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Nonideal Polymerization Kinetics of Styrene in Acetone

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ABSTRACT

Deviations from the "ideal" behavior have been observed in the polymerization of styrene in acetone. Both monomer and initiator exponents differ from the expected values. The poor thermodynamic properties of acetone as a solvent for the polystyrene chain seem responsible for the decrease of the initiation rate exponent, owing to the presence of a noticeable primary termination reaction. The strong effect of the reaction medium on monomer exponent can be related to the electron-donating tendency of acetone. The sharp decrease of the fractional rate of polymerization as a function of dilution has been interpreted in terms of lowering of the propagation rate constant, presumably due to solvent complexation of the growing chains.

INTRODUCTION

According to the simplest kinetic scheme for radical polymerizations [1], monomer and initiation rate exponents in the equation giving the rate of polymerization should be 1 and 0.5, respectively. Although the above kinetic relationships hold in a number of cases, they are not observed in many polymerization experiments.

In particular, the anomalies are very marked when solution polymerization is concerned.

Several factors can cause deviations from the expected behavior, and they involve some modifications of the initiation, propagation, or termination steps. For instance, the cage effect in initiation causes an increase of the monomer exponent and leaves unchanged the initiation rate exponent. Monomer and radical solvation, complex formation, or microphase separation give apparent deviations from the first-order dependence of polymerization rate from monomer concentration. Primary radical termination and degradative chain transfer affect both exponents in a very complex way, while neglecting the diffusion control on the termination reaction causes a substantial deviation of the monomer exponent from unity. An extensive review of this topics has recently been published [2].

The approaches for a better understanding of the factors which affect solution polymerization are based on the comparison of experimental data and equations, deduced from various kinetic models, for rates and degrees of polymerization. Quite often, the equations based on molecular weight data disregard the role of the various chain transfer reactions and do not consider changes of the propagation and termination rate coefficients as functions of medium composition [3-7]. These oversimplifications, therefore, might provide ambiguous answers and conclusions. On the other hand, more general equations are too complex to be workable. At present, a careful analysis of data on polymerization rates seems the only approach which can be used for comprehensive interpretation of the behavior of most solution polymerizations.

The kinetics of solution polymerization of acrylate and methacrylate monomers, which show strong solvent effects, has been investigated very extensively [3-6, 8-13], whereas similar studies on styrene have received less attention [7, 14, 15]. The choice of styrene and acetone as the polymerizing system is based on two considerations: 1) the thermodynamic properties of acetone, which is a very poor solvent for polystyrene [16], could affect the termination rate coefficient much more than the simple hydrodynamic effect related to the viscosity of the reaction medium [17]; and 2) acetone is a relatively strong electron-donor molecule [18], capable to form complexes with the growing polystyrene chain [19]. The composition of the reaction medium has been varied within the homogeneity range in order to avoid phenomena of phase separation and polymer precipitation. Under such conditions the growing chain should assume conformations which are more or less tightly coiled, depending on medium composition.

Literature data on chain transfer constant to acetone [20-22], as well as some recent values for monomer and initiator chain transfer constants [23, 24] confirm that simplified equations based on molecular weight data can provide erroneous information.

EXPERIMENTAL

Purification of styrene, acetone, and α,α'-azobisisobutyronitrile (AIBN), as well as sampling, polymerization procedure, and polymer recovery, have been carried out following previously described techniques [25, 26]. The polymerization temperature was 50 ± 0.05°C. Rates of polymerization, R_p, were varied by changing the initiator concentration or the solvent/monomer ratio, [S]/[M]. The maximum conversion was less than 5%. Mean values of R_p, [M], and [S] were calculated from conversion yields and literature data on densities of styrene [27] and acetone [28] as functions of temperature. Corrections due to the relatively high vapor pressure of acetone [29] at the polymerization temperature have been taken into account. The viscosity of the reaction medium has been evaluated by linear interpolation between the limiting values ($\eta^{50°}_{St} = 0.552$ cP; $\eta^{50°}_{acetone} = 0.26_2$ cP) [27, 29]. The validity of the linear interpolation has been confirmed experimentally.

