

The effect of benzyl alcohol on pulsed laser polymerization of styrene and methylmethacrylate

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The Effect of Benzyl Alcohol on Pulsed Laser Polymerization of Styrene and Methylmethacrylate

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SYNOPSIS

The homo- and copolymerizations of styrene (STY) and methylmethacrylate (MMA) have been studied in the presence of several levels of benzyl alcohol (BA). From pulsed laser polymerizations it has been found that the apparent propagation rate constant increased with increasing BA for all systems. In copolymerization it has been found that the reactivity ratios for STY decrease somewhat, but those for MMA change little with increasing BA. The tacticity of poly(MMA) formed in the presence of BA is affected, the amount of mm diads increasing with increasing BA. The results are interpreted as supporting the hypothesis that BA forms a strong complex with radical chain ends terminating in MMA and a weak complex with those terminating in STY. © 1997 John Wiley & Sons, Inc.

Keywords: pulsed laser polymerization • kinetics • solvent effects

INTRODUCTION

It has long been recognized that solvents may affect free radical homo- and copolymerization kinetics.^{1,2} Most of the data available have been obtained either by measuring the overall rate of homopolymerization or by estimating the reactivity ratios obtained in copolymerization. In a few cases, rotating sector measurement of propagation rate constants, k_p , have been made to explore solvent effects. Unfortunately, these methods are either inappropriate or too inaccurate to explore the subtle effects that solvents seem to have on free radical polymerization. In the case of overall rate measurements, it is impossible to separate effects on termination from those on propagation. In copolymerization, the reactivity ratios are estimated in accord with some reaction schemes that describes propagation, such as the Mayo-Lewis model. Because reactivity ratios are only ratios of propagation rate constants and often

have large inaccuracies, it is difficult to infer mechanistic effects from their solvent dependence. Rotating sector methods have often given unreliable or imprecise results for a variety of reasons. As a result of all this, the literature contains many, varied attempts to explain experimental results on solvent effects which invoke such diverse phenomena as solvent polarity, complex formation between solvent and chain end, preferential solvation of the polymer coil by one of two monomers or by the solvent, etc. The explanations are as diverse as the data, and it is not possible to generalize on the topic.

In an effort to provide some unambiguous data, we have used pulsed laser polymerization (PLP) to measure the effect of solvent on the apparent propagation rate constant, $\langle k_p \rangle$, in the homopolymerizations and copolymerization of styrene (STY) and methylmethacrylate (MMA). PLP is a robust technique which has been found capable of measuring $\langle k_p \rangle$ with a precision often better than 5%. It depends on measuring a particular chain length, ν_p , in a photopolymerization where the laser is pulsed at a time interval τ . In typical experiments, the laser is pulsed at a frequency of about 1 Hz, τ is about 1 s, and ν_p is the inflection point on a peak measured

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by gel permeation chromatography (GPC). The ratio of the two easily measured experimental quantities is related to $\langle k_p \rangle$ and the monomer concentration $[M]$ by the equation:

$$\frac{\nu_p}{\tau} = \langle k_p \rangle [M] \quad (1)$$

In the context of eq. (1), $[M]$ refers to the monomer concentration used in a homopolymerization or to the sum of the two monomer concentrations used in a copolymerization. In the latter case, $\langle k_p \rangle$ is a mean rate constant which is expected to be a function of the molar ratio of the two monomers used in a given experiment.

In preliminary work³ with a variety of solvents, it was observed that benzyl alcohol (BA) had a strong effect on $\langle k_p \rangle$ in the homopolymerizations of STY and MMA. Previously, Otsu and Ito⁴ had shown for the copolymerization of STY and MMA in various solvents that there is a trend in the reactivity of the MMA radical toward STY which is a function of the solvent polarity. In BA, Otsu found the reactivity ratios to be $r_{\text{STY}} = 0.44$ and $r_{\text{MMA}} = 0.39$, values which may be compared with the bulk reactivity ratios of 0.454 and 0.472.⁵ We have recalculated the reactivity ratios using Otsu's data and a nonlinear least squares technique.⁶ This gives $r_{\text{STY}} = 0.446$ and $r_{\text{MMA}} = 0.414$, with a 95% confidence interval that includes the bulk values cited. This suggests that the relative reactivities of the STY and MMA radicals toward these two monomers are only slightly affected by BA. Kratochvil and co-workers⁷ have considered preferential solvation effects in polymer-monomer-solvent systems, and, in the particular case of poly(MMA) in a MMA-BA mixture, show that there is no preferential solvation of BA or MMA by the poly(MMA).

