Macromolecules **1995,** *28,* 5405−5410

Solvent Effects on Free-Radical Polymerization. 6.[†] Solvatochromic (LSER) Analysis of the Solvent Effect on the Homopolymerization Rate on the Basis of the Reaction−Solvent Complex Model

Wojciech Krzysztof Czerwinski[‡]

Deutsches Kunststoff-Institut, Schlossgartenstrasse 6R, D-64289 Darmstadt, Germany

Received December 19, 1994; Revised Manuscript Received May 16, 1995[⊗]

ABSTRACT: Evaluation results of the homopolymerization rate in solution taken from previous papers are analyzed by two solvatochromic correlation methods taking into account the scale E_T by Dimroth and scales by Taft. From available data a nearly linear correlation between $\log(1/r_{11'})$ ($r_{11'}$ = relative monomer reactivity change increment) and E_T is found for styrene (St) and methyl methacrylate (MMA). Linear solvent susceptibility equations are established for these monomers and tentatively estimated for *N*-vinylpyrrolidone (NVP), ethyl acrylate (EA), and acrylonitrile (AN). It follows from solvatochromic analyses of St and MMA polymerizations by Taft that the aliphatic, more polar, and electron-deficient MMA is 3 times more susceptible against solvent polarity and is considerably more susceptible against solvent nucleophilicity than St. St is about 5 times more susceptible against solvent polarizability than MMA. Furthermore, two independent methods of separate radical susceptibility estimation are presented. Polar solvents reduce the reactivity of growing PMMA radicals. This reactivity lost is recompensed by a much stronger reactivity increase of the monomer.

1. Introduction

As was found very early for reactions in the condensed phase, solvents are able to change the reaction rate within several orders of magnitude,[1] contrary to reactions in the gaseous phase. Processes involving ionic or highly polar reactants or intermediates are of particular concern. This is the case because the molecular orbital energy of reacting partners may be markedly affected by solvation processes.

Free-radical chain reactions were found to be much less sensitive to solvent effects. Later, it was observed that reactions of such type are not fully unaffected by solvents.[2] At present, numerous solvent effects are known, but no systematic explanation of the mechanism of the solvent effect exists.

At first, general attempts were made to correlate measured (often relative) rate constants or energy of activation with such characteristic solvent constants as dielectric constant ϵ, dipole moment μ, or refraction index n.

Because of a lack of a general or specific relationship,[1] several workers looked for a new strategy of investigation. They chose, on the one hand, model reactions to follow the rate or equilibrium point or, on the other hand, model compounds to use their physical properties like optical absorption in different solvents. In the last case dyes were often used; this is why the characteristic solvent numbers obtained in this way were called solvatochromic parameters.

Furthermore, other methods such as calorimetric[3] and chromatographic[4] measurements were proposed to get characteristic solvent reference quantities (scales). The reader is referred to ref 1 for a review of scales presently available.

Solvatochromic scales are commonly used because of their high accuracy.

The aim of the present work is the solvatochromic analysis of the homopolymerization low-conversion rate presented in ref 11. Special attention is paid to modeling of the chain propagation. The solvent effect on the initiation rate was judged to be negligible because exclusively systems initiated with azobis(isobutyronitrile) (AIBN) as a nearly solvent-insensitive initiator were taken into consideration.

Apart from chain initiation and propagation, solvents affect the overall reaction rate via chain-termination reaction. The rate of this reaction depends on the dynamic viscosity of the reacting system. In this paper this influence could not be taken into consideration since no systematic viscosity data are available at the present time. Thus, certain interference of the solvent effect on chain propagation and termination should be expected in the present work.

In refs 12−14 the solvent effects on chain initiation and termination of some systems are presented, and it is shown how such dependences affect the overall polymerization rate. Furthermore, detailed kinetical treatment is discussed.

The solvatochromic methods were applied to analyze the relative monomer reactivity increment r_{11}, calculated in ref 11 by means of the reactant−solvent complex (RSC) model. In the following section solvatochromic scale E_T by Dimroth[2−8] and scales by Taft[8−10] are briefly presented.

2. Theoretical Part

2.1. Solvatochromic Scale E_T by Dimroth. The solvatochromic parameter E_T (energy transition) was measured by Dimroth in a wide range of solvents on dye *N*-(4-hydroxy-3,5-diphenylphenyl)-2,4,6-triphenylpyridinium betaine.[1,5−7] Its absorption frequency was measured by means of UV−vis spectroscopy and yielded:

$$E_T\ (\mathrm{kJ{\cdot}mol^{-1}}) = hcN\nu = 2.859 \times 10^{-3}\nu \qquad (1)$$

(h = Planck constant, c = velocity of light, N = Avogadro's number, and ν = wavenumber in cm^{-1}).

