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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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To cite this Article Talpur, Mir Munsif Ali and Kaim, Andrzej(1994) 'Investigation of Methyl Methacrylate-Styrene Copolymerization System in the Presence of Methyl Cyanoacetate', *Journal of Macromolecular Science, Part A*, 31: 5, 535 – 541

To link to this Article: DOI: 10.1080/10601329409349736

URL: <http://dx.doi.org/10.1080/10601329409349736>

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INVESTIGATION OF METHYL METHACRYLATE-STYRENE COPOLYMERIZATION SYSTEM IN THE PRESENCE OF METHYL CYANOACETATE

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ABSTRACT

The copolymerization of the methyl methacrylate-styrene system was studied at 75°C in the absence of any free radical initiator in pure methyl cyanoacetate (MCA) and in a methyl cyanoacetate/benzene mixture. The reactivity ratios were calculated by the YBR and EVM methods. An increasing dielectric constant of the reaction medium influenced the reactivity ratios and enhanced the alternating tendency of monomers in a copolymer. A comprehensive comparative study of the *r*-parameters achieved for these copolymer systems with the reactivity coefficient values for the same monomer system initiated by free radical initiators and with those obtained for thermal bulk in pure cyclohexanone and in a cyclohexanone/cyclohexane mixture are presented. It was found that the initiating activity of MCA closely resembles those of free radical initiators. The specific interactions of methyl methacrylate monomer and methyl cyanoacetate are explained by the facts that the reactivity ratios obtained for the monomer system in the presence of methyl cyanoacetate are in reasonable agreement with the data reported in the literature for the same monomer system initiated by conventional free radical initiators. In the absence of any radical initiator, copolymerization of the monomer system does not proceed in highly polar and nonpolar solvents

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containing no mobile hydrogen atom. By increasing the concentration of methyl methacrylate in the monomer feed and/or by increasing the concentration of methyl cyanoacetate, the reaction rate is also increased.

INTRODUCTION

The radical homopolymerization of polar vinyl monomers in the presence of active compounds containing acid hydrogen atom has been subject of many publications [1-7]. It has been reported that ethyl cyanoacetate can initiate the polymerization of methyl methacrylate (MMA) without the use of any conventional free radical initiator [8].

The mechanism of the reaction involving transfer of a hydrogen radical abstracted from an active compound to a monomer was originally proposed by Ouchi et al. [3-5] for the polymerization of MMA initiated with aldehydes and later discussed for MMA polymerization started by cyclohexanone still remains uncertain for several reasons. For example, the so-called thermal polymerization problem of MMA systems is still being discussed [9, 10]. The proof of the mechanism as obtained from electron paramagnetic resonance (e.p.r.) investigations performed by Sato [2] and Ouchi [5] seems to be indecisive [11]. Moreover, we suspect that compounds with acid hydrogen atoms can undergo some thermal transformations which liberate radicals which can then initiate polymerization, e.g., the thermal radical self-condensation of cyclohexanone [12].

Very recently we have been studying [13] the initiating activity of these hydrogen compounds in copolymerization reactions in the absence of any conventional initiator. In this paper we discuss the reactivity ratios of the methyl methacrylate-styrene copolymerization system in the presence of methyl cyanoacetate (MCA).

EXPERIMENTAL

Pure grade methyl cyanoacetate (Aldrich Chemie) was dried over molecular sieves type 3Å and distilled twice at reduced pressure in a dry, oxygen-free nitrogen atmosphere. The middle portion of distillate was taken for use.

Benzene was purified [14] by shaking it with concentrated H_2SO_4 acid until free from thiophene. It was washed with distilled water, then with a dilute (10%) aqueous solution of sodium hydroxide, and again washed several times with distilled water. Benzene was then dried over molecular sieves type 3A for 72 hours. It was distilled under a dry oxygen-free nitrogen stream after refluxing for 3 hours at 79°C. The middle part of the distillate was taken for use and kept under oxygen-free nitrogen in a dark bottle.

Purification of monomers as well as the procedures for polymerization and copolymer composition analysis were described previously [13]. Conversion was kept below 8% of the total monomer weight.

RESULTS AND DISCUSSION

Copolymer composition data for the methyl methacrylate-styrene system in different solvents are listed in Table 1 together with the corresponding weight-% conversion.

Methyl methacrylate-styrene copolymer composition curves as a function of monomer feed are shown in Fig. 1 and refer to methyl cyanoacetate and methyl cyanoacetate/benzene (1:1.16 by volume) solutions.

