Polymerizable tautomers: 5. Solvent effects on radical polymerization and copolymerization of 5-hexene-2,4-dione

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5-Hexene-2,4-dione (AA) has been polymerized and copolymerized at 60°C in different solvents. An initiator order of 0.5 and monomer order above unity were obtained for the polymerization of AA in benzene and acetonitrile. A strong influence of the solvents on monomer reactivity ratios for the AA–styrene copolymerization system was observed. The contribution of electrostatic field effect and solute–solvent hydrogen bonding interactions was estimated separately and critically discussed using multiparametric regression analysis and empirical polarity parameters, according to the linear solvation energy relationship developed by Taft *et al.*

(Keywords: 5-hexene-2,4-dione; polymerization kinetics; copolymerization; solvent effect; regression analysis)

INTRODUCTION

There have been many reports on solvent effects on radical polymerization and copolymerization. The reaction medium affects propagation and termination reactions, and consequently causes deviation from the conventional model of radical polymerization[1] and changes in monomer reactivity ratios in copolymerizations[2]. These solvent effects have been considered to arise from a change in the dielectric constant of the reaction mixture and interaction between monomer and solvent.

Our previous papers[3,4] have presented a remarkable solvent effect on radical polymerization and copolymerization of unsaturated keto-esters, such as ethyl 3-oxo-4-pentenoate, which coexist as the ketonic and enolic forms. In these cases, the keto–enol tautomerism is an important factor governed by the apparent reactivity of the keto-esters, and the solvents function as an agent which shifts the tautomeric equilibrium. On the other hand, 5-hexene-2,4-dione (acryloylacetone, AA), a polymerizable unsaturated β-diketone, is not tautomeric but exists only in the enolic form. The enolic form of AA has carbonyl and hydroxyl groups, which are liable to interact with the solvents. From the viewpoint of interactions, the former group may serve as a hydrogen-bond acceptor and the latter as hydrogen-bond donor. Therefore, the hydrogen-bond accepting and donating powers of the solvents are expected to have an effect on the reactivity of AA.

In this paper, the kinetics of free radical polymerization of AA in benzene and acetonitrile are described, and parameters for the copolymerization of AA with styrene in different solvents are determined. In addition, on the basis of copolymerization results obtained, the factors governing the reactivity of AA are estimated, using multiparametric regression analysis and empirical polarity parameters, according to the 'linear solvation energy relationship' proposed by Taft *et al.*[5].

EXPERIMENTAL

AA was prepared according to the procedure of Ponticello and Furman[6]. B.p. 51°C/667 N m^{-2}. ^{1}H n.m.r. (CDCl$_3$) δ 2.07 (3H, s, –C*H*$_3$), 5.68 (1H, s, –C(OH)=C*H*–CO–), 5.72 (1H, m, CH$_2$=C*H*–), 6.26 (2H, m, C*H*$_2$=CH–), and 14.50 (1H, s, –O*H*); ^{13}C n.m.r. (CDCl$_3$) δ 27.27 (–CH$_3$), 101.12 (–C(OH)=CH–CO–), 125.28 (CH$_2$=CH–), 133.14 (CH$_2$=CH–), 176.28 (–C(OH)=CH–CO–), 199.55 (–CO–). Other reagents were commercially available and purified by the standard methods prior to use.

The ^{1}H and ^{13}C n.m.r. spectra were recorded on a Hitachi R-42 FT spectrometer, using tetramethylsilane as the internal standard.

Homopolymerization of AA and the copolymerization with styrene were carried out at 60°C in sealed tubes under vacuum. Monomer(s), solvent, and initiator (2,2′-azobisisobutyronitrile, AIBN) were added to the tube, and the mixture was degassed by successive freeze–pump–thaw cycles. After a given time, polymers were precipitated by pouring the reaction mixture into a large

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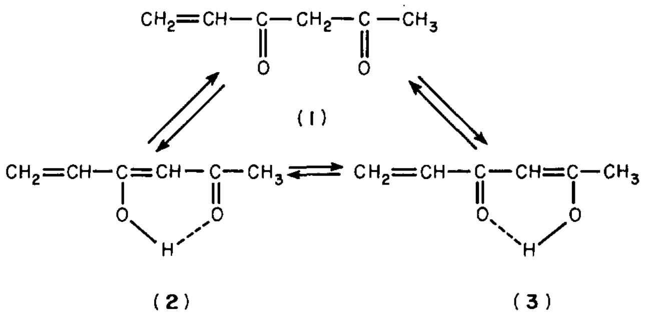
excess of methanol. The precipitates were filtered off, dried under reduced pressure, and weighed. The rate of polymerization was determined gravimetrically and copolymer composition by elemental analysis.