[†] Part 5: Reference 11.

[‡] Present address: Silcherstrasse 22, D-22761 Hamburg, Germany.

[⊗] Abstract published in *Advance ACS Abstracts,* July 1, 1995.

0024-9297/95/2228-5405$09.00/0

E_T is generally considered as a measure of solvent polarity. Since other solvent properties like polarizability, hydrogen-bond acceptance, or donor ability are not separately considered in this treatment, further scales were proposed to make the solvatochromic analysis more precise. As will be later shown, the E_T scale is still valuable for simplified solvatochromic analysis of the LFER type (see below). It yields good correlations valuable for preliminary conclusions.

2.2. LFER (Linear Free Energy Relationship) and LSER (Linear Solvent Energy Relationship) Analyses. Linear free energy relationships (LFER) are a useful tool in the investigation of the reaction mechanism by means of correlation analysis. The first relationship of this type was established by Hammet, was later extended by Taft[15,16] and Otsu et al.,[17] and was discussed by several other authors.[18] By means of LFER it was possible to establish quantitatively substituent effects on reactivity in low and high molecular chemistry.

LSER analysis operates in analogy to LFER. In the present work the following LSER equation is proposed, making use of the E_T scale:

$$\log \frac{k_{p11'}}{k_{p11}} = \log \frac{1}{r_{11'}} = \zeta E_T + \tau \tag{2}$$

where k_{pij} = propagation rate constant of radical i to monomer j, $r_{11'}$ = relative monomer reactivity change increment, index i = component i not complexed by solvent, index i' = component i complexed by solvent, ζ = solvent susceptibility of the monomer, and τ = constant. Further LSER relationships are presented in the following part of this section.

2.3. Solvatochromic Scales by Taft. In analogy to the multiparameter extension of the Hammet equation,[18] Koppel and Palm[19] proposed a multiparameter LSER equation, taking into account not only solvent polarity Y corresponding to E_T in eq 2 but also its polarizability P, electrophilicity E (Lewis acidity), and nucleophilicity B (Lewis basicity):

$$x = x_0 + yY + pP + eE + bB \tag{3}$$

where x = observed property, x_0 = property x observed in the reference state, and y, p, e, b = reaction sensibilities against the corresponding characteristic solvent parameters (scales) Y, P, E, and B. Y, P, and E scales were computed using dielectric constant ϵ, refraction index n, and the E_T scale, respectively. The B scale was estimated on the basis of frequency shift $\Delta\nu_{OD}$ of C_6H_5-OD or CH_3OD in different solvents related to the gaseous phase.

Since correlations obtained by means of eq 3 were not satisfactory, Taft and co-workers[8-10] elaborated on new solvent scales expressing the same solvent properties but adopting a new strategy of the scale estimation. In analogy to eq 3, they proposed a new eq 4:

$$x = x_0 + s(\pi^* + d\delta) + a\alpha + b\beta \tag{4}$$

The π^* scale stands for a scale of solvent polarities. It was determined by means of UV spectroscopy with 5 primary (high-accuracy) indicators and about 40 secondary indicators. As indicators aromatic compounds with single or multiple substituents were used. Frequency shift $\Delta\nu_{max}$ of a chosen absorption was followed in about 60 solvents. The linear π^* scale was normalized to be 0.0 in cyclohexane and 1.0 in dimethyl sulfoxide (DMSO). Polarizability δ was set to 0.0 for nonhalogenated aliphatic solvents, 0.5 for polyhalogenated aliphatics, and 1.0 for aromatic solvents.[10]

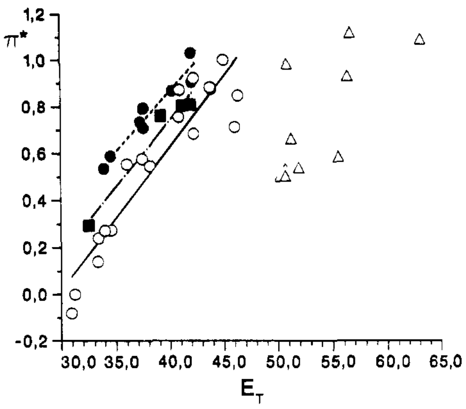


Figure 1. Relationship between the solvatochromic scale π^* by Taft and E_T by Dimroth including classification for solvents: class 1, (△) hydrogen-bond-donating solvents; class 2, (○—) aliphatic, nonhalogenated solvents (R = 0.930); class 3, (■ – · –) aliphatic, halogenated solvents (R = 0.981); class 4, (● ···) aromatic solvents (R = 0.967). Overall correlation coefficient for classes 2–4: R = 0.861.