For comparison, we show some earlier results [13] for the same comonomer system in cyclohexanone and a cyclohexanone/cyclohexane mixture (1:1.16 by volume). For the present work we employed benzene as the neutral solvent instead of cyclohexane. This choice was affected by the fact that cyclohexane is immiscible with methyl cyanoacetate. Furthermore, the dielectric constants of benzene ($\delta^{20} = 2.28$) and cyclohexane ($\delta^{20} = 2.02$) are very close [14].

The analytical data were used to determine the reactivity ratios for methyl methacrylate (r_1) and styrene (r_2) by the Yezielev, Brokhina, and Roskin method (YBR method) [15] and the error-in variable model method (EVM method) [16], as shown in Table 2. Reactivity ratios were generated using random errors of 5 and 1% for the monomer feed composition and copolymer composition, respectively, with the EVM method.

Although the methods employed gave somewhat different values for r_1 and r_2 , it is evident that the direction of change with changing reaction media is the same (Table 2). For example, increasing tendency for both r_1 and r_2 increased when the solvent was changed from pure methyl cyanoacetate ($\delta^{20} = 29.30$) [14] to methyl cyanoacetate/benzene (see the discussion below).

The reactivity ratios obtained for the copolymerization of the MMA-St system in pure methyl cyanoacetate agree well with data given in the literature [17] for free radical initiated copolymerization in a polar solvent.

The r -parameters could not be found in the literature for the conventional free radical copolymerization of the monomer system in mixed solvents. However, for the same system in dioxane initiated with aliphatic aldehydes, the reported r_1 and r_2 values are in the 0.51–0.59 and 0.46–0.53 ranges, respectively [5]. The reactivity ratio for styrene (r_2) in the MCA/benzene (1:1.16 by volume) mixture is in excellent agreement with most of the data given in the literature [17–22, 24] for the free radical copolymerization of the MMA-St system in inert solvents. However, the reactivity coefficient for MMA (r_1) is higher than what is reported for the free radical copolymerization system [17–22, 24] or when compared with thermal bulk copolymerization or when MCA is used in the absence of a conventional free radical initiator. Thus, variation of the reactivity ratios caused by changing the reaction medium can be interpreted as dependent on the dielectric constant of the reaction medium. It is well known that the reactivity ratios for the free radical initiated copolymerization of methyl methacrylate and styrene can be correlated with the variation in the dielectric constant of the solvent [17, 23, 24].

Thus, the r -parameters calculated by the older YBR method as well as by the more reliable and recent EVM method for systems with pure MCA become smaller, particularly r_2 . As seen in Table 2, the same result was observed by using cyclohexanone [13] instead of MCA. For both MCA and cyclohexanone the $r_1 r_2$ product is always smaller when compared with bulk thermal copolymerization. Thus, the

TABLE 1. Copolymerization of Methyl Methacrylate (M_1) and Styrene (M_2) at 75°C

Mole fraction in feed		Copolymerization of MMA (M_1) with St (M_2) in the presence of methyl cyanoacetate/benzene (1:1.16 by volume) mixture		Copolymerization of MMA (M_1) with St (M_2) in the presence of methyl cyanoacetate		Copolymerization of MMA (M_1) with St (M_2) in the presence of methyl cyanoacetate				
M_1	M_2	Reaction time, minutes	Conversion, wt%	Reaction time, minutes	Conversion, wt%	Reaction time, minutes	Conversion, wt%			
		Results of elemental analysis of copolymer		Results of elemental analysis of copolymer		Results of elemental analysis of copolymer				
		Carbon, %	Hydrogen, %	Carbon, %	Hydrogen, %	Carbon, %	Hydrogen, %			
		Mole fraction of M_1 in copolymer		Mole fraction of M_1 in copolymer		Mole fraction of M_1 in copolymer				
0.90	0.10	120	7.263	63.81	7.72	0.883	4.463	63.655	7.781	0.888
0.80	0.20	240	3.452	67.50	7.91	0.772	3.275	66.395	7.692	0.805
0.70	0.30	240	3.447	70.83	7.71	0.670	2.341	68.935	7.841	0.728
0.60	0.40	480	3.791	74.15	7.68	0.558	2.455	71.330	7.885	0.655
0.50	0.50	480	3.462	74.73	7.23	0.550	2.040	73.985	7.815	0.570
0.40	0.60	540	2.433	75.47	7.16	0.530	2.196	77.622	7.811	0.460
0.30	0.70	540	2.179	78.16	7.21	0.444	1.783	80.211	7.625	0.380

