

ESTIMATION AND COMPARISON OF Q-e PARAMETER OF METHYL METHACRY- LATE AND ACRYLAMIDE COPOLYMER- IZED WITH STYRENE IN THE PRESENCE OF CYCLOHEXANONE AND METHYL CYANOACETATE

Mir Munsif Ali Talpur ^{*a}, Tajnees Pirzada and Mir
Sajjad Hussain Talpur ^b,

^aDepartment of Chemistry, Shah Abdul Latif
University, Khairpur (Mirs), Pakistan

^bDepartment of Chemical Engineering, Mehran
University of Engineering and Technology, Jamshoro,
Sindh, Pakistan

(Received 9 October 1995; accepted 31 August 1998)

The role of some organic compounds (having active hydrogen atom) initiating radical polymerization of some polar vinyl monomers involving the transfer of hydrogen radical has been reported (Imto *et al* 1975; Ouchi *et al* 1980; Kaim 1984 a & b; Kaim 1986; Kaim and Munsif 1993; Munsif and Kaim 1994). The proof of discussed mechanism has been recently obtained from spectroscopic, excess enthalpy investigations (Wilczura *et al* 1995) and copolymerization reactions of the monomers (Kaim and Munsif 1993; Munsif and Kaim 1994; Munsif *et al* 1994; Munsif and Kaim 1995 and 1996). Besides the reactivity ratios which have been evaluated by error-in-variable model (EVM) (Dube *et al* 1991), the free radical character of the vinyl monomers in copolymerization can be sought by "Q" and "e" parameters. Where "Q" is a measurement of the general reactivity/resonance stabilization of the monomer and "e" depends on polar properties of the monomer.

The purpose of the present study is to report and compare the "Q" and "e" values obtained for the copolymerization of monomers performed in the absence of conventional free radical initiators (Kaim and Munsif 1993; Munsif and Kaim 1995 and 1996).

The e_2 and Q_2 values were calculated (Young 1961) by applying the following two equations:

$$e_2 = e_1 \pm (-\ln r_1 r_2)^{1/2}$$

$$Q_2 = Q_1 / r_1 \exp [-e(e_1 - e_2)]$$

The values of r_1 and r_2 calculated by EVM method for each copolymer system were taken from our previous work (Munsif and Kaim 1993 and 1994; Munsif *et al* 1994; Munsif and Kaim 1995 and 1996). The Q_2 and e values for styrene (sty) have been taken as that of Alfrey and Price (1947) ($Q_1 = 1.0$ and $e = -0.80$) for calculating the Q_2 and e_2 values.

There are also two methods (Greenly 1975; Laurier *et al* 1985), however, according to Laurier *et al* the precision of Q-e values depends upon r-parameter data if it is exact, any Q-e estimation procedure including Young's will give equivalent results.

The calculated Q_2 and e_2 values for the monomers have been placed in Table 1 whereas those reported in literature are listed in Table 2.

The Q_2 value for methyl methacrylate in all our copolymer systems is in the range of 0.5307-0.6449, which is much less than the Q_2 data that is in the range of 0.74-0.78 \pm 0.02-0.06 for the same monomer system reported in literature (Young 1961; Greenly 1980; Laurier *et al* 1985) for the free radical copolymerization of MMA and Styrene. Thus our results suggest the low reactivity of the methyl methacrylate as compared with the reactivity of monomer initiated by conventional free radical initiators. These results also indicate that as the concentration of the cyclohexanone increases in the reaction mixture the Q_2 value for MMA decreases as in case of MMA-Sty + Chan system. This is not true in case of methyl cyanoacetate (MCA) as shown in Table 1. This is in contradiction with the result of Kaim (Kaim 1984 a and b) which shows an increase of polymerization rate by increasing concentration of cyclohexanone. Moreover, it is noted from data in Table 1 that by replacing a portion of cyclohexanone by cyclohexane the Q_2 value increases. This has also been confirmed from the results of copolymerization systems where benzoyl peroxide has been used as initiator i.e. Q_2 is higher when mixture of both of them has been used as a solvent.