RESULTS AND DISCUSSION

Primary Radical Termination

The polymerization rate of styrene in acetone as a function of initiator concentration at constant [M] is shown in Fig. 1. An initiator order of 0.45, evaluated by using the least-square method, has been found. The "normal" half-order dependence (dotted line) has been reported as the reference.

An initiator order less than 0.5 can be found when the primary radical termination becomes important. Various kinetic schemes, including primary radical termination, have been proposed in the literature [30-34]. We have used the following equation, recently suggested by Deb and Meyerhoff [34]:

$$\ln \frac{R_p^2}{[I][M]^2} = \ln \frac{2f_K k_d k_p^2}{k_t} - 2\frac{k_t'}{k_i k_p}\,\frac{R_p}{[M]^2} \qquad (1)$$

where f_K is the fraction of primary radicals escaping the solvent cage and taking part in initiation and termination of growing chains.

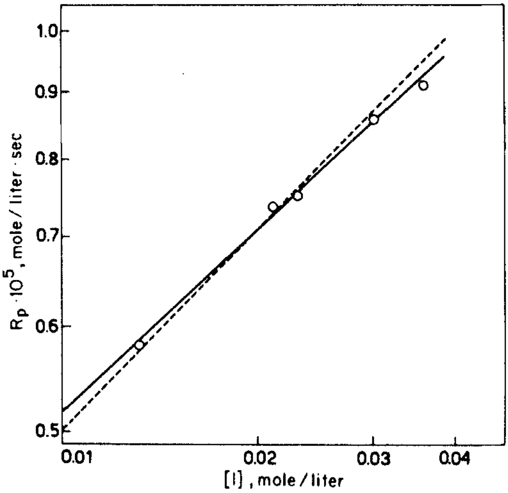

FIG. 1. Polymerization rate of styrene in acetone as a function of initiator concentration, at [S]/[M] ~3.2. (Dotted line corresponds to the "ideal" initiator order of 0.5, solid line to the value of 0.45, found experimentally).

k_d, k_p, and k_t are the rate constants related to the processes of primary radical production, propagation of the polymer chain, and polymer-polymer termination, respectively. k_i is the rate constant for initiation of a polymer chain, and k_t' represents the rate constant for primary radical termination. In deriving Eq. (1) the various processes of chain transfer have been considered to produce no peculiar effect on the overall rate of polymerization. The validity of this assumption is supported by the absence of any degradative chain transfer in our system.

Our data are plotted in Fig. 2. A good linearity is obtained only when experimental data referred to the same [S]/[M] ratio (open circles) are considered. A strong solvent effect on the various parameters present in Eq. (1) is clearly evident from the scattering of the other data related to different dilutions. Literature data on bulk polymerization [25] have been reported for comparison. From the slope and the intercept of the straight line we obtained the values

$$\frac{k_t'}{k_i k_p} = 0.35 \times 10^5$$

and

$$\frac{f_K k_d k_p^2}{k_t} = 1.74 \times 10^{-10}$$

Of course, their validity is confined to a solvent/monomer ratio of about 3.2. From the data of Fig. 2 related to other compositions of the reaction medium (including bulk), both slope and intercept values seem to be affected by dilution. It is therefore impossible to evaluate f_K because most of the rate constants seem subject to change as functions of the medium composition. An extrapolation of literature data [34, 35] to 50°C yields $f_K \simeq 0.75$.

By writing

$$f_K = f_i + f_t' \tag{2}$$

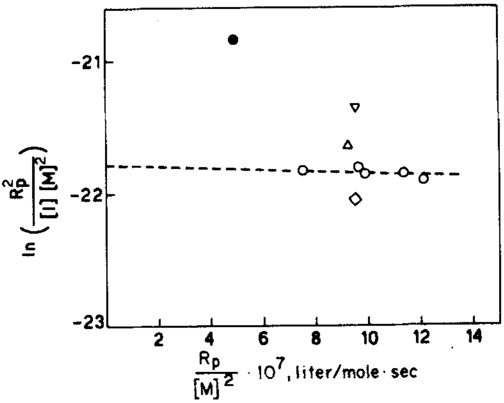

FIG. 2. Semilog plot of $R_p^2/[I][M]^2$ vs $R_p/[M]^2$, according to Eq. (1){open circles refer to the same [S]/[M] ratio, equal to 3.2; filled circle value refers to the bulk polymerization [25]; (▽) [S]/[M] = 1.6; (△) [S]/[M] = 2.4; (◇) [S]/[M] = 4.7}.

