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“BOOTSTRAP MODEL” FOR THE COPOLYMERIZATION OF THE METHYL METHACRYLATE–STYRENE SYSTEM IN THE PRESENCE OF METHYL CYANOACETATE

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Key Words: Methyl methacrylate; Styrene; Copolymerization; Bootstrap model; Solvent effect; Sequence distribution

ABSTRACT

The methyl methacrylate–styrene system in pure methyl cyanoacetate and in a methyl cyanoacetate/benzene mixture was examined by testing the theoretical calculations of the “bootstrap model” for the solvent effect in the copolymerization of the system. Methyl methacrylate centered triads calculated according to the procedure given by Harwood plotted against the methyl methacrylate ratio in copolymer showed that for the copolymer with the same composition, a different copolymer microstructure was obtained. A similar but smaller effect can be observed for reexamined data in the literature for free-radical-initiated copolymerization of the system in butyl alcohol and phenol. The inadequacy of the “bootstrap model” to describe exactly the solvent effects in the monomer–solvent systems investigated here is explained by the active H-atom in the solvents involved in the initiation and/or complexation reaction with methyl methacrylate.

INTRODUCTION

It was recently shown that the composition and sequence distributions of the monomers in a chain are sensitive to the solvent utilized during polymerization [1, 2]. Harwood [1] showed in his theoretical development that the relative concentrations of monomer unit sequences in a copolymer can be calculated from the monomer reactivity ratios and the monomer feed ratios only. Thus, Harwood described four comonomer pairs consisting of polar and nonpolar monomers showing different reactivity ratios in different solvents. The monomer triads in the corresponding copolymers, theoretically calculated by him from the monomer reactivity ratios and the monomer feed ratios, showed that copolymers of the same composition have the same microstructure irrespective of the solvent used during copolymerization. He explained this solvent effect with the "bootstrap model" and proposed the distribution coefficient *K* for quantification of the phenomena. He did not mention any limitations on the validity of his model.

We recently studied the copolymerization of the methyl methacrylate–styrene system in the presence of pure methyl cyanoacetate and a methyl cyanoacetate/benzene mixture [3]. It was found that the initiating activity of methyl cyanoacetate resembles those of free-radical initiators. Some differences in the reactivity ratios obtained from comparisons with data reported in the literature for the same monomer system initiated by conventional free-radical-initiators has been explained by the specific interactions of methyl methacrylate and methyl cyanoacetate.

Although the influence of the solvent on the radical copolymerization of the methyl methacrylate–styrene system has been the subject of numerous studies, important problems remain in the quantitative description of the solvent effect upon both copolymer composition and sequence distributions in the polymer chain. This subject is of great importance because it supplies valuable information regarding the polymerization processes [4]. Thus, it was of interest to examine if the "bootstrap model" is also valid for the methyl methacrylate–styrene system in the presence of methyl cyanoacetate.

In the present paper we refer to experimental data given before [3] and propose a critical revaluation of the "bootstrap model" based on theoretical calculations. The results of the test are correlated with the recalculated data presented in the literature concerning the solvent effects for the methyl methacrylate–styrene system.

EXPERIMENTAL

All experimental data used for calculation of the monomer unit sequence in the copolymers obtained have been given previously [3].

RESULTS AND DISCUSSION

All reactivity ratios for the methyl methacrylate (M_1)–styrene (M_2) system in different solvents used for further calculation of the relevant conditional probabili-

TABLE 1. Reactivity Ratios for Methyl Methacrylate (r_1) and Styrene (r_2) Calculated by the EVM Method [9] from Data by San Román et al. [5,6] (data recalculated by Klumperman et al. [10], Ito et al. [7], and Talpur et al. [3]

Solvent	Author	r_1	r_2
Bulk	San Román et al. [5][a,b]	0.45	0.47
Benzene	San Román et al. [6][a]	0.43	0.51
	Ito et al. [7][a]	0.47	0.58
Benzonitrile	San Román et al. [6][a]	0.62	0.38
	Ito et al. [7][a]	0.51	0.49
Chlorobenzene	San Román et al. [6][a]	0.49	0.47
Benzyl alcohol	Ito et al. [7][a]	0.42	0.45
Phenol	Ito et al. [7][a]	0.36	0.36
Methyl cyanoacetate	Talpur et al. [3][c]	0.59	0.26
Methyl cyanoacetate/benzene mixture (1:1.16 by volume)	Talpur et al. [3][c]	0.95	0.55

[a] Reaction initiated with 2,2′-azoisobutyronitrile at 60°C.