RESULTS AND DISCUSSION

Though AA has three theoretically possible tautomers, one ketonic (**1**) and two enolic (**2** and **3**) forms, its n.m.r. spectra, shown in *Figures 1* and *2*, reveal that it is only in the enolic form in $CDCl_3$. The signals at 5.68 ppm in the ^1H n.m.r. spectrum and at 101.12 ppm in the ^{13}C n.m.r. spectrum are assigned to methyne proton and carbon adjacent to the carbon–oxygen groups, respectively, but the spectra have no peaks corresponding to the methylene proton and carbon lying between two carbonyl groups. Because tautomeric equilibrium generally shifts with solvents, n.m.r. measurements were also carried out in neat and in dimethylsulphoxide-d_6, acetonitrile-d_3, benzene-d_6, and carbon tetrachloride. Similar spectra to that in the system of AA/$CDCl_3$ were obtained, and signals corresponding to the ketonic methylene proton and carbon were not detectable. Therefore, AA is concluded to take only the enolic form in most solvents.



In order to obtain further information about the chemical structure of the enolic AA, a selective decoupled method was applied. As can be seen from *Figure 3*, the peak at 199.55 ppm in non-decoupled ^{13}C n.m.r. spectrum which is assigned to the carbonyl carbon appears as a quintet with the coupling constant of 5.2 Hz. The coupling of the carbonyl carbon is removed by irradiating the methyl proton at its resonance frequency so that the carbonyl carbon appears as a doublet due to spin–spin splitting only by the methyne proton on the adjacent carbon. This observation clearly shows that the carbonyl carbon is adjacent to the methyl group, i.e. the structure of AA may be represented by chemical formula (**2**).

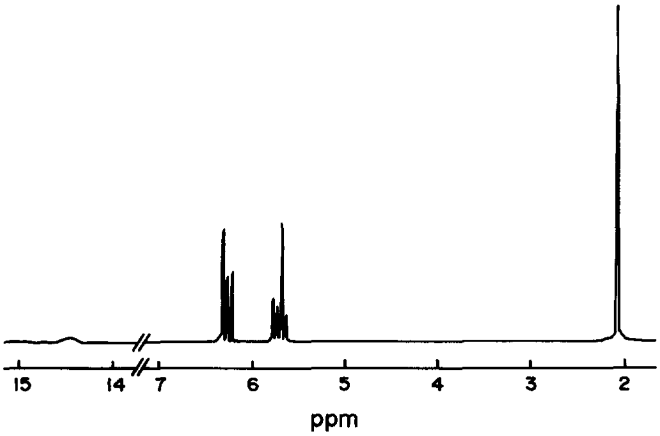


Figure 1 ^1H n.m.r. spectrum of AA. Measurement was carried out at 35°C in $CDCl_3$ with [AA] = 33 vol.%

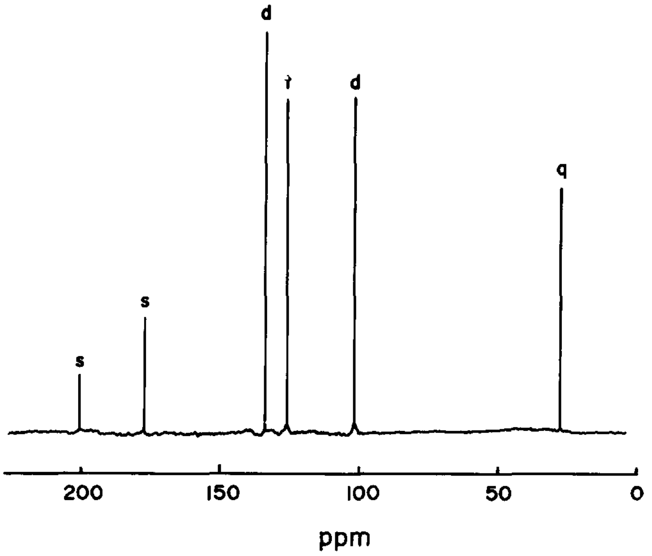


Figure 2 ^{13}C n.m.r. spectrum of AA. s, d, t, and q represent singlet, doublet, triplet, quartet, respectively