where f_i is the fraction of primary radicals escaping the solvent cage and capable to initiate the polymerization and f_t' is the fraction implied in primary radical termination, we obtained [34]

$$F^2 \frac{1 + F}{1 - F} = \left(\frac{k_t'}{k_i}\right)^2 \frac{2f_K k_d}{k_t} \frac{[I]}{[M]^2} \tag{3}$$

where $F = f_t'/f_i$.

Figure 3 shows the variation of $1/1 + F$, i.e., $f_i/f_i + f_t'$, as a function of $[I]/[M]^2$, at constant $[S]/[M]$. The regular decrease of $1/1 + F$ shows the relevance of primary radical termination, which is enhanced by increasing the ratio $[I]/[M]^2$. In the range of $[I]/[M]^2$ values we used experimentally, the fraction of primary radicals involved in termination, as compared to the efficiency of initiation, varies between 2.6 and 4.3%. The correction factor, proposed by Olaj [33], by also taking in account the small amount of monomer consumed in initiation for a more precise evaluation of R_p to be used in Eq. (1), is almost negligible in our case (less than 2%).

The presence of a noticeable primary termination process in the polymerization of styrene in acetone suggests that the above process is important not only at high [I] and low [M], as is usually indicated in the literature, but also when the termination reaction between two growing macrochains is hindered owing to the very

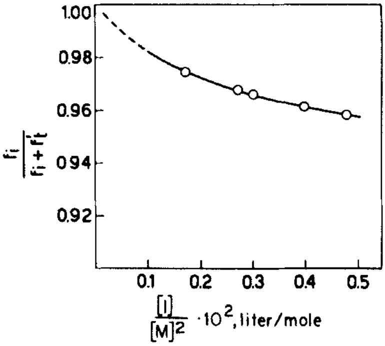

FIG. 3. Variation of $1/1 + F$ as a function of $[I]/[M]^2$ ($[S]/[M] = 3.2$).

poor solvent power of the reaction medium. Deviations from the "ideal" dependence of R_p on the square root of the initiator concentration or incident light intensity have not been noticed in other similar studies related to the effect of poor solvents on the polymerization kinetics [17]. Direct inspection of Fig. 1 suggests that these deviations are not very marked; quite easily, therefore, a square root dependence might be erroneously assumed to be valid. It should be remembered that the effect of primary termination reaction is twofold: 1) the primary radical is not used for initiating a chain; thus the effective initiation rate is lowered; and 2) the primary radical stops a growing chain and acts as an added inhibitor, decreasing the polymerization rate.

Influence of the Reaction Medium

A more detailed picture of the effect of the reaction medium on the polymerization rate of styrene in acetone is shown in Fig. 4 where the fractional rate of polymerization divided by the square root of the initiator concentration is plotted as a function of

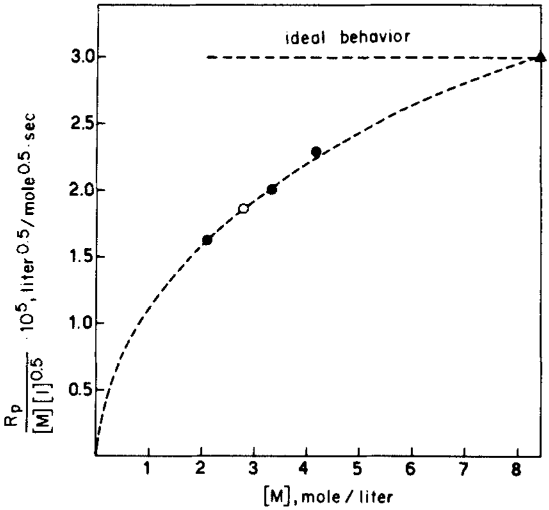

FIG. 4. Fractional rate of polymerization divided by $[I]^{0.5}$ as a function of monomer concentration in the reaction medium {(●) $[I]/[M] = 0.71 \times 10^{-2}$; (○) extrapolated value (see text); (▲) bulk polymerization}.