The experimentally observed variation of $\langle k_p \rangle$ with reaction conditions such as solvent or monomer concentration or composition must be interpreted in terms of some explicit model. For example, numerous PLP studies (building on the rotating sector work of Fukuda and co-workers⁸) have interpreted the composition dependence of $\langle k_p \rangle$ in copolymerization in terms of an implicit penultimate unit effect (IPUE). Others^{9,10} have suggested that solvent effects in copolymerization could be explained by preferential solvation of the polymer coil by one of two monomers (the "Bootstrap effect"⁹). The small effect of BA on reactivity ratios of STY and MMA found by Otsu and Ito, and the negligible preferential solvation of PMMA by BA in a MMA-BA mixture are at variance with the relatively strong solvent

effect on $\langle k_p \rangle$ observed in the preliminary work. Therefore we have examined this system carefully using PLP.

EXPERIMENTAL

The PLP experiments were conducted at 30°C as previously described¹¹ with the laser providing 20 mJ/pulse and flash frequencies varying from 1 to 10 Hz. Reagent-grade benzyl alcohol was freshly distilled prior to use. In a typical experiment, a total of 4 mL of solvent plus monomer were polymerized using 2,2'-azobisisobutyronitrile (AIBN) as an initiator.

GPC analysis was also done as previously described,¹¹ weighting the calibration for the molecular weight of the copolymer of STY and MMA by the mole fractions of the two homopolymers. The GPC data were plotted as suggested by Hutchison,¹² and ν_p taken as the inflection point of the PLP peak.

Copolymerization experiments were done at several levels of BA: 30, 50, and 75% by volume. In all experiments, the mole fraction of the two monomers employed was calculated using the *D*-optimal criteria of Tidwell and Mortimer¹³ for the conventional Mayo-Lewis model of copolymerization. Copolymerizations were carried out at 60°C using AIBN as a thermal initiator. Copolymer compositions were determined by NMR on a Bruker AMX-500 spectrometer at room temperature using an inverse 5 mm broadband probe. Samples (10% w/v in CDCl₃) were typically subjected to 64 scans, acquiring 16384 data points over a sweep width of 12 ppm. A pulse time of 10.8 μs was used (90° pulse), with a relaxation delay of 5 s between pulses. Data were processed with a 0.1 Hz line broadening factor in the exponential multiplication. Integration was completed on baseline corrected spectra using the UXMNMR software integration routine. Chemical shift assignments for the polymer were confirmed with literature values reported by German and colleagues.¹⁴

RESULTS

Table I shows the values of $\langle k_p \rangle$ determined from PLP over a wide range of BA concentrations for homopolymerizations of STY and MMA and also for an equimolar, "azeotropic" copolymerization of the two monomers. The effect of BA on copolymer composition is shown in Table II, from which the reactivity ratios and associated 95% confidence in-

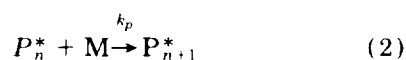
tervals shown in Figure 1 were calculated. In Table III we show the effect of BA on the tacticity of poly(MMA).

DISCUSSION OF RESULTS

Effect of BA on Kinetics

It is clear from Tables I and II that BA has a strong effect on the apparent rate constant, $\langle k_p \rangle$, of the homo- and copolymerizations of STY and MMA and a weaker effect on the copolymerization compositions. The values of $\langle k_p \rangle$ are increased by increasing the ratio of BA to monomer, but, as shown in Figure 1, the reactivity ratio for addition to STY is decreased only slightly, while that for addition to MMA remains essentially unchanged. The effect of BA on tacticity of the formed poly(MMA) is small, but well beyond experimental error. On the balance of evidence, we hypothesize that BA complexes the propagating radical chain end and so affects its reactivity. The following discussion sets forward the reasons for this hypothesis and seeks to quantify the complexation in terms of the data we have observed.

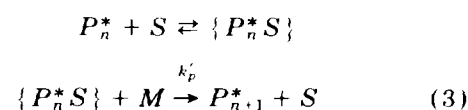
Let us consider that a propagating polymer chain, P_n^* , can either add monomer with rate constant k_p



or can enter into reversible complex formation with solvent S , and then add monomer, displacing

Table II. Effect of BA on Copolymer Composition, F_{MMA}

| f_{MMA} | BA | | |
|-----------|----------|----------|----------|
| | 30% | 50% | 75% |
| 0.174 | 0.252526 | 0.310778 | 0.321591 |
| 0.174 | 0.251322 | 0.317069 | 0.325235 |
| 0.174 | 0.252075 | 0.311500 | 0.334216 |
| 0.174 | 0.255959 | 0.323613 | 0.333403 |
| 0.816 | 0.714723 | 0.739243 | 0.728859 |
| 0.816 | 0.713975 | 0.739845 | 0.729059 |
| 0.816 | 0.716676 | 0.737608 | 0.729649 |
| 0.816 | 0.715351 | 0.731799 | 0.728753 |



the solvent and forming chain end P_{n+1}^* with rate constant k_p' .