Our e_2 for methyl methacrylate using cyclohexanone pure as initiator and benzoyl peroxide match well with the e_2 reported in literature (Young 1961; Greenly 1980; Laurier *et al* 1985) which is in the range 0.38-0.40 \pm 0.3-0.8. In the thermal copolymerization and in methyl cyanoacetate/benzene (mixture) reaction medium the e_2 values for MMA are much less even minus in cyclohexanone/cyclohexane as compared with that reported in the literature (Young 1961; Green 1980; Laurier *et al* 1985). This supports our previous results (Kaim and Munsif 1993; Munsif and Kaim 1994; Munsif *et al* 1994; Munsif and Kaim 1995; Munsif *et al* 1996) which indicate the alternating tendency of monomers in copolymer that has been accounted for (Braun and Czerwinski 1989) in terms of

*Author for correspondence

differing electrical polarities. However, e_2 value in pure methyl cyanoacetate as well as in chn/cyclohexane and cyclohexane using benzoyl peroxide is surprisingly higher than that reported in the literature (Young 1961; Greenly 1980; Laurier *et al* 1985).

In acrylamide-styrene system Q_2 for acrylamide in chn/benzene (mixture) is in close relation to the data for the same monomer (Greenly 1975) which suggests the almost similar reactivity of acrylamide monomer in the copolymer system initiated by cyclohexanone to that of initiated by conventional free radical initiators. However, the Q_2 values for acrylamide in all our remaining systems do not match with the data reported in the literature (Young 1961; Greenly 1975). These Q_2 values were in contradiction to that of MMA discussed above which indicate that as the concentration of chn increases the (Q_2 value) increases. However, it Q_2 value) decreases by replacing cyclohexanone partially by dioxane or benzene.

Table 1

The Q_2 and e_2 values for methyl methacrylate copolymerized with styrene in various reaction media in the absence of any conventional radical initiator at 75°C

Reaction Media	Q_2	e_2
Thermal in bulk	0.6176	0.113
Cyclohexanone	0.5307	0.385
Cyclohexanone/Cyclohexane (1:1.16 in volume) mixture	0.5816	-0.018
Methyl Cyanoacetate	0.5668	0.569
Methyl Cyanoacetate/benzene (1:1.16 in volume) mixture	0.5503	0.003

The Q_2 and e_2 values for methyl methacrylate copolymerized with styrene in various reaction media using benzoyl peroxide as initiator at 60°C.

Cyclohexanone	0.6035	0.399
Cyclohexanone/Cyclohexane (1:1.16 in volume) mixture	0.6178	0.487
Cyclohexane	0.6449	0.462

The Q_2 and values for acrylamide copolymerized with styrene in various reaction media in the absence of any conventional radical initiator 75°C.

Dioxane	0.5994	0.458
Cyclohexane	0.7049	0.048
Cyclohexanone/benzene (1:1.6 in volume) mixture	0.2525	1.392
Cyclohexanone/dioxane (1:1.6 in volume) mixture	0.5916	0.176

Table 2

The Q_2 and e_2 parameters for methyl methacrylate reported in literature

Reaction Media	Q_2	e_2	Reference No.
Bulk	0.78±0.04	0.38±0.03	(Greenly 1975)
Bulk	0.76±0.02	0.38±0.03	(Greenly 1980)
Bulk	0.74	0.40	(Young 1961)
Not mentioned	0.78±0.06	0.40±0.08	(Braun and Czerwinski 1989)

The Q_2 and e_2 parameters reported in literature for acrylamide

Bulk	1.18	1.30	(Young 1961)
Not mentioned	0.23	0.54	(Braun and Czerwinski 1989)

Our e_2 values for acrylamide in various reaction media are in the range 0.048-1.392. The only e_2 data obtained for the copolymer system in cyclohexanone/benzene is nearer to that of reported by Young (1961). All other e_2 values are smaller than those found in the literature (Young 1961; Greenly 1975), which indicate an alternating tendency of monomers in copolymer.

