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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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To cite this Article Ghosh, Premamoy and Biswas, Samir(1982) 'Photopolymerization of Methyl Methacrylate Initiated by Pyridine-Sulfur Dioxide Charge Transfer Complex in the Presence of Carbon Tetrachloride', *Journal of Macromolecular Science, Part A*, 18: 4, 503 – 510

To link to this Article: DOI: 10.1080/00222338208082063

URL: <http://dx.doi.org/10.1080/00222338208082063>

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Photopolymerization of Methyl Methacrylate Initiated by Pyridine-Sulfur Dioxide Charge Transfer Complex in the Presence of Carbon Tetrachloride

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ABSTRACT

Photopolymerization of methyl methacrylate in visible light was studied at 40°C using a pyridine-sulfur dioxide charge transfer complex as the initiator in the presence of carbon tetrachloride. In this study the [Py-SO₂] used was high (0.5-3.2 mol/L), i.e., 6-40% (V/V), and the [CCl₄] ranged between 0 and 1.4 mol/L, i.e., 0-10% (V/V). At a fixed [Py-SO₂], R_p followed an increasing trend with increasing [CCl₄] until the latter was about 2-3% of the total volume. The polymerization rates may be expressed as

$$(R_p - R_{p_0}) = \frac{k_p k_1}{k_t^{0.5}} [\text{Py-SO}_2]^{0.5} [M]^{1.5} \left(\frac{[\text{CCl}_4]}{k_2/k_3 + [\text{CCl}_4]} \right)^{0.5}$$

where R_p and R_{p₀} are rates of photopolymerization in the presence and in the absence of CCl₄, respectively. The overall rate, R_p, is proportional to [CCl₄]^{0.5} for [CCl₄] ≤ 0.2 mol/L, but it is independent of [CCl₄] > 0.2 mol/L.

INTRODUCTION

It has been recently reported [1, 2] that pyridine (donor) and sulfur dioxide (acceptor) readily react with each other to form a 1:1 pyridine-sulfur dioxide (Py-SO₂) charge transfer complex which can act as a good photoinitiator of vinyl polymerization. Kinetics of photopolymerization of methyl methacrylate (MMA) using this photoinitiator in the concentration range of 10⁻¹ to 10⁻³ mol/L have also been studied. The present paper reports the kinetics of photopolymerization of methyl methacrylate in largely diluted systems using Py-SO₂ complex photoinitiator in a much higher concentration range, 0.5 to 3.2 mol/L, in the presence of different concentrations of carbon tetrachloride. Experimental set up and procedures are similar to those described before [2-4].

RESULTS

The Py-SO₂ complex is not quite miscible with MMA when used in concentrations > 0.2 mol/L. We used some known quantities of methanol, a polar solvent in polymerization systems, to make them homogeneous.

Variation of Rate of Polymerization (R_p) with
Variation in [Py-SO₂] at Fixed [M] and [CCl₄]

Photopolymerization was usually studied at 40 ± 0.05° C. Table 1 shows the effect of variation of Py-SO₂ on the initial steady rate, R_p , at fixed [M] and [CCl₄], where [M] is the monomer concentration. The initiator exponent obtained from the slope of the log R_p vs log [Py-SO₂] plot is 0.5 (Fig. 1). It may be clearly seen (Table 1) that the presence of about 2-3% CCl₄ (0.2-0.3 mol/L) greatly enhances the rate of the photopolymerization process. Almost instantaneous polymerization was observed even with low [CCl₄], < 0.5%, while there was usually an inhibition period (10-20 min) in systems containing no CCl₄.

k_p^2/k_t -Value

The kinetic parameter k_p^2/k_t , evaluated graphically in the usual manner from R_p and \bar{P}_n data, where \bar{P}_n is the degree of polymerization determined viscometrically [1], is 1.37×10^{-2} L/mol·s (Fig. 2). This value is in agreement with some reported values [2-4].

TABLE 1. Variation of R_p with Initiator Concentration in the Photopolymerization of MMA using Py-SO₂ Complex as the Photoinitiator Activated by a Fixed Concentration of CCl₄ (Diluent: methanol; [M] = 3.68 mol/L; [CCl₄] = 0.689 mol/L)

Py-SO ₂ (mol/L)	$R_p \times 10^4$ (mol/L·s)	$[\eta]$ (dL/g)	$(1/\bar{P}_n) \times 10^3$	Initiator exponent	$(k_p^2/k_t) \times 10^2$ (L/mol·s)
3.18	3.308	0.132	6.472		
2.65	3.020	0.139	6.083		
2.12	2.660	0.148	5.596	0.50	1.37
1.59	2.300 ^a	0.159	5.109		
1.06	1.875	0.175	4.535		
0.53	1.350	0.190	4.100		
1.59 ^b	0.137 ^c				

^aInhibition period: nil (for 0.689 mol/L of CCl₄).