[b] These data have been used for further calculation. Recalculation of the data of San Román [5] gave slightly different results: $r_1 = 0.447$ and $r_2 = 0.446$.

[c] No free-radical initiator used at 75°C.

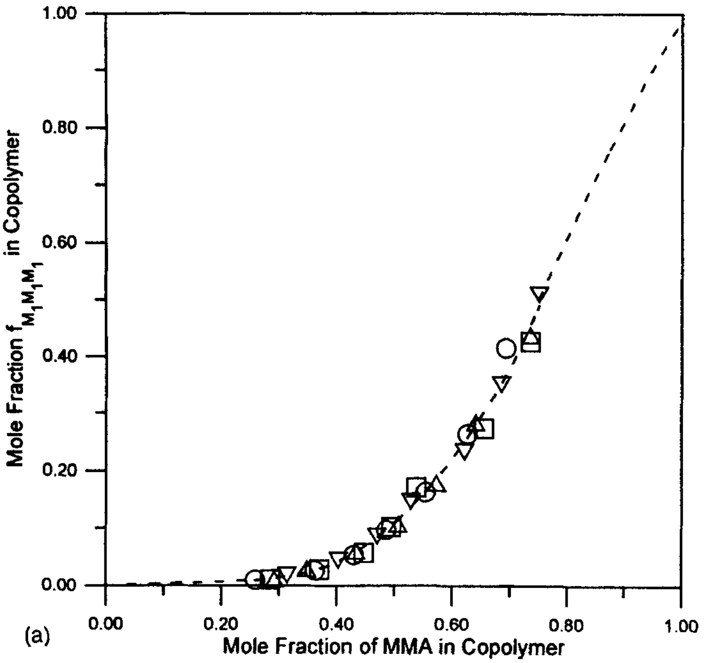
ties appearing in the "bootstrap model" are presented in Table 1. The reactivity ratios measured in pure methyl cyanoacetate and in a methyl cyanoacetate/benzene mixture are taken from a previous paper [3]. For comparison, data of San Román et al. [5, 6] and of Ito et al. [7], originally calculated by the Fineman-Ross method [8] and recalculated with the error-in-variable-model (EVM method) [9] by Klumperman et al. [10] and by us, respectively, have been taken into consideration.

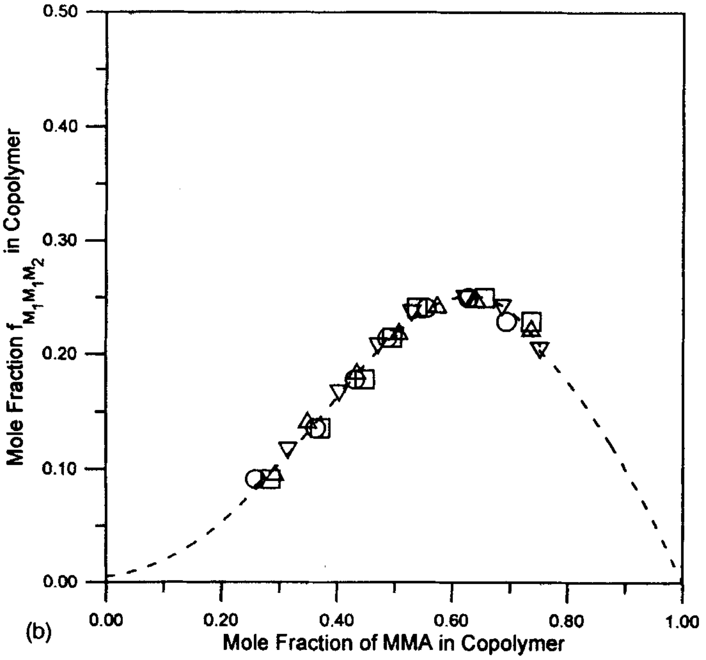
Assuming the Mayo-Lewis terminal copolymerization model for the free-radical copolymerization of the methyl methacrylate-styrene system, the conditional probabilities were calculated in as follows:

