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Propagation rate coefficients for styrene solution polymerization in dimethyl formamide and acetonitrile

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Abstract

The technique of pulsed-laser polymerization was used to measure the propagation rate coefficient (k_p) of styrene in dimethyl formamide and acetonitrile over a range of monomer concentrations at 40°C. A significant solvent effect was observed in both solvents. In dimethyl formamide, the k_p value systematically falls, as the monomer concentration decreases, to a value that is (at 1 mol l^{-1} of styrene) approximately 75% of the bulk k_p. In acetonitrile, the k_p is also reduced. In this case, however, the k_p value has a minimum at an intermediate dilution. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Solvent effects on radical polymerization have been the subject of numerous articles over the past 50 years. Such effects are known to be widespread (though often small) and many theories have been suggested to account for them, including polarity effects, the formation of various types of monomer– and/or radical–solvent complexes, and monomer-partitioning for a description of these different theories, as applied to free-radical copolymerization see Ref. [1]. In the past, studies on solvent effects in propagation may have been regarded as somewhat academic. However, as new controlled and living radical polymerizations have become commonplace, the focus of research effort is shifting towards the possible control of stereochemistry in radical polymerization, and the use of radical complexes would seem to be a promising research direction. In the past, radical–solvent complexes have been suggested to explain solvent effects on the propagation step even for common monomers such as styrene (STY) and methyl methacrylate (MMA) [2]. Clearly, if complexes of this nature are present, then it suggests that the control of stereochemistry in free-radical polymerization may be viable through the appropriate selection of solvent and/or Lewis acid. Indeed, in modern organic radical chemistry, some degree of stereo-selectivity is being achieved through this approach [3].

Although there have been many studies of the effects of solvents on the propagation step in free-radical homopolymerization, most of these studies have been performed using the now superseded technique of rotating sector polymerization. As the experimental errors associated with k_p determination by rotating sector are commonly around 40% [4], it is likely that in some cases the previously observed 'solvent effects' are attributable to systematic errors. In other cases, solvent effects on k_p may have been overlooked as they may have been subsumed in the random or systematic error of the rotating sector experiment. Since the invention of pulsed-laser polymerization by Olaj et al. [5] in 1987, it has become possible to probe the propagation reaction in free-radical polymerization with enhanced accuracy, and a few articles have found significant solvent effects on propagation reactions [6–8]. In recent work, we studied

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the propagation reactions of several *para*-substituted STYs to investigate the penultimate unit's effect in copolymerization [9]. As a part of this work, we diluted some of the monomers with solvents to minimize possible absorption of the laser light (355 nm) by the monomer. The purpose of this short article is to report some significant solvent effects on the STY propagation reaction that we observed during the course of these studies.

2. Experimental

2.1. Materials

STY (Aldrich) was passed through a column of activated basic alumina, Brockmann 1 (Aldrich) and refrigerated until required. The photoinitiators, 2,2′-azobisisobutyronitrile (AIBN) and benzoin, were recrystallized from ethanol. Dimethyl formamide (DMF) (Aldrich, HPLC grade, 99.9+%) and acetonitrile (ACN) (Ajax, HPLC grade) were used as received. The SEC eluent, HPLC grade tetrahydrofuran (THF) (BDH, Hipersolv) was triply filtered through a 0.02 μm pore size filter and then stored in the dark until required.

2.2. Polymerizations

Propagation rate coefficients (k_p) were measured using the technique of pulsed laser polymerization (PLP). Details of this technique may be found in the original article of Olaj et al. [5], or in recent reviews [10,11]. Purified monomer, photoinitiator and solvent were weighed into pyrex sample tubes (10 mm in diameter and 60 mm in height), which were then sparged by bubbling with nitrogen for 5 min and sealed with rubber septa. The reaction mixtures were equilibrated at the reaction temperature (i.e. 40°C) prior to laser exposure. The polymerizations were initiated by a pulsed Nd:Yag laser (Continuum Surelite I-20) with a harmonic generator (a Surelite SLD-1 and SLT in series), which was used to produce the 355 nm UV laser radiation, and a wavelength separator (Surelite SSP-2), which was used to isolate the 355 nm beam. The laser beam was directed at a constant pulsing rate through the sensitized monomer solution. The laser pulsing rate was controlled internally, as follows. The frequency of the flash lamp discharge, measured at 19.96 ± 0.04 Hz using a photodiode in conjunction with an oscilloscope, was controlled by a software oscillator, and the Q-switch (and thus the laser) was pulsed at various fractions of this rate, as set by a software divider function. In this way, the darktime, T_f, between laser flashes was varied. During the polymerizations, the sample was held in a thermostatted copper cell, the design and calibration of which have been described previously [12]. Polymerization activity was terminated by removing the sample from the laser, and precipitating the polymer into methanol. Conversion was restricted to 2%, so as to satisfy the assumption of constant monomer concentration that is inherent in the PLP technique. The polymer was then isolated, further purified of residual monomer via a redissolution–reprecipitation technique, and then dried to constant mass in vacuo at 60°C.

