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 Masuda, Seizo , Minagawa, Keiji , Tanaka, Masami and Asahi, Yutaka(1992) 'Polymerizable Tautomers. VII. Radical Copolymerization of Ethyl 3-oxo-4-Pentenoate and Ethyl 4-Methyl-3-oxo-4-Pentenoate with Methyl Methacrylate', Journal of Macromolecular Science, Part A, 29: 9, 821 — 829

To link to this Article: DOI: 10.1080/10601329208054119

URL: http://dx.doi.org/10.1080/10601329208054119

J.M.S.—PURE APPL. CHEM., A29(9), pp. 821–829 (1992)

POLYMERIZABLE TAUTOMERS. VII. RADICAL COPOLYMERIZATION OF ETHYL 3-OXO-4-PENTENOATE AND ETHYL 4-METHYL-3-OXO-4-PENTENOATE WITH METHYL METHACRYLATE

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ABSTRACT

Ethyl 3-oxo-4-pentenoate (EAA) and ethyl 4-methyl-3-oxo-4-pentenoate (EMAA) exhibit the coexistence of the ketonic and enolic forms in most organic solvents. Radical copolymerizations of EAA and EMAA with methyl methacrylate (MMA) were carried out at 60°C in various solvents, and monomer reactivity ratios were estimated. There are minor solvent effects on monomer reactivity ratios r_{MMA} in both EAA/MAA and EMAA/MMA systems. On the other hand, r_{EAA} and r_{EMAA} values greatly change with the solvent: The values decrease with an increase in the ketonic fraction of the polymerizable tautomers (EAA and EMAA). Regression analysis of the monomer reactivity ratios with the solvatochromic parameters reveals that polarity of the solvent is the major factor governing the relative reactivity.

INTRODUCTION

It is generally said that solvents have no effect on radical reactions. However, several reports have been published on the solvent effect in radical polymerization and copolymerization [1-5], where the constant for the propagation and termination rates change with solvent.

Vinyl compounds having a β-ketoester group (polymerizable tautomers) exhibit the coexistence of the ketonic and enolic forms, and their tautomeric equilibria shift with the solvent. The ketonic and enolic tautomers are expected to differ in their reactivities, and thus the reactivity of the polymerizable tautomer apparently changes with the solvent. In fact, there is a remarkable solvent effect in the homopolymerization of ethyl 3-oxo-4-pentenoate (ethyl acryloylacetate, EAA) and ethyl 4-methyl-3-oxo-4-pentenoate (ethyl methacryloylacetate, EMAA) [6, 7] and in their copolymerization with styrene [8, 9]. In homopolymerization, the rate of homopolymerization becomes slower and the monomer reactivity ratio for the copolymerization with styrene decreases as the ketonic fraction of the polymerizable tautomer increases.

This paper deals with solvent effect on the copolymerization of EAA and EMAA with methyl methacrylate (MMA). The solvent effect is discussed by using multiparametric regression analysis of monomer reactivity ratios with solvatochromic parameters according to the "Linear Solvation Energy Relationship" proposed by Kamlet and Taft [10].

EXPERIMENTAL

EAA and EMAA were prepared according to the methods reported previously [6, 7]. EAA: bp 78-80°C (2.4 kPa); ^{1}H NMR ($CDCl_3$, TMS) 3.65 (s, <2H, $-CO-\underline{CH_2}-CO-$), 5.10 (s, <1H, $-C(OH)=\underline{CH}-CO$), 10.99 (s, <1H, $-C(O\underline{H})=CH-CO-$). EMAA: bp, 70-72°C (0.67 kPa); ^{1}H NMR (neat, TMS) 3.73 (s, <2H, $-CO-\underline{CH_2}-CO-$), 5.23 (s, <1H, $-C(OH)=\underline{CH}-CO-$), 12.16 (s, <1H, $-C(O\underline{H})=CO-$). Other monomer (MMA) and solvents were commercially available and purified by the standard methods prior to use. 2,2′-Azobisisobutyronitrile (AIBN) was purified by recrystallization from methanol.