$$p(M_1/M_1) = \frac{k_{11}[PM_1^\bullet][M_1^0]}{k_{11}[PM_1^\bullet][M_1^0] + k_{12}[PM_1^\bullet][M_2^0]} = \left(1 + \frac{[M_2^0]}{r_1[M_1^0]}\right)^{-1}$$

$$p(M_1/M_2) = \frac{k_{21}[PM_2^\bullet][M_1^0]}{k_{21}[PM_2^\bullet][M_1^0] + k_{22}[PM_2^\bullet][M_2^0]} = \left(1 + \frac{r_2[M_2^0]}{[M_1^0]}\right)^{-1}$$

$$p(M_2/M_1) = \frac{k_{12}[PM_1^\bullet][M_2^0]}{k_{12}[PM_1^\bullet][M_2^0] + k_{11}[PM_1^\bullet][M_1^0]} = \left(1 + \frac{r_1[M_1^0]}{[M_2^0]}\right)^{-1}$$


1.00
0.80
0.60
0.40
0.20
0.00
Mole Fraction $f_{M_1M_1M_1}$ in Copolymer
0.00
0.20
0.40
0.60
0.80
1.00
Mole Fraction of MMA in Copolymer
(a)


0.50
0.40
0.30
0.20
0.10
0.00
Mole Fraction $f_{M_1M_1M_2}$ in Copolymer
0.00
0.20
0.40
0.60
0.80
1.00
Mole Fraction of MMA in Copolymer
(b)

