Aqueous Polymerization of Methyl Methacrylate Initiated by Pyridine-Sulfur Dioxide Complex

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ABSTRACT

The aqueous polymerization of MMA was studied kinetically at
$40°C$ using low concentrations of Py-SO$_2$ complex as initiator.
For $[Py\text{-}SO_2] < 2 \times 10^{-2}$ mol/L, $R_p \propto [Py\text{-}SO_2]^{0.5}[M]^{1.5}$,
and for $[Py\text{-}SO_2] > 2 \times 10^{-2}$ mol/L, $R_p \propto [Py\text{-}SO_2]^{0.0}[M]^{1.08}$.
Polymerization is considered to proceed by a radical mechanism.
The radical generation or the initiation step is believed to proceed
through equilibrium complexation between the Py-SO$_2$ complex
and monomer molecules. For $[Py\text{-}SO_2] < 2 \times 10^{-2}$ mol/L, the
polymerization is characterized by bimolecular termination.
Above this $[Py\text{-}SO_2]$, chain termination by a degradative initiator
transfer process assumes prominence.

INTRODUCTION

In low concentrations, sulfur dioxide is reported [1, 2] to play
different roles in vinyl and related polymerizations. It acts as (1) an
initiator in suitable monomer systems in nonaqueous media, (2) an
effective chain transfer agent, and (3) a comonomer. In aqueous
solution, SO$_2$ remains as sulfurous acid (H$_2$SO$_3$) and it is unable to

initiate polymerization as such. Sodium bisulfite (NaHSO₃), on the other hand, is a reasonably good initiator [3] of aqueous polymerization of methyl methacrylate (MMA) and some other monomers, but sodium sulfite (Na₂SO₃) fails to initiate aqueous vinyl polymerization.

Thus the capacity to initiate aqueous polymerization by the SO_2 initiator system is dependent on pH or acidity of the system and polymerization is not favored in acidic or strongly basic conditions. Pyridine, a weak base, was chosen as a donor compound to form a charge transfer complex [2] with SO_2 (acceptor), and the suitability of the pyridine-sulfur dioxide (Py-SO_2) complex as an initiator of aqueous polymerization of MMA was examined. Results of the kinetics of polymerization are reported in the present paper.

EXPERIMENTAL

Preparation of Pyridine-Sulfur Dioxide (Py-SO_2) Complex

Five millileters of purified pyridine was taken in a test tube, cooled to about -5°C, and purified SO_2 gas was then gently bubbled through the cooled pyridine. SO_2 gas was generated in the laboratory by heating fresh copper turnings with reagent grade concentrated H_2SO_4. The liberated gas was subsequently purified by passing it through a scrubber of concentrated H_2SO_4. Bubbling of SO_2 in cooled pyridine was stopped when no more absorption of SO_2 in the liquid was apparent. Excess SO_2 was allowed to bubble out of the resultant yellow liquid at room temperature condition (25-30°C), occasionally aided by slowly stirring the liquid with a glass rod. The theoretical SO_2 content in 1:1 Py-SO_2 complex is 44.75%; analysis showed that the SO_2 percentage in the prepared complex was 45%.

UV spectra of dilute aqueous solutions of pyridine (1.5×10^{-4} mol/L) and of Py-SO_2 complex prepared (1.5×10^{-4} mol/L) are given by Curves 1 and 5, respectively, Fig. 1(A). λ_{max} for each spectrum is 258 nm. SO_2 (1.5×10^{-4} mol/L) shows little absorption in the wavelength range studied. For a fixed pyridine content (1.5×10^{-4} mol/L) in water, the absorbance at λ_{max} increases progressively with an increasing proportion of SO_2 added to the system until the latter is used in an equimolar proportion (1.5×10^{-4} mol/L), Fig. 1(A). With a further increase in SO_2 content, no further changes in the absorption spectra are visible. None of the spectra in Fig. 1(A) changed measurably with time.