Two further scales were expressed separately: hydrogen-bond acceptor ability (Lewis basicity) as the β scale and hydrogen-bond donor ability (Lewis acidity) of solvents as the α scale. The first one was established by measuring frequency shift $\Delta\nu_{max}$ for 4-nitroaniline and *N,N*-diethyl-4-nitroaniline in a series of solvents.[8] Both $\Delta\nu_{max}$ values were compared with each other, yielding $\Delta\Delta\nu_{NH_2}$—the so-called enhanced solvatochromic displacement. Each solvent got its characteristic β value:

$$\beta = -\Delta\Delta\nu_{NH_2}/2.80 \tag{5}$$

The factor 2.80 was chosen to normalize obtained β values so that β = 1 in hexamethylphosphoramide. Four other indicator systems were applied, and β values were averaged for each solvent after normalization.

The α scale was determined[9] by taking into consideration the E_T scale by Dimroth.[1] For this purpose solvatochromic displacements of frequency $\Delta\nu_{max}$ of 4-nitroanisole in a wide range of solvents were measured. It was found in ref 9 that they are insensitive to the hydrogen-bond donor ability of alcoholic solvents contrary to $\Delta\nu_{max}$ values of betaine used by Dimroth. Owing to this finding, the difference $\Delta\Delta\nu$ between both values was believed to be a measure of the hydrogen-bond donor ability of protic solvents. The new scale was normalized for methanol to be α = 1.0, and it was fixed at

$$\alpha = \Delta\Delta\nu/6.24 \tag{6}$$

Five other indicator pairs were used. Normalized α values were then averaged for each solvent, yielding the final α scale.

Quantities s, d, a, and b in eq 4 represent sensitivities of property x to the four solvent scales cited above.

As was pointed out in ref 10, the π^* scale correlates directly with the E_T scale for distinct solvent classes; i.e., separate correlations were found for aliphatic (not halogenated) solvents, for aliphatic halogenated solvents, and for aromatic solvents. Obtained linear correlations are presented in Figure 1. It can be seen from the same figure that for protic solvents (alcohols)

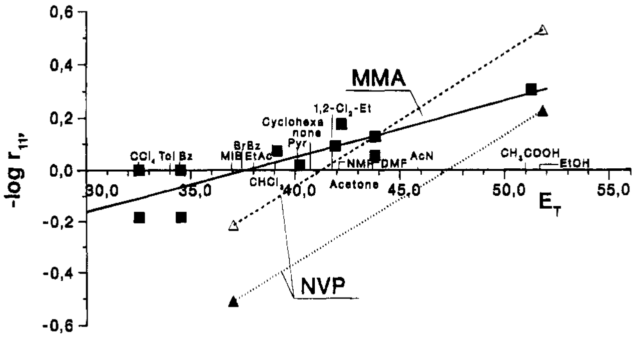


Figure 2. Solvatochromic analyses of the relative reactivity ratio $r_{11'}$ in terms of the E_T scale by Dimroth. For MMA: (■) $\log(1/r_{11'})$ calculated from ref 11; (—) eq 8. For NVP: (▲) $\log(1/r_{11'})$ taken from ref 11; (···) eq 9; (△ - - -) for reaction rate normalized to constant feed viscosity (ref 11, Table 3), $\log(1/r_{11'}) = 0.050E_T - 2.079$.

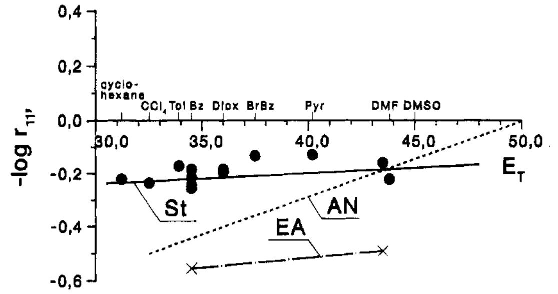


Figure 3. Solvatochromic analyses of the relative reactivity ratio $r_{11'}$ in terms of the E_T scale by Dimroth. For styrene: (●) $\log(1/r_{11'})$ calculated from ref 11; (—) eq 8. For ethyl acrylate: (x) $\log(1/r_{11'})$ from ref 11; (– • –) eq 10. For AN: (- - -) eq 11.

no direct trend can be found. This is probably so because of the self-association of these solvents. For nonprotic solvents both scales correlate directly and should indeed express the same solvent property, in this case polarity.

Betaine used in refs 1, 6, and 7 behaves similarly with changing solvents as a number of other common compounds. This is why the E_T scale correlates better with reactivity increments than the π^* scale. It seems to be advantageous to apply the E_T scale for first orientation, even if it does not allow analytical conclusions approachable from the Taft equation (eq 4). Results on free-radical polymerization obtained in terms of both analytical methods are presented in the following section.