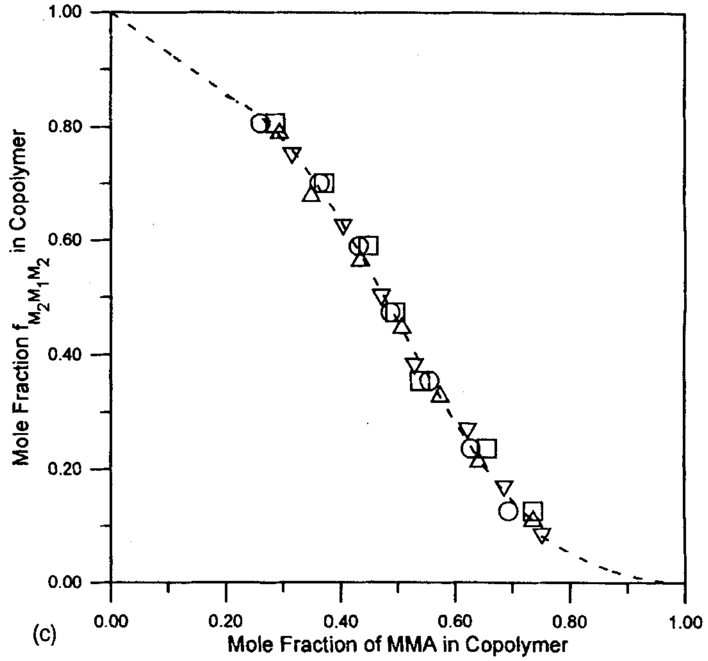


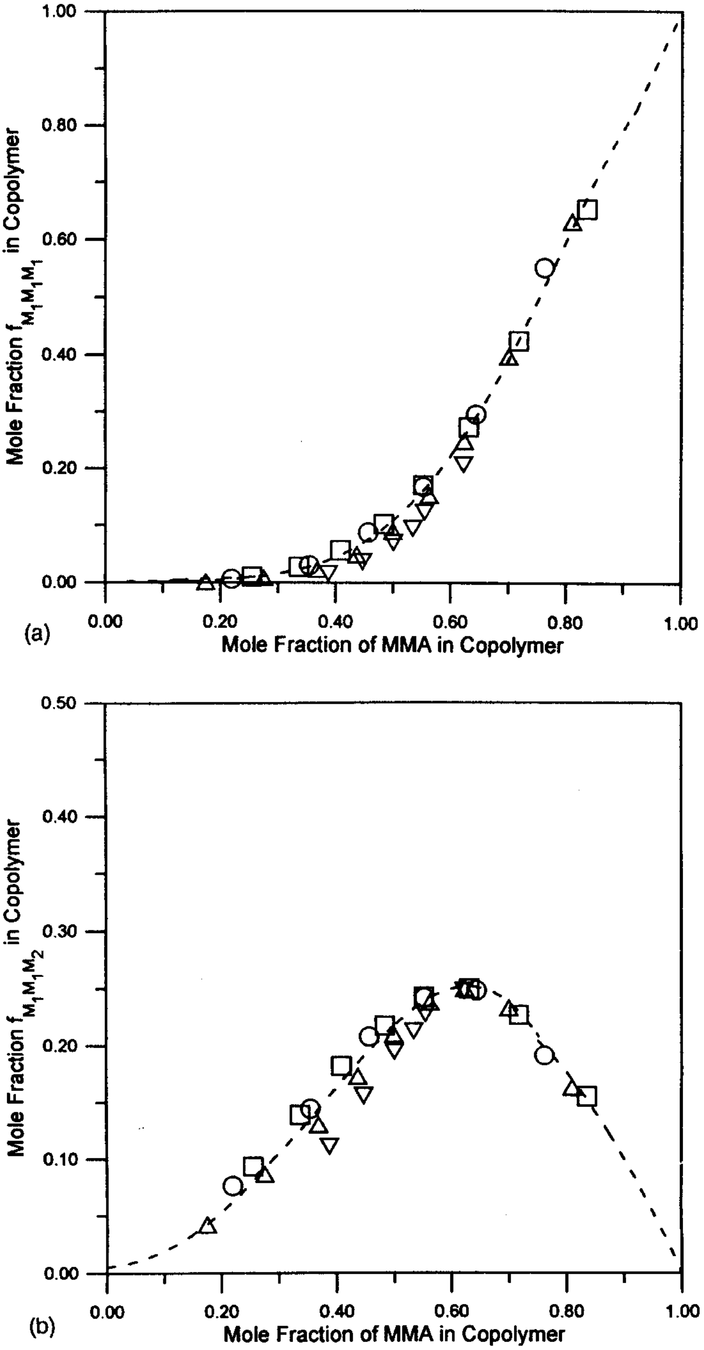
FIG. 1 Methyl methacrylate (M_1)-centered triad fractions for methyl methacrylate–styrene copolymer by San Román et al. [5,6]. Reaction medium: (□ bulk, (○) benzene, (△) chrorobenzene, (▽) benzonitrile. Dashed lines are polynomial curves fitting data for all solvent used. (a) Methyl methacrylate (M_1)-centered triad fraction $f_{M_1M_1M_1}$. (b) Methyl methacrylate (M_1)-centered triad fraction $f_{M_1M_1M_2}$. (c) Methyl methacrylate (M_1)-centered triad fraction $f_{M_2M_1M_2}$.

$$p(M_2/M_2) = \frac{k_{22}[PM_2^{\bullet}][M_2^0]}{k_{22}[PM_2^{\bullet}][M_2^0] + k_{21}[PM_2^{\bullet}][M_1^0]} = \left(1 + \frac{[M_1^0]}{r_2[M_2^0]}\right)^{-1}$$

where r_1 and r_2 are the reactivity ratios of M_1 and M_2, respectively; $[M_1^0]$ and $[M_2^0]$ are total monomer concentrations; $PM_1^{\bullet}$ and $PM_2^{\bullet}$ are macroradicals ending with monomer M_1 and M_2, respectively; $p(M_1/M_1)$, $p(M_1/M_2)$, $p(M_2/M_1)$, and $p(M_2/M_2)$ are conditional probabilities of the corresponding addition reaction to the growing macroradical [$p(M_2/M_1)$ means the conditional probability of addition of monomer 2 to a macroradical ending with monomer 1]. Particular M_1-centered triads were calculated by

