SOLVENT EFFECT ON
THE FREE-RADICAL COPOLYMERIZATION OF
METHYL METHACRYLATE–STYRENE SYSTEM

Mir Munsif Ali Talpur*

Department of Chemistry
Shah Abdullatif University
Khairpur (MIRS), Sindh, Pakistan

A. Kaim, T. Kaspryzycka-Guttman, and Tajnees Pirzada

Warsaw University
Faculty of Chemistry
U.L. Pasteura-01-02903 Warsaw, Poland

الخلاصة :

ندرس في هذا البحث البلمرة المشتركة للوحدات الأساسية الحرة لـ ميثيل ميثا أكريلان (MMA) –

ستايرين في كل من سيكلوهيكسانون، حيث خليط سيكلوهيكسانون – سيكلوهيكسان بنسبة حجمية قدرها

(١,١٦:١) وسيكلوهيكسان عند درجة حرارة (٦٠ ± ١) درجة مئوية وذلك باستخدام بادئ التفاعل بنزويل

بيروكسايد. قمنا بحساب النسبة التفاعلية (r) باستخدام طرق: YBR و KT و EVM، ووجدنا أن هذه

القيم تتفق مع النتائج المنشورة في هذا المجال، وأنها تشير إلى النزعة الأُحادية في البلمرة المشتركة. وأبانت

هذه الدراسة أن الزيادة في ثابت العزل لوسط التفاعل لا تؤثر على قيم النسبة التفاعلية خاصة قيم (r₂) كما

تبيّن لنامن خلال قيم Q–e. أضف الى ذلك أن الاحتمالية الشَّرطية والتي تتحكم بتوالي التوزيع لم تتأثر

بالوسط المبلمر.

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*To whom correspondence should be addressed.

M.M. Ali Talpur, A. Kaim, T. Kaspryzycka-Guttman, and T. Pirzada

ABSTRACT

The free radical copolymerization of the methyl methacrylate (MMA)–styrene (Sty) system is studied in cyclohexanone, cyclohexanone–cyclohexane (1:1.16 by volume) mixture, and cyclohexane at 60°C ± 1°C using benzoyl peroxide initiator. The reactivity ratios are evaluated by Yezrielev, Brokhina, and Roskin (YBR), Kelen and Tüdös (KT), and Error-in-variable model (EVM) methods. The r-parameter values are in reasonable agreement with those reported in the literature for the free radical copolymerization of the present monomer system. The r-product values suggest the alternating tendency of the monomers in copolymerization. The increasing dielectric constant of the reaction medium does not influence the reactivity ratios, particularly the r_2 value which is also evident from $Q-e$ parameters. Moreover, the conditional probabilities governing sequence distribution are unaffected by the polymerization medium. These factors support the operation of a bootstrap model.

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INTRODUCTION

The effect of the reaction medium on the reactivity of monomers and their radicals in free-radical copolymerization has been reported in the literature [1–23]. Several interpretations for the change of reactivity ratios as a function of reaction medium were proposed; the most common among them are monomer solvation [19], complex formation [9, 24], solvent dielectric constant [9, 13, 15, 20], hydrogen bonding [1, 3–8, 11] and hot radical theory [14]. However, none of these can satisfactorily explain the variation of the reactivity ratios.

We have been studying [24, 28] the initiating activity of some organic compounds containing an active hydrogen atom in the copolymerization of some polar vinyl monomers. We investigated the solvent effect of these compounds in the presence of conventional radical initiator at a temperature where the initiating activity of the hydrogen-containing compounds was not pronounced [29].

The present paper reports the solvent effect on the free radical copolymerization of methyl methacrylate (MMA)–styrene (Sty) system.

EXPERIMENTAL

Materials

The purification of monomers, cyclohexanone, and cyclohexane was carried out as described in our previous work [24–26]. Benzoyl peroxide was purified [30] by recrystallizing it twice from purified chloroform. The crystals of benzoyl peroxide were dried under vacuum over phosphorus peroxide for two days. The melting point was taken as the criterion of purity.