Copolymerizations of EAA and EMAA with MMA in various solvents were carried out at 60°C in sealed tubes. Monomer (4 mL), solvent (10 mL), and AIBN (which was dissolved in the solvent to give a concentration of 5×10^{-3} mol/L) were placed in the tube, and the mixture was degassed by successive freeze-thaw cycles. After a given time, copolymerization was stopped and isolated by pouring the reaction mixture into a large excess of methanol. The resulting copolymer was filtered, dried under reduced pressure, and weighed. Copolymer composition was determined by means of an NMR spectrometer.

^{1}H-NMR spectra were obtained with a JEOL GX-400 spectrometer (400 MHz), with tetramethylsilane (TMS) used as the internal standard. Monomer reactivity ratios were estimated by the Kelen–Tüdös method [11].

RESULTS AND DISCUSSION

EAA and EMAA are mixtures of ketonic and enolic tautomers as described in previous papers [7, 8], and the tautomeric equilibria vary with the solvent.

Radical copolymerizations of EAA and EMAA with MMA were carried out at 60°C in various solvents. The relationship between the compositions of the feed monomer and the resulting copolymer is listed in Tables 1 and 2. The copolymer compositions were determined by the NMR spectroscopic method from a comparison of the areas obtained by integration of the peak at δ = 4.20 ppm (corresponding to methylene protons for ethyl group of EAA) and the whole proton peaks for the EAA–MMA system, and the peak at δ = 4.16 ppm (corresponding to methylene protons for the ethyl group of EMAA) and the whole proton peaks for the EMMA–MMA system. Tables 3 and 4 show monomer reactivity ratios determined according to the Kelen–Tüdös method [11] on the basis of the monomer–copolymer composition relationships shown in Tables 1 and 2, respectively.

In the EAA–MMA system, the monomer reactivity ratio, r_{MMA}, on the whole, appears to be unchanged, although a few exceptional cases, e.g., in acetonitrile and methanol solutions, give a slightly smaller value. The monomer reactivity ratio r_{MMA} represents the rate constant of MMA addition relative to that of the addition of EAA to the polymer radical with the MMA unit at the terminal position. Unchanged r_{MMA} values suggest that the solvents do not have much of an effect on the reactivities of EAA monomer, MMA monomer, and propagating MMA radical.

On the other hand, there is a significant solvent effect on the monomer reactivity ratio r_{EAA}. The r_{EAA} values have a tendency to decrease with an increase in polarity of the solvent. This tendency is similar to that in the copolymerization of EAA with styrene [8]. A change in r_{EAA} does not appear to have an associated solvent effect on EAA monomer, but it is possible that the propagating EAA radical is sensitive to its environment. As seen from Table 4, a change in monomer reactivity ratios for the copolymerization of EMAA and MMA shows a similar tendency to that for the EAA–MMA system.

As a quantitative description of the solvent effects on chemical processes and spectroscopic properties, linear multiparametric equations have been proposed by many authors [12–16]. Taft et al. also proposed a "Linear Solvation Energy Relationship" as the empirical solvent scale [10]

$$x = x_0 + s(\pi^* + d\delta) + a\alpha + b\beta$$

where x_0 is the value of the given property x in a standard solvent. π^* (polarity), δ (polarizability), α (hydrogen-bond donor acidity), and β (hydrogen-bond acceptor basicity) are referred to as the solvatochromic parameters, and s, d, a, and b are the

TABLE 1. Monomer-Copolymer Composition Relationship for the Copolymerization of EAA with MMA in Various Solvents[a]

Mole fraction of EAA in the feed	Mole fraction of EAA in the copolymer									
	Toluene	Ethanol	AcOEt	THF	Methanol	Benzene	Acetone	AcCN	DMF	DMSO
0.844	0.947	0.917	0.946	0.901	0.867	0.905	0.912	0.808	0.894	0.870
0.698	0.883	0.822	0.856	0.819	0.777	0.801	0.779	0.718	0.792	0.729
0.562	0.782	0.729	0.772	0.687	0.693	0.676	0.674	0.613	0.636	0.627
0.435	0.656	0.644	0.636	0.580	0.583	0.580	0.550	0.561	0.538	0.528
0.316	0.532	0.500	0.502	0.468	0.484	0.439	0.434	0.445	0.398	0.406
0.204	0.380	0.362	0.359	0.358	0.347	0.322	0.311	0.363	0.250	0.297
0.099	0.191	0.195	0.182	0.189	0.210	0.157	0.155	0.233	0.147	0.163

[a] AcOEt = ethyl acetate; THF = tetrahydrofuran; AcCN = acetonitrile; DMF = dimethylformamide; DMSO = dimethylsulfoxide.