$$f_{M_1M_1M_1} = p(M_1/M_1)^2$$
$$f_{M_1M_1M_2} = p(M_1/M_1)p(M_2/M_1)$$
$$f_{M_2M_1M_2} = p(M_2/M_1)^2$$

where $f_{M_1M_1M_1}$, $f_{M_1M_1M_2}$, and $f_{M_2M_1M_2}$ are M_1-centered triads in the copolymer chain.


1.00
0.80
0.60
0.40
0.20
0.00
Mole Fraction $f_{M_1M_1M_1}$ in Copolymer
0.00
0.20
0.40
0.60
0.80
1.00
(a)
Mole Fraction of MMA in Copolymer
0.50
0.40
0.30
0.20
0.10
0.00
Mole Fraction $f_{M_1M_1M_2}$ in Copolymer
0.00
0.20
0.40
0.60
0.80
1.00
(b)
Mole Fraction of MMA in Copolymer

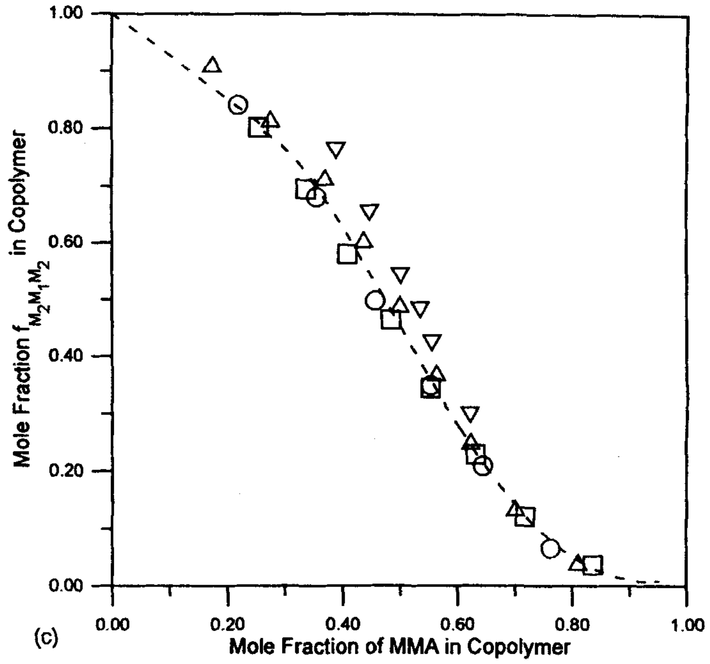


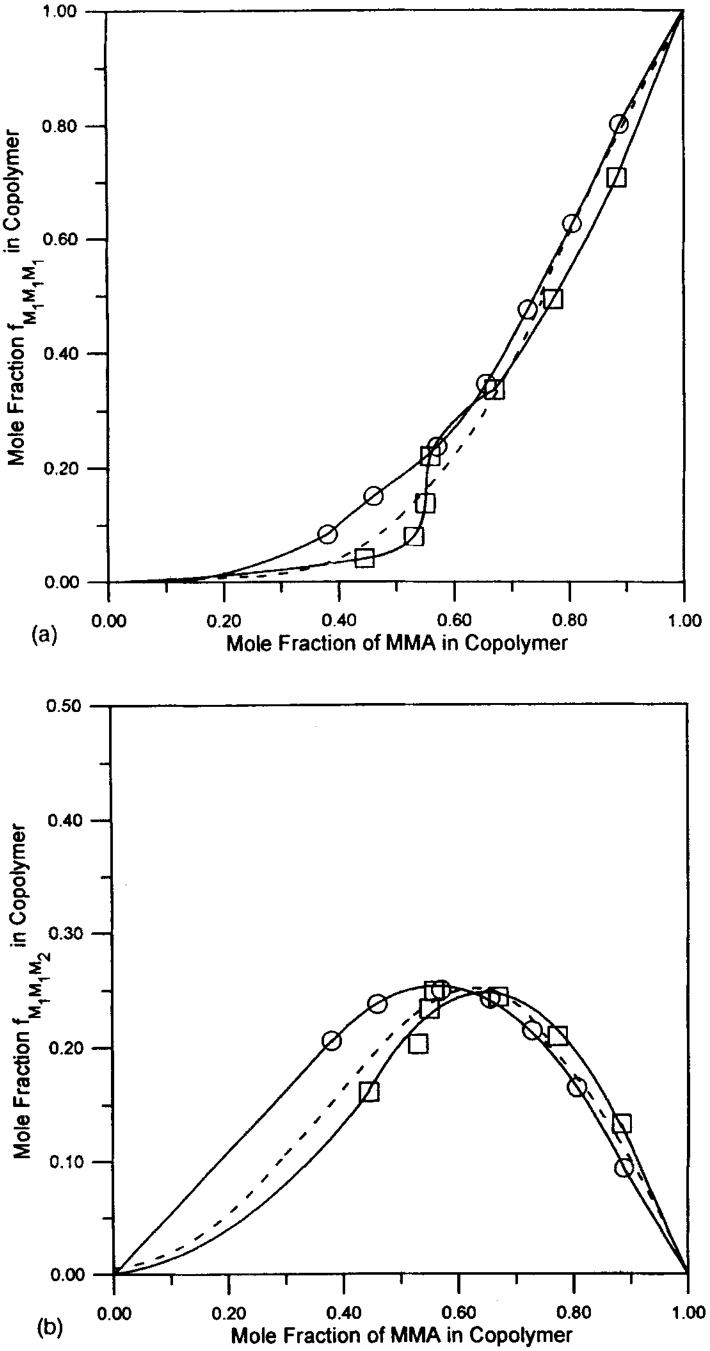
FIG. 2. Methyl methacrylate (M_1)-centered triad fractions for methyl methacylate-styrene copolymer by Ito et al. [7]. Reaction medium: (□) benzene, (○) benzonitrile, (△) benzyl alcohol, (▽) phenol. Dashed lines are polynomial curves taken for comparison from Figs. 1(a-c). (a) Methyl methacrylate (M_1)-centered triad fraction $f_{M_1M_1M_1}$. (b) Methyl methacrylate (M_1)-centered triad fraction $f_{M_1M_1M_2}$. (c) Methyl methacrylate (M_1)-centered triad fraction $f_{M_2M_1M_2}$.

In Figs. 1(a-c), 2(a-c), and 3(a-c) the compositional mole fractions of MMA-centered triads are plotted as a function of MMA in the copolymers obtained by San Román et al., by Ito et al., and by us, respectively.

From the data shown in Figs. 1(a-c) it is clear that copolymers of the same composition, irrespective of the solvent used during polymerization, have the same microstructure. In Figs. 1(a-c) the dashed lines are polynomial curves fitting data for all solvent used by San Román et al. [5, 6]. This finding, which refers to the work of San Román et al. [5, 6], was previously reported by Davis [2] who reexamined the results of San Román using data originally calculated by the Fineman-Ross method.

In Figs. 2(a-c) the compositional mole fractions of the MMA-centered triads are plotted as a function of MMA in the copolymers obtained by Ito et al. [7] and are compared with polynomial curves from Figs. 1(a-c). It is shown that despite some differences in r-values for benzene and benzonitrile (see Table 1), the molar fractions of MMA triads in the copolymers obtained by Ito et al. in these solvents lay on the lines from Figs. 1(a-c) while the data for benzyl alcohol and phenol solvents differ distinctly.

