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Solvent Effect in Radical Copolymerization of Methyl Methacrylate with Styrene

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SUMMARY

A study of the copolymerization of methyl methacrylate and styrene in monosubstituted benzenes such as benzene, benzonitrile, benzyl alcohol, and phenol was made at 60°C. It was found that the copolymerization parameters changed significantly with the polarity of solvents, and the relative reactivity of methyl methacrylate toward the polystyryl radical was correlated with the E_T values of solvents. These results and spectroscopic data suggest that in the transition state of this copolymerization the polarized structure ($\gt C^+-O^-$) of methyl methacrylate monomer became important, enhancing its reactivity, as the solvents became more protic.

INTRODUCTION

In previous papers, it was shown that the reactivities of alkyl acrylates [1], alkyl methacrylates [2], and nuclear-substituted phenyl methacrylates [3] toward the polymer radical are dependent on the polar nature of the substituents in their ester groups; this can be explained in terms of the effect of the ester substituents on the polarization of the carbonyl group. Actually, the differences in the spectroscopic data of the carbonyl band in these esters are small, but there are significant differences with regard to their substituents [4].

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Since the polarization of the carbonyl group is known to be sensitive to the nature of the solvents [5] used, it is interesting to compare the reactivity of methyl methacrylate monomer in radical copolymerizations in various solvents.

It is well known, however, that the solvent effect is not so significant in radical copolymerization [6]. For example, Lewis et al. [7] and Price and Walsh [8] indicated that there were no effects from solvents such as benzene, acetonitrile, and methanol on the radical copolymerization of styrene (M_1) and methyl methacrylate (M_2) at 60°C. Recently Nikolaev and Galperin [9] reported that the copolymerization parameters for the same system changed significantly in the presence of basic solvents such as pyridine and dimethyl sulfoxide.

The present paper deals with an example of the solvent effect on the radical copolymerization of methyl methacrylate with styrene in four kinds of monosubstituted benzenes.

EXPERIMENTAL

Materials

Methyl methacrylate and styrene were purified by the usual methods [10] and distilled under reduced pressure immediately before use. α, α'-Azobisisobutyronitrile (AIBN) was recrystallized twice in ethanol. Benzene, benzonitrile, benzyl chloride, and phenol were used after fractional distillation of these materials which were purified by ordinary methods [10].

Copolymerization

Copolymerizations were carried out in a sealed glass tube of about 30-ml capacity. The required amounts of comonomer, solvent, and initiator solution were placed in the polymerization tube. After being thoroughly degassed by repeated cycles of freezing and thawing, the tube was sealed off under vacuum. Then the tube was set in a thermostat maintained at 60°C to start the polymerization. After polymerization for a given time, the resulting copolymer was obtained by pouring the contents of the tube into a large amount of methanol. The copolymer thus obtained was purified by a reprecipitation method from a benzene-methanol system and dried under vacuum. Conversion attained was within ca. 6% with respect to the initial monomer concentration. The composition of the copolymer was determined by an elementary analysis of carbon, and the monomer reactivity ratio was calculated by the equation derived by Fineman and Ross [11].

Infrared Spectra

The carbonyl stretching frequency of methyl methacrylate was measured in various solvents using a Hitachi EPI-2 infrared spectrophotometer with a 100 η NaCl cell.

RESULTS AND DISCUSSION

Table 1 shows the results of copolymerization of styrene (M_1) with methyl methacrylate (M_2) initiated by AIBN (6.1×10^{-3} moles/liter) in benzene, benzonitrile, benzyl alcohol, and phenol at 60°C.

From Table 1 it can be seen that phenol does not act as terminator and the rate of copolymerization at the same monomer composition increases with an increased polar nature of solvents used. Similar results were obtained in the rate of homopolymerization of methyl methacrylate in these solvents (see Table 1). It was also found that the composition of the copolymers obtained at the same monomer mixture changed with the solvents.

The copolymerization parameters obtained are shown in Table 2, in which the r_1 and r_2 values reported by Price and Walsh [8] are also given. In this table, Alfrey-Price Q and e values for methyl methacrylate were calculated by assuming that those of styrene did not change with the nature of solvents used. From Table 2, it was noted that the copolymerization parameters changed significantly with the solvents, depending on the polar natures of the solvents, as was the case with the rates of copolymerization (see Table 1).

In previous papers [1-4], it was pointed out that the relative reactivities of alkyl acrylates and methacrylates toward the polystyryl radical increased with the increasing polar nature of their ester substituents, i.e., their reactivities increased as the carbonyl group became more polar ($\gt C^{+}—O^{-}$) as a result of the introduction of electron-attracting ester substituents. These considerations were also supported by the spectroscopic data [4].

The results of Table 2 might also be explained in terms of the same consideration. Spectroscopic data of styrene and methyl methacrylate are shown in Table 3, which also gives data for methyl acetate. From this table, the vinyl stretching frequency in styrene is not shifted with the solvents, but the carbonyl stretching frequencies in methyl methacrylate and also in methyl acetate are shifted to shorter wave numbers as the solvent polarity increases. These results coincide with those observed for some aldehydes, ketones, and esters by several workers [12].