If we denote the rate constants of formation and decomposition of the complex, $\{P^* S\}$, by k_1 and k_2 , then we may write at steady state

$$\frac{d[\{P^* S\}]}{dt} = 0 = k_1[P^*][S] - k_2[\{P^* S\}] - k_p'[\{P^* S\}][M]$$

$$[\{P^* S\}] = \frac{k_1[P^*][S]}{k_2 + k_p'[M]} \quad (4)$$

Consider a PLP experiment where a chain grows to length v_p following the model of eqs. 2 and 3. At times it will propagate as the free radical with rate

Table I. Effect of Benzyl Alcohol on the Apparent Values of k_p in PLP Experiments for MMA, STY, and a 1 : 1 Copolymerization

| Reaction (mL) | BA in 4 mL | | $\langle k_p \rangle$ (L/mol s) | [STY] (mol/L) | [BA]/[STY] | $\langle k_p \rangle$ (L/mol s) | [MMA] + [STY] (mol/L) | [BA]/([MMA] + [STY]) | $\langle k_p \rangle$ (L/mol s) |
|---------------|---------------|------------|---------------------------------|---------------|------------|---------------------------------|-----------------------|----------------------|---------------------------------|
| | [MMA] (mol/L) | [BA]/[MMA] | | | | | | | |
| 0 | 9.27 | 0.00 | 358.0 | 8.71 | 0.00 | 106.5 | 9.02 | 0.00 | 111.4 |
| 0.6 | 7.87 | 0.18 | 368.8 | 7.42 | 0.20 | 104.1 | 7.65 | 0.19 | 133.5 |
| 1.2 | 6.45 | 0.45 | 372.9 | 6.09 | 0.48 | 120.6 | 6.30 | 0.46 | 145.5 |
| 2 | 4.62 | 1.04 | 435.6 | 4.34 | 1.11 | 152.9 | 4.49 | 1.08 | 185.1 |
| 2.6 | 3.28 | 1.92 | 438.1 | 3.06 | 2.05 | 148.2 | 3.45 | 1.82 | 185.9 |
| 3 | 2.34 | 3.10 | 488.9 | | | | 2.99 | 2.42 | 186.6 |
| 3.4 | 1.35 | 6.08 | 582.1 | 1.26 | 6.51 | 153.4 | 1.31 | 6.27 | 193.3 |

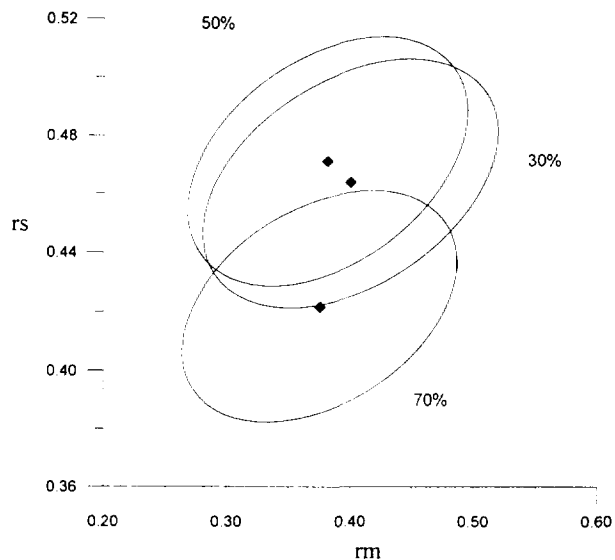


Figure 1. Reactivity ratios for STY/MMA: 95% confidence ellipses at various volume % BA, with following point estimates: 30% BA, $r_m = 0.400$, $r_s = 0.464$; 50% BA $r_m = 0.381$, $r_s = 0.471$; 75% BA, $r_m = 0.375$, $r_s = 0.422$.

constant k_p , and at other times as the complexed radical with rate constant k'_p . The mean value of the apparent rate constant for propagation, $\langle k_p \rangle$, will be given by the weighted sum of the k_p values for each of the two states:

$$\langle k_p \rangle = p_f(k_p) + p_c(k'_p) \quad (5)$$

where p_f and p_c are the fractions of chain ends in the free or complexed state.

