity of the terminal model as seen here. The choice of the correct model (terminal, penultimate, or complex participation) is arrived at usually by the sequence anlaysis of the copolymers or from the polymerization parameters.[15–18]

Since the present polymerization system contains a bulky, electron-withdrawing monomer as one of the components (MBA), the possibility for a penultimate group effect especially for the radical terminated in monomer 2 was considered. The complex participation was not considered since the polymerization was done in solution. In the penultimate model each pair is associated with four reactivity ratios defined as $r_1 = k_{111}/k_{112}$, $r_1' = k_{211}/k_{212}$, $r_2 = k_{222}/k_{221}$, and $r_2' = k_{122}/k_{121}$. (e.g., k_{hij} = rate constant for the addition of a polymer radical terminated in monomer i whose penultimate group is monomer h to monomer j.)

Table III
Penultimate Model Reactivity Ratios

system	method of polymer analysis	method of data treatment	reactivity ratios r_1	r_1'	r_2	r_2'
MBA–MMA	acid value	linear	0	0	1.19	2.09
		nonlinear	0.01	0.04	1.19	2.09
	elem anal.	linear	0	0	1.13	1.83
		nonlinear	0.03	0.08	1.11	2.10
MBA–BuA	acid value	linear	0.36	0.36	0.98	1.09
		nonlinear	0.41	0.43	1.00	1.22
	elem anal.	linear	0.44	0.44	0.82	1.04
		nonlinear	0.43	0.43	0.60	1.45

In the terminal model it is assumed that the radical activity is unaffected by the penultimate group; i.e., $r_1 = r_1'$ and $r_2 = r_2'$.

The equation relating the copolymer compositions to the feed composition when a kinetic penultimate effect is operative is given as

$$x = \frac{f_1}{f_2} = \frac{1 + \dfrac{r_1'X(r_1X + 1)}{(r_1'X + 1)}}{1 + \dfrac{r_2'(r_2 + X)}{X(r_2' + X)}} \tag{5}$$

$$X = F_1/F_2$$

The various penultimate reactivity ratios could be resolved based on eq 5 using a nonlinear method with the help of a computer program.[19] The values are tabulated in Table III. Prior to the computer analysis, the values of r_2 and r_2' for the two systems could also be determined by a graphical method based on the original method of Fenn and Barson,[20] which was modified by us. In this method it is assumed that the penultimate group effect is felt only with respect to the radicals terminated in one particular monomer. In our case it is correct to assume that the reactivity of the MBA-terminated radical is independent of its preceding moiety, because of their bulky size and strong electron-withdrawing nature. In other words, $r_1 = r_1'$. (The r_1 values obtained later by the nonlinear method confirmed this assumption to be correct.) The r_1 values are calculated from the experiments conducted at $[M_1] \ll [M_2]$. In that case a value of r_1 independent of the penultimate effect is obtained by conventional methods since there is very little chance for existence of radicals of the type M_1M_2. The r_1 value so calculated by the FR method for MMA is 0 and that for BuA is 0.36.

The Fenn–Barson equation is given as[20]

$$r_2 = \frac{Xk}{x} + \frac{X^2k}{xr_2'} - X \tag{6}$$

where $k = 1 + r_1X - x$. In their original publications, they have recommended a hyperbolic plot using the above equation for different values of r_2 and r_2', whose intersection would give the true values of r_2 and r_2'. We,

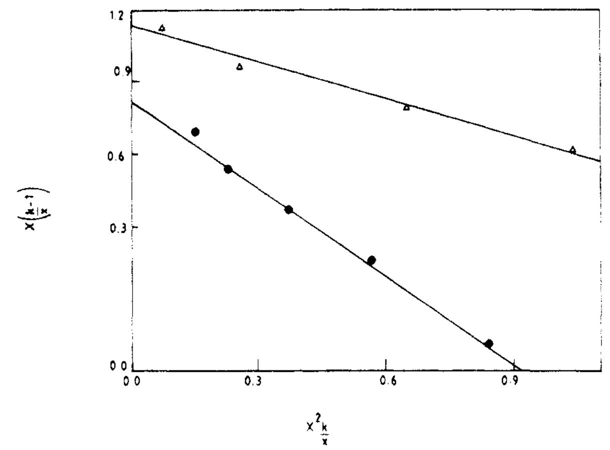


Figure 3. Determination of reactivity ratios by a modified. Fenn–Barson method (elemental analysis); (Δ) MBA–MMA; (●) MBA–BuA.

