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Solvent Effects on the Propagation Rate Coefficient for Free Radical Polymerization

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ABSTRACT: The effect of solvent on the propagation rate coefficient (k_p) for styrene and methyl methacrylate was examined using pulsed laser polymerization. Solvents used were ethanol and methanol over the range 25–50 °C. Solvent:monomer ratios were increased until phase separation of the polymer was observed during the polymerization. A block copolymer was also used to stabilize the formed particle phase, thereby simulating the early-time nucleation behavior of dispersion polymerization systems. There were no observable solvent effects on k_p. This can be rationalized in terms of the transition state for propagation, where the reaction coordinate comprises the incipient bond in a configuration such that solvent molecules can play no direct role in the reaction dynamics.

Introduction

Knowledge of any solvent effects on the polymerization kinetics is important for modeling the aqueous-phase component of emulsion polymerizations[1] and in nonaqueous dispersion polymerizations where somewhat polar solvents, such as ethanol, are sometimes utilized.[2] In addition, the development of *a priori* models of the rate coefficients important in polymer kinetics will be aided with a knowledge of effects induced by various solvents. This communication examines solvent effects on the propagation rate coefficients for free-radical polymerizations in the presence of relatively polar solvents such as alcohols. The monomers used are styrene and methyl methacrylate (MMA), for which the rate coefficient for propagation, k_p, has been well characterized in recent years,[3] particularly with the introduction of the pulsed laser polymerization (PLP) technique. The first appearance in the literature of the technique seems to be a suggestion in a theoretical paper in 1977,[4] but the technique was developed independently and properly implemented for the determination of k_p by Olaj and co-workers.[5–7] Some data have been published on the effect solvents have on k_p, mostly by Davis et al.,[8] who used the PLP technique with inert monomer analogues such as ethylbenzene for styrene and ethyl acetate for MMA and showed that there was no effect on the measured k_p's. Methanol was also used over a limited concentration range (5–20% (v/v)) and again no effect of solvent was observed. Barton and co-workers[9] also examined the effect of a range of nonsolvents utilizing the rotating sector method. These included C_1 to C_4 alcohols for which a range of k_p's were considered to be the same within experimental error. The improved accuracy of the PLP technique should enable the effects of solvent to be investigated more thoroughly. Since the rate coefficients of many radical–molecule reactions in the gas and solution phases are similar (e.g., refs 10 and 11), it is generally expected that there will be minimal solvent effects as long as there are no strong solvent interactions.

The k_p measurements in this communication were performed using PLP. This technique has the advantage of providing k_p independent of other polymerization rate coefficients such as that for termination. A pulsed-UV laser source is used to generate a rapid burst of initiator radicals which undergo polymerization until the next laser pulse. This simplifies the kinetic analysis of the polymerization process to the following equation

$$\nu_p = k_p[M]t_f \qquad (1)$$

where [M] is the monomer concentration, t_f is the time between pulses, and the chain length, ν_p, is obtained from the inflection point on the molecular weight distribution of the polymer formed between successive pulses, determined by gel permeation chromatography (GPC). The use of the inflection point has been justified elsewhere.[6,12–14]

Here we present an investigation into the effects of varying the solvent polarity in styrene and MMA homogeneous polymerizations utilizing ethanol and methanol as diluents. Both these solvents are significantly more polar than monomer and polymer. These experiments were extended to include the effect of polymer precipitation, including the use of a nonionic surfactant added to stabilize any polymer precipitates formed. Such events mirror the conditions found prior to nucleation in the dispersion polymerization of monomers such as styrene and MMA.[15]

Experimental Section

Reagents. Styrene (Aldrich) and MMA (Baker) were distilled under reduced pressure prior to use. The initiator 2,2′-azobis(isobutyronitrile) (AIBN) was recrystallized 3 times from methanol. The block copolymer used in these studies was a poly(styrene)-*block*-poly(ethylene oxide) (PS-*b*-PEO) with a polystyrene section of number-average molecular weight (M_n) of 5800 and a PEO block of 13 500. It had a final polydispersity (M_w/M_n) of about 1.4. Other reagents (ethanol, methanol, and 2,6-di-*tert*-butylphenol) were AR grade (Aldrich) and used as received. GPC measurements utilized tetrahydrofuran (THF) as the continuous phase for both polystyrene and pMMA analysis.