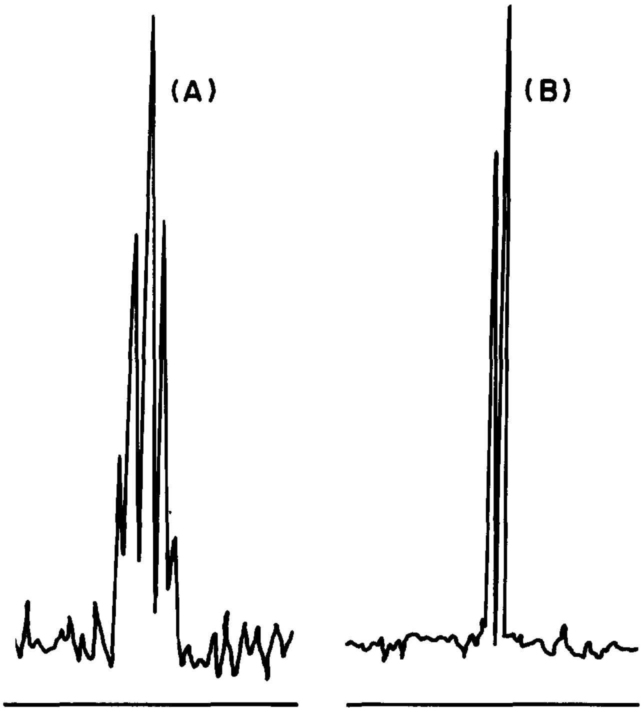


Figure 3 (A) Non-decoupled and (B) single frequency selective decoupled ^{13}C n.m.r. spectra for the carbonyl carbon

The polymerization of AA was kinetically investigated at 60°C in benzene and acetonitrile. *Figure 4* shows time-conversion curves for the polymerization in benzene at various temperatures. An Arrhenius plot of the polymerization rate (R_p) is shown in *Figure 5*. The overall activation energy of the polymerization was calculated to be 66.9 kJ mol^{-1}. *Figures 6* and *7* show the dependence of the rate on monomer and initiator concentrations, respectively. At low concentration of the monomer, the polymerization rate is higher in benzene than in acetonitrile, but the difference between the polymerization rates becomes smaller as the monomer concentration

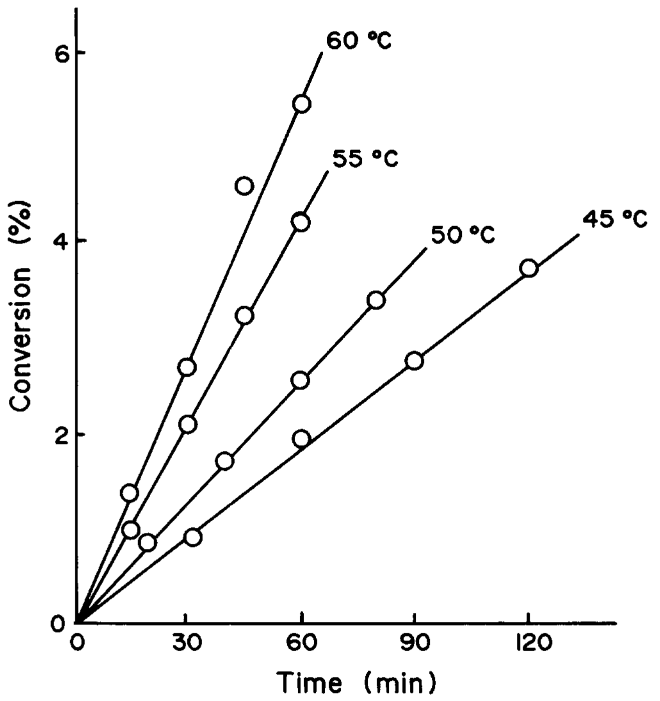


Figure 4 Time-conversion curves for the polymerization of AA at various temperatures