3. Solvatochromic Analysis by Means of the E_T Scale

3.1. Analysis in Terms of the E_T Scale. The solvent effect on the homopolymerization rate was analyzed in ref 11 in terms of the RSC model. It was shown that an almost linear relationship between the monomer exponent n and $\log(1/r_{11'})$ can be achieved (for $r_{11'}$, see eq 2).

Only a few monomers summarized in Table 2 in ref 11 were investigated in a wide range of solvents. For the following monomers, plots according to eq 2 ($\log(1/r_{11'})$ values against E_T) are presented: for methyl methacrylate (MMA) and *N*-vinylpyrrolidone (NVP) in Figure 2 and for styrene (St) and ethyl acrylate (EA) in Figure 3. In other scientific literature a relatively large number of data for monomer exponent n measured for MMA and St in other solvents as cited in ref 11 can be found. In these cases $\log(1/r_{11'})$ was approximately determined via eq 3 in ref 11 and the corresponding points were also traced in Figures 2 and 3. For MMA and St, experiments carried out at temperatures of 60 and 50 °C, respectively, were selected. In both figures an increasing tendency in $\log(1/r_{11'})$ with a E_T increase is observed for both MMA and St. A linear description of this tendency by means of eq 2 was hypothetically suggested, and, in addition, it was preliminarily applied to monomers NVP and EA, for which only two points per monomer were available, and to acrylonitrile (AN), where a tentative prediction was made.[20] The following equations were obtained:

$$\text{St:}\qquad \log\frac{1}{r_{11'}} = 0.004E_T - 0.358 \qquad (7)$$

$$\text{MMA:}\qquad \log\frac{1}{r_{11'}} = 0.021E_T - 0.802 \qquad (8)$$

$$\text{NVP:}\qquad \log\frac{1}{r_{11'}} = 0.049E_T - 2.338 \qquad (9)$$

$$\text{EA:}\qquad \log\frac{1}{r_{11'}} = 0.008E_T - 0.861 \qquad (10)$$

$$\text{AN:}\qquad \log\frac{1}{r_{11'}} = 0.028E_T - 1.403 \qquad (11)$$

The following conclusions can be drawn from Figures 2 and 3 and eqs 7–11:

1. Solvent susceptibility equations (eq 7–11) show that NVP is highly susceptible, MMA and AN exhibit a medium susceptibility, and St and EA exhibit a low solvent susceptibility. This corresponds to observations made until the present time on these monomers.

2. Only a few systems behave classically. One of them is MMA in benzene for which authors report consistently $n = 1$.[21–25] The straight line constructed for MMA in Figure 2 crosses the E_T axis in the domain of low E_T, indicating consistency of the reactant–solvent complex modeling with experimental results.

3. As mentioned in the Introduction, rate modeling requires modeling of all elementary reaction steps.[14] This requirement concerns also the solvent effect on these reaction steps. As was proposed in ref 14, the solvent effect on chain propagation can be separately analyzed after normalizing the overall polymerization rate by dividing it by the square root of the chain initiation rate and/or dynamic viscosity of the reaction system (solvent effect on chain termination).

Viscosity differences between monomers and solvents could not be considered in the present calculations of $r_{11'}$ in ref 11. This should be one of the reasons for observed scatter of points in Figures 2 and 3. As can be seen in Figure 2, the fine dotted straight line for NVP found without taking the solvent viscosity into account shifts considerably and is presented as a dashed line after reducing the reaction rate by the square root of the solvent viscosity. It is a rather drastic example of viscosity differences between monomer and solvent.

4. Since it was proposed that monomers do not influence themselves and are not influenced by solvents which are very similar to them, straight lines proposed in Figures 2 and 3 should cross the E_T axis in a region corresponding to the E_T value of monomers or of the above-mentioned solvents. E_T values for monomers were not measured until the present time and are approximately estimated to lie in the region of about

37 for MMA, 42 for NVP, probably very low for St, and near to that for acetonitrile (≈46) for AN. The above expectation could be confirmed for MMA and NVP (after viscosity reduction of the NVP polymerization rate) and almost for AN. This is yet not confirmed for St.

3.2. Analysis According to Taft. The solvent effect on the polymerization of styrene (St) and methyl methacrylate (MMA) was investigated in terms of eq 4. The following expressions were obtained:

$$\text{for St:}\quad \log\frac{1}{r_{11'}} = -0.267 + 0.146(\pi^* - 0.293\delta) + 0.034\beta \quad (12)$$

$$\text{for MMA:}\quad \log\frac{1}{r_{11'}} = -1.137 + 0.468(\pi^* - 0.059\delta) + 1.338\beta \quad (13)$$

Monomer responses on solvent properties are very different. Aliphatic and more polar MMA is 3 times more susceptible to solvent polarity than St. It is known as an electron-deficient monomer, and it is considerably more susceptible to solvent nucleophilicity than St.

