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Radical Copolymerization of Acrylic Monomers. II. Effect of Solvent on Radical Copolymerization of Methyl Methacrylate and Styrene

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ABSTRACT

The influence of various solvents on the copolymerization behavior of methyl methacrylate with styrene has been investigated. In these systems there is a significant solvent effect on both r_S and r_M which may be attributed to changes in the dielectric constant of the solvents used. The calculated relative reactivity of the polystyryl radical towards the methyl methacrylate monomer increases with increasing solvent polarity, whereas the reactivity of poly(methyl methacrylate) radical towards styrene monomer decreases. The results obtained are discussed taking into account the behavior of both monomers in homopolymerization with the same experimental conditions as in copolymerization.

INTRODUCTION

Some recent papers [1, 2] at variance with earlier reports in the literature [3, 4], show an appreciable effect of the reaction medium on the reactivity ratios for the pair methyl methacrylate-styrene.

In the same way, a great number of papers described the effect of solvent on radical copolymerization of nonionizable pairs [5-23]. Several interpretations have been proposed to explain the variation of the reactivity ratios with the reaction medium: changes in monomer reactivity, enhanced form of chain growing radical solvation in the transition state and monomer association in solution.

In the present paper we refer to the influence of solvent on the reactivity ratios for the pair methyl methacrylate-styrene as copolymerized at 60°C. The solvents used were benzene, chlorobenzene, and benzonitrile.

EXPERIMENTAL

Materials

Purification of styrene and methyl methacrylate were carried out by conventional methods.

Benzene, chlorobenzene, and benzonitrile were purified by appropriated chemical methods [24]. The solvents were freshly distilled immediately prior to use.

2,2'-Azobisisobutyronitrile (AIBN) was purified as described previously [25].

Copolymerization

All experiments were performed in glass ampoules covered by aluminum foil. Copolymerization were conducted at $60 \pm 0.1^\circ\text{C}$ under high vacuum. The required volumes of solvent, initiator, and monomers were added to the glass ampoules and the mixtures were degassed by successive freeze-pump-thaw cycles. Monomer and initiator concentrations were 3 mole/liter and 0.3 mole % of the total monomer concentration, respectively. Polymer conversion were kept lower than 6 weight %.

The resulting copolymer were isolated by pouring the content of the glass ampoules into methanol containing hydroquinone. The precipitated materials were purified by reprecipitation from benzene-methanol system and then filtered and dried under vacuum at 50°C to constant weight.

Copolymer Analysis

Copolymer composition was determined by elemental analysis by using a Perkin-Elmer elemental analyzer, model 240.

TABLE 1. Composition (as Mole Fraction of Styrene F_S) and Conversion of Styrene-Methyl Methacrylate Copolymers Prepared in Various Solvents at 60°C

Solvent	f_S (feed)	Conversion (weight %)	F_S (copolymer)	
			Carbon analysis	NMR spectra
Benzene	0.800	5.08	0.741	0.732
	0.700	5.06	0.638	0.652
	0.600	5.08	0.570	0.573
	0.500	5.20	0.514	0.514
	0.400	4.97	0.446	0.449
	0.300	4.73	0.373	0.378
	0.200	4.87	0.307	0.284
Chlorobenzene	0.800	4.37	0.708	0.709
	0.700	4.48	0.652	0.616
	0.600	4.59	0.569	0.570
	0.500	4.62	0.494	0.486
	0.400	4.37	0.427	0.431
	0.300	4.43	0.359	0.360
	0.200	4.34	0.264	0.274
Benzonitrile	0.800	4.96	0.686	0.715
	0.700	5.19	0.597	0.616
	0.600	5.20	0.530	0.551
	0.500	5.47	0.472	0.462
	0.400	5.34	0.379	0.403
	0.300	5.27	0.315	0.326
	0.200	5.17	0.249	0.249