Substitution of eq. (4) into eq. (5) and rearrangement gives:

$$\langle k_p \rangle = \frac{k_p + \left(\frac{k_1[S]}{k_2 + k'_p[M]} \right) k'_p}{1 + \left(\frac{k_1[S]}{k_2 + k'_p[M]} \right)} \quad (6)$$

Two limiting cases are easily envisioned: in the case of weak complex formation, $k_1/k_2 \ll 1$ and one may assume that $k_2 \gg k'_p[M]$; in the case of strong complex formation, postulating a high propagation reactivity of the complex, we assume $k_2 \ll k'_p[M]$. This postulate is justified below. Our experimental work with STY and MMA show that $\langle k_p \rangle$ is increased by BA, indicating that the complexation of the radical, in these monomers, enhances the propagation rate constant, thus making $k'_p > k_p$. Therefore it is worthwhile to note that eq. (6) takes on

Table III. Effect of BA on Tacticity of MMA

| BA (%) | mm | rm | rr | P_m |
|--------|----------|----------|----------|----------|
| 0 | 0.029003 | 0.298163 | 0.672834 | 0.170303 |
| 25 | 0.027904 | 0.290723 | 0.681373 | 0.167045 |
| 50 | 0.034289 | 0.317178 | 0.648533 | 0.185173 |
| 75 | 0.044796 | 0.295724 | 0.65948 | 0.211651 |

the following forms for weak and strong complexation respectively:

Weak Complexation:

$$\langle k_p \rangle = k_p + k'_p \left(\frac{k_1[S]}{k_2} \right) \quad (7)$$

Strong Complexation:

$$\langle k_p \rangle = k_p + \frac{k_1[S]}{[M]} \quad (8)$$

To arrive at eq. (8), the further assumption is made that $k_1[S]/k'_p \ll 1$; this assumption is justified below by experimental data for MMA homopolymerization.

The $\langle k_p \rangle$ results for MMA homopolymerization shown in Table I indicate that the apparent value of $\langle k_p \rangle$ increases steadily as the BA concentration increases. By contrast the results for STY and the "azeotropic" copolymerization approach a maximum value as the BA concentration increases. The MMA results do not conform to eq. (7) but are well described by eq. (8) for strong complex formation and are plotted in the form of eq. (8) in Figure 2. The slope of Figure 2 gives $k_1 = 36$ L/mol/s according

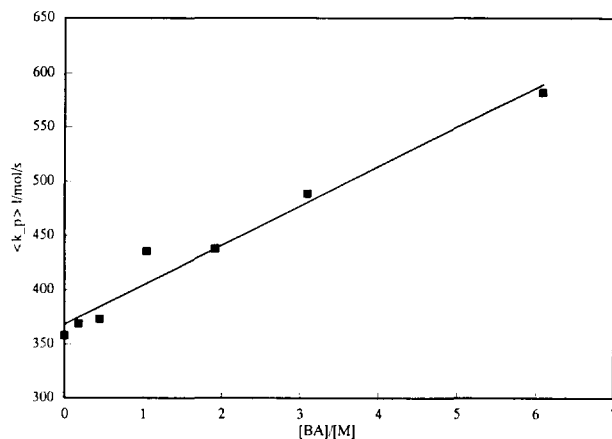


Figure 2. Apparent k_p for MMA as a function of BA, plotted according to eq. (8) for strong complex formation.

to eq. (8), one-tenth the value of k_p for MMA, which in turn is less than k'_p , thus justifying the assumption made above in deriving eq. (8).

The $\langle k_p \rangle$ results for STY homopolymerization and for the "azeotropic" copolymerization do not conform to eq. (8), but do appear to be well described by eq. (7) for weak complex formation as shown in Figures 3 and 4. In Figures 2-4 the straight lines are best fits to the data from a linear least-squares regression according to eqs. (7) or (8).

If the function of BA is to form a complex which propagates as postulated in the mechanism of eqs. (2), (3), and (5), then the reactivity ratios determined by the ordinary Mayo-Lewis equation are only "apparent" reactivity ratios, and they should be interpreted more carefully, rather than assuming they are absolute measures of changes in reactivity of the single, uncomplexed chain ends assumed in the Mayo-Lewis model.