In two separate sets of experiments, absorbance values at λ_{max} for solutions of pyridine and Py-SO_2 complex in water at several concentrations were determined and the data were plotted as in Fig. 1(B). In each case the plot, passing through origin, is linear,
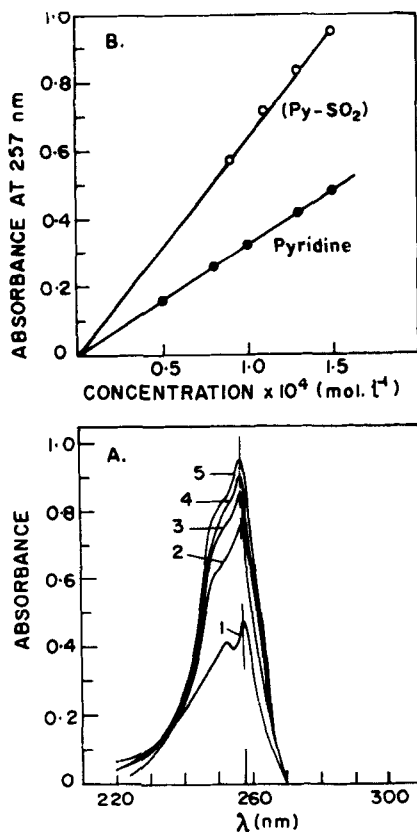
FIG. 1.   A.   UV absorption spectra of SO_2, Py-SO_2 complex, and different mixtures of SO_2 and pyridine in aqueous solution using water in the reference cell in each case.   1, Pyridine = 1.5×10^{-4} mol/L; 2, pyridine = 1.5×10^{-4} mol/L and SO_2 = 0.90×10^{-4} mol/L; 3, pyridine = 1.5×10^{-4} mol/L and SO_2 = 1.10×10^{-4} mol/L; 4, pyridine = 1.5×10^{-4} mol/L and SO_2 = 1.30×10^{-4} mol/L; 5, pyridine = 1.5×10^{-4} mol/L and SO_2 $\geq$ 1.50×10^{-4} mol/L, and Py-SO_2 complex = 1.5×10^{-4} mol/L.   B: Plot of absorbance at 258 nm vs concentration for pyridine and Py-SO_2 complex, each in water solution (water in the reference cell).

the Py-SO_2 plot giving a higher slope than the pyridine plot.   The overall absorbance at λ_{max} (258 nm) for each of the various mixtures of pyridine and SO_2, Fig. 1(A), is equal to the summation of the absorbances corresponding to the calculated amount of 1:1 Py-SO_2 complex in the system and that of pyridine present in excess of SO_2 on a
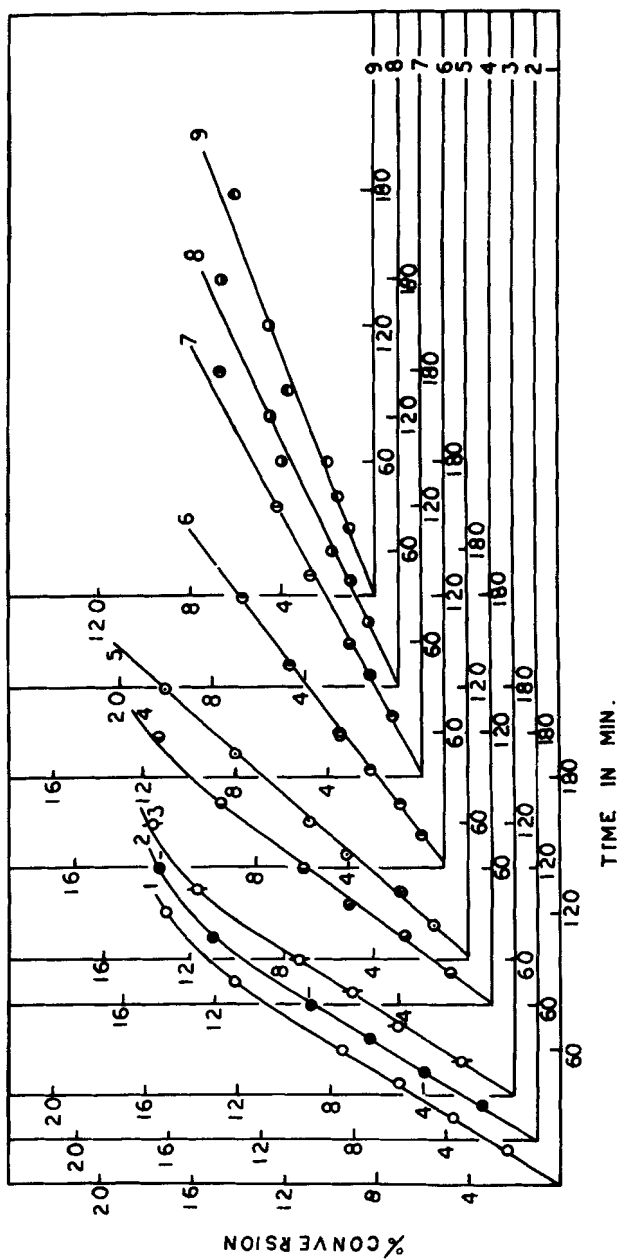
FIG. 2. Aqueous polymerization of MMA at 40°C using Py-SO$_2$ complex as initiator. Plot of % conversion vs time in min. Data given for each curve is Py-SO$_2$, mol/L: (○) 4.80 × 10^{-2}, (●) 3.20 × 10^{-2}, (◔) 2.10 × 10^{-2}, (◑) 1.52 × 10^{-2}, (◉) 1.08 × 10^{-2}, (◍) 0.48 × 10^{-2}, (◉) 0.24 × 10^{-2}, (◉) 0.18 × 10^{-2}, (◉) 0.12 × 10^{-2} M.