TABLE 2. Monomer–Copolymer Composition Relationship for the Copolymerization of EMAA with MMA in Various Solvents[a]

Mole fraction of EMAA in the feed	Mole fraction of EMAA in the copolymer								
	Toluene	AcOEt	THF	Methanol	Benzene	Acetone	AcCN	DMF	DMSO
0.831	0.927	0.792	0.855	0.825	0.894	0.853	0.854	0.789	0.785
0.678	0.825	0.697	0.725	0.737	0.779	0.693	0.698	0.669	0.643
0.539	0.736	0.607	0.624	0.610	0.686	0.600	0.587	0.546	0.548
0.413	0.598	0.517	0.511	0.518	0.563	0.490	0.483	0.438	0.438
0.296	0.449	0.390	0.421	0.387	0.450	0.378	0.381	0.338	0.351
0.190	0.303	0.298	0.278	0.299	0.331	0.267	0.257	0.240	0.236
0.091	0.162	0.186	0.148	0.176	0.158	0.137	0.131	0.118	0.132

[a] AcOEt = ethyl acetate; THF = tetrahydrofuran; AcCN = acetonitrile; DMF = dimethylformamide; DMSO = dimethylsulfoxide.

TABLE 3. Monomer Reactivity Ratios for the EAA-MMA System

No.	Solvent	r_{EAA}	r_{MMA}
1	Toluene	3.48	0.60
2	Ethanol	2.01	0.41
3	Ethyl acetate	2.98	0.56
4	Tetrahydrofuran	1.66	0.43
5	Methanol	1.11	0.29
6	Benzene	1.73	0.56
7	Acetone	1.75	0.62
8	Acetonitrile	0.65	0.22
9	Dimethylformamide	1.60	0.74
10	Dimethylsulfoxide	1.14	0.60

solvatochromic coefficients. This equation is regarded as a general representation of the solvent effect because of a better correlation between solvatochromic parameters and other empirical solvent scales [17].

Regression analysis of monomer reactivity ratios with the solvatochromic parameters gives the following equations with a good linear correlation.

For the EAA-MMA system:

$$\begin{array}{lcccc} \ln(1/r_{EAA}) = -1.212 + & 2.919(\pi^*-0.406\delta) & + 0.999\alpha & - 2.502\beta & \\ & (4.35)\quad(3.32) & (3.67) & (3.82) & \end{array} \tag{1}$$

R (correlation coefficient) = 0.929
F (Snedecor F value) = 7.90
t values are shown in parenthesis

For the EMMA-MMA system:

TABLE 4 Monomer Reactivity Ratios for the EMAA-MMA System

No.	Solvent	r_{EMAA}	r_{MMA}
1	Toluene	2.57	0.60
3	Ethyl acetate	0.73	0.37
4	Tetrahydrofuran	1.12	0.50
5	Methanol	0.93	0.42
6	Benzene	1.68	0.48
7	Acetone	1.11	0.60
8	Acetonitrile	1.01	0.61
9	Dimethylformamide	0.72	0.65
10	Dimethylsulfoxide	0.64	0.60

$$\begin{array}{llllll} \ln(1/r_{\mathrm{EMMA}}) = & -0.530 + & 0.740(\pi^* & - 0.853\delta) & - 0.011\alpha & + 0.252\beta \\ & & (0.94) & (1.50) & (0.03) & (0.30) \end{array} \quad (2)$$

$R = 0.912$
$F = 4.93$
t values are shown in parenthesis

The EAA-MMA system possesses significant F and t values for the solvatochromic parameters. For the EMAA-MMA system, the regression equation is reliable with a significance level of 7.5%, but t values are small. Regression analysis of r_{MMA}'s is meaningless, because it is hardly affected by the solvent for both copolymerization systems.

Equations (1) and (2) are illustrated graphically in Figs. 1 and 2, respectively. In the copolymerization of EAA with MMA, increases in polarity (π^*) and hydrogen-bond donor acidity (α), and decreases in polarizability (δ) and hydrogen-bond acceptor basicity (β) of the solvent result in reducing r_{EAA} values. In addition, comparison of the solvatochromic coefficients reveals that polarity and hydrogen-bond acceptor basicity of the solvent are important factors governing the relative reactivity r_{EAA}. The contribution of the solvent factors shows a tendency similar to the case for the copolymerization of EAA and styrene.