Pulsed Laser Polymerizations. Solutions of the relevant solvent/monomer mixtures were prepared with AIBN (5×10^{-3} mol dm^{-3}). The polymerizations were carried out in cylindrical, flat-bottomed Pyrex sample tubes (approximately 1 cm diameter) charged with ≈1 cm^3 of sample, which was degassed by bubbling with high-purity argon. The ampules were placed in a thermostated cell holder with a thermocouple to monitor the temperature. Most runs were carried out at 298 K with some conducted at temperatures up to 323 K.

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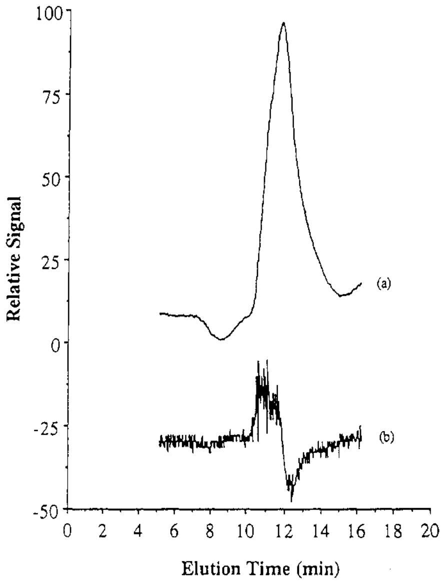

Figure 1. GPC trace (a) and its differential (b) showing the inflection point, which is the minimum in the differential from the right-hand side of the trace. The sample trace was for the polymerization of styrene in ethanol (25% (v/v)) where $t_f = 0.2197$ s and $\nu_p \approx 120$.

Table I. Measured Propagation Rate Coefficients k_p at 25 °C

monomer	solvent (% volume)	[monomer], mol dm^{-3}	[PS-*b*-PEO], mol dm^{-3}	k_p, dm^3 mol^{-1} s^{-1}
styrene		8.66		84
styrene	ethanol (25%)	6.52		76
styrene	ethanol (50%)	4.35		80
styrene	ethanol (75%)	2.17		101
styrene	ethanol (50%)	4.35	5.2×10^{-5}	74
styrene	ethanol (75%)	2.17	5.2×10^{-5}	87
styrene	methanol (25%)	6.52		70
MMA		9.35		306
MMA	ethanol (25%)	7.01		300
MMA	ethanol (50%)	4.67		292
MMA	ethanol (75%)	2.35		414
MMA	ethanol (75%)	2.35	5.2×10^{-5}	432

The pulsed laser system used here has been described elsewhere.[8,16] The polymerization was initiated with laser pulses (15 ns wide at half height) of 35 mJ at 355 nm generated by a Quanta-Ray DCR2 pulsed Nd:YAG laser. The beam diameter of approximately 9 mm was directed through the base of the cell in order to minimize dead volume. The radical flux was equivalent to a radical concentration of approximately 6.5×10^{-7} mol dm^{-3}. Dark times, t_f, were varied from 0.1 to 5 s and the number of pulses was chosen to obtain ≈1% conversion for the duration of the experiment. Chemical inhibitor, 2,6,di-*tert*-butylphenol in isopropyl alcohol was then added to prevent further polymerization.

Subsequent analyses of the molecular weight of the polymer produced were performed using a Waters GPC fitted with three μ-Styragel columns with pore sizes 10^5, 10^3, and 10^2 Å. Calibration of the traces was performed using well-characterized polystyrene and pMMA standards. The detector used was an online differential refractometer. The inflection point (shown as a minimum in the differential of the GPC trace) on the GPC traces was used as the estimate of ν_p (Figure 1).

Results and Discussion

Table I summarizes the measured k_p's for the various solvent conditions with both styrene and MMA at 25 °C. The changing polarity of the polymerization media had little effect on k_p for either MMA or styrene. The k_p values agreed well with previous estimates ($10^{7.04} \exp\{-29.5 \text{ kJ mol}^{-1}/RT\}$ dm^3 mol^{-1} s^{-1}) found under bulk polymerization conditions for styrene.[3] The MMA result at 25 °C is in excellent agreement with the results of O'Driscoll and Mahabadi[17,18] of 315 dm^3 mol^{-1} s^{-1} using SIP and the result of 299 dm^3 mol^{-1} s^{-1} measured by Olaj and co-workers.[19] The errors in the molecular weight analysis are likely to be relatively large (approximately ±10%), as a result of the need to calibrate the system and the ability to determine the inflection point accurately. It is seen that all the measured rate coefficients for polymerization in both bulk and polar solvent conditions (<50% (v/v) ethanol) are the same (for a given monomer) within the precision of the data.