mole to mole basis. As expected, excess SO_2, wherever present, has little influence on the overall absorbance. Thus it is clearly indicated that complexation between pyridine and SO_2 takes place almost instantly and that the complex is of the 1:1 kind.

Aqueous Polymerization of MMA

Monomer MMA was purified and aqueous polymerization was carried out in 150 mL stoppered conical flasks under nitrogen following the usual procedures [4, 5]. The initial monomer content was usually 1.5% v/v. The monomer was allowed to dissolve in the aqueous media under a blanket of nitrogen for about 20 h before the addition of the initiator. Most of the experiments were carried out at 40°C. Rate measurements were done following standard procedures [5]. Molecular weight ($\overline{M}_n$) or degree of polymerization ($\overline{P}_n$) of polymethyl methacrylate was obtained viscometrically [1].

RESULTS AND DISCUSSION

The results of polymerization are presented in Figs. 2–6. The aqueous polymerization of MMA initiated by the $Py-SO_2$ complex at 40°C was associated with inhibition periods (IP) of 5–15 min, higher [$Py-SO_2$] giving lower IP in general. Percent conversion vs time plots (not showing the inhibition periods) are presented in Fig. 2.

Rates of polymerization (R_p) calculated from the slopes of the initial linear zones of these curves showed an increasing trend with increasing [$Py-SO_2$] up to [$Py-SO_2$] of about 0.02 mol/L, and beyond this point R_p remained practically constant with a further increase in [$Py-SO_2$].

Initiator Exponent, Monomer Exponent, and Activation Energy

A plot of $\log R_p$ vs $\log$ [$Py-SO_2$] is shown in Fig. 3A. The slope of this plot giving the initiator exponent is 0.5 for [$Py-SO_2$] $\leq$ 0.02 mol/L. For [$Py-SO_2$] $>$ 0.02 mol/L, the initiator exponent is practically zero.

R_p values were also measured at several monomer concentrations using a fixed [$Py-SO_2$]. A linear plot of $\log R_p$ vs $\log$ [M] is shown in Fig. 3B. The slope of this plot, giving the monomer exponent, is 1.50.