Finally, we compared the microstructure of polyMMA obtained in the presence of pure methyl cyanoacetate and in a methyl cyanoacetate/benzene mixture in


(a)
Mole Fraction $f_{M_1M_1M_1}$ in Copolymer
Mole Fraction of MMA in Copolymer
0.00
0.20
0.40
0.60
0.80
1.00
(b)
Mole Fraction $f_{M_1M_1M_2}$ in Copolymer
Mole Fraction of MMA in Copolymer
0.00
0.10
0.20
0.30
0.40
0.50

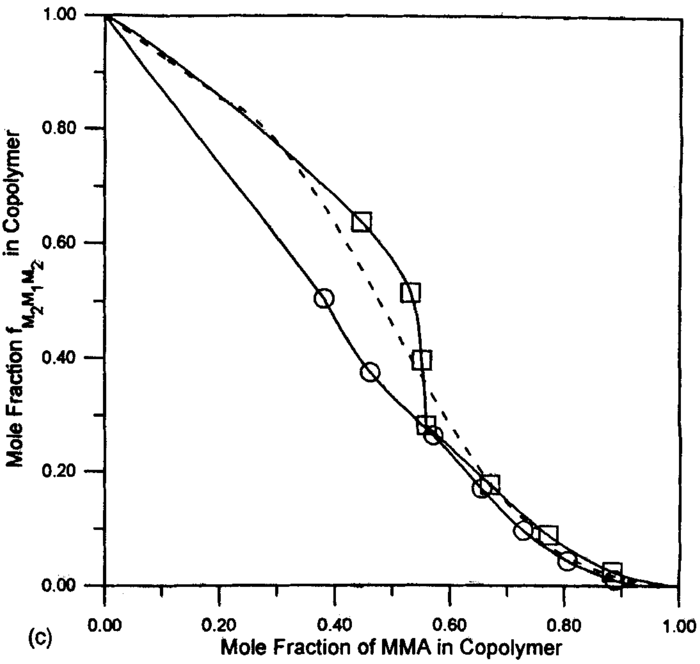


FIG. 3. Methyl methacrylate (M_1)-centered triad fractions for methyl methacrylate–styrene copolymer by Talpur et al. [3]. Reaction medium: (□) methyl cyanoacetate, (○) methyl cyanoacetate/benzene mixture (1:1.16 by volume). Dashed lines are polynomial curves taken for comparison from Fig. 1(a–c). (a) Methyl methacrylate (M_1)-centered triad fraction $f_{M_1M_1M_1}$. (b) Methyl methacrylate (M_1)-centered triad fraction $f_{M_1M_1M_2}$. (c) Methyl methacrylate (M_1)-centered triad fraction $f_{M_2M_1M_2}$.

the absence of a conventional free-radical initiator [3] with the plots of Figs. 1(a–c) (Figs. 3a–c). The comparison shows that the content of MMA-centered triads differs significantly from the comparative data from Figs. 1(a–c).

The above results lead to the belief that the "bootstrap model" has some limitations as a successful explanation of solvent effects in the methyl methacrylate–styrene system.

It should be emphasized that insufficient accuracy of the experimental data used for the calculation of the relative concentrations of monomer unit sequences in the copolymer cannot be the origin for the observed effect. Reactivity ratios used for calculation of the triad sequences were generated with the EVM method by using random errors of 5 and 1% for the monomer feed composition and copolymer composition, respectively [3]. The error in the composition configurations of the copolymer obtained by San Román et al. [11], which have been used by us for comparative calculation of the compositional mole fractions of MMA-centered triads, was not estimated. However, the precision of the measurement of the peaks areas in the ^{1}H-NMR spectroscopy used by San Román et al. [11] was probably about 5%. This same precision was estimated by Maxwell et al. [12] for their ^{1}H-NMR measurements of the microstructure of the styrene–methyl methacrylate copolymer.

By taking into account the shapes of the curves formed by the data obtained from the calculation of the triads and the data points scattering presented in Figs. 1-3, we conclude that the experimental errors cannot have a significant influence on the final conclusion.