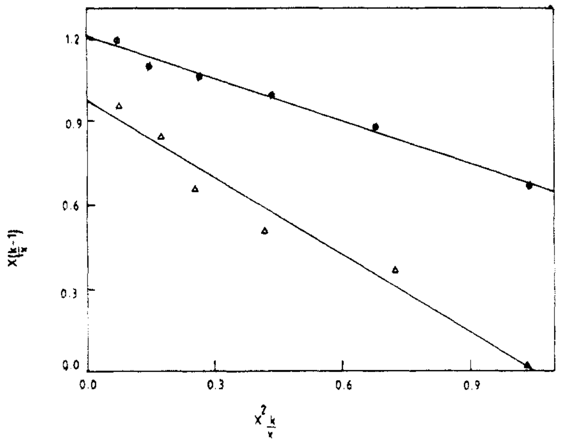


Figure 4. Determination of penultimate reactivity ratios based on acid values by a linear Fenn–Barson method, (Δ) MBA–MMA; (Φ) MBA–BuA.

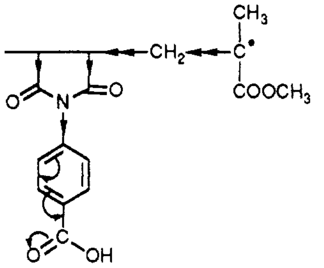
however, noticed that the same equation can be linearized by appropriate restructuring of the equation assuming the value of r_1, as follows.

$$X[k/x - 1] = \frac{-X^2k}{xr_2'} + r_2 \qquad (6a)$$

A plot of the left-hand side versus X^2k/x gives the intercept as r_2 and the slope as $-1/r_2'$. The linear plots for the two cases are shown in Figures 3 and 4, and it can be seen that the fit is excellent for MMA and reasonably good for BuA. The values obtained from the computer method match very well with those from this method for MMA–MBA. A slight difference is seen for BuA–MBA.

The different reactivity ratios based on both the terminal (Table II) and penultimate models (Table III) were calculated independently depending upon the method of copolymer composition analysis. The values from N estimation and acid values are complied separately for comparison. The values differ with the estimation method. Since the acid value determination is more reliable, the results based on it are considered as more correct. The reactivity ratios show that both the systems are prone to exhibit the penultimate group effect for the radical terminated with the acrylate, to different extents.

As a whole for the pair MBA–MMA, the former has a markedly reduced reactivity particularly at high MBA concentration. MBA-terminated radicals add exclusively to the MMA monomer. This is a consequence of the fact that MBA is bulky and strongly electron-withdrawing in nature. Therefore, its preference goes exclusively to the electron-rich, sterically nonhindered MMA monomer. The possibility for the existence of a donor–acceptor charge transfer complex between the MBA radical and MMA monomer in the transition state further augments the preference. The MMA-terminated radical prefers to add to its own monomer, the preference doubling when its penultimate group is the imide. However, the MMA–MMA radical has considerable reactivity toward MBA, since the former is an electron-rich radical whose addition to the electron-deficient MBA is facilitated by the possible charge-transfer complexation in the transition state. When the MMA radical is neighbored by MBA, the latter renders the former electron-deficient because of its strong electronegativity, thereby increasing the radical's preference for the electron-rich MMA.



Additionally, the bulky MBA group can sterically hinder the approach of an MBA molecule to its neighboring MMA radical.