^bFor zero CCl₄ concentration.

^cInhibition period: 15 min (for no CCl₄).

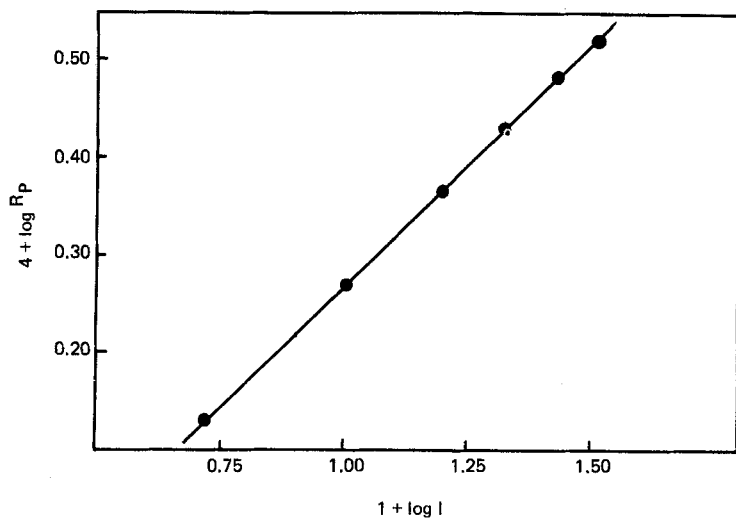


FIG. 1. Photopolymerization of methyl methacrylate initiated by the pyridine-sulfur dioxide charge transfer complex in the presence of carbon tetrachloride.

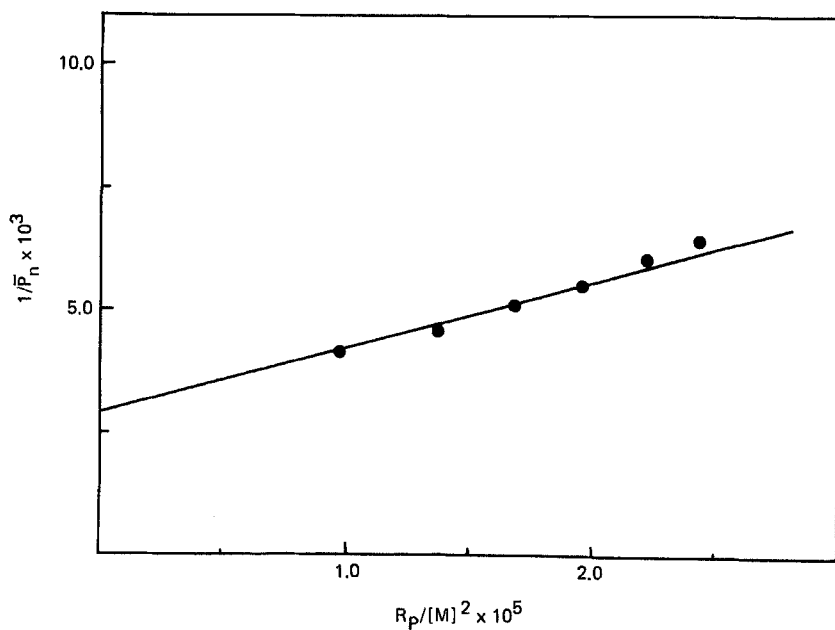


FIG. 2. Photopolymerization of methyl methacrylate initiated by the pyridine-sulfur dioxide charge transfer complex in the presence of carbon tetrachloride.