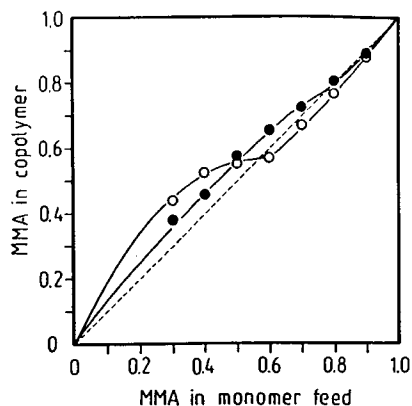


FIG. 1. Copolymerization of methyl methacrylate (r_1) and styrene (r_2) at 75°C. Reaction medium: (O) methyl cyanoacetate; (●) methyl cyanoacetate/benzene mixture (1:1.16 by volume).

alternating tendency of a copolymer produced in the presence of two compounds containing acid hydrogen atoms is much more pronounced when compared with bulk thermal copolymerization. This statement is valid regardless of the method used for r -parameters calculation. The growing alternating tendency of a copolymer is due to enhancement by polar solvents of the oppositely polarized form of both monomers at the growing ends of the copolymer chain (Bonta et al. [24] and the references therein). In our case the relative diminution of the r_2 (St) value in comparison to the r_1 (MMA) value can be attributed to the incapability of styrene to interact strongly with methyl cyanoacetate (or cyclohexanone). The kinetic consequences of this is that no homopolymerization of styrene in the presence of cyclohexanone has been noted [6].

TABLE 2. Reactivity Ratios of Methyl Methacrylate (r_1) and Styrene (r_2) Polymerized in Different Media at 75°C

Reaction medium	YBR method		EVM method	
	r_1	r_2	r_1	r_2
Thermal in bulk	0.67 ± 0.03	0.52 ± 0.02	0.78	0.55
Cyclohexanone/ cyclohexane mixture (1:1.16 by volume)	0.74 ± 0.01	0.50 ± 0.02	0.92	0.59
Cyclohexanone	0.56 ± 0.00	0.26 ± 0.10	0.73	0.33
Methyl cyanoacetate/ benzene mixture (1:1.16 by volume)	0.86 ± 0.01	0.48 ± 0.02	0.95	0.55
Methyl cyanoacetate	0.68 ± 0.03	0.30 ± 0.05	0.59	0.26

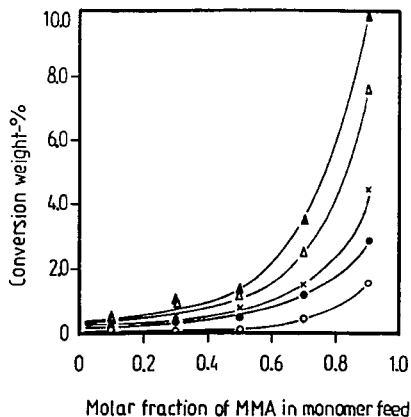


FIG. 2. Conversion of copolymerization of methyl methacrylate and styrene vs mole fraction of MMA in monomer feed at 75°C, reaction time 4 hours, in the presence of different concentrations of methyl cyanoacetate (MCA). [MCA] = 0 mol·dm⁻³, no copolymer. (○) [MCA] = 0.09 mol·dm⁻³, (●) [MCA] = 0.26 mol·dm⁻³, (×) [MCA] = 0.44 mol·dm⁻³, (△) [MCA] = 0.61 mol·dm⁻³, (▲) [MCA] = 0.79 mol·dm⁻³.

Partial replacement of a polar solvent by an inert solvent increases the reactivity ratio of both monomers to some extent. This effect, previously observed by Fujihara et al. [18], is probably due to the fact that an inert solvent like benzene or cyclohexane lowers the polarity of the reaction medium. This can be considered as another aspect of the r -parameters dependence on the polarity of solvents, as discussed by Bonta et al. [24].

The rate of copolymerization decreases when methyl cyanoacetate is replaced by benzene, as illustrated in Fig. 2. It is evident from Fig. 2 that only the simultaneous presence of methyl methacrylate monomer and methyl cyanoacetate in the reaction mixture starts the copolymerization reaction. Furthermore, we determined previously [13] that at the same temperature and concentrations, the present comonomer system did not undergo a copolymerization reaction in the absence of a free radical initiator, be it nonpolar (e.g., benzene and cyclohexane) or highly polar (e.g., benzonitrile) solvents. This is because these solvents do not dispense any mobile hydrogen atom.

Thus, it is concluded that the specific type of interaction between methyl methacrylate and methyl cyanoacetate involving hydrogen radical transfer from the molecule with a mobile hydrogen atom to the monomer molecule, as discussed previously [3–6], can be one of the primary radical sources in the copolymerization reaction.

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Received July 16, 1993