Procedure

The procedure for copolymerization and experimental conditions, except for the temperature which was kept at $60 \pm 1°C$, were similar to those reported earlier [24]. The concentration of benzoyl peroxide was $2\,g/l$ of monomers.

RESULTS AND DISCUSSIONS

The copolymer composition data for the MMA-Sty system in different solvents are listed in Table 1 together with corresponding weight-% conversion. The MMA–Sty copolymerization curves as a function of monomer feed *versus* copolymer composition are shown in Figure 1 and labeled as benzoyl peroxide copolymerization of MMA–Sty system in cyclohexanone, cyclohexanone/cyclohexane (1:1.16 in volume) mixture, and cyclohexane at $60 \pm 1°C$ respectively. A plot of the mole fraction of MMA centered triads as a function of the mole fraction of MMA in the copolymer is shown in Figure 2.

The analytical data (percent carbon) of the copolymer was used to determine the *r*-parameters. The reactivity ratios of MMA (r_1) and Sty (r_2) for all the investigated copolymerization systems were calculated by the Yezerielev, Brokhina, and Roskin method (YBR method) [31], Kelen and Tüdös method (KT method) [32], and by the method using the error-in-variable Model (EVM method) [33]. The reactivity parameters were generated using random errors of 5% and 1% for the monomer feed composition and copolymer composition respectively, with the EVM method. The reactivity coefficient data estimated by the above mentioned methods for all the copolymerization systems investigated are reported in Table 2. The $Q-e$ parameters are calculated by Young's method [36] from the values of r_1 and r_2 data calculated by the EVM method (for the present monomer system in all the solvents) and are shown in Table 3.

The reactivity coefficient values for the monomers obtained in cyclohexane are in reasonable agreement with the reactivity ratio data reported by Nazoki $(r_1 = 0.55 \pm 0.01$ and $r_2 = 0.47 \pm 0.01)$ [34] and KinSinger *et al.* $(r_1 = 0.53$ and $r_2 = 0.51$ in benzene) [35]. The *r*-parameter values in cyclohexanone/cyclohexane (1:1.16 by volume) mixture or in the mixture of other solvents for the present monomer system have not been reported in the literature. The r_1 and r_2 values in pure cyclohexanone

are in good agreement with the r-values ($r_1 = 0.62 \pm 0.03$, $r_2 = 0.38 \pm 0.02$) reported by Madruga *et al.* [17] for the same monomer system in benzonitrile.

The r-product values for the monomer system in pure cyclohexanone, cyclohexanone/cyclohexane, and in cyclohexane are 0.235, 0.191, and 0.203 respectively. These values are closer to zero, which suggests an alternating tendency of monomers in the copolymer.

Table 1. Results of Copolymerization of Methyl Methacrylate (M1) and Styrene (M2) Initiated by Benzoyl Peroxide in Various Reaction Media at 60°C.

Copolymerization of MMA (M1) with Sty (M2) in Cyclohexane

Mole fraction in feed		Reaction time, minutes	Conversion weight %	Results of elemental analysis of copolymer		Mole fraction of M1 in copolymer
M1	M2			C%	H%	
0.70	0.30	240	6.757	70.635	8.105	0.677
0.60	0.40	240	6.511	73.425	8.225	0.591
0.50	0.50	240	6.264	75.275	8.285	0.534
0.40	0.60	240	5.595	77.755	7.925	0.457
0.30	0.70	240	5.270	79.040	7.885	0.417

Copolymerization of MMA (M1) with Sty (M2) in the mixture of Cyclohexanone/Cyclohexane (1:1.16 by volume)

Mole fraction in feed		Reaction time, minutes	Conversion weight %	Results of elemental analysis of copolymer		Mole fraction of M1 in copolymer
M1	M2			C%	H%	
0.70	0.30	240	7.738	70.87	7.85	0.670
0.60	0.40	240	7.499	72.52	7.73	0.619
0.50	0.50	240	7.024	75.51	7.55	0.527
0.40	0.60	240	6.622	77.09	7.76	0.478
0.30	0.70	240	6.178	78.91	7.91	0.421