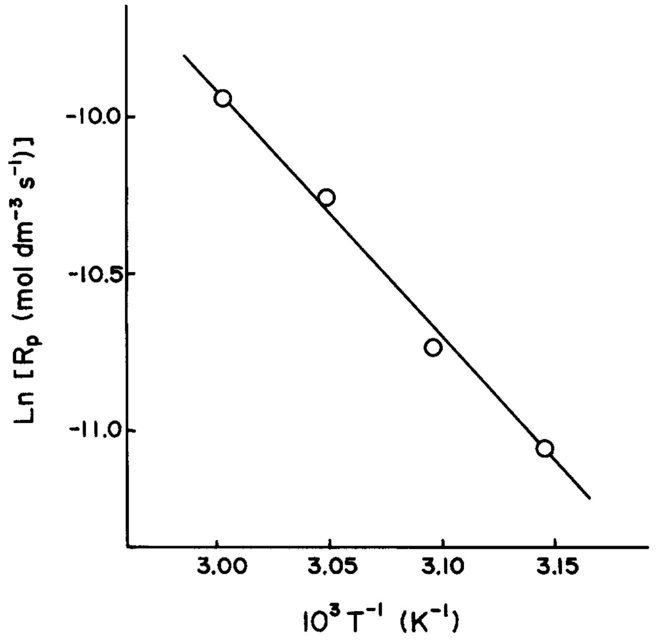


Figure 5 Arrhenius plot of the polymerization rate

increases. From these results, the following rate equations are obtained for the polymerization of AA.

$$R_p = k[\mathrm{AA}]^{1.47}[\mathrm{AIBN}]^{0.45} \quad \text{in benzene}$$

$$R_p = k[\mathrm{AA}]^{1.67}[\mathrm{AIBN}]^{0.48} \quad \text{in acetonitrile}$$

According to the conventional model of radical polymerization, the rate is directly proportional to the monomer concentration and to the square root of the initiator concentration. For several monomers, especially acrylic and methacrylic acid esters, however, the orders with respect to the monomer concentration have been recognized to be different from the theoretical values[7]. The absolute rate constants for the radical polymerization of the esters have been determined in various solvents by using the rotating-sector method, and it has been revealed that the solvents have an effect on the propagation reaction rather than the termination reaction[8].

Our investigations also give the order more than unity with respect to the monomer concentration. Such a deviation of the kinetic order from the theoretical value may be explained by a change in the rate constant of propagation reaction owing to monomer–solvent and polymer radical–solvent interactions.

Copolymerization of AA (M_1) and styrene (M_2) was carried out at 60°C in various solvents. Composition of the copolymer obtained was determined by carbon

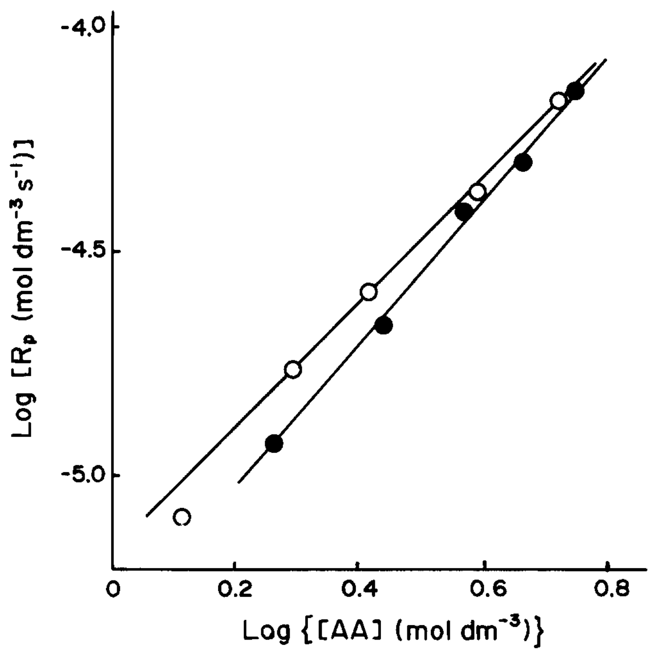


Figure 6 Dependence of the rate of polymerization in benzene (○) and acetonitrile (●) on the monomer concentration