2.3. Size-exclusion chromatography

Size-exclusion chromatography (SEC) analyses were performed on a modular system comprising GBC Instruments LC1120 HPLC pump operating at room temperature; a SCl-10A Shimadzu autoinjector with a 99 position sample rack and variable injection loop facility; a column set, which consisted of a PL 3.0 mm bead-size guard column (50 × 7.5 mm) followed by four PL fixed pore size columns (a 10^6, 10^5, 10^4 and 10^3 Å), an in-line filter (0.02 μm), and a Viscotek Model 250 detector set. The detector set consisted of a differential viscometer (DV) and differential refractive index detector (DRI) connected in parallel. The data from both detectors were collected using PL data capture units at a rate of 2 points s^{-1} using PL Caliber version 6.0 GPC/SEC software [13], though only the DRI data were used in the present work. The eluent was THF at a flow rate 1 ml min^{-1}. Polymer analyte solutions were prepared with (accurately known) concentrations in the range 2–3 mg ml^{-1}, while sample injection volumes in the range 50–100 μl were used, depending upon the injection loop that was installed at the time. Lower concentrations were used for the narrow standards, depending upon their molecular weights.

The molecular weights of all samples were measured against a polystyrene (PSTY) calibration curve, compiled using a set of PSTY (PL 1.25×10^3–9.80×10^5) narrow polydispersity index standards. The calibration and analysis was performed using PL Caliber version 6.0 GPC/SEC software [13]. The k_p values were obtained from the low-molecular weight-side inflection point of the primary peak in the (linear scale) molecular weight distributions. In calculating the k_p values from the inflection point chain lengths (υ_{ip}), previously published densities of DMF [14] (data kindly supplied by Dr. R. Hutchinson) and STY [15] were used while, for ACN, the density at 40°C was measured at 0.7602 g cm^{-3} using a density metre.

3. Results and discussion

The k_p data obtained for STY in DMF and ACN at 40°C, together with the corresponding experimental conditions, are given in Tables 1 and 2, respectively. All of the PLP samples met with the IUPAC consistency criteria [16], and this is demonstrated for typical exam-

Table 1
k_p values and corresponding experimental conditions for STY in DMF at 40°C

[STY] (mol l^{-1})	Initiator	[I] (mmol l^{-1})	Pulse energy (mJ)	T_f (s)	υ_{ip}	k_p (l mol^{-1} s^{-1})
8.150	AIBN	5.15	4	1.00	1223	150
7.432	AIBN	6.05	4	1.05	1147	147
6.541	AIBN	6.80	4	1.00	909	139
6.529	AIBN	3.54	25	0.50	477	146
6.389	AIBN	11.16	20	0.50	466	146
4.915	AIBN	2.10	25	0.50	347	141
4.883	AIBN	4.89	15	1.00	664	136
4.455	AIBN	3.28	25	0.50	307	138
3.112	AIBN	3.97	25	0.50	204	131
2.975	AIBN	4.52	25	0.50	198	133
1.970	AIBN	2.19	20	0.70	174	126
1.824	AIBN	4.26	25	0.80	181	124
1.012	AIBN	2.62	20	0.70	81	115
0.736	AIBN	4.75	20	1.50	128	116

Table 2
k_p values and corresponding experimental conditions for STY in ACN at 40°C

[STY] (mol l^{-1})	Initiator	[I] (mmol l^{-1})	Pulse energy (mJ)	T_f (s)	υ_{ip}	k_p (l mol^{-1} s^{-1})
7.476	Benzoin	3.942	7	0.30	339	151
7.432	Benzoin	3.421	7	0.40	437	147
7.277	AIBN	19.449	8	0.30	312	143
7.105	AIBN	14.622	8	0.30	313	147
6.295	AIBN	18.298	8	0.40	342	136
6.165	Benzoin	3.064	7	0.40	345	140
5.111	Benzoin	3.768	7	0.60	423	138
4.948	Benzoin	3.526	7	0.50	346	140
4.206	Benzoin	3.693	7	0.60	346	137
3.935	Benzoin	2.603	7	0.50	283	144
3.001	Benzoin	3.644	7	0.60	266	148
2.910	Benzoin	3.375	7	0.40	170	146
1.775	Benzoin	1.991	7	0.30	79	148

ples from each system in Figs. 1 and 2, respectively. A plot of the k_p data for each system is given in Fig. 3. Also plotted in Fig. 3 is the bulk value for STY at 40°C (160 l mol^{-1} s^{-1}). This value, measured at the same time as the present work but reported elsewhere [4], is identical to the corresponding IUPAC benchmark value [16] – thereby providing confidence in the accuracy of the present work.