As far as the BuA–MBA system is concerned, the pair behaves like an ideal random copolymerization system with $r_1r_2 < 1$ (terminal). The r_1 value is far higher than zero, showing that MBA is capable of homopolymerization. The preference of the MBA-terminated radical for BuA is only 2.5 times that for its own monomer, and the BuA radical has practically no preference for any monomer. This is because both monomers are equally electron-deficient like their respective radicals. No donor–acceptor complexation is likely here. The reduced preference of the MBA radical for MBA arises from steric hindrance and electron deficiency of the latter. The BuA radical is too reactive to differentiate between the electron-deficient MBA or BuA; i.e., it adds onto both at equal rates. The penultimate model reactivity ratios (acid value based) show that, in this system, the penultimate effect is not as pronounced as in the case of MBA–MMA, r_1' and r_2' differing only slightly from their respective r_1 and r_2 values which are in turn close to the terminal-mode values. The slightly enhanced tendency for homopolymerization of a BuA radical with a penultimate MBA group arises mostly from the enhanced electron-withdrawing nature of the imide. Since BuA is relatively more electron-rich than MBA, the above electron-deficient BuA radical (thanks to its neighbor) prefers its own monomer. The contribution of the steric factor is not significant in both cases, since, if that were the case, a substantial penultimate group effect would have been felt in the case of MBA–BuA as well.

Copolymer Composition Curves. The feed–copolymer composition curves are shown in Figures 5 and 6for the two systems. The theoretical curves based on both the terminal (KT) and the penultimate models are shown for both systems along with the experimental points. In the case of MMA, for the terminal model r_1 was taken as zero since a negative value is an impossibility. It is seen that, in this case, the experimental points conform exclusively to the penultimate model. For BuA, the composition curve is the same for both models and the experimental points conform equally well to both.

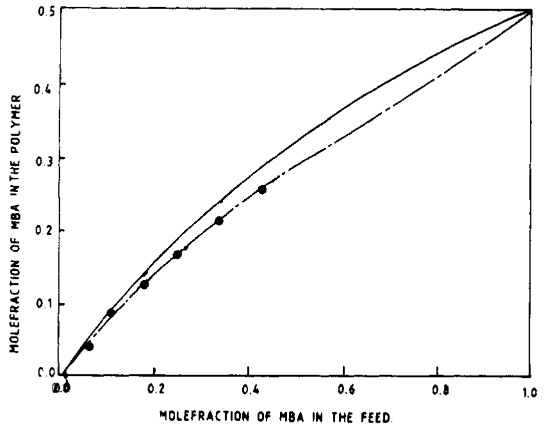


Figure 5. Variation of the copolymer composition with the feed composition for a MBA–MMA system: (—) terminal model; (- · -) penultimate model; (●) experimental points.

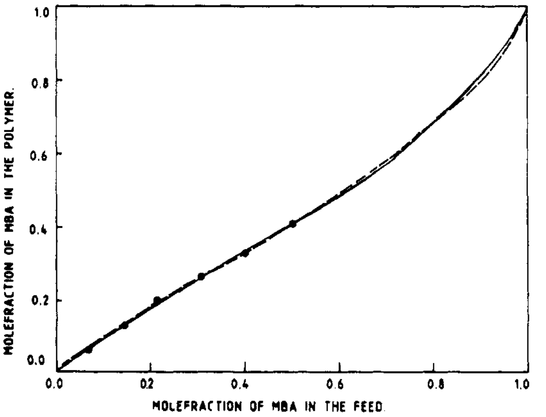


Figure 6. Variation of copolymer composition with feed composition for MBA–BuA: (—) terminal model; (- - -) penultimate model; (●) experimental points.

Statistical Prediction of Microstructure. The copolymerization behavior for MMA–MBA predicts that the copolymer cannot accommodate more than 50% of MBA and that, in the chain, MBA sequences will be absent. At lower concentrations of MBA one can expect long sequences of MMA bridged by MBA units. Since MBA is the carrier for the COOH functions, the COOH groups will be distributed at intervals in the chain. The probabilities of finding the sequences of the type MBA-(MMA)$_n$MBA are given as

$$N_{(\mathrm{A})n} = P_{\mathrm{BAA}}P_{\mathrm{AAA}}^{\;n-2}(1 - P_{\mathrm{BAA}})$$

where A = MMA and B = MBA.