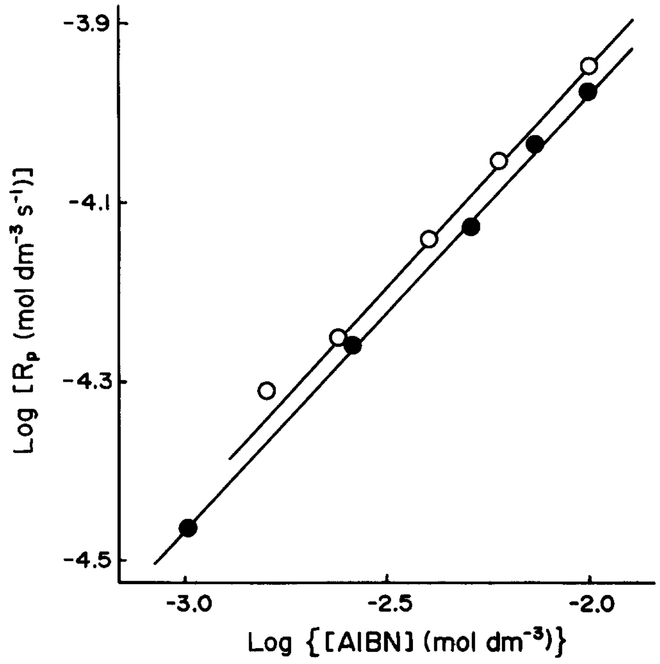


Figure 7 Dependence of the rate of polymerization in benzene (○) and acetonitrile (●) on the initiator concentration

Table 1 Monomer reactivity ratios for the copolymerization of AA(M_1) and styrene(M_2)

No.	Solvent	r_1	r_2
1	Toluene	1.22	0.031
2	Benzene	1.38	0.049
3	Ethanol	1.52	0.066
4	Methanol	1.73	0.070
5	Ethyl acetate	1.91	0.171
6	Tetrahydrofuran	1.91	0.179
7	Dioxane	2.07	0.173
8	Acetone	2.46	0.121
9	Acetonitrile	2.69	0.240
10	Hexamethylphosphoramide	2.93	0.014
11	Dimethylformamide	3.19	0.044
12	Dimethylsulphoxide	4.11	0.028

analysis. *Table 1* shows monomer reactivity ratios estimated by the method of Fineman and Ross[9]. There is a remarkable solvent effect on monomer reactivity ratios r_1 and r_2. The r_1-values increase with an increase in the r_2-values, with a few exceptions. The change in the r_1- and r_2-values suggests that the solvents interact with both AA monomer and terminal AA radical along the polymer chain.

r_2 is the ratio of the rate constant of AA to that of styrene for the addition of the polymer radical with styrene unit at its terminal position. Since it is considered in copolymerizations that the solvents have no effect on the reactivities of styrene and polystyryl radical, the change in the r_2-values can be reduced to interaction between AA and the solvents. On the other hand, r_1 represents the ratio of the rate constant of AA to that of styrene for the addition of the polymer radical with AA unit at its terminal position. The solvent effect on r_1 is complicated because the solvents affect the reactivities both AA monomer and polymer radical having AA unit as the terminal group.

As a quantitative description of the solvent effects on chemical processes and spectroscopic properties, linear multiparametric equations have been proposed by many authors. Abboud and Taft[7] have derived a dielectric function $\theta(\varepsilon)$. Dimroth's E_T-values[10] are widely used as a measure of the solvent effect. E_T actually combines solvent polarity and a solvatochromic electrophilicity parameter, which is a measure of hydrogen-bond donor acidity of the solvents. However, plots of r_1 and r_2 against $\theta(\varepsilon)$ and E_T parameters lead to poor linear correlations:

$$\mathrm{Ln}(1/r_1) = -0.164 - 1.747\theta(\varepsilon) \quad R = 0.659$$

$$\mathrm{Ln}(1/r_2) = 2.402 + 0.262\theta(\varepsilon) \quad R = 0.047$$

$$\mathrm{Ln}(1/r_1) = -0.183 - 0.013E_T \quad R = 0.249$$

$$\mathrm{Ln}(1/r_2) = 2.193 + 0.007E_T \quad R = 0.064$$

These findings suggest that factors other than polarity and electrophilicity play an important role in the solvent effects.

In their 'linear solvation energy relationship' (LSER), Taft *et al.*[5] have proposed the following equation.

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

where x_0 is the value of the given property x in the 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 as the solvatochromic coefficients. Taft *et al.* have also found a better correlation between their solvatochromic parameters and other empirical solvent scales[11]. For example, the G-value[12] is a function of π^*, and the A_N-value is expressed as a function of π^* and α (ref. 13). Therefore, LSER can be regarded as general expression of the solvent effect.