Two main observations may be made concerning the effects of DMF and ACN on STY homopropagation. Firstly, during the course of this work, it was found that for the STY/DMF system, the STY concentration could be reduced to very low levels (<1 mol l^{-1}) – beyond which PLP experiments became unfeasible, owing to the long reaction times and minuscule amounts of polymer produced at low conversion. However, in the case of the STY/ACN system, the STY concentration could only be reduced to around 2 mol l^{-1} as, beyond this level, the polymer precipitated out during polymerization. Secondly, examining Fig. 3, it is clear that, on dilution with

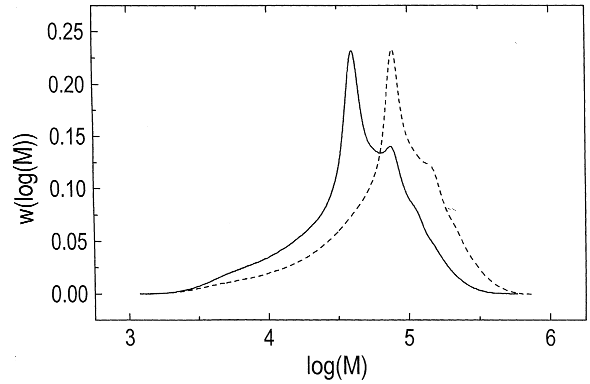

Fig. 1. Molecular weight distributions for two typical STY/DMF samples from this study: (—) 4.9 mol l^{-1} and $T_f = 0.50$ s (A), (- - -) 4.9 mol l^{-1} and $T_f = 1.00$ s (B). The inflection point molecular weight of B (69 052) is approximately twice that of A (36 052), which is thus in accordance with the IUPAC consistency criteria [16].

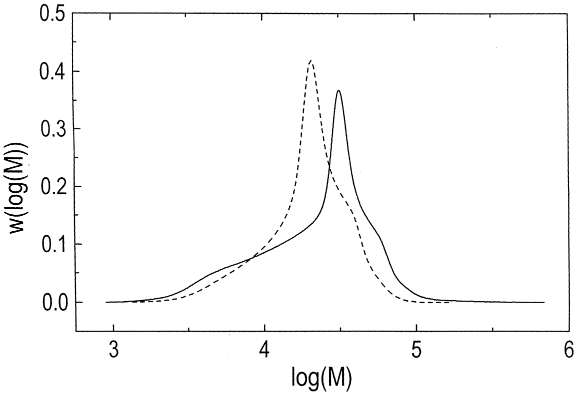

Fig. 2. Molecular weight distributions for two typical STY/ACN samples from this study: (- - -) 2.9 $\mathrm{mol\,l^{-1}}$ and $T_f = 0.40$ s (A), (—) 3.0 $\mathrm{mol\,l^{-1}}$ and $T_f = 0.60$ s (B). The inflection point molecular weight of B (27 875) is approximately twice that of A (17 737), which is thus in accordance with the IUPAC consistency criteria [16].

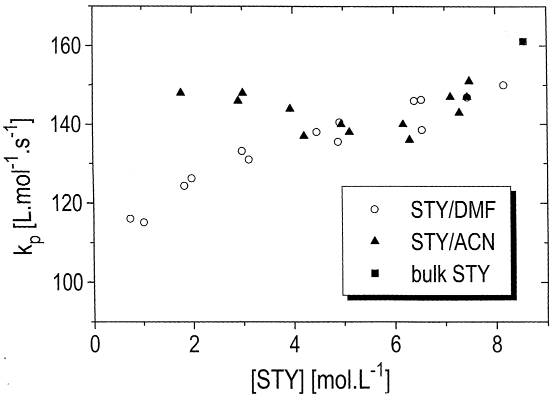

Fig. 3. Plot of k_p versus monomer concentration for the STY/ACN and STY/DMF solutions at 40°C. Also shown is the corresponding k_p value for bulk STY [16].

either solvent, substantial and significant decreases in the k_p occur – results which are consistent with the early findings of Burnett et al. [17]. In DMF, the k_p value systematically falls as the monomer concentration decreases, to a value (at 1 $\mathrm{mol\,l^{-1}}$ of STY) approximately 75% of the bulk k_p. In ACN, the k_p is also reduced, though the k_p value has a minimum at an intermediate dilution. In what follows, the possible explanations for the observed solvent effects will be explored.