Solvent effects are however apparent on the observed k_p's where the formed oligomers precipitated from the reacting solution. This occurred for reaction in the 75% (by volume) ethanol mixtures. For the MMA polymerization in particular, this resulted in an increase in the *apparent* k_p. In the case of styrene, while some increase is observed, it is within the experimental uncertainty of these measurements. The origin of this increase in k_p may result from two effects: (1) there may be preferential solvation of the polymer by monomer, thereby increasing the monomer concentration at the free radical site, or (2) as the polymer phase forms it will scatter more light, causing a decrease in the ability of the next pulse to fully terminate all the chains formed. Although such an effect is possible, it is unlikely to influence greatly the inflection point (and hence k_p) but rather result in a stronger second peak ($2\nu_p$) as some chains will grow until the next pulse (as pointed out by reviewers). Thus it would seem that preferential solvation is the most likely explanation of the apparent increased k_p. This result also mitigates against the occurrence of substantial preferential solvation of the radical end (e.g. ref 20) before precipitation occurs, as there is no change in k_p with addition of solvent. While it does not rule out the possibility that there is a fortuitous cancellation of the effect of any preferential solvation of the chain end, with some other unknown effect (e.g. the viscosity effect discussed in the next section), such a cancellation is unlikely. These results are therefore most consistent with preferential solvation only occurring with the whole polymer chain (e.g. precipitation), rather than of the radical end. The molecular weights of the chains produced in the cases where precipitation occurred were approximately 10 000 amu for the pMMA and up to 5000 amu for the polystyrene.

The addition of the block copolymers, to stabilize the heterogeneous system produced, showed similar results to the system without the stabilizer. This would indicate that the surfactant played little role in forming the aggregates that were observed in this system. In particular it has been suggested that nucleation in dispersion polymerization systems occurs within micelles of the stabilizer.[15] If block copolymers did exhibit micellization, they should swell with monomer and this high local concentration should be reflected in observed k_p. At the block copolymer concentrations used (≈ 5×10^{-5} mol dm^{-3}), no effect on k_p was observed, although this is not a definitive result.

The temperature dependence of the propagation rate coefficient for styrene was examined in 50% (v/v) ethanol mixtures. Figure 2 compares the temperature dependence found previously by Lansdowne et al.[21] with that data found in this study. Again solvent is found to have little effect on k_p in the range 25–50 °C, although the temperature range over which the present data were measured is too small to report meaningful Arrhenius parameters.

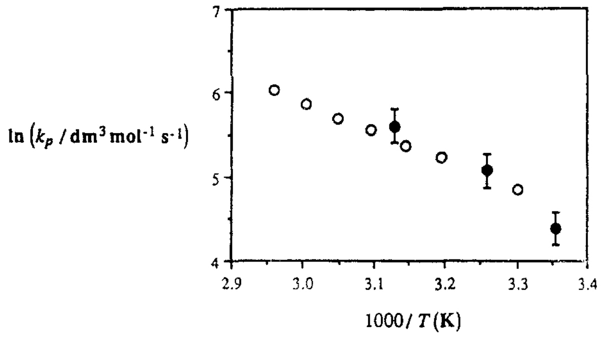

Figure 2. Temperature variation of the propagation rate coefficient, k_p, for styrene: data from Lansdowne et al.[21] (○); average results using a 50/50 (v/v) ethanol/styrene mixture (●).

Theoretical Description of Solvent Effects on the Propagation Rate Coefficient

The data here are consistent with a negligible solvent effect on the observed rate coefficient, except in the situation where precipitation of the polymer occurred (probably due to preferential solvation with monomer, rather than a changing k_p). Thus for a considerable range of solvent conditions no effect of k_p was observed. We now examine the implications of this for the nature of the transition state for the situation where the polymer remains solvated. We note that it has been observed that many radical–molecule reactions (including propagation) have similar rate coefficients in the gas and liquid phases (e.g., refs 10 and 11), and so we expect the nature of the transition-state dynamics to be such that there will be minimal solvent/transition-state interaction and, hence, minimal solvent effects on k_p.

There is good evidence (e.g., ref 22, p 183) that the transition state typical of a radical/(closed-shell) molecule reaction such as propagation consists of a geometry qualitatively similar to that of the product (i.e., a propagated macroradical in the present case) with the incipient bond slightly elongated from its value in the product. The reaction coordinate, at large distances, consists of the center-of-mass motion of the two moieties (in these cases, the styrene monomer and the macroradical); on the other hand, the reaction coordinate in the neighborhood of the transition state is largely composed of this incipient bond. In solution, one could imagine two extreme cases for the effect of solvent:

Case 1. The reaction is governed by the relatively slow "docking" of the styrene with the macroradical, with the solvent impeding this docking: the reaction coordinate will be that appropriate to relatively large distances, viz., the styrene/chain-end distance.