The activation energy for the present polymerization is 8.28 kcal/mol, and this value is close to some reported values of activation energy for aqueous polymerization of MMA [6-9].
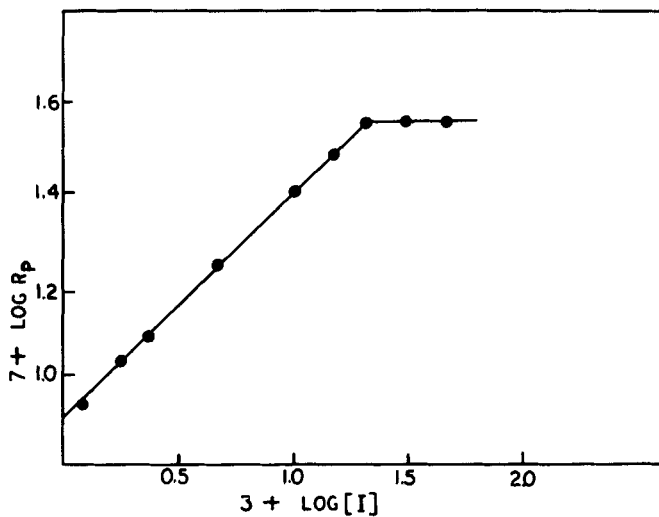
FIG. 3A. Aqueous polymerization of MMA at 40°C using Py-SO₂ complex as initiator. Plot of log R_p vs log [Py-SO₂].
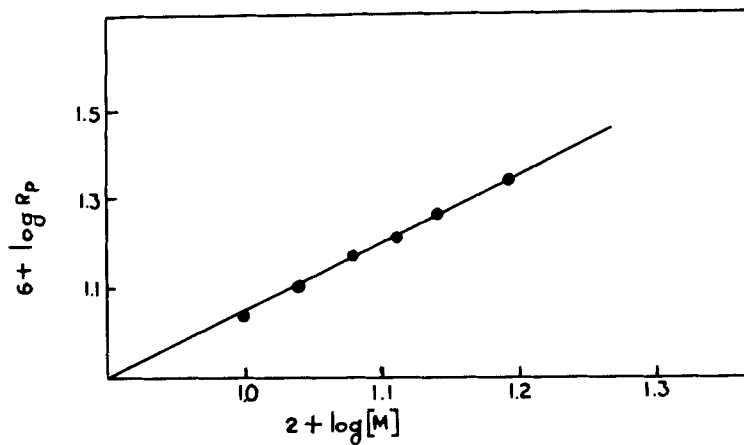

FIG. 3B. Aqueous polymerization of MMA at 40°C using Py-SO₂ complex as initiator. Plot of log R_p vs log [M].

TABLE 1A. Variation of R_p and Intrinsic Viscosity with pH of the Solution of Aqueous Polymerization of MMA at 40°C Using Py-SO$_2$ Complex as Initiator. $[Py-SO_2] = 8.00 \times 10^{-3}$ mol/L, $[M] = 13.85 \times 10^{-2}$ mol/L

pH	$R_p \times 10^6$ mol/L/s	Intrinsic viscosity $[\eta]$ (dL/g)
3.60	2.040	6.50
4.40	2.208	6.30
5.00	2.570	5.80
8.10	2.970	5.40
10.00	3.100	5.15
12.40	2.110	5.40

TABLE 1B. Effect of polymerization Time on Intrinsic Viscosity $[\eta]$ of the Polymer Product. $[Py-SO_2] = 1.08 \times 10^{-2}$ mol/L, $[M] = 13.8 \times 10^{-2}$ mol/L

Time (h)	% conversion	$[\eta]$ (dL/g)
4	16.20	5.62
10	25.10	6.64
22	39.70	7.95
34	46.50	8.70

Effect of pH and Other Features

In the present aqueous polymerization, R_p was found to follow a slowly increasing trend with an increase in pH of the medium up to pH 10. pH variation was done by adding different volumes of a dilute NaOH solution to the system. A falling trend in the intrinsic viscosity of the polymer formed with an increase in pH was also observed. Further, the intrinsic viscosity $[\eta]$, and hence the average chain length of the polymer formed under a given initial set of conditions, increased significantly with the progress of polymerization to higher conversions, a feature similar to that observed in SO$_2$-initiated bulk polymerization of MMA [1]. All relevant data are given in Tables 1A and 1B.