The Taft equation was applied to our copolymerization systems. As shown in *Figures 8* and *9*, regression analysis of the monomer reactivity ratios with the solvatochromic parameters gives a good linear relationship:

$$\mathrm{Ln}(1/r_1) = 0.202 - 1.895(\pi^* - 0.318\delta) + 0.122\alpha + 0.390\beta \quad R = 0.999$$

$$\mathrm{Ln}(1/r_2) = -0.963 + 1.998(\pi^* + 1.544\delta) + 0.173\alpha + 3.399\beta \quad R = 0.971$$

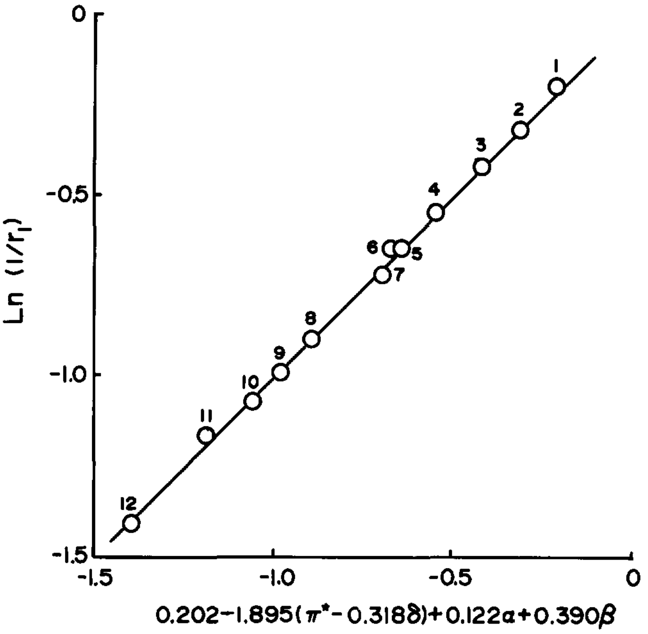


Figure 8 Regression analysis of r_1 with the solvatochromic parameters. Same symbols as in *Table 1*

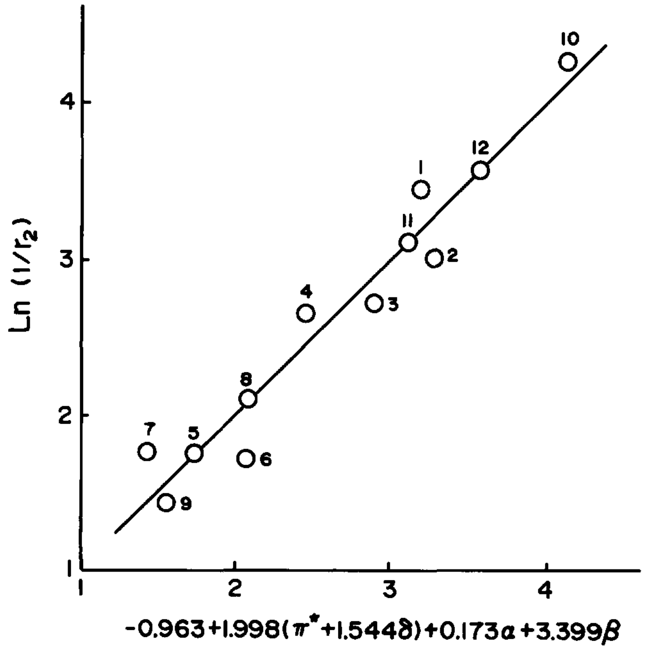


Figure 9 Regression analysis of r_2 with the solvatochromic parameters. Same symbols as in *Table 1*

Increase in polarity of the solvents results in increasing r_1-values, whereas an increase in hydrogen-bond donating and accepting powers of the solvents should produce the opposite effect. For r_2-variations, increasing polarity, polarizability, hydrogen-bond donor acidity and hydrogen-bond acceptor basicity all decrease the relative reactivities. The relative magnitude of the coefficients is a measure of the contribution of the solvent properties to the r_1- and r_2-variations. It can be seen from a comparison of the solvatochromic coefficients that the most important factors of the solvents governing the reactivities of AA monomer and propagating AA radical are hydrogen-bond accepting power and polarity, respectively. However, it is not clear at present what such a difference originates in.

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