Case 2. The reaction in solution behaves the same as in the gas-phase: only motion in the vicinity of the transition state is important, and here the reacting moieties are so close that there is no room for solvent to have much influence on the reaction dynamics, apart from possible polarization effects on the energies of reactants and/or transition state.

The observed lack of solvent effects on k_p can be used to distinguish between these two extremes. Although at first sight it might appear that the first possibility (solvent-mediated motion of the reacting moieties) is automatically eliminated by this observation, a more detailed treatment shows that this is not necessarily the case.

Case 1. To examine the dynamics of the supposition that the reaction coordinate consists of the styrene/macroradical-chain-end distance, a simple yet rigorous approach is through the Kramers equation.[23] This invokes the assumption that the rate of a condensed-phase reaction involving two large moieties can be obtained from that of the dynamics of the corresponding reaction in the gas phase are as follows. The effect of the condensed phase is supposed to be only on motion along the reaction coordinate, by superimposing solvent effects upon the gas-phase dynamics as viscous drag (treating the microscopic moieties as macroscopic particles moving in a bulk medium) together with a random force corresponding to Brownian motion. Hamilton's equations are then replaced by a Fokker–Planck equation.[24] If it supposed that the reaction profile is composed of parabolic segments, then this Fokker–Planck equation can be solved,[23] leading to the simple result that the gas-phase transition-state theory expression for the rate coefficient can be modified to find the corresponding condensed-phase rate coefficient by

$$k_{\text{condensed}} = \frac{1}{\omega}\left(\left(\frac{\beta_2}{4} + \omega^2\right)^{1/2} - \frac{\beta}{2}\right)k_{\text{gas phase}} \qquad (2)$$

where for a reaction involving two identical moieties with reduced mass m, the coefficient β is given by the Stokes–Einstein relationship, with slip boundary conditions as $4\pi\eta d/m$, η being the bulk viscosity, d the hydrodynamic radius of the moving moieties, and ω the curvature of the reaction coordinate at the saddle point. That is, ω is the imaginary frequence at the saddle point which characterizes the transition state (e.g., ref 22). In the case of a propagation reaction where one of the reacting moieties is an essentially immobile chain end, then[25] m is the mass and d the van der Waals radius of the monomer.

As stated, there are a number of more sophisticated approaches to the dynamics of reactions in solution (particularly through the use of frequency-dependent friction coefficient: see, e.g., refs 26 and 27) and, indeed, improvements to Kramers' approximate solution to the Fokker-Planck equation (e.g., ref 28). There are also more "traditional" approaches such as that of transfer free energy[29] and group interaction parameters of the transition state.[30,31] However, eq 2 not only has the advantage of simplicity but also has provided excellent fits to sensitive data (e.g., from picosecond experiments[25,32,33] and simulations[34,35]). These data show that eq 2 provides a good representation of the movement of a relatively bulky group such as styrene moiety in solvent.

In the present context of examining solvent effects on k_p, it is most useful to consider the predictions of eq 2 for the change in k_p with viscosity for two solvents A and B

$$\frac{k_{p,A}}{k_{p,B}} = \frac{({}^1/_4\beta_A{}^2 + \omega^2)^{1/2} - {}^1/_2\beta_A}{({}^1/_4\beta_B{}^2 + \omega^2)^{1/2} - {}^1/_2\beta_B} \qquad (3)$$

This expression has two simple limits: when $\omega \gg \beta$ $k_{p,A} = k_{p,B}$, while when $\omega \ll \beta$, the rate coefficients are proportional to the viscosity ratio of the two solvents. This is why one cannot assume that the supposition that the reaction dynamics are controlled by the relative motion of the two moieties automatically implies a viscosity dependence of the rate coefficient: in the first limit ($\omega \gg \beta$)k_p would be independent of viscosity.