Application of the dye-partition test of Palit et al. indicated the incorporation of anionic sulfoxy end groups in the polymers [10].

Mechanism

Kinetic data, the presence of a sulfoxy end group in the polymers prepared, and the pronounced inhibitory effect of hydroquinone indicate a radical mechanism. The radical generation step may be described as [11]

$$Py\text{-}SO_2 + M \underset{}{\overset{K}{\rightleftharpoons}} [Py\text{-}SO_2 \ldots M] \xrightarrow{k_d} \text{pair of radicals}$$

$$\text{Initiating complex}$$

$$I$$
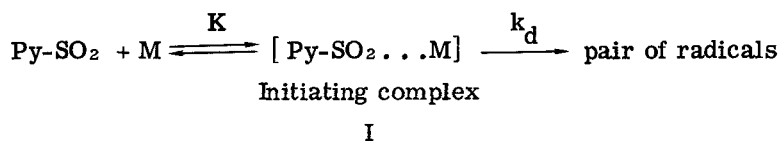
Assuming bimolecular termination, the rate of polymerization (propagation), R_p, may be expressed as

$$R_p = k_p \left(\frac{k_d K}{k_t} \right)^{0.5} [Py\text{-}SO_2]^{0.5} [M]^{1.5}$$

The radical generation process is considered to be preceded by a complexation reaction between monomer and Py-SO₂ complex molecules which is characterized by an equilibrium constant K such that the initial concentration of the actual initiating complex I is given by $[I] = K[Py\text{-}SO_2][M]$, and k_p, k_d, and k_t have their usual significances. The above expression explains well [11] the observed dependence of R_p on $[M]$ and $[Py\text{-}SO_2]$.

With initiator exponent of 0.5 in the lower range of $[Py\text{-}SO_2]$ ($< 2 \times 10^{-2}$ mol/L), termination appears to take place bimolecularly; however, for $[Py\text{-}SO_2] > 2 \times 10^{-2}$ mol/L, the initiator exponent becomes practically zero, indicating that the termination under this condition is very much dependent on the initiator.
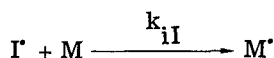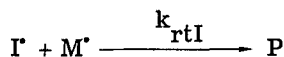
Analysis of Primary Radical Termination and Degradative Initiator Transfer Processes

The equation of Deb and Meyerhoff [12], developed to analyze the primary radical termination effect in the absence of any degradative chain transfer, will assume the following form for the present polymerization:

$$\log \frac{R_p^{\,2}}{[\,Py\text{-}SO_2\,][\,M\,]^3} = \log \frac{fKk_dk_p^{\,2}}{k_t} - 0.8684 \frac{k_{prt}}{k_ik_p} \frac{R_p}{[\,M\,]^2} \tag{1}$$

where k_{prt} is the rate constant for the primary radical termination reaction and all other terms have their usual significance.

On the other hand, assuming a negligible primary radical termination effect, the following equations may be considered to describe the overall degradative initiator transfer process:

$$M^\bullet + I \xrightarrow{\;\;k_{trI}\;\;} P + I^\bullet$$

$$I^\bullet + M^\bullet \xrightarrow{\;\;k_{rtI}\;\;} P$$

$$I^\bullet + M \xrightarrow{\;\;k_{iI}\;\;} M^\bullet$$

For R_p becoming independent of $[\,Py\text{-}SO_2\,]$ at a fixed $[\,M\,]$, the equation of Ghosh et al. [13], suitable for detecting the degradative initiator transfer effect, will assume the following form for the present polymerization:

$$\log \frac{R_p^{\,2}}{[\,Py\text{-}SO_2\,][\,M\,]^3} = \log \frac{fKk_dk_p^{\,2}}{k_t} - 0.434 \frac{k_p^{\,2}}{k_t} \frac{k_{rtI}}{k_{iI}k_p} C_IK[\,Py\text{-}SO_2\,] \tag{2}$$

Equations (1) and (2) permit separate plots of $\log R_p^{\,2}/[\,Py\text{-}SO_2\,][\,M\,]^3$ against $R_p/[\,M\,]^2$ and against $[\,Py\text{-}SO_2\,]$ for the analysis of the primary radical termination effect and the degradative initiator transfer effect, respectively, and such plots are shown in Figs. 4 and 5.

