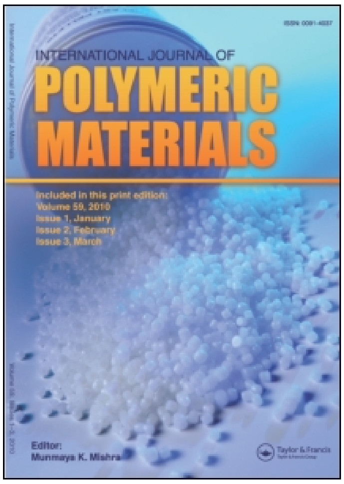

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Study on the Copolymerization Kinetics of 8-Quinolinyl Methacrylate with Methyl Methacrylate, *n*-Butyl Methacrylate and Styrene

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The 8-quinolinyl methacrylate (8-QMA) monomer was prepared and characterized by the conventional methods of analysis. The 8-QMA monomer was copolymerized with methyl methacrylate (MMA), *n*-butyl methacrylate (BMA) and styrene under different monomer feed ratio using azobisisobutyronitrilic (AIBN) as an initiator by solution copolymerization. The polymerization reaction was allowed to proceed only upto ~ 10%. The composition of the resulting copolymers was determined by UV-visible spectrophotometry and reactivity ratio for each monomer pair was calculated. The relative reactivity of the monomers was discussed on the basis of the size of alkyl group in methacrylates and effect of resonance on the stability of the styryl radicals during the copolymerization.

Keywords: Copolymerization; UV-visible spectrophotometry; copolymer composition; reactivity ratio

INTRODUCTION

The copolymers of acrylic and other related monomers are of great technological importance because they often have properties significantly different from their respective homopolymers. The various properties of a polymers such as melting temperature, degree of

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crystallinity, glass transition temperature, phase separation and sites for crosslinking can often be closely controlled by adjusting the composition and monomer sequences in the polymer chain. That being show, it is important to study and understand the various factors which affects and controls these features. It is also become equally important to be able to predict the tendency of one monomer to react with the other during the copolymerization. Mayo *et al.* [1 – 3], during their kinetic studies on copolymerization reactions, noted that certain monomer pairs exhibits a tendency to alter during the copolymerization which resulted from either steric effects or differences in the electron donor-acceptor properties of the radical and polarity of the double bond of the incoming monomer. It was also observed that the relative reactivities of the monomers were controlled by two main factors *viz.* resonance stabilization and polarity.

The present work discribes copolymerization kinetic study of 8-QMA with MMA, *n*-BMA and styrene. The effect of experimental condition on the polymerization rate has been discussed. The effect of reactivity ratio on the resulting copolymer structure and properties have also been discussed.

Kinetic of 8-QMA Copolymerization

Solution copolymerization of 8-QMA with MMA, BMA and styrene was carried out in dimethylformamide (DMF) at 70°C using AIBN initiator and different monomer feed ratios for each monomer pair (as listed in Tabs. I – III). The polymerization reaction was allowed to proceed only upto ~10%. The reaction was stopped at ~10% conversion and the copolymer was isolated from the solution by precipitation using methanol as a non-solvent. The precipitated copolymer was washed and dried in vacuum at 50°C.

Copolymer Composition

The copolymer composition was determined by UV-visible spectrophotometry. Shimadzu-160A recording UV-VIS spectrophotometer was used for this purpose. Then dilute solutions of 8-QA with known and exact concentration were prepared in chloroform and absorption of each solution at 282 nm (λ_{max} for 8-QMA in chloroform) was

TABLE I Solution copolymerization of 8-QMA and MMA for determination of reactivity ratio, Solvent: Dimethyl formamide (DMF); Initiator: AIBN (1% w/w of monomers weight); Temperature: 70 ± 2°C

Sr. No.	*Monomer feed composition*		*Conversion* (%)	*Composition* 8-*QMA in the copolymer* $[m_1]$	*Reactivity ratio*	
	8-*QMA* $[M_1]$ (*Mole*)	*MMA* $[M_2]$ (*Mole*)			r_1	r_2
1	0.015	0.035	9.5	0.026	0.76	0.52
2	0.020	0.030	10.3	0.033		
3	0.025	0.025	11.2	0.035		
4	0.030	0.020	10.6	0.037		
5	0.035	0.015	12.2	0.041		

TABLE II Solution copolymerization of 8-QMA and Styrene for determination of reactivity ratio, Solvent: Dimethyl formamide (DMF); Initiator: AIBN (1% w/w of monomers weight); Temperature: 70 ± 2°C

Sr. No.	*Monomer feed composition*		*Conversion* (%)	*Composition* 8-*QMA in the copolymer* $[m_1]$	*Reactivity ratio*	
	8-*QMA* $[M_1]$ (*Mole*)	*Styrene* $[M_2]$ (*Mole*)			r_1	r_2
1	0.015	0.035	11.3	0.039	0.50	0.01
2	0.020	0.030	10.8	0.040		
3	0.025	0.025	12.1	0.041		
4	0.030	0.020	9.8	0.039		
5	0.035	0.015	10.5	0.040		

TABLE III Solution copolymerization of 8-QMA and BMA for determination of reactivity ratio, Solvent: Dimethyl formamide (DMF); Initiator: AIBN (1% w/w of monomers weight); Temperature: 70 ± 2°C

Sr. No.	*Monomer feed composition*		*Conversion* (%)	*Composition* 8-*QMA in the copolymer* $[m_1]$	*Reactivity ratio*	
	8-*QMA* $[M_1]$ (*Mole*)	*BMA* $[M_2]$ (*Mole*)			r_1	r_2
1	0.015	0.035	8.7	0.029	0.79	0.26
2	0.020	0.030	9.8	0.050		
3	0.025	0.025	10.3	0.054		
4	0.030	0.020	9.5	0.047		
5	0.035	0.015	10.6	0.029		

recorded using chloroform as a reference. The absorption values were plotted against corresponding concentration values to construct a calibration curve.