For the EMAA-MMA system, on the other hand, solvent polarity and polarizability are the most important factors governing the relative reactivity r_{EMAA}, and the hydrogen-bond donating and accepting powers have no significant effect. The results of the t-test revealed that the π^* and δ parameters possess significance levels of 20%, but the α and β parameters possess no significance.

Our previous papers presented the solvent effect on the tautomeric equilibria of EAA [6] and EMMA [7] in which the following regression equations for the equilibrium constant (K_T) were given.

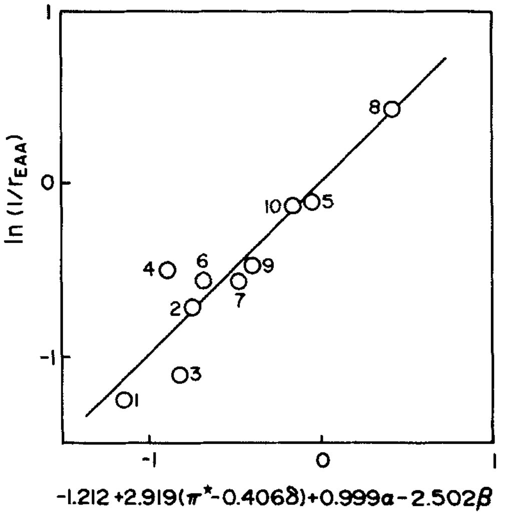

FIG. 1. Regression analysis of r_{EAA} for the EAA-MMA system with the solvatochromic parameters. Same symbols as in Table 3.

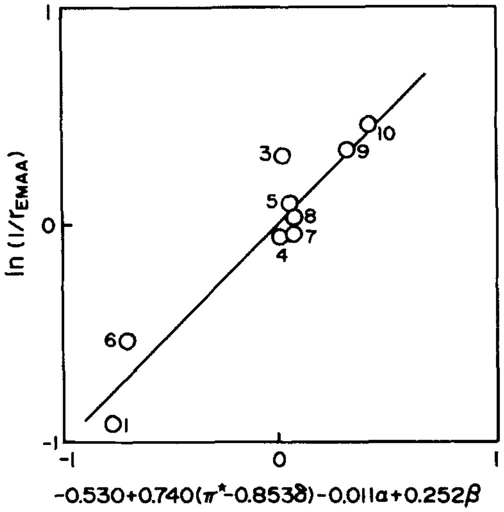

FIG. 2. Regression analysis of r_{EMAA} for the EMAA-MMA system with the solvatochromic parameters. Same symbols as in Table 4.

For EAA:

$$\ln K_T = 0.711 - \underset{(5.86)}{1.199}(\pi^* - \underset{(1.94)}{0.299}\delta) - \underset{(4.27)}{0.709}\alpha + \underset{(0.35)}{0.192}\beta \tag{3}$$

$R = 0.936$
$F = 19.43$
t values are shown in parenthesis

For EMAA:

$$\ln K_T = -0.648 + \underset{(5.36)}{2.811}(\pi^* - \underset{(2.43)}{0.262}\delta) + \underset{(1.70)}{0.737}\alpha + \underset{(0.89)}{0.059}\beta \tag{4}$$

$R = 0.967$
$F = 18.32$
t values are shown in parenthesis

where K_T = [enol form]/[keto form] for EAA and [keto form]/[enol form] for EMAA. It can be seen by reference to Eqs. (3) and (4) that r_{EAA} and r_{EMAA} values decrease with an increase in the ketonic fraction of EAA and EMAA, respectively. The decrease in the r_{EAA} values means a decrease in the rate constant for the addition of the EAA monomer to the polymer radical with an EAA unit at its terminal position or an increase in the rate constant for the addition of the MMA monomer to the propagating EAA radical. It has been reported that homopolymerization of EAA is faster in a nonpolar solvent that in a polar solvent [6]. Therefore, although we cannot definitely conclude that the solvent can have an effect on the former reaction (the addition of EAA to its own radical), we suggest more research is needed.

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Received September 16, 1991
Revision received February 6, 1992