In each plot the value of the ordinate remains practically constant (zero slope) for $[\,Py\text{-}SO_2\,] < 2 \times 10^{-2}$ mol/L, indicating that either of the nonideal termination mechanisms considered is inconsequential. But for $[\,Py\text{-}SO_2\,] > 2 \times 10^{-2}$ mol/L, the experimental points fall on a straight line with a negative slope in each case, indicating that under this condition each of the nonideal termination mechanisms envisaged becomes very significant. The relative significance of the two nonideal termination mechanisms cannot be properly judged from the analysis given above. But it was found that the monomer exponent value of 1.5, determined with low $[\,Py\text{-}SO_2\,]$, i.e., 5.5×10^{-3} mol/L, changed to a value of 1.08 when determined using high $[\,Py\text{-}SO_2\,]$, i.e.,
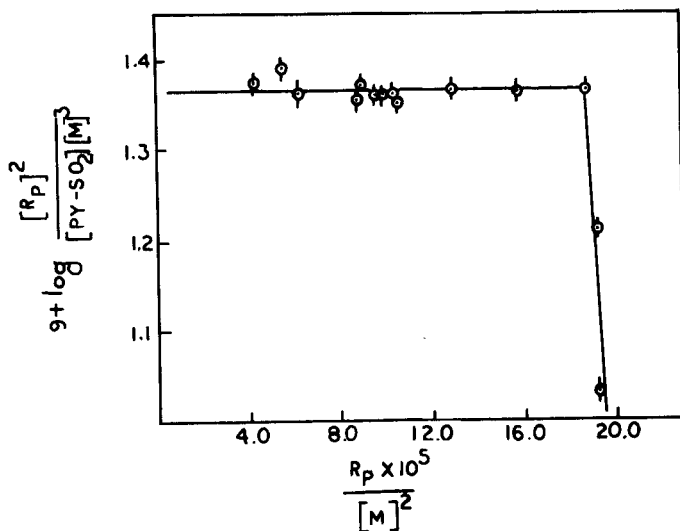
FIG. 4. Analysis of primary radical termination effect in aqueous polymerization of MMA at 40°C using Py-SO$_2$ complex as initiator. Plot of log $\dfrac{R_p^{\,2}}{[\,Py\text{-}SO_2\,][\,M\,]^3}$ vs $R_p/[\,M\,]^2$.
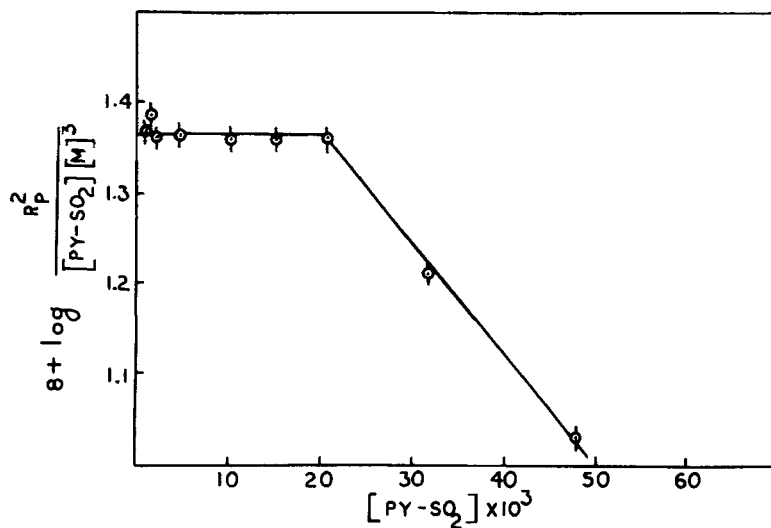