We found only one paper in the literature showing the deviation of the methyl methacrylate-styrene system from the "bootstrap model." San Román et al. [11] reported without explanation that the very high (total) conversion in suspension polymerization has a significant influence on both the sequence composition and the stereochemical configuration of methyl methacrylate-styrene copolymers. We recently showed [13] that in copolymerization of the methyl methacrylate-acrylamide system performed in solvent by Orbay et al. [14] with conversion up to 75%, the high conversion did not influence the calculated sequence composition of the polymer obtained. In order to interpret the influence of the conversion on the microstructure of the copolymer, new experimental results are needed because the data now available refer to different monomer systems and report nonequal degrees of conversion and different solvent conditions. (In the case of suspension polymerization done by San Román et al., no solvent was present in the chain-growing site.)

What, then, are the reasons for the more or less pronounced failure of the "bootstrap model" in the case of a methyl methacrylate-styrene system polymerized in the presence of benzyl alcohol, phenol, and methyl cyanoacetate? The discrimination of the terminal model of copolymerization for the calculation of the conditional probabilities probably cannot be the reason, because the result of recent discussions about the applicability of terminal and penultimate models to the methyl methacrylate-styrene system concluded that the monomer system behaves according to the Mayo-Lewis terminal copolymerization model with respect to the composition as well as to the microstructure of the copolymer [15-17]. It is possible, however, that in the case of some complexing solvents like benzyl alcohol, phenol, and methyl cyanoacetate, organic compounds with active H-atom become attached to the electron-withdrawing atom or group, such as oxygen atom, carbonyl group, or/and cyano group, so some of the new complex participation models in radical polymerization [18, 19] should be used for calculation of the reactivity ratios. Ito et al. suggest in their work [7] that the polarized structure ($>C^{+}-O^{-}$) of methyl methacrylate monomer becomes more important, enhancing its reactivity as the solvent becomes more protic. Among the solvents investigated by Ito et al., phenol was considered to be the most protic, which corresponds to the greatest deviation of the microstructure of copolymer obtained in phenol from the copolymer presented in Figs. 1(a-c) (Figs. 2a-c). The effect described above probably influences the microstructure of the copolymer much more when the copolymerization reaction is not conventionally initiated as in the case of the reaction performed in the presence of methyl cyanoacetate (Figs. 3a-c). We assume that the compositional mole fractions of MMA-centered triads are especially strongly influenced when they are produced from MMA molecules complexed with methyl cyanoacetate in the absence of conventional free-radical initiators. This means that MMA molecules complexed with methyl cyanoacetate take part in the copolymerization reaction comparatively more often when compared with the conventional free-radical-initiated copolymerization of MMA with the simultaneous presence of the complexing agent and a conventional free-radical initiator. Results published in our previous paper seem to support these ideas [20]. The chain-transfer constants to the monomer, solvent, and initiator have been evaluated as $C_M = 1.1 \times 10^{-3}$, $C_I = 2.2 \times 10^{-4}$, $C_S = 1.8 \times 10^{-4}$, respectively. The chain-transfer constants of the poly(MMA) radical with monomer during free-radical-initiated polymerization in bulk, ethyl methyl ketone, ethyl acetate, and benzene as calculated by Gopalan et al. [21] were 0.33×10^{-4}, 0.60×10^{-4}, 0.27×10^{-4}, and 0.70×10^{-4}, respectively. We interpreted the very high C_M value in systems containing compounds with active H-atoms in terms of the increased reactivity of the MMA molecules complexed with an organic compound with an active H-atom, like cyclohexanone, toward the chain-transfer reaction.

In conclusion, it can be said that the accuracy of the "bootstrap model" for describing the solvent effects in a copolymerization reaction probably depends on the nature of the monomer–solvent interactions in the reaction system.

CONCLUSION

The methyl methacrylate–styrene system in pure methyl cyanoacetate and in a methyl cyanoacetate/benzene mixture was examined by testing the theoretical calculations of the "bootstrap model" for the solvent effect in the copolymerization of the system. Results were compared with calculations performed for data in the literature for the free-radical-initiated polymerization of the monomer system. From the relative concentrations of monomer unit sequences in the copolymer it was concluded that the active H-atom in solvents like methyl cyanoacetate, benzyl alcohol, and phenol can lead to failure of the "bootstrap model" as a description of the methyl methacrylate–styrene monomer system.

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