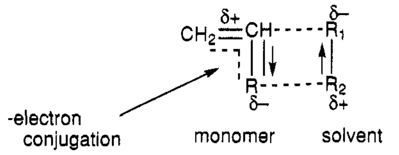
The aromatic St is about 5 times more susceptible to solvent polarizability than MMA which corresponds to the scale adopted by Taft.

It follows that the solvent susceptibility of monomers depends on several factors and that they can contribute differently to the overall monomer reactivity. Monomer constitution plays an important role in this connection. Investigations on a greater number of monomers should bring more light into the solvent effect nature.

4. Discussion

4.1. Interaction Monomer/Solvent. The present considerations are restricted to single α-substituted vinyl compounds. In contrast to α,β-disubstituted monomers, this class of monomers is less concerned by sterical or tensional effects at the double bond and for this reason is more appropriate for studies of the solvent effect.

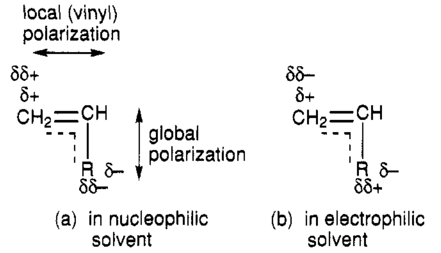
The substituent R adjacent to the vinyl group polarizes the whole monomer molecule, enabling it to interact with other polar molecules like solvent molecules. Let's consider an interaction between a monomer with an electron-withdrawing substituent and a solvent molecule. In the case of conjugation between R and the vinyl group, this interaction can be presented as follows:



(14)

δ+,δ− = partial charges before the establishment of the interaction

Depending on the nature of the solvent, monomer responses to the solvent effect are different, if one considers the bulk state as the reference state. As indicated in formula (15a), nucleophilic solvents bring about an electron release from the vinyl group to the substituent.[26] This is followed by electronic deshielding of β−C atoms measured by means of ^{13}C-NMR spectroscopy for MMA.[26,27] The reactivity of the monomer increases in reaction with a nucleophilic radical.[28] Since the polarity of the vinyl bond increases at the same time, its strength decreases slightly. It may be followed by means of IR spectroscopy, where the C=C bond vibration shifts to lower frequencies.[27]



(a) in nucleophilic solvent (b) in electrophilic solvent

(15)

δ+,− = the same as in eq 14
δδ+,− = partial charges induced by solvent only; it is imposed δδ << δ

Opposite effects are observed in electrophilic solvents as presented in eq 15b. In this case the solvent reduces slightly the global monomer polarity. Because of an increased electron density on the β-C atom, the monomer becomes less reactive. Simultaneously, the strength of the vinyl bond increases and the C=C valence bond vibration shifts in the direction of higher frequencies.

With the help of schemes in eq 15, the kinetical results can be explained in accord with NMR and IR observations.

4.2. Interaction Radical/Solvent. 4.2.1. Thermodynamic Aspects. The radical/solvent interaction is assumed to have mainly the same cause and character as the monomer/solvent interaction but a different effect on reactivity. Growing radicals in polymerization are mainly kinetically unstable. As Leroy et al.[29] pointed out, such radicals may be thermodynamically stable. They found a good linear relationship between the thermodynamic stability of radicals and enthalpy $\Delta H_0°$ and activation energy E_a of dissociation of the azo initiators yielding the above radicals.

The stabilization energy SE° of a compound was defined in ref 29 as the difference between the heat of atomization $\Delta H_a°$ (experimental bond energy) and the standard bond energy $\sum N_{AB}E°_{AB}$ (N_i = stoichiometric coefficient, $E°_i$ = standard energy of bond i):

$$\mathrm{SE}° = \Delta H_a° - \sum N_{AB}E°_{AB} \quad (16)$$

The stabilization energy SE° is positive or negative depending on whether the corresponding species is stabilized or destabilized.

It was found in ref 29 for dissociation of the symmetrical azo compounds similar to azobis(isobutyronitrile) (AIBN):

$$\Delta H_0° = 34.748 - 2.198\mathrm{SE}°(\mathrm{R}^\bullet) \quad (17)$$

$$E_a = 48.395 - 1.361\mathrm{SE}°(\mathrm{R}^\bullet) \quad (18)$$

Authors pointed out, further, that the stability of the radicals depends on the configuration of the substituents adjacent to the radical carbon atom. Enhanced stabilization was observed when both a donor and an acceptor (captor) group are present at a C-centered radical. They called this stabilization the captodative effect.

It is assumed in the present work that solvents may support the captodative effect by enhancing the delocalization of the single electron and then stabilizing the radicals.