FIG. 5. Analysis of degradative initiator transfer effect in aqueous polymerization of MMA at 40°C using Py-SO$_2$ complex as initiator. Plot of log $\dfrac{R_p^{\,2}}{[\,Py\text{-}SO_2\,][\,M\,]^3}$ vs $[\,Py\text{-}SO_2\,]$.
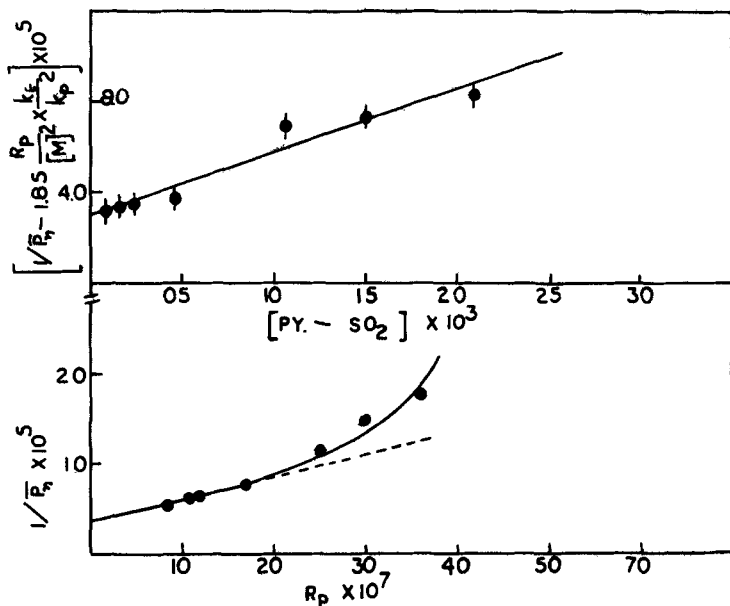
FIG. 6. Aqueous polymerization of MMA at 40°C using Py-SO₂ complex as initiator. Bottom: Plot of $1/\overline{P}_n$ vs R_p. Top: Plot of $(1/\overline{P}_n - (1.85R_p(k_t/k_p^2[M]^2)))$ vs $[Py-SO_2]$.

3.20×10^{-2} mol/L. It is therefore strongly indicated that the initiator dependent termination, appearing prominent for $[Py-SO_2] > 2 \times 10^{-2}$ mol/L, is largely due to degradative initiator transfer.

k_p^2/k_t Value

The value of the kinetic parameter k_p^2/k_t was obtained from the initial slope of the plot of $1/\overline{P}_n$ vs R_p, Fig. 6 (bottom), following the usual procedures and assumptions, with the help of the Mayo equation:

$$\frac{1}{\overline{P}_n} = 1.85 \frac{k_t}{k_p^2} \frac{R_p}{[M]^2} + C_M + C_I \frac{[I]}{[M]} \qquad (3)$$

C_M and C_I are the monomer and initiator transfer constants, respectively. Assuming that the initial slope would not change measurably

due to transfer processes, the calculated k_p^2/k_t value is 3.65 L/mol/s for the aqueous polymerization of MMA at 40°C, which is in close agreement with some reported values [14-16].

Initiator Transfer

The above equation may be transformed into the following form to calculate the initiator transfer parameter ($C_I K$) in the aqueous system, taking the transfer constant of water to be zero [17] and [I] = K[Py-SO$_2$][M]:

$$\frac{1}{\overline{P}_n} - 1.85 \frac{k_t}{k_p^2} \frac{R_p}{[M]^2} = C_M + C_I K[\text{Py-SO}_2] \tag{4}$$

A plot of the left-hand side of this equation vs [Py-SO$_2$] is given in Fig. 6 (top), and the value of $C_I K$ obtained from the slope of this plot is 0.28 L/mol. The intercept of the plot giving the value of C_M is 3.0×10^{-5}.

With knowledge of k_p^2/k_t and $C_I K$ values, Eq. (2) and the corresponding plot given in Fig. 6 was used to calculate the kinetic parameters $f k_d K$ and $k_{rtI}/k_{iI} k_p$ and the calculated values are 6.54×10^{-8} and 1.80×10^3 L/mol/s, respectively.

ACKNOWLEDGMENT

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