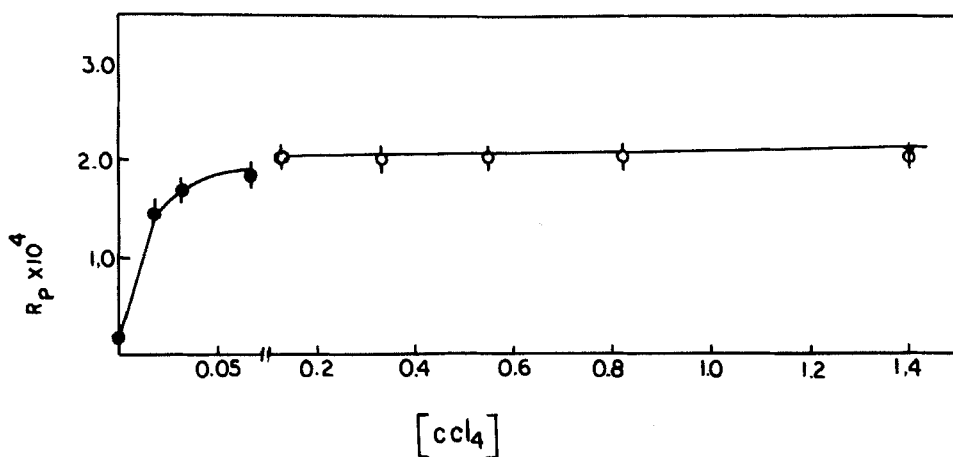


FIG. 3. Photopolymerization of methacrylate initiated by the pyridine-sulfur dioxide charge transfer complex in the presence of carbon tetrachloride.

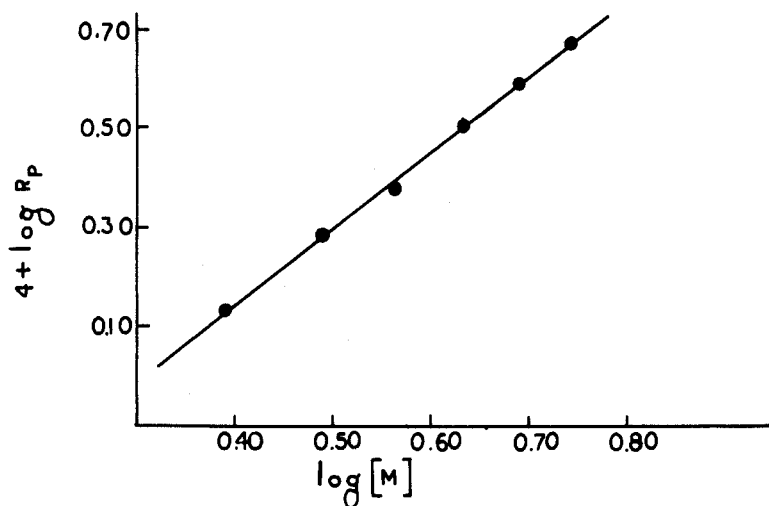


FIG. 4. Photopolymerization of methyl methacrylate initiated by the pyridine-sulfur dioxide charge transfer complex in the presence of carbon tetrachloride.

Effect of Carbon Tetrachloride

For a fixed $[\text{Py-SO}_2]$ and $[\text{M}]$, R_p was found to increase sharply with an increase in $[\text{CCl}_4]$ up to about 0.03-0.05 mol/L $[\text{CCl}_4]$, Fig. 3; for higher $[\text{CCl}_4]$, R_p remains practically independent of $[\text{CCl}_4]$. The CCl_4 exponent changes from nearly 0.5 in a low $[\text{CCl}_4]$ range (< 0.04 mol/L) to practically zero in a high $[\text{CCl}_4]$ range (> 0.2 mol/L).

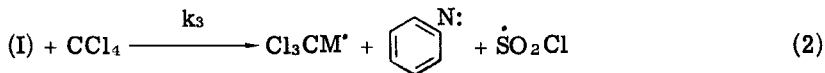
Monomer Exponent

In the CCl_4 -activated systems, variation of monomer concentration with methanol at a fixed $[\text{Py-SO}_2]$ and $[\text{CCl}_4]$ produced variation of R_p such that the monomer exponent obtained from the $\log R_p$ vs $\log [\text{M}]$ plot is 1.5, Fig. 4.

Mechanism

With R_p proportional to $[\text{C}]^{0.5}$ (where C stands for the Py-SO_2 complex) and to $[\text{CCl}_4]^{0.5}$ and $[\text{CCl}_4]^{0.0}$ in low or high concentrations of

CCl_4 , respectively, the overall reaction steps for radical generation and chain initiation may be expressed as [5]



The formation of the initiator-monomer complex is presumed to be reversible. Complex (I) enters into reaction with CCl_4 to generate a pair of radicals very easily. The second reaction is considered to be highly photosensitive.