The various P's represent the probabilities of the concerned triads calculated from the penultimate reactivity ratios.[21] $N_{(\mathrm{A})n}$ is the number fraction of n sequences of A. The weighted probabilities of such sequences are

$$\frac{N_{(\mathrm{A})n}n}{\sum N_{(\mathrm{A})n}n} = \frac{N_{(\mathrm{A})n}n}{W_{\mathrm{A}}}$$

where W_{A} = weighted composition of all such A's given as

$$W_{\mathrm{A}} = 1 + P_{\mathrm{BAA}}/P_{\mathrm{AAB}}$$

It is seen from Figure 7 that, for a copolymer containing about 4.5% MBA, large sequences of MMA with length in the range of 15–40 units can be found, the maximum occurring at 25. As the composition rises, the sequence length of maximum population shifts to the lower side and the distribution becomes narrower. However, copolymers of BuA are completely random with the possibility for all monomer combinations and sequences.

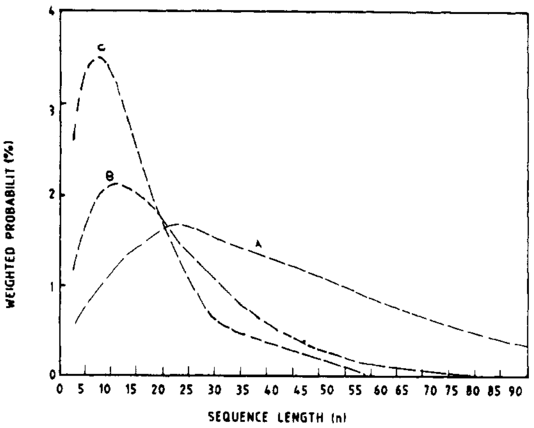


Figure 7. Distribution of MMA sequences in a MBA–MMA copolymer with MBA of (A) 4.3, (B) 8.1, and (C) 11.6 mol %.

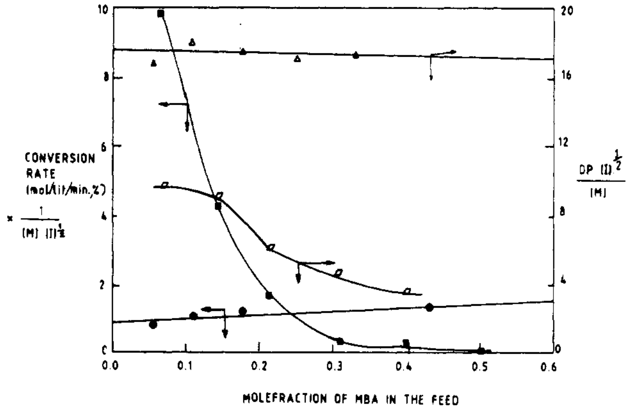


Figure 8. Variation of the apparent polymerization rate and polymer molecular weights with feed composition; (●) conversion rate for MBA–MMA; (△) molecular weight for MBA–MMA; (■) conversion rate for MBA–BuA; (◊) molecular weight for MBA–BuA.

Apparent Copolymerization Rate. From the polymer yield and the time of polymerization, it was possible to get the trend in the rate of polymerization, although the values cannot be absolute, as they have been determined from a one-point experiment. The apparent copolymerization rate as a function of the feed composition is shown in Figure 8. Since the total monomer concentration varies progressively down the series (Table I), a true representation is given by the factor R_{p}, (conversion rate)/$[\mathrm{I}]^{1/2}[\mathrm{M}]$. It is seen that, in the case of MMA, the polymerization rate remains more or less constant as the MBA loading increases, whereas, in the case of BuA, there is an abrupt fall in the rate. Interestingly, the variation in the copolymerization rate is strictly in conformation with the observed reactivity ratios. As for MMA, if we consider the terminal model, the cross propagation rate k_{12} is far higher than k_{11} and k_{21} is more or less the same as k_{22}. The result is that an increase in the concentration of MBA enhances the rate of cross propagation of the MBA radical considerably, resulting in an overall increase in the rate of propagation. Although the penultimate effect is operative at higher concentration, the decrease in the cross propagation rate for the MMA radical as a result of it is only by a factor of 2 and that also only for the fraction of MMA radicals neighbored by MBA molecule. The constancy in the rate must be a consequence of the fact that cross termination is also as equally favored as the cross propagation as the feed is enriched in MBA.