In the following part the dissociation of alkyl azobis(isobutyrates) (RAIB) in different solvents according to Otsu and Yamada[30] is considered. Authors demon-

Table 1. Solvent Effect on the Stability of the Methyl Isobutyryl Radical Estimated According to Leroy et al.[29] for Dissociation Data of Methyl Azobis(isobutyrate) (MAIB) at 60 °C in Several Solvents[30]

solvent	E_T	$k_d \times 10^5$ (s^{-1})	$\ln(k_{d,solv}{}^a/k_{d,c\text{-}hex})$	ΔE_a (kcal·mol^{-1})	$\Delta SE°(R^•)$ (kcal·mol^{-1})
cyclohexane	31.2	0.586	0	0	0
benzene	34.5	0.885	0.412	−0.273	0.20
acetonitrile	46.0	1.010	0.544	−0.360	0.26
methanol	55.5	1.439	0.898	−0.594	0.44
acetic acid	51.2	1.564	0.982	−0.650	0.48

[a] $K_{d,solv}$ = dissociation constant for MAIB in a given solvent. $k_{d,c\text{-}hex}$ = dissociation constant in cyclohexane.

strated that this group of azo compounds is more sensitive to solvent influence as AIBN, but it is insensitive to the bulkiness of the ester substituent R.

In Table 1, the results of dissociation of methyl azobis(isobutyrate) (MAIB) in several solvents at 60 °C are listed with the corresponding E_T values, differences of activation energy of dissociation ΔE_a, and differences in $\Delta SE°(R^•)$ of produced radicals. The two last values were calculated by means of eq 18 with cyclohexane as the reference solvent. It was assumed for the determination of ΔE_a that the frequency factor in the Arrhenius equation is not affected by solvents.

From Table 1 it follows that with increasing E_T (1) the dissociation rate of MAIB increases, (2) the activation energy of MAIB dissociation decreases, and (3) the stability of the emerging radicals increases.

4.2.2. Estimation of the Solvent Susceptibility of the Radical ζ_{rad} for MMA and St Homopolymerizations. Solvent susceptibilities under discussion in the present work represent very low slopes which are therefore additive (for St $\zeta_{mon} = 0.004$, and for MMA $\zeta_{mon} = 0.021$; eqs 7 and 8).

It can therefore be

$$\zeta_{homo} = \zeta_{rad} + \zeta_{mon} \tag{19}$$

The solvent susceptibility of the homopolymerization ζ_{homo} could be calculated if the logarithm of the absolute propagation rate constant k_p as function of E_T were known. For this purpose eq 20 was used to calculate k_p:

$$\frac{k_p}{k^{\circ}{}_t^{0.05}} = \frac{r_{11'}M_1{}^2 + 2M_1M_{1'} + (1/r_{11'})M_{1'}{}^2}{\dfrac{k^{\circ}{}_t^{0.05}}{k_{p11}}r_{11'}M_1 + \dfrac{k^{\circ}{}_t^{0.05}}{k_{p1'1'}}(1/r_{11'})M_{1'}} \tag{20}$$

for polymerizations in different solvents. M_1 and $M_{1'}$ represent mole ratios of uncomplexed and complexed monomers, $r_{11'}$ is referred to eq 2, and ratios $k^{\circ}{}_t^{0.05}/k_{p11}$ (bulk polymerization) and $k^{\circ}{}_t^{0.05}/k_{p1'1'}$ (infinite dilution) were taken from ref 11. $k^{\circ}{}_t$ is assumed to be a chain termination constant independent of solution viscosity. Using $k^{\circ}{}_t$ values typical for both homopolymerizations (for MMA 2.5×10^7 L·mol^{-1}·s^{-1} at 60 °C and for St 10^8 L·mol^{-1}·s^{-1} at 50 °C), log k_p as a function of E_T was finally calculated for both polymerizations and is given in eqs 21 and 22:

$$\text{for MMA, 60 °C:} \quad \log k_p = 0.013E_T = 2.368 \tag{21}$$

$$\text{for St, 50 °C:} \quad \log k_p = -0.003E_T + 2.365 \tag{22}$$

(eq 21 at $[M]_0 = 2.0$ mol·L^{-1} and eq 22 at $[M]_0 = 0.4$ mol·L^{-1}) whereby linearity was observed ($R^2 = 0.890$ for MMA and 0.734 for St).