Effect of BA on MMA Tacticity

Quantitative consideration of the effect of BA on the tacticity of PMMA as observed by NMR is hampered by the fact that the relative concentrations of the complexed and uncomplexed chain ends, p_c and p_f as defined in eq. (5), are equilibrium values, but the configurations of the terminal diads, as measured on dead polymer, reflect a kinetic "locking in" of configurations and therefore may not reflect the equilibrium values. (This is quite analogous to the situation in reversible copolymerization where copolymer composition reflects a blend of kinetic and thermodynamic control.¹⁵)

The probability of an uncomplexed terminal meso diad adding another monomer unit to generate an-

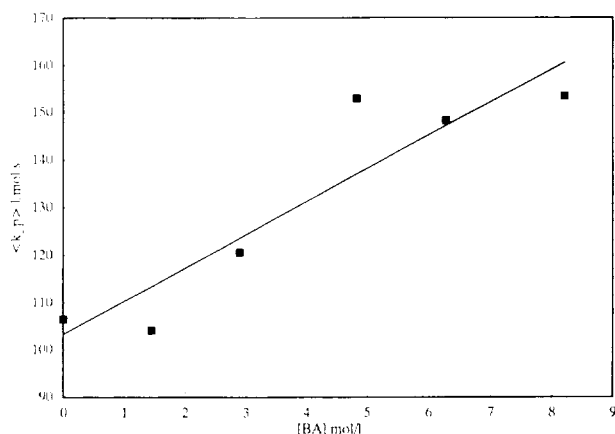


Figure 3. Apparent k_p for STY as a function of BA, plotted according to eq. (7) for weak complex formation.

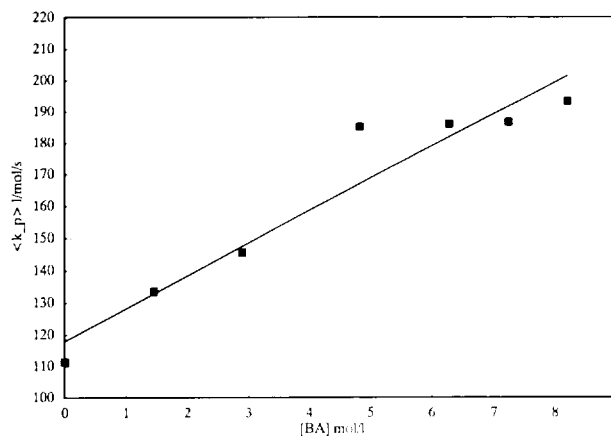


Figure 4. Apparent k_p for STY/MMA azeotropic copolymerization as a function of BA, plotted according to eq. (7) for weak complex formation.

other meso unit is P_m and the probability to generate a racemic unit is P_r , normalized so that $P_m + P_r = 1$. Similarly, normalized, P_m^* and P_r^* denote the probabilities for addition to a terminal meso diad complexed by BA. The normalized diad fractions found in dead polymer can now be represented by the equations:

$$\begin{aligned} mm &= (p_f P_m + p_c P_m^*)^2 \\ mr &= 2(p_f P_m + p_c P_m^*)(p_f P_r + p_c P_r^*) \\ rr &= (p_f P_r + p_c P_r^*)^2 \end{aligned} \quad (9)$$

Given the experimental values of the PMMA diad fractions in Table III, a trial-and-error solution of eq. (9) yields values for the fraction of uncomplexed chain ends, $p_f = 0.94$ and 0.91 at BA = 50 and 75%, respectively. No solution was obtainable at BA = 25%. These values are not true values because, as noted above, the actual concentration of particular diads in dead polymer is determined by a mix of kinetics and thermodynamics and may be different from that of the live terminal diads. In principle, knowing $\langle k_p \rangle$ and k_p , one might check these numbers using a trial and error solution of eq. (8) for k'_p as a function of p_f . This was attempted, but no physically real solution could be found.

CONCLUSIONS

The types of complexes that may exist between a chain end and solvent are numerous.¹ Bamford and Brumby,¹⁶ in their rotating sector measurements of k_p , have given particular attention to the possible

interactions between MMA and aromatic solvents. (Their article is one of the few to respect the ambiguity of overall rate measurements with respect to understanding solvent effects.) They concluded that specific interactions between the π electrons of the various aromatic solvents and the MMA chain end radical might account for the increase in k_p observed, but regarded results with anisole as anomalous. Unfortunately, they did not consider BA.

It is clear that more data are needed to refine ideas on chain end complexation and to distinguish between effects such as complexation, the "Boots-trap" effect¹⁵ and the implicit penultimate unit effect⁸ which have come to complicate our understanding of homo- and copolymerization kinetics.

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