Copolymerization of MMA (M1) with Sty (M2) in Cyclohexanone

Mole fraction in feed		Reaction time, minutes	Conversion weight %	Results of elemental analysis of copolymer		Mole fraction of M1 in copolymer
M1	M2			C%	H%	
0.70	0.30	165	5.768	70.46	7.63	0.682
0.60	0.40	165	5.798	73.12	7.83	0.600
0.50	0.50	165	5.528	75.28	7.71	0.534
0.40	0.60	165	5.370	76.98	7.79	0.480
0.30	0.70	165	5.097	78.80	7.74	0.420

As cyclohexanone is a highly polar compound compared to cyclohexane, it is evident from Table 2 that r-parameter values, especially r_2 (Sty), are very close in both the solvents; this precludes the idea of other investigators [2, 9, 15, 17–18] that the polarity of the reaction medium causes the variation of reactivity ratios in the free radical copolymerization of methyl methacrylate–styrene system. These authors suggest that an increase in solvent dielectric constant causes a decrease in both the reactivity ratios which is more pronounced for styrene than for methyl methacrylate. However, in our case there is no indication of any significant effect on r_2 (Sty). This suggests that the dielectric constant of the reaction medium (*i.e.* polarity) does not significantly influence the r_2-value of styrene.

The data in Table 3 show that the Q_2 value for MMA is smaller when pure cyclohexanone is used as a solvent; however, Q_2 values increase when cyclohexanone is replaced partially and eventually completely by cyclohexane. This can be explained
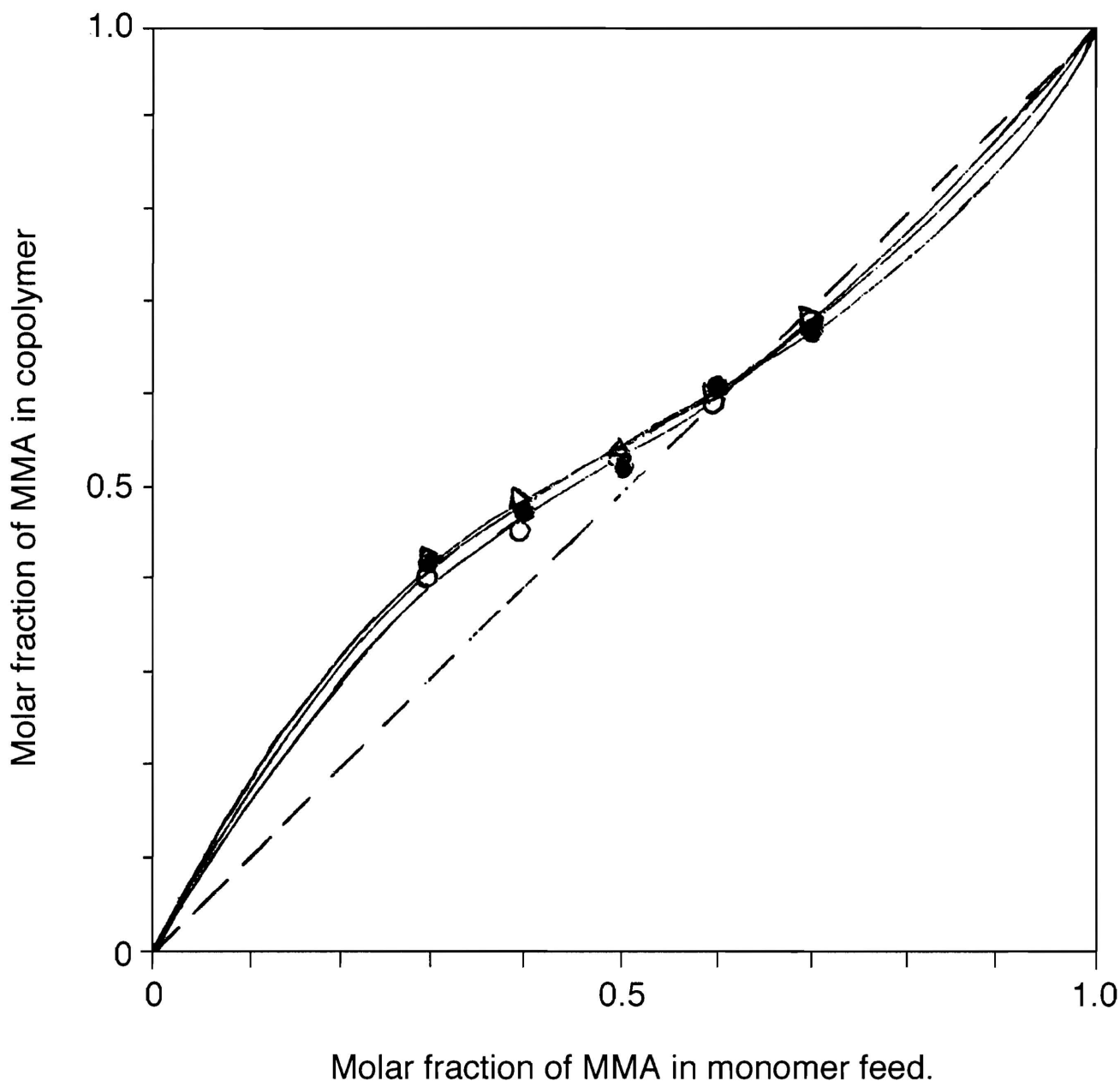