To estimate viscosity effects with eq 3, it is necessary to evaluate the various parameters therein. The hydrodynamic radius was taken to be the styrene van der Waals radius of 3 Å. This correlates well with that calculated from the diffusion coefficients measured for styrene and using slip boundary conditions. The viscosities used were those of ethanol (1.2 cP; 1 cP = 10^{-3} kg m^{-1} s^{-1}) and ethylbenzene (0.6 cP) at 17 °C. These are representative of the typical viscosity changes encountered in these experiments. The results of the calculation of the ratio

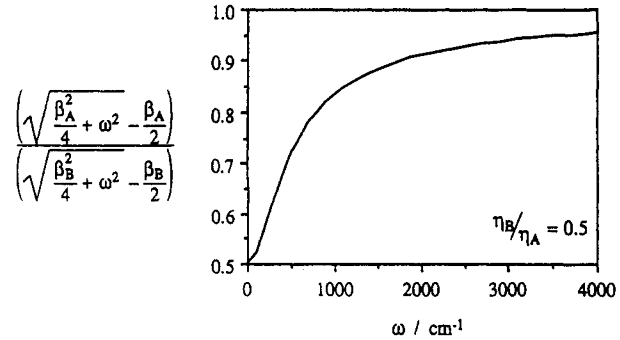

Figure 3. Variation of the ratio of Kramers ratio (eq 3) with the barrier frequency ω, where the viscosity ratio $\eta_A/\eta_B = 2$.

of eq 3 with these parameter values are shown in Figure 3, as a function of ω.

There is at present no information on the value of ω for a typical propagation reaction being examined here, and it is necessary to use what limited information is available for similar processes. Accurate quantum chemistry calculations have been carried out for the reactions $CH_3^\bullet + C_2H_3X \rightarrow CH_3C_2H_3X^\bullet$, where X is a series of atoms such as H, Cl, etc. These are radical–molecule processes with transition states expected to be archetypical for the propagation reaction of a macroradical with a vinyl monomer. These quantum calculations gave an imaginary frequency ω in the range 400–500 cm^{-1}; this is similar to that of the corresponding real frequency for a stable molecule, viz., the 675 cm^{-1} of a C·C stretch.[36] Comparison with Figure 3 would predict that there is a significant change in k_p for imaginary frequencies of this magnitude. In particular, the change in viscosity that results from changing from 100% styrene to 50% styrene/ethanol mixture is approximately 35% for 50% (v/v) ethanol/styrene compared to pure styrene. This change was calculated using[9]

$$\log \eta_{MIX} = \chi_{STY} \log \eta_{STY} + \chi_{ETH} \log \eta_{ETH} \qquad (4)$$

where χ_{STY} and χ_{ETH} are the mole fractions of styrene and ethanol, and the η's the corresponding viscosities, with η_{STY} (25 °C) = 0.696 cP and η_{ETH} (25 °C) = 1.10 cP. The change in k_p given by the Kramers relationship is 18%, which would be observable in the present experiments.

Since the examples quoted above show that the Kramers equation successfully describes condensed phase reactions whose reaction coordinate involves center-of-mass motion of a moiety the size of styrene, the present data show that it appears to be inapplicable to the polymerization reaction. That is, the original supposition that the reaction coordinate involves center-of-mass motion "docking" of the styrene onto the chain end is rigorously disproved.

Case 2. The reaction in solution behaves the same as in the gas phase: only motion in the vicinity of the transition state is important. The reaction coordinate for the propagation reaction consists of the distance between the carbon on the styrene and the carbon of the macroradical on which the free radical is largely delocalized, consistent with the quantum calculations on smaller species.[36] There is no space between the carbons (each attached to a bulky group) for significant solvent penetrations and this therefore would predict no solvent effects. This is in accord with experiment. These results strongly indicate that the transition state involves a relatively short intermoiety C·C distance rather than the general proximity of the two moieties.

While the foregoing theoretical considerations, in conjunction with the lack of significant solvent effects on the propagation rate coefficient at low conversion, indicate that the solvent plays no major role in the reaction dynamics, it must be borne in mind that solvent effects in propagation are important at very high polymer fraction (when the polymer becomes glassy), when the monomeric diffusion coefficient is so small that the approach of the moieties to become trapped in a relatively long-lived solvent cage becomes rate-determining. This has been directly observed by measurement of k_p at very high conversion.[37]

Conclusions

The PLP data show that changing solvent viscosity and polarity has no significant effect on the propagation rate coefficient of styrene or MMA. This is consistent with the transition state, and reaction dynamics overall, for the propagation reaction, being unaffected by the presence of polar solvents. Also no preferential solvation of the polymer by the monomer can occur, as this would have resulted in an apparent increase in k_p. Preferential solvation of the radical site seems to occur when polymer precipitation takes place and results in an apparent increased k_p. This effect may be worthy of further study both experimentally and theoretically.

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