monomer concentration at fixed [I]/[M]. The value corresponding to the bulk polymerization [25] has been reported for comparison. An extrapolated value of $R_p/[I]^{0.5}[M]$ from the data related to $[S]/[M] \sim 3.2$ (open circle) has been evaluated from the intercept of the straight line in Fig. 2. On this basis, primary radical termination can be deleted and direct comparison with bulk polymerization is possible. A marked deviation from the ideal behavior is evident. The sharp and regular decrease of $R_p/[I]^{0.5}[M]$ as a function of dilution reflects the strong influence of the reaction medium, already foreseen from the data of Fig. 2, on some (or all) kinetic steps.

A major effect of the reaction medium should concern the rate coefficients for propagation and/or polymer-polymer termination, whereas a minor influence can be expected on f_K, k_d, k_i, and k_t'. In fact, despite some conflicting results [36, 37], it is generally accepted that the decomposition rate constant of AIBN and the primary radical production are not very strongly affected by modifications of the reaction medium composition [3, 5, 6]. k_i is directly related to f_i and follows the irrelevant changes of the latter, shown in Fig. 3. The primary radical termination rate constant seems to be independent of the medium fluidity [38, 39]. Moreover, direct measurements of the initiation rates in bulk and in acetone solution by using [^{14}C]-AIBN and the radioactive tracer method [40] did not show any appreciable solvent effect for the system under study.

By assuming, after our results [40],

$$(2fk_d)_{\text{solution}} \sim (2fk_d)_{\text{bulk}} \tag{4}$$

we have

$$\left(\frac{R_p}{[I]^{0.5}[M]}\right)_{\text{solution}} \Bigg/ \left(\frac{R_p}{[I]^{0.5}[M]}\right)_{\text{bulk}} = \left(\frac{k_p}{k_t^{0.5}}\right)_{\text{solution}} \Bigg/ \left(\frac{k_p}{k_t^{0.5}}\right)_{\text{bulk}} = \frac{\delta_{\text{bulk}}}{\delta_{\text{solution}}} \tag{5}$$

In Fig. 5 the ratios between the $R_p/[I]^{0.5}[M]$ values in acetone solution and in bulk (open circles) are plotted as functions of

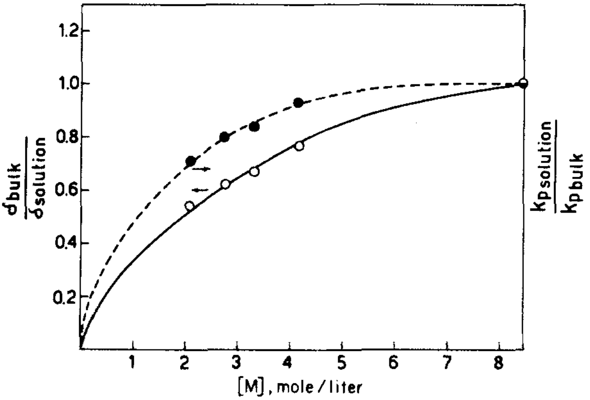

FIG. 5. $\delta_{bulk}/\delta_{solution}$ values (open circles) and $k_{p\ solution}/k_{p\ bulk}$ values (filled circles) as functions of the monomer concentration in the reaction medium (k_p values calculated by assuming $k_t \propto 1/\eta_{mix}$).