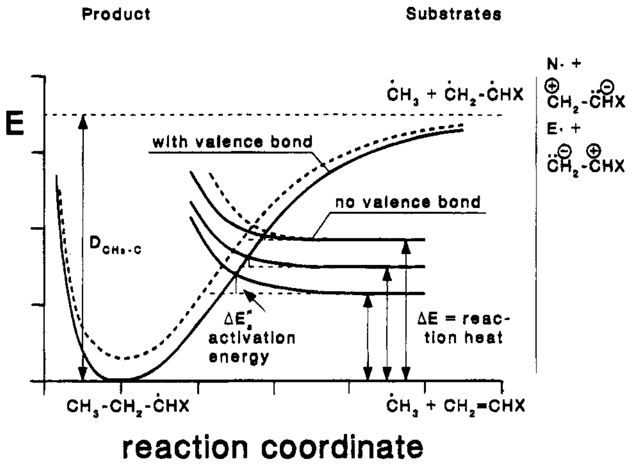


Figure 4. Energy-reaction-way diagram for addition of methyl radical to an olefinic monomer (continued and dashed curves, see text).

No measurements of k_p at 60 °C in different solvents could be found in the literature for MMA. Comparison data obtained at 25 °C[31] are evaluated, and the result is given in eq 23:

$$\log k_p = 0.010E_T + 2.105 \quad \text{at } [M]_0 = 2.0 \text{ mol·L}^{-1} \tag{23}$$

A good linearity was obtained in this case ($R^2 = 0.902$). In spite of the temperature differences, eq 23 could be considered as an indication of the accuracy of the results estimated by means of the RSC modeling (eq 20).

According to eq 19, it follows for the radical solvent susceptibility:

$$\zeta_{rad} = 0.013 - 0.021 = -0.008 \quad \text{for MMA radicals}$$

$$\zeta_{rad} = -0.003 - 0.004 = -0.007 \quad \text{for St radicals}$$

Polar solvents reduce the reactivity of both growing radicals.

For MMA polymerization reactivity loss of the radical caused by polar solvents is compensated by a much stronger reactivity increase of the monomer. Due to this a higher polymerization rate is obtained as compared to rate predictions in terms of the classical model.

The higher solvent susceptibility of the monomer should originate in the closer conjugation between the C=C and C=O π-bonds in MMA than conjugation of the single electron with the C=O group in the radical. For St the susceptibility of the monomer does not fully compensate the susceptibility of the radical. PSt grows slower in polar media as compared to rate predictions in terms of the classical model.

An alternative way of examination of the ζ_{rad} value is presented in the Appendix.

4.3. Energy-Reaction-Way Diagram. All observed and discussed effects of solvents on monomer and radical reactivity can be presented and rationalized in terms of the energy-reaction-way presentation. In this connection a diagram proposed by Fueno and Kamachi[32] for addition of a methyl radical to an olefinic monomer was adopted and is presented in Figure 4. The energies of both bonded and nonbonded radical-monomer systems are indicated in this diagram (continued curves).

The energy of the olefinic monomer increases with increasing the degree of homolytic dissociation of the double bond or with its polarization (Figure 4, continued curves on the right side). This work can be performed partially by polar solvents. As a result, reduction of the activation energy is observed and both the exothermicity and the rate of the addition reaction are increased.[33] In the case of nucleophilic radicals $N^\bullet$ polarization of the vinyl group with a positive partial charge at the β carbon atom will facilitate the reaction. The opposite will be valid for an electrophilic radical $E^\bullet$.

The reactivity of the radical may be reduced under solvent influence as a result of enhanced delocalization of the single electron. In this case polar solvents delay the addition reaction under renewed enlargement of the activation energy (see dashed curves in Figure 4).

The energy-reaction-way diagram allows a reasonable summarization of all aspects of the solvent effect on free-radical chain propagation.

Appendix: An Alternative Way for ζ_{rad} Estimation in Application to the MMA Radical

This independent way makes use of model radicals resulting from MAIB dissociation.

After transforming the natural logarithm (see Table 1, column 4) into a decadic one, the following solvent susceptibility equation of MAIB dissociation was obtained:

$$\log \frac{k_{\mathrm{d,solv}}}{k_{\mathrm{d,c\text{-}hex}}} = 0.015E_{\mathrm{T}} - 0.418 \qquad (24)$$

Factors governing this reaction are thermodynamic instability of the initiator, on the one hand, and stability of the products (two radicals and one N_2 molecule), on the other. Solvation of MAIB and of the radicals can be regarded as very similar because both interact with solvents via ester carbonyl groups. Polar solvents increase the polarity of MAIB and therefore its instability. Simultaneously, the polarity of the radical increases. As a result the delocalization of the free electron and consequently the stability of the radical increases. Both factors are considered to support the MAIB dissociation to nearly equal parts, so that:

$$\zeta_{\mathrm{diss}} = \zeta_{\mathrm{MAIB}} + \zeta_{\mathrm{rad}} = 0.015 \quad \text{and} \quad \zeta_{\mathrm{MAIB}} = \zeta_{\mathrm{rad}} \approx 0.008 \qquad (25)$$

Since radicals produced in MAIB decomposition can be regarded as a model of the growing MMA radical, the obtained value ζ_{rad} can be considered as a support of this value obtained earlier above.