Regarding BuA, the r_1 value shows that cross propagation of the MBA radical is favored only by a factor of

2 vis-à-vis its homopropagation which is by itself very slow (as seen from its δ value). Cross propagation of the BuA radical is at the same rate as its homopropagation. The result is that the significance of k_{11} in the rate expression increases as the feed becomes richer in MBA; i.e., the overall cross propagation rate falls. The cross termination rate naturally increases with an increase in the concentration of the comonomer. The two effects collectively causes a sharp decrease in the polymerization rate when MBA is present in increasing quantities.

Copolymer Molecular Weights. The variation of copolymer molecular weight with feed composition is shown in Figure 8. For obtaining a nearly true trend, the factor $\mathrm{DP}[\mathrm{I}]^{1/2}/[\mathrm{M}]$ has been considered, where [M] is the total monomer concentration. It is seen that the trend is similar to the one observed for the conversion rate, as would normally be anticipated for similar reasons. The variation of the copolymer molecular weight with feed composition has been studied in some cases, but the studies have been rare when the penultimate unit effect is present.

In conventional copolymerization, when the termination is chemically controlled, the copolymer molecular weight in the terminal model is given as[22]

$$\mathrm{DP}_0 = \frac{(r_1M_1^{\,2} + 2M_1M_2 + r_2M_2^{\,2})}{(r_1^{\,2}M_1^{\,2}\delta_1^{\,2} + 2\Phi r_1r_2M_1M_2 + r_2^{\,2}M_2^{\,2}\delta_2^{\,2})^{1/2}R_i^{\,1/2}} \tag{7}$$

where Φ is the Wallings cross termination factor

$$\delta_1 = \frac{2k_{\mathrm{t}11}^{\,1/2}}{k_{\mathrm{p}11}^{\,2}} \qquad \delta_2 = \frac{2k_{\mathrm{t}22}^{\,1/2}}{k_{\mathrm{p}22}^{\,2}}$$

$$\Phi = \frac{k_{\mathrm{t}12}}{(k_{\mathrm{t}11}k_{\mathrm{t}22})^{1/2}}$$

In the case of BuA, the above equation could be used to describe the copolymer molecular weight since the reaction is not much subjected to the penultimate effect and that it is done in solution where termination may not be diffusion controlled. When chain transfer to the solvent is possible, eq 7 has to be modified as

$$\frac{1}{\mathrm{DP}} = \frac{1}{\mathrm{DP}_0} + \frac{f_1C_{\mathrm{s}1}[\mathrm{S}]}{M_1 + M_2/r_1} + \frac{f_2C_{\mathrm{s}2}[\mathrm{S}]}{M_2 + M_1/r_2} \tag{8}$$

$C_{\mathrm{s}1}$ and $C_{\mathrm{s}2}$ are the chain-transfer constants of the radicals 1 and 2 to the solvent, S. Simplifying

$$1/\mathrm{DP} = 1/\mathrm{DP}_0 + 1/\Delta \tag{8a}$$

where Δ representing the chain-transfer term. I.e.

$$\mathrm{DP}_0 = \frac{1}{\{1/\mathrm{DP} - 1/\Delta\}} \tag{9}$$

DP_0 is the corrected degree of polymerization after accounting for the chain transfer, and DP is the observed one. Equation 7 was used to describe the molecular weight variation with feed composition. However, prediction of the copolymer molecular weight warrants determination of Φ and δ_1. In some cases it is reported that Φ is composition-dependent. We found that the above eq 7 can be transformed to a linear form as

$$\frac{(4K^2 - L)}{\mathrm{DP}_0^{\,2}R_i}\,\frac{1}{M_1^{\,2}} = \frac{J}{M_1^{\,2}\Phi\delta_1} + r_1^{\,2}\delta_1^{\,2} \tag{10}$$

where

$$K = r_1M_1^{\,2} + 2M_1M_2 + r_2M_2^{\,2}$$

$$L = r_2^{\,2}M_2^{\,2}\delta_2^{\,2}$$

$$J = r_1r_2M_1M_2$$

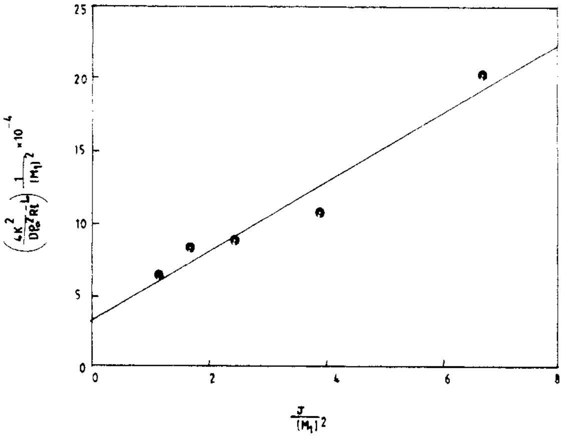


Figure 9. Determination of Φ and δ for MBA–BuA according to eq 10.