From the above reaction scheme the expression of R_i (the rate of initiation) in the presence of CCl_4 may be given as

$$R_i = 2 \frac{k_1 k_2 [\text{C}] [\text{M}] [\text{CCl}_4]}{k_2 + k_3 [\text{CCl}_4]} \quad (3)$$

Therefore, R_p in the presence of carbon tetrachloride may be expressed as

$$R_p = k_p \left(\frac{R_i}{2k_t} \right)^{0.5} [\text{M}] = \frac{k_p}{k_t^{0.5}} [\text{M}]^{1.5} [\text{C}]^{0.5} k_1^{0.5} \left(\frac{[\text{CCl}_4]}{k_2/k_3 + [\text{CCl}_4]} \right)^{0.5} \quad (4)$$

provided there is no polymerization at 40°C in the absence of CCl_4 . However, if R_{p_0} is the rate observed in the absence of CCl_4 at the polymerization temperature, then the expression for R_p takes the form

$$R_p = R_{p_0} + \frac{k_p}{k_t^{0.5}} [\text{M}]^{1.5} [\text{C}]^{0.5} k_1^{0.5} \left(\frac{[\text{CCl}_4]}{k_2/k_3 + [\text{CCl}_4]} \right)^{0.5} \quad (5)$$

For a given value of $[\text{C}]$ (1.59 mol/L) at a fixed value of $[\text{M}]$ (3.68 mol/L), R_{p_0} was found to be 0.137×10^{-4} mol/L's, and the overall rate, R_p , was largely dependent on $[\text{CCl}_4]$ when $[\text{CCl}_4]$ was < 0.2 mol/L but it was more or less independent of $[\text{CCl}_4]$ for $[\text{CCl}_4] > 0.2$ mol/L, Fig. 3, Table 2. The mean upper limiting value of R_p for $\text{CCl}_4 > 0.2$ mol/L was 2.05×10^{-4} mol/L's.

TABLE 2. Effect of CCl_4 on R_p in the Photopolymerization of MMA Using Py-SO_2 Complex as the Photoinitiator at 40°C ($[M] = 3.68$ mol/L, $[\text{Py-SO}_2] = 1.59$ mol/L)

CCl_4 (mol/L)	$R_p \times 10^4$ (mol/L·s)
1.400	2.100
0.827	2.083
0.550	2.045
0.344	2.000
0.138	1.971
0.069	1.865
0.034	1.698
0.017	1.472
0.000	0.137

For high $[\text{CCl}_4]$, (> 0.2 mol/L) and $[C]$ and $[M]$ as above, the value of k_1 was readily calculated from Eq. (5) using the given values of $[C]$ and $[M]$ and taking a k_p^2/k_t value equal to 1.40×10^{-2} L/mol·s. The calculated value of k_1 is 3.474×10^{-8} L/mol·s. Now, with knowledge of $k_p/k_t^{0.5}$ and the given values of $[M]$ and $[C]$, and from various values of R_p at different $[\text{CCl}_4]$ for $[\text{CCl}_4] < 0.2$ mol/L, the corresponding values of k_2/k_3 were calculated. The average value of this parameter is 0.021 mol/L. For polymerization of MMA at 50°C in the dark using the $(\text{Py-SO}_2)\text{-CCl}_4$ system as initiator, Matsuda et al [5] reported a value of 4.69×10^{-9} L/mol·s for k_1 and a value of 0.0224 mol/L for the ratio k_2/k_3 , the value of R_{p0} in the dark being zero, i.e., they observed no polymerization if CCl_4 was not included in the system, and their reported R_p values were in the range of $(0.2\text{-}0.35) \times 10^{-4}$ mol/L·s.

Thus photoactivation of the polymerization of MMA using the (Py-SO_2) complex and CCl_4 combination as the initiator system largely influences the overall kinetics including the initial (Py-SO_2) -monomer complexation reaction and the subsequent radical generation

process activated by CCl_4 , the net result being a many-fold increase in the rate of polymerization R_p and a significant value for R_{p0} . The enhancement in the rate due to photoactivation over the rate observed in the dark is seen to be largely due to a much higher k_1 value under the photo set up, and changes in the values of k_2 and k_3 seem to produce little or marginal effect on the overall kinetics.

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Accepted by editor August 22, 1981

Received for publication August 30, 1981