The relationship between the relative reactivity of methyl methacrylate toward the polystyryl radical and the polarities of the solvents used is shown in Fig. 1, in which the E_T values [13] of

Table 1. Copolymerization of Styrene (M_1) with Methyl Methacrylate (M_2) in Various Solvents at 60°C

Solvents[a]	$[M_2]$ in comonomer, mole %	Time, min	Conversion, %	Carbon in copolymer, %	$[M_2]$ in copolymer mole %
Benzene	0.0	45	1.7	92.04	0.0
	20.0	55	2.1	84.05	25.5
	30.0	55	1.8	81.46	33.6
	40.1	55	1.8	79.17	40.8
	50.1	55	2.0	76.75	48.3
	60.1	55	2.2	74.52	55.2
	70.0	55	2.5	71.98	63.1
	80.0	55	3.0	69.18	71.7
	90.0	55	4.0	65.26	83.6
	100.0	45	7.1	59.77	100.0
Benzonitrile	0.0	30	1.3	92.04	0.0
	15.1	30	1.3	84.97	21.9
	29.4	30	1.3	80.62	35.4
	45.1	30	1.5	77.31	45.6
	57.6	30	1.6	74.22	55.2
	70.0	30	1.8	71.29	64.3
	85.0	30	2.6	67.44	76.2
	100.0	30	6.2	59.77	100.0
Benzyl alcohol	0.0	45	2.4	92.04	0.0
	9.9	35	1.9	86.61	17.4
	20.0	35	2.0	83.44	27.5
	30.0	35	2.1	80.44	36.8
	40.1	35	2.2	78.29	43.6
	50.1	35	2.2	76.26	49.9
	60.1	35	2.5	74.21	56.2
	70.0	35	2.7	72.24	62.3
	80.0	35	3.1	69.72	70.0
	90.1	35	4.2	66.11	81.0
	100.0	45	10.9	59.77	100.0
Phenol	0.0	170	4.8	92.04	0.0
	29.0	75	6.4	79.89	38.7
	40.0	75	7.1	77.96	44.6
	50.1	75	7.1	76.24	50.0
	55.3	70	7.1	75.10	53.4
	60.1	70	5.8	74.50	55.4
	70.0	70	6.7	72.71	62.2
	100.0	60	8.5	59.77	100.0

[a] In all cases, the solvent was used at 50 vol. %.

Table 2. Copolymerization Parameters for Styrene (M_1) and Methyl Methacrylate (M_2) in Various Solvents at 60°C: [AIBN] = 6.1×10^{-3} moles/liter

Solvents	r_1	r_2	$1/r_1$	Q_2	e_2
Benzene	0.57 ± 0.032	0.46 ± 0.032	1.75	0.70	0.36
Benzene[a]	0.54 ± 0.04	0.42 ± 0.10	1.85	–	–
Benzonitrile	0.48 ± 0.045	0.49 ± 0.045	2.08	0.78	0.42
Acetonitrile[a]	0.44 ± 0.08	0.50 ± 0.04	2.27	–	–
Benzyl alcohol	0.44 ± 0.054	0.39 ± 0.054	2.27	0.78	0.53
Phenol	0.35 ± 0.024	0.35 ± 0.024	2.86	0.90	0.65

[a] Data of Price and Walsh [8].

Table 3. Solvent Effect in Infrared Spectra of Styrene and Methyl Methacrylate[a]

Solvent	Styrene C=C	Methyl methacrylate C=C	Methyl methacrylate C=O	Methyl methacrylate C–O	Methyl acetate C=O
n-Heptane	1629	1639	1730	1162	1754
Benzene	1629	1636	1722	1162	1754
Chloroform	1629	1636	1717	1167	1736
Tetrachloroethane	–	1637	1715	1169	1736
None	–	1639	1725	1166	–

[a] All units: cm^{-1}.

solvents, which are empirical values of proton-donating ability of solvents, were used as a measure of solvent polarity. From this figure, a straight line relationship was observed, and the plots for benzene and acetonitrile (see Table 2) reported by Price and Walsh [8] were also fitted on this line. Although the E_T value of phenol was not found in the literature [13], it is expected to have a larger value than that of benzyl alcohol. Accordingly this fact might suggest that the polarized structure ($\rangle C^{+}-O^{-}$) of methyl methacrylate monomer became important in the transition state of the radical copolymerization when the solvents became more

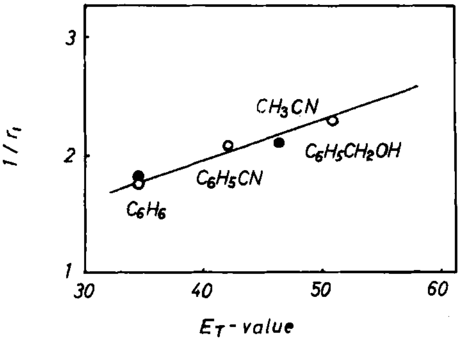

Fig. 1. Relationship between the relative reactivity of methyl methacrylate toward the polystyryl radical and the E_T values of solvents used. Black circles show the plots by the data of Price and Walsh [8].

protic, and resulted in an enhancement of its reactivity, similar to the effect of ester alkyl groups in alkyl methacrylate [4].

Recently we have found that the first-order rate constants of methyl azobisisobutyrate, whose radical is a model of poly(methyl methacrylate) radical, in its thermal decomposition are changed with the solvents and also correlated with their E_T values [14].

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