δ_2 is known in the literature (=1.02). $C_{\mathrm{s}1}$ and $C_{\mathrm{s}2}$ were taken as 50×10^{-4} and 0.1×10^{-4}, respectively. A plot of the left-hand side of eq 10 versus $J/M_1^{\,2}$ is shown in Figure 9. A comparatively good linear fit of the experimental points shows that ϕ is relatively insensitive to composition. δ_1 and ϕ were calculated from the slope and intercept as

$$\delta_1 = 1.375 \times 10^3\ \mathrm{L}^{-1/2}\cdot\mathrm{mol}^{1/2}\cdot\mathrm{s}^{1/2}$$

$$\Phi = 17.5$$

The unusually high value of δ_1 for MBA in contrast to that of the acrylates ($\delta \approx 1$) points toward the sluggishness in the self-propagation of MBA. MBA undergoes random polymerization with BuA, and as the MBA concentration is enhanced, its δ term contributes significantly to the polymerization kinetics with a consequent fall in both R_{p} and molecular weight. The high value of Φ indicates a highly favored cross termination reaction.

In the case of MMA, the homopropagation of MBA does not practically arise in the polymerization rate expression since $r_1 = 0$. In this case, based on a terminal model the relationship between DP and the feed composition can be reduced to the form

$$\mathrm{DP}_0 = \frac{2M_1}{R_i^{\,1/2}} + \frac{r_2M_2}{r_2\delta_2} \tag{11}$$

On the basis of the penultimate model, this equation is modified as

$$\mathrm{DP}_0 = \frac{2M_1}{R_i^{\,1/2}} + \frac{\bar{r}_2M_2}{\bar{r}_2\delta_2} \tag{12}$$

where

$$\bar{r}_2 = \frac{r'_2(M_2r_2 + M_1)}{(M_2r'_2 + M_1)}$$

assuming that the penultimate effect does not affect the termination rates. DP_0 is the corrected DP as per eq 9.

The calculated variations of the polymer molecular weight (DP) with feed composition for both models are shown in Figure 10. It is seen that the experimental points conform better to the penultimate model than to the

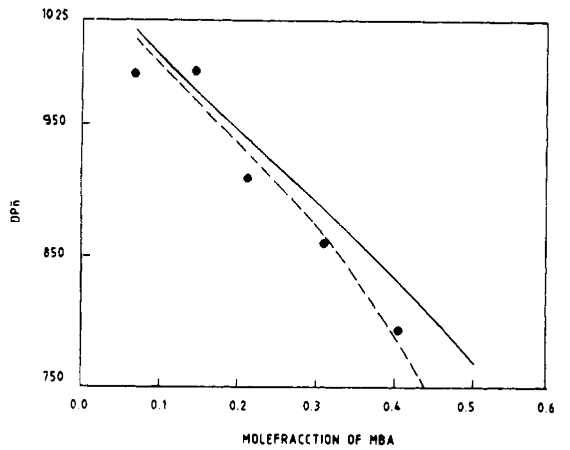


Figure 10. Variation of the copolymer molecular weight with feed composition for MBA–MMA; (—) theoretical molecular weight according to the terminal model; (- - -) molecular weight according to the penultimate model; (O) experimental points.