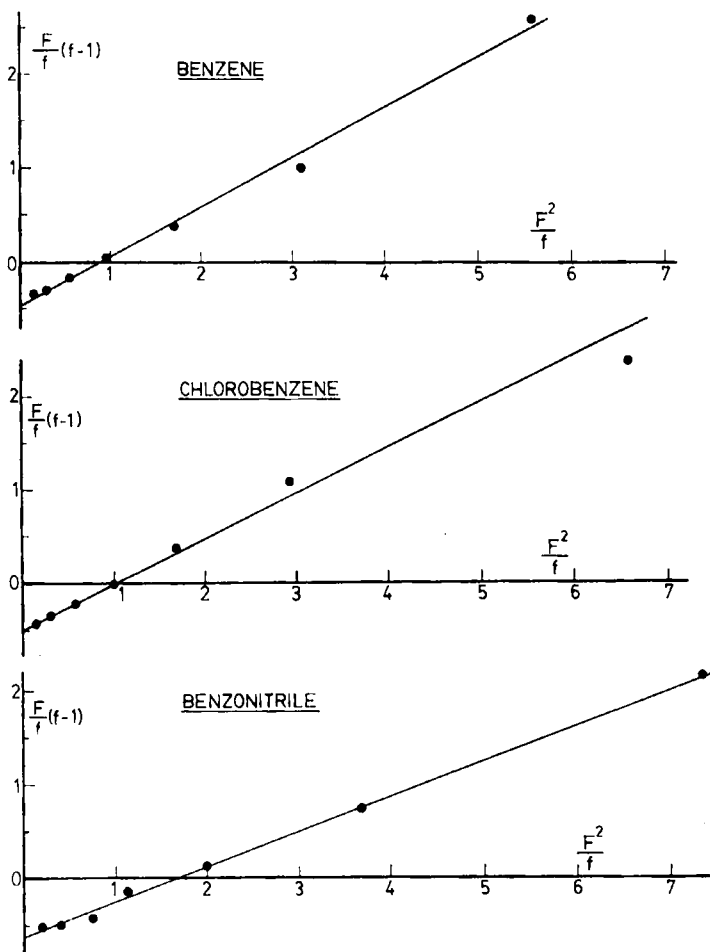


FIG. 1. Fineman-Ross plots of composition results from copolymerization of styrene-methyl methacrylate in benzene, chlorobenzene, and benzonitrile.

TABLE 2. Reactivity Ratios for Copolymerization of Styrene and Methyl Methacrylate in Various Solvents at 60°C

Solvent	r_S	r_M
Benzene	0.52 ± 0.03	0.47 ± 0.04
Chlorobenzene	0.48 ± 0.05	0.50 ± 0.03
Benzonitrile	0.38 ± 0.02	0.62 ± 0.03

¹H-NMR spectroscopy was also used to determine the copolymer composition. The spectra were obtained at 60°C from about 8% solutions in deuteriochloroform for all copolymers by use of a Varian XL 100 spectrometer. Hexamethyldisiloxane was used as internal standard reference.

RESULTS AND DISCUSSION

The copolymer compositions (as mole fraction of styrene) are shown in Table 1 with the corresponding weight % conversions. These analytical data were used to determine r_S and r_M by the Fineman-Ross method [26]; the corresponding plots are shown in Fig. 1 and the values of r_S and r_M are given in Table 2. The errors were derived from standard deviations in the slopes and the intercepts of the straight lines obtained by the Fineman-Ross method.

The monomer feed composition practically does not change during the copolymerization time irrespective of the solvent used; nevertheless from the data of Table 1 it follows that all the solvents used in the copolymerization experiments affect the copolymer composition.

Both reactivity ratios change with the solvents, but the variations observed for methyl methacrylate and for styrene are reversed, that is, r_M increases while r_S decreases when the solvent dielectric constant increases.