As noted in Section 1, solvent effects on k_p are often attributed to monomer partitioning – an effect, which is also known as a 'bootstrap' effect. However, the results for the STY/ACN system seem to refute this possible explanation as at very high ACN concentrations the polymer precipitates, and hence, ACN is clearly a poor solvent for the polymer. As a result of this, in this system, the thermodynamic driving force for preferential absorption should in fact increase the concentration of STY around the polymer at high ACN concentrations (and hence increase, rather than decrease, the observed k_p). Although the results indicate that, at the very high ACN concentrations, the k_p does start to increase again towards its bulk value (which may indicate a minor role for preferential solvation in this system), partitioning effects cannot account for the fact that (at all concentrations of ACN) the k_p is lower than the bulk value for STY.

Another possible explanation for the observed solvent effects is the formation of a solvent–radical (or solvent–monomer) complex, which somehow stabilises the propagating radical (or monomer). However, if the effect is simply to stabilize the radical (or monomer) then it is unlikely that this would result in the substantial drop in k_p that is observed for the STY–DMF system. For, free-radical propagation, reactions are very exothermic – consonant with an early transition state – and thus, a substantial effect on the reaction barrier is unlikely to be explained by a simple radical (or monomer) stabilisation argument – this is analogous to an argument recently presented for the penultimate unit effect in copolymerization [18].

Solvent effects have also been attributed to polarity effects. However, while such effects are likely to be important in copolymerizations involving STY (correlations between the monomer reactivity ratios and solvent dielectric constants having been observed for its copolymerization with MMA [19–21] and with acrylonitrile [22,23] in various solvents), such effects are unlikely to be important in the homopolymerization of this monomer as the charge-transfer configurations of its transition structure are likely to be relatively high in energy as the electron-rich phenyl substituent is attached to both the monomer and the radical. In any case, the dielectric constants for ACN and DMF are very similar, and hence, on this basis, similar behaviour should have been predicted for each system. Furthermore, previous work by Davis et al. [24] found that the solvent polarity (methanol or ethyl benzene), exerted no significant effect on the k_p of STY – a result, which would appear to rule out the influence of polarity effects in the homopropagation reaction of STY.

Given the failure of these other possible explanations, it would appear (by default) that the solvent is playing a specific role in the transition state of the reaction. That is, it is not only (de)stabilizing the radical and/or monomer but possibly also affecting the geometry of the transition state via specific interactions. Of course, the present results do not provide direct evidence for this conclusion, and further studies (examining, for instance, the stereochemistry of the resulting polymers and the Arrhenius parameters of the propagation reaction) are required. These results are worthy of further investigation for, if this conclusion is valid, it suggests the possibility of exerting control over the propagation step via a complexation strategy.

What is perhaps most surprising in these data, is the large size of the observed solvent effects for a monomer such as STY. In general, it would be expected that strong solvent effects would be more likely to occur in relatively unstable propagating radicals as the scope for stabilisation is much stronger. This seems to be true for monomers such as vinyl acetate [25] and the intriguing example of vinyl benzoate, which as Kamachi et al. [26] showed, propagates more slowly than expected (a result, which can be attributed to the stabilization of the radical by the benzene ring of the monomer itself). However, STY forms relatively stable propagating radicals and hence the fact that a 25% decrease in STY k_p can be induced by DMF suggests that radical–solvent complexes may be commonplace. Whether complexes can be exploited to gain some control over polymer stereochemistry will depend on the ability to design complexing agents, which exert a very specific effect in the transition state – analogous to the gegen ion in ionic polymerization. Clearly, ionic interactions are very strong and finding a non-ionic equivalent may be challenging – although, as already mentioned in Section 1, specific control in organic small-radical chemistry is being exerted via the use of Lewis acids [3].

4. Conclusions

In this work, it was shown that both DMF and ACN can exert substantial solvent effects on the bulk homopropagation rate coefficient of STY at 40°C. It was argued that the results obtained could not be wholly explained by partitioning, polarity or simple radical stabilization effects. Thus, it appears that these solvents may be directly interfering in the transition structure of the propagation reaction, though further studies are required to confirm this result.

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