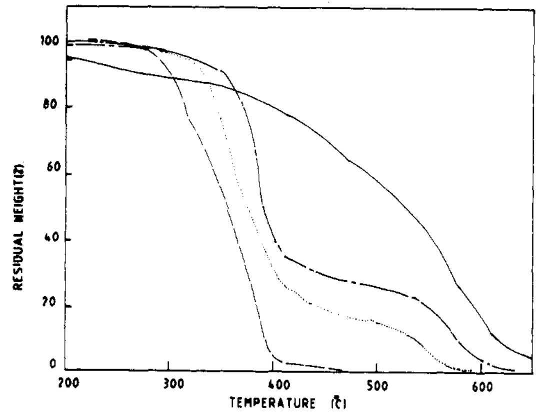


Figure 11. TGA (N_2) of (- - -) PPMA, (···) a MBA–MMA copolymer with a MBA content of ~20 mol %, (- · -) a MBA–MMA copolymer with a MBA content of 31 mol %, and (—) PMBA. Heating rate 10 °C/min.

terminal one especially at high MBA loading. The deviation of the experimental values from the calculated one is accommadable within the experimental limits.

For precise calculation of the {M_1} and {M_2}, the partial molal volume of MBA in DMF and densities of solutions of BuA (or MMA) in DMF were calculated.

Thermal Characteristics. The copolymers were subjected to DSC analyses. In most of the cases, the glass transitions could not be clearly seen in the thermogram. Wherever they were visible it was seen that the T_gs were enhanced considerably by the incorporation of a small amount of MBA. Thus PBuA, incorporating about 20 mol % MBA showed at T_g of 165 °C, while PMMA containing 10 mol % MBA showed a glass transition around 210 °C. Since the polymers bear COOH groups, association of polymer chains through them may be leading to the inconsistancies and probably also to the very high T_gs observed. Similar observations have been made for other COOH-bearing polymers.[22]

The copolymers were evaluated for their thermal stability by thermogravimetric analyses. The thermograms for various copolymers are shown in Figures 11 and 12. It is seen that incorporation of MBA enhances the initial decomposition temperature of the polymers by a factor of 20–30 °C vis-à-vis the acrylate homopolymers. Improvement in thermal stability is observed at high temperature also, in the sense that the rate of decomposition is slowed down. Poly(MBA) has a significantly higher thermal stability.

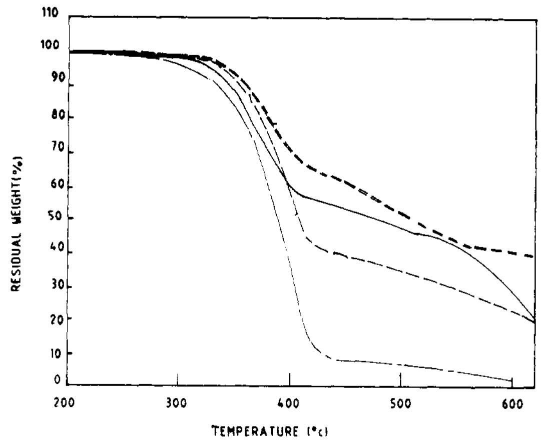


Figure 12. TGA (N_2) of (- · -) PBuA, (- - -) a MBA–BuA copolymer with a MBA content of 27 mol %, (—) a MBA–BuA copolymer with a MBA content of 40 mol %, (= = =) a MBA–BuA copolymer having a MBA content of 60 mol %. Heating rate 10 °C/min.

Conclusion

Copolymerization of MBA with MMA or BuA is associated with a marked penultimate group effect especially for the radicals terminated in the acrylates. The effect is more pronounced in MMA than in BuA for electronic and steric reasons. Studies show that MBA is an ideal vehicle for the cross-linkable functional groups for its copolymers with MMA.

In fact a good fit of experimental points to the various equations based on the ML model is no indication of the validity of the model. For selection of the correct model other methods like the determination of sequence distribution, copolymer molecular weight, etc., may have to be resorted to. Incorporation of MBA enhanced the thermal stability of the copolymer. The COOH group of the copolymers have been successfully transformed to photofunctional groups whose synthesia and photo-cross-linking/degradation will be the subject of a subsequent paper.

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Registry No. MBA, 17057-04-4; MMA, 80-62-6; BuA, 141-32-2; (BuA)(MBA) (copolymer), 144565-02-6; (MBA)(MMA) (copolymer), 138780-74-2; PMBA, 37452-86-1; PMMA, 9011-14-7; PBuA, 9003-49-0; p-$NH_2C_6H_4CO_2H$, 150-13-0; 2,5-furandione, 108-31-6.