Figure 1. The copolymer composition curve for the copolymerization of methyl methacrylate (M1)–Styrene (M2) system at 60°C initiated by benzeyl peroxide in: (O) cyclohexane; (●) cyclohexanone/cyclohexanane mixture; (Δ) cyclohexanone.

on the grounds that the reactivity of MMA increases in cyclohexane due to the increased resonance stabilization and the same reasons (less resonance stabilization) leads to less reactivity of the monomer in cyclohexanone due to its polarity.

The e_2 value is higher in a mixture of cyclohexanone and cyclohexane than the e_2 value obtained in cyclohexanone or cyclohexane. Moreover, the e_2 value of MMA obtained in all the solvents is higher than that reported by Young [35], Greenly [37], and Laurier [38], for reasons we do not understand.

It is clear from Figure 2 that copolymers of same composition have the same microstructure. Therefore the conditional probabilities governing sequence distribution are unaffected by the polymerization medium. A natural consequence of this assertion is that the reactivity ratios are not affected by the reaction medium.
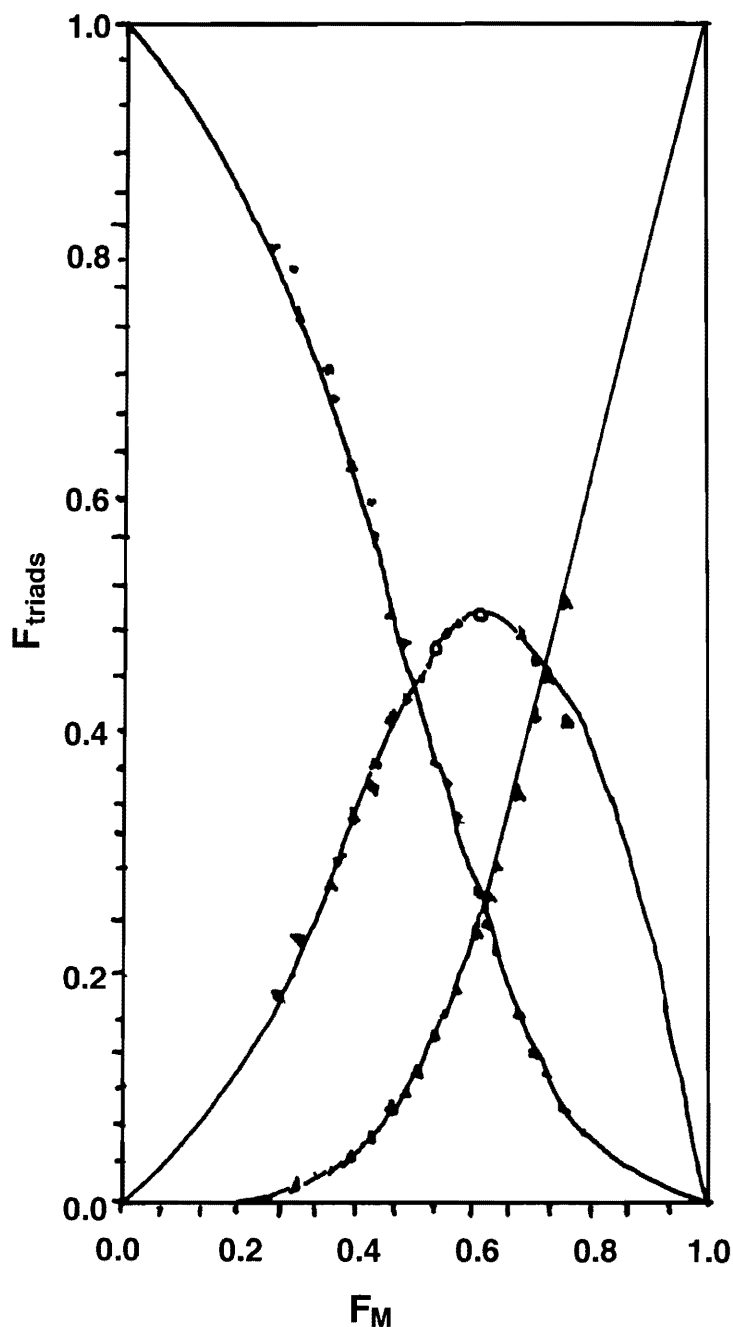

*Figure 2. A plot of the mole fraction of MMA centered triads as a function of the mole fraction of MMA in the copolymer:
(O) cyclohexane; (●) cyclohexanone/cyclehexane mixture; (△) cyclohexanone.*

Table 2. The r_1 (Methyl Methacrylate) and r_2 (styrene) Values Calculated
by Various Methods for the Methyl Methacrylate-Styrene
Copolymerization System in Various Reaction Media at 60°C Initiated
by Benzoyl Peroxide.

Reaction Medium		YBR Method	KT Method	EVM Method	$r_1 . r_2$
Cyclohexane	r_1	0.56 ± 0.07	0.56 ± 0.05	0.565	**0.203**
	r_2	0.35 ± 0.01	0.36 ± 0.05	0.360	
Cyclohexanone/ cyclohexane	r_1	0.57 ± 0.01	0.57 ± 0.05	0.578	**0.191**
(1:1.16 by volume mixture)	r_2	0.32 ± 0.01	0.33 ± 0.05	0.330	
Cyclohexanone	r_1	0.65 ± 0.09	0.64 ± 0.05	0.635	**0.235**
	r_2	0.38 ± 0.08	0.37 ± 0.05	0.374	

Table 3. $Q\text{-}e$ Parameters of MMA Copolymerized with Styrene
in Various Solvents Initiated by Benzoyl Peroxide.

Solvent	Q_2	e_2
Cyclohexanone	0.6035	0.399
Cyclohexanone/Cyclohexane (1:1.16 by volume)	0.6178	0.487
Cyclohexane	0.6449	0.462

CONCLUSIONS

The reactivity ratios particularly r_2 (Sty) in cyclohexane together with conditional probabilities and $Q\text{-}e$ parameters support the appropriate operation of Harwood's Bootstrap model in the present copolymerization system.

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