References and Notes

(1) Reichardt, C. *Lösungsmitteleffekte in der organischen Chemie*; Verlag-Chemie: Weinheim, 1969; *Angew. Chem.* **1965**, *77*, 30.
(2) Huyser, E. S. *Free-Radical Chain Reactions*; Wiley-Interscience: New York, 1970.
(3) Gutman, V. *Angew. Chem.* **1970**, *82*, 858.
(4) Kováts, E.; Weiss, P. B. *Z. Elektrochem., Ber. Bunsen-Ges. Phys. Chem.* **1965**, *69*, 812.
(5) Brooker, L. G. S.; Keyes, G. H.; Heseltine, D. W. *J. Am. Chem. Soc.* **1951**, *73*, 5350.
(6) Dimroth, K.; Reinhardt, C.; Siepmann, T.; Bohlmann, F. *Liebigs Ann. Chem.* **1963**, *661*, 1.
(7) Dimroth, K.; Reihardt, C.; Schweig, A. *Liebigs Ann. Chem.* **1963**, *669*, 95.
(8) Kamlet, M. J.; Taft, R. W. *J. Am. Chem. Soc.* **1976**, *98*, 377.
(9) Taft, R. W.; Kamlet, M. J. *J. Am. Chem. Soc.* **1976**, *98*, 2886.
(10) Kamlet, M. J.; Abboud, J. L.; Taft, R. W. *J. Am. Chem. Soc.* **1977**, *99*, 6027.
(11) Czerwinski, W. K. *Makromol. Chem.* **1993**, *194*, 3015−3029.
(12) Czerwinski, W. K. *Makromol. Chem.* **1991**, *192*, 1285.
(13) Czerwinski, W. K. *Makromol. Chem.* **1992**, *193*, 359.
(14) Czerwinski, W. K. *Makromol. Chem., Theory Simul.* **1993**, *2*, 577.
(15) Wells, P. R. *Linear Free Energy Relationships*; Academic Press Inc.: London, 1968.
(16) Matyjaszewski, K. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1986**, *C26*, 1.
(17) Otsu, T.; Ito, T.; Fuji, Y.; Imoto, *Bull. Chem. Soc. Jpn.* **1968**, *41*, 204.
(18) Shorter, J. Multiparameter Extension of the Hammet Equation. In *Correlation Analysis in Chemistry*; Chapman, N. B., Shorter, J., Eds. Plenum Press: New York, 1972.
(19) Koppel, I. A.; Palm, V. A. In *Advances in Linear Free Energy Relationships*; Chapman, N. B., Shorter, J., Eds.; Plenum Press: London, 1972.
(20) Article in preparation.
(21) Cernobaj, A. V.; Grinakovskaja, A. V. *Izv. Vyss. Ucheb. Zav., Chim. Chim. Techn.* **1982**, *25*, 1131.
(22) Karapetjan, Z. A.; Smirnov, B. R. *Vysokomol. Soedin.* **1987**, *A29*, 2102.
(23) Yokota, K.; Itoh, M. *J. Polym. Sci.* **1968**, *B6*, 825.
(24) Fenyvesi, G.; Fehérvári, A.; Földes-Berezsnich, T.; Tüdös, F. *J. Macromol. Sci., Chem.* **1985**, *A22*, 203.
(25) Arnett, L. M. *J. Am. Chem. Soc.* **1952**, *74*, 2027.
(26) Bune, E. V.; Zhuravleva, I. L.; Sejnker, A. P.; Bogatchev, Ju. S.; Teleshov, E. N. *Vysokomol. Soedin.* **1986**, *A28*, 1279.
(27) Czerwinski, W. K. *Makromol. Chem.* **1991**, *192*, 1297.
(28) Giese, B. *Angew. Chem.* **1983**, *95*, 771.
(29) Leroy, G.; Peeters, D.; Sana, M.; Wilante, C. A Theoretical Approach to Substituent Effects in Radical Chemistry. In *Substituent Effects in Radical Chemistry*; Viehe, H. G., Janousek, Z., Merényi, R., Eds.; Reidel: Dordrecht, The Netherlands, 1986.
(30) Otsu, T.; Yamada, B. *J. Macromol. Sci., Chem.* **1969**, *A3*, 187.
(31) Kamachi, M.; Liaw, D. J.; Nozakura, S. *Polym. J.* **1981**, *13*, 41.
(32) Fueno, T.; Kamachi, M. *Macromolecules* **1988**, *21*, 908.
(33) Karapetjan, Z. A.; Smirnov, B. R. *Vysokomol. Soedin.* **1987**, *A29*, 2102.

MA946330J