The polarity of the solvent has been considered by Ito and Otsu [1] to explain the observed variations of the reactivity ratios in the copolymerization of methyl methacrylate and styrene. These authors suggest the polarized structure of methyl methacrylate monomer to become important in the transition state when the solvent polarity increases. On the other hand, the variations of the reactivity ratios in the copolymerization of the above mentioned monomers have been claimed by Bontà and al. [2] to result from the enhancement of polarized forms of the growing radicals by the polar solvents.

Cameron and al. [5] have pointed out that in the copolymerization of methacrylonitrile with styrene, the reactivity ratio of methacrylonitrile is a function of the solvent dielectric constant. They have suggested the polarity of the propagating methacrylonitrile radical to be sensitive to its environment.

Many other authors [16, 18, 19] in the study of the influence of solvent on the copolymerization of vinyl monomers have stated the physic phenomena of the formation of molecular aggregates and the polarization of the functional groups in the monomeric state. In this way, Bamford [27] in the radical copolymerization of methacrylonitrile and styrene have suggested that methacrylonitrile can form hydrogen bonds with high polar solvents like benzyl alcohol, giving rise to a decrease of the electronic density of the double bond so that the cross propagation coefficient should increase with decreasing r_S .

In a similar system, Guyot et al. [6] have found not only that the reactivity ratios change with solvent but also that the solvent concentration influences the reactivity ratios. They assumed the nitrile groups to be associated with dipolar bonds [27], and consequently the acrylonitrile can polymerize as a free monomer or in the associated form, depending on both the concentration and polarity of the solvent.

In a general sense, on treating the problem from a kinetic point of view, an effect of solvent on the reactivity ratios implies a change in the ratio k_{ii}/k_{ij} , where k_{ii} and k_{ij} are the rate coefficients for the addition of *i* and *j* monomers to growing *i* radicals, respectively. Variations in the propagation rate constants for the homopolymerization of styrene [29, 30] and methyl methacrylate [30-33] in several solvents have been described; the solvent effect was reported to be quite different for both monomers, as k_p was found to decrease or to increase depending on whether the polymerizing monomer is styrene or methyl methacrylate respectively.

In a previous paper [34] we have calculated the kinetic coefficients of radical homopolymerization for methyl methacrylate and styrene in benzene, chlorobenzene, and benzonitrile. The kinetic coefficients, shown in Table 3, were obtained by using the same monomer concentration as in the copolymerization experiments and its values were derived from dilatometric and viscometric data taking into account the North diffusion theory [35, 36] on the termination step.

The opposite effect of the solvent on the propagation rate constants of both monomers has been attributed to the different stability and reactivity of the complex between the growing radical and the solvent as compared to the reactivity of the growing chain towards the monomer [37-41] and the complexing polymer radical can be regarded as an enhanced form of the radical solvation by the monomer and/or the solvent. On the other hand the solvents change the thermodynamic kinetic parameters, which indicates enhancement of polarized

TABLE 3. Rate Coefficients for Methyl Methacrylate and Styrene Homopolymerizations Initiated by AIBN at 60°C in Various Solvents

Monomer	Solvent	$(k_p^2/k_t) \times 10^2$ (liter/ mole-sec)	$k_t \times 10^{-7}$ (liter/ mole-sec)	k_p (liter/ mole-sec)
Methyl methacrylate	Benzene	1.01	2.66	518.3
	Chlorobenzene	1.29	2.15	526.6
	Benzonitrile	2.40	1.59	617.7
Styrene	Benzene	5.56	8.2	213.5
	Chlorobenzene	7.93	6.7	230.5
	Benzonitrile	7.23	4.9	188.2

TABLE 4. Cross-Propagation Coefficients in the Styrene-Methyl Methacrylate Radical Copolymerization Initiated by AIBN at 60°C in Various Solvents

Solvent	k_{pSM}	k_{pMS}
Benzene	410.6	1102.8
Chlorobenzene	480.2	1053.2
Benzonitrile	495.3	996.3

forms of the growing radical in the transition state, although no charged species are directly involved in the propagation [2, 42]. Data shown in Table 3 clearly indicate that the methyl methacrylate radical is more reactive towards methyl methacrylate monomer when the solvent dielectric constant increases, contrary to what happens with the styrene radical, whose reactivity towards the styrene monomer decreases with the increasing dielectric constant of the solvent.