It can be concluded that lower reactivity of methyl methacrylate is due to initiation by the active hydrogen containing organic compounds, while the reactivity of acrylamide is unaffected. The e_2 values for both the monomers (MMA and Aam) confirm the alternative tendency of monomers in copolymers that also supports our previous results (Kaim and Munsif 1993; Munsif and Kaim 1994; Munsif and Kaim 1995; Munsif *et al* 1996).

Key words: Acrylamide, Styrene, Copolymerization, Cyclohexanone.

References

- Alfery T, Jr Price C C 1947 Determination of reactivity of vinyl monomers in copolymer. *J Polym Sci* **2** 101-107.
- Braun D, Czerwinski W K 1989 Comprehensive polymers science **3** 321-324.
- Dube M, Amin S R, Penlidis A, O'Driscoll K F, Reilly P M 1991 A microcomputer program for estimation of copolymerization reactivity ratio *J Polym Sci* part (part A) **29** 703-708.
- Greenly R Z 1975 Determination of Q and e values by a least squares techniques. *J Macromol Sci-Chem* **A9** (4) 505-516.
- Greenly R Z 1980 An expanded listing of revised Q and e values. *J Macromol Sci-Chem* **A14** 427-443.

- Imoto M, Oishi M, Ouchi T 1975 Polymerization of methyl methacrylate initiated with poly (styrene-co-acroleins) or poly (styrene-co-methyl vinyl ketone). *Die Makromol Chem* **B176** 3287-3294.
- Kaim A 1984 Polymerization of vinyl monomers initiated with cyclohexanone. *J Polym Sci* **22** 203-208.
- Kaim A 1984 Kinetics of polymerization of methyl methacrylate initiated with cyclohexanone. *J Polym Sci* **22** 1891-1895.
- Kaim A 1986, Activity of some methylene compounds in radical polymerization of methyl methacrylate. *J Polym Matter* **3** 73-77.
- Kaim A Mir Munsif A 1993 Copolymerization of methyl methacrylate styrene system in presence of cyclohexanone. *J Polym Matter* **10** 95-98
- Laurier G C, O' DrisColl K F, Reilly P M 1985 Estimating reactivity in free radical copolymerization. *J Poly Sci* **72** 17-26.
- Mir Munsif A, Kaim A, Kasprzyzcha-guttman T 1994 *Solvent effect on the free radical copolymerization of methyl methacrylatestyrene system*. In the Abstract of **6th** National Chem: Conference pp 69.
- Mir Munsif A, Kaim A 1994 Investigation of methyl methacrylate-styrene copolymerization system in the presence of methyl cyanoacetate. *J Macromol Sci Chem* **A31** (2) 241-249.
- Mir Munsif A, Kaim A 1995 Investigation of acrylamide-styrene copolymerization system in cyclohexanone in the absence of a conventional radical initiator. *J Macromol Sci-Chems* **A32** (2) 241-249.
- Mir Munsif A, Oracz P, Kaim A 1996 Study of methyl methacrylate-acrylamide copolymerization system in cyclohexanone in the absence of conventional radical initiator *J Polym Sci* **37** (81) 4149-4154.
- Ouchi T, Murayama N, Imoto M 1980 Radical polymerization of vinyl monomer initiated by aliphatic aldehyde. *Bull Chem Soc Jpn* **53** 748-752.
- Wilczura H, Mir Munsif A T, Kaim A, Kasprzyzcha-guttman T 1995 Excess enthalpies of cyclohexane + cyclohexanone, cyclohexane + methyl methacrylate and cyclohexanone + methyl methacrylate at 298.15k. *J Chem Engg Data* **40** (6) 1233-1236.
- Young I J 1961 Copolymerization parameters. *J Polym Sci* **54** 411-455.