A dilute solution of each copolymer, containing different amount of 8-QMA, was prepared in chloroform and its absorption was recorded at 282 nm using chloroform as a reference. By using these absorption values, the corresponding concentration values for P8-QMA content in the copolymers were determined from the calibration curve and converted into the appropriate units. By using this copolymer composition data, the reactivity ratios for each monomer pair was calculated by Finmann-Ross method [4].

RESULTS AND DISCUSSION

For determining the reactivity ratios, solution copolymerization of 8-QMA with MMA, BMA and styrene was carried out using 1% AIBN initiator and DMF solvent at 70°C. The total monomer concentration was maintained at 0.05 mole while the monomer feed ratio was varied. The copolymerizations were allowed to proceed only upto 10% conversion and the copolymers were isolated at low degree of conversion to minimize errors in the differential form of the copolymerization equation. The copolymerization equation speaks only of the instantaneous molar composition of the copolymer formed from a given monomer feed with particular values of r_1 and r_2 at low conversions only and cannot predict the copolymer composition formed at higher conversions, say 50–60%. This is so, because the moment copolymerization begins, the ratio of the unconsumed monomers continuously drifts away from the initial feed ratio. The continuous change in the monomer feed ratio is the result of the relative rate of consumption of the two monomers, not being the same and, hence, the two monomer do not enter into the copolymer chain in the same ratio as that of the initial feed. Usually, the monomer with a higher reactivity ratio consumed sooner and, hence the monomer mixture becomes progressively poorer in that monomer. The continuous change in the monomer composition also continuously changes the copolymer composition thereby introducing a composition inhomogenity as polymerization progresses, which depends on a percentage conversion. The higher the conversion the broader the distribution of extent of inhomogenity [5].

Tables I to III shows copolymerization parameters and calculated values of the reactivity ratios for 8-QMA-MMA, 8-QMA-styrene and

8-QMA-BMA system. It is observed from the results that for all the three systems $r_1 > r_2$ and the value of r_1 is less than one. This indicates that the copolymers are weakly ordered with predominantly a random distribution of the monomer units in the polymer chain. The copolymer formed will be richer in 8-QMA. The rate of polymerization depends on the nature of the comonomers. This can be understand from the $(1/r_1)$ values (where $r_1 = k_{11}/k_{12}$) that gives a measure of the relative reactivity of the comonomers *i.e.*, MMA, BMA and styrene towards the P8-QMA radicals. The higher the value of $1/r_1$ the greater the chance that comonomer will add to the P8-QMA radical. On the basis of the reactivity ratios the order of reactivity of the comonomers towards 8-QMA radical is MMA > BMA > Styrene. The relative reactivities of the methacrylates towards 8-QMA radical is governed by steric factors. It is observed that as the size of the alkyl group in alkyl methacrylates increases the tendency to react with 8-QMA radical decreases. Similar observation has been made by Dhal *et al.* [6] in case of copolymers of GMA and alkylmethacrylates and by Murthy *et al.* [7] in case of copolymers of N-methyl acrylamide and alkyl methacrylates. The lower relative reactivity of styrene may be attributed to the stability of the styryl radicals due to resonance effects [8]. The results of reactivity ratios also lead to the conclusion that in order to synthesize the copolymers with narrow compositional distribution for specific applications, the following factors should be considered: (i) monomer pair should be selected with r_1 and r_2 values close to unity, so that the monomer ratio is distributed to the minimum throughout the polymerization (ii) if possible, copolymerization should be carried out at or close to azeotropic composition (iii) copolymerization should be restricted to low conversions only and (iv) the monomer concentration should be maintained by controlled addition of the monomer which gets consumed faster.

CONCLUSION

The 8-QMA monomer was copolymerized with MMA, *n*-BMA and styrene by solution polymerization using different monomer feed ratio. From the results of reactivity ratio it is observed that 8-QMA monomer has a tendency to form a random copolymers with MMA, *n*-BMA and styrene during free radical copolymerization. The copolymers formed are slightly richer in 8-QMA content. It is also observed that the reactivity of comonomers was affected by the nature of alkyl group in methacryalates and resonance effect of styrene during copolymerization with 8-QMA.

References

[1] Mayo, F. R., Lewis, F. M. and Hulse, W. F. (1945). *J. Am. Chem. Soc.*, **67**, 1701.
[2] Mayo, F. R. and Walling, C. (1947). *Discuss. Faraday Soc.*, **2**, 295.
[3] Mayo, F. R., Walling, C., Briggs, E. R. and Wolfstirn, K. B. (1948). *J. Am. Chem. Soc.*, **70**, 1537.
[4] Fineman, M. and Ross, S. D. (1950). *J. Poly. Sci.*, **5**, 259.
[5] Govarikar, V. R., Viswanathan, N. V. and Sreedhar, J. (1986). *Polymer Science*, Wiley Eastern Ltd., India p. 208.
[6] Dhal, P. K., Ramkrishna, M. S. and Babu, G. N. (1982). *J. Polym. Sci.-Polym. Chem. Ed.*, **19**, 581.
[7] Murthy, S. N. and Rao, P. R. (1994). *J. Ind. Concil Chem.*, **X**(1), 53.
[8] Boyd, R. H. and Phillips, P. J. (1996). The Science of Polymer Molecules, Cambridge University Press. London p. 132.