Data shown on Tables 2 and 3 enabled us to calculate the k_{ij} coefficients, which, as shown in Table 4, vary with the polarity of the solvent in reverse way depending on the growing radical.

Figure 2 shows the variation of $1/r_M$ and $1/r_S$ against the solvent

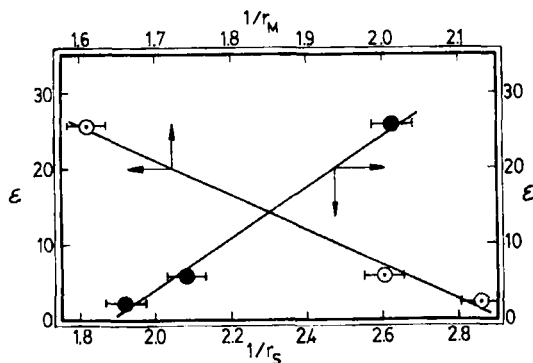


FIG. 2. Relative reactivity of poly(methyl methacrylate) and polystyryl radicals toward (○) styrene and (●) methyl methacrylate monomers, respectively, as a function of dielectric constant of the solvent.

dielectric constant. The obtained straight lines indicate that there is a direct correlation between the radical reactivity towards monomers and the solvent dielectric constant. These results are in good agreement with those obtained from homopolymerization studies reported in Table 3. The reactivity of polystyryl radicals towards the methyl methacrylate monomer increases with increasing solvent polarity, whereas the reactivity of poly(methyl methacrylate) radicals towards styrene monomer decreases.

Linear ratios between copolymerization parameters and solvent dielectric constants have been stated by Cameron and al. [5] and Bontà et al. [2] in the copolymerization of styrene with methacrylonitrile and methyl methacrylate, respectively. These authors have explained their results on the basis of the polarized forms of the growing radicals by the electron-donating or electron-withdrawing character of its functional groups.

However the observed variations of reactivity ratios do not have the same trend for the two systems above mentioned, and their results are dissimilar to those reported in this paper.

It is possible to state that the "complexing" radicals are involved in the propagation step. In this way propagation must involve three different radical species [43, 44]: uncomplexed macroradicals and macroradicals complexed with either solvent or monomer molecules.

In a previous paper [45], we studied the solvent effect in the radical copolymerization of a pair of acceptor monomers and the changes of reactivity ratios have been attributed to a simultaneous

k_{ii} increase and a k_{ij} decrease. In the same way variation of r_M with the solvent is due to a k_{PMM} increase and a k_{PMS} decrease, while donor monomer styrene shows an opposite trend and the variation of r_S with the solvent is due to a decrease in k_{PSS} and an increase in k_{PSM} when the polarity of the solvent increases.

Results reported in this paper can be related to those obtained from $^1\text{H-NMR}$ spectroscopy as published elsewhere [46], which enabled us to study the composition and the sequence stereochemical configuration in methyl methacrylate-styrene copolymers prepared in the solvents above mentioned. From these results we can state that the presence of the solvents in the radical copolymerization of methyl methacrylate and styrene not only affects the kinetics of the reaction but also modifies the composition and the stereochemical sequence configuration in the copolymers. It is noteworthy that the "coisotactic" stereochemical configuration of alternating SMS triads is favored by the increasing solvent polarity.

As we have pointed out above, the homopolymerization analysis has allowed us to state that the reactivity of the methyl methacrylate radical towards the methyl methacrylate monomer increases when the solvent dielectric constant increases, whereas the styrene radical diminishes its reactivity towards the styrene monomer. This fact is in connection with an increase of the methyl methacrylate homotriads when the solvent polarity increases, which we have verified from $^1\text{H-NMR}$ spectroscopy results [46].

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