monomer concentration. The strong effect of dilution on the above ratios cannot be explained in terms of medium control on the termination rate coefficient. The assumption of the usual dependence of k_t on medium viscosity, i.e., $k_t \propto 1/\eta_{mix}$, contributes in part to the decrease of $R_p/[I]^{0.5}[M]$, because k_t is increased when a solvent (like acetone) of lower viscosity than the monomer is added to the reaction medium, but it cannot entirely account for the sharp decrease of the ratios, as shown in Fig. 5 (filled circles). Moreover, this assumption is valid only for flexible chains surrounded by a reaction medium characterized by good thermodynamic power [3, 5, 7, 8, 10, 41-49], as pointed out by Cameron et al. [17]. According to his results, thermodynamically poor solvents reduce the termination rate coefficients, regardless of changes in medium fluidity. In our system the relevance of the primary termination reaction, shown in the previous section, has been attributed to the very poor solvent power of the reaction medium. Thus the contribution connected with the variation of the termination rate constant due to the thermodynamic control of the medium would produce an increase, instead of a decrease, of the above ratios as a function of dilution. Whatever assumption is valid, we can conclude that the major effect of dilution is a regular decrease of the propagation rate coefficient.

Recent data on the overall copolymerization kinetics of styrene and methyl methacrylate in solution [49] show a marked solvent effect on the self-propagation rate constants. The solvents used were dioxane, dimethylformamide, and acetone. This effect is more pronounced for styrene than for methyl methacrylate, and it shows an opposite trend for the two monomers. As compared to the bulk polymerization, k_p of styrene is decreased whereas k_p of methyl methacrylate is increased, in full agreement with the pattern already found in bromobenzene [3, 7], diethyl malonate [6, 7], and benzonitrile [3, 7]. The applicability of a simple hydrodynamic effect of the reaction medium on the termination rate constants, assumed valid in Ref. 49 for styrene-rich monomer feeds in acetone solution, should not belittle the complete agreement between polymerization and copolymerization data.

Similar results have been obtained from the monomer reactivity ratios [26], which show a noticeable influence of the solvent on the composition of styrene-methyl methacrylate random copolymers. This effect has been correlated to changes in the dielectric constant of the reaction mixture: polar solvents enhance the role of polarized forms of the growing chains and increase the alternation tendency in the copolymer. The stronger solvent effect on r_1 (monomer 1, styrene) in comparison to r_2 has been tentatively ascribed to a decrease of the propagation rate constant of styrene in solution as compared to bulk polymerization. The present results confirm the validity of that assumption.

CONCLUSIONS

A relevant influence of the reaction medium on the polymerization kinetics of styrene in acetone has been evidenced in the present work. Owing to the poor thermodynamic properties of acetone as a solvent for polystyrene, the termination reaction between a polystyrene growing chain and a primary radical is important and the initiation rate exponent is lowered from the "ideal" value of 0.5 to about 0.45. Thus primary radical termination is confined not only in the ranges of high initiator and low monomer concentrations, as is usually stated in the literature, but is present also when favorable thermodynamic conditions in the reaction medium are realized.

The strongest effect of the reaction medium, however, is exerted on the propagation rate constant. The exact nature of this effect cannot be ascertained more precisely. A reasonable interpretation of these interactions is based on solvent complexation of the growing polymer radical. Recent work in this field [50] provides some support to the above hypothesis and shows a parallel complexing power of some monomers. The relatively strong electron-donating tendency of acetone [18] can justify the capability of forming complexes with the growing chains in competition with styrene complexation of the macroradicals. Therefore, the propagation stage can involve three different macroradicals: uncomplexed growing chains, and radicals complexed with the monomer and solvent molecules, respectively. Consequently, the overall value of the propagation rate constant is dependent on the composition of the reaction medium.

Henrici-Olivé and Olivé [15, 19, 51, 52] proposed a simplified scheme for this type of polymerization kinetics by assuming that all growing chains are complexed with solvent or monomer molecules, with only the latter complex leading to propagation. As pointed out by Cameron et al. [11], Olivé's equations do not take in account the effects of the reaction medium on the rate constants for bimolecular termination. A modified equation, based on the usual dependence of k_t on solution viscosity, i.e., $k_t \propto 1/\eta_{mix}$, has been derived [11] but its applicability to our system is questionable because acetone is a poor solvent for the polystyrene chain. Indeed, a tentative plot, based on our data and the equation proposed in Ref. 11, does not give the straight line predicted by Olivé's model. However, before questioning on the validity of Olivé's model, direct evaluation of the solvent effect on k_t is necessary. At present, therefore, a quantitative interpretation of our data in terms of solvent complexation does not seem possible.

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