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Polymerization of Methyl Methacrylate by Charge-Transfer Mechanism with Amines and Carbon Tetrachloride

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ABSTRACT

The charge-transfer complex formed between an amine and carbon tetrachloride can initiate the polymerization of vinyl monomers in a nonaqueous solvent such as dimethylsulfoxide. Here we use cyclopentylamine (CPA) and heptylamine (HA) as the donor compounds for charge-transfer initiation of the polymerization of methyl methacrylate (MMA). The rate of polymerization $R_p = k[\text{MMA}]^{\frac{1}{2}}[\text{amine}]^{0.5} [\text{CCl}_4]^{0.5}$ when $[\text{CCl}_4]/[\text{amine}] \leq 1$; when $[\text{CCl}_4]/[\text{amine}] > 1$, R_p becomes independent of $[\text{CCl}_4]$ and $R_p = k[\text{MMA}]^{1.5} [\text{amine}]^{0.5}$. The average constant at 60°C for the polymerization of MMA in terms of monomer were $(1.66 \pm 0.03) \times 10^{-5}$ and $(1.46 \pm 0.04) \times 10^{-5} \text{ s}^{-1}$ with CPA and HA, respectively, when $[\text{CCl}_4]/[\text{amine}] \leq 1$, and $(1.16 \pm 0.04) \times 10^{-5}$ and $(1.39 \pm 0.08) \times 10^{-5} \text{ L/mol} \cdot \text{s}$ when $[\text{CCl}_4]/[\text{amine}] > 1$.

INTRODUCTION

It is well known that the charge-transfer complex formed between a compound containing a donor atom and an acceptor like SO_2 can initiate the polymerization of vinyl monomers [1-3]. Maleic anhydride can initiate the charge-transfer polymerization of styrene in the presence of such solvent as ethylbenzene, cymene, and p-cymene [4]. It has been reported that vinyl monomers can be initiated by n-butylamine [5], isopropylamine [6], 2,4-dinitrophenyl hydrazine [7], sodium cyanide [8], urea [9], melamine [10] etc. in the presence of carbon tetrachloride by a charge-transfer mechanism. Such a charge-transfer polymerization can be accelerated by Lewis acids. Here we report the polymerization of MMA initiated by cyclopentylamine (CPA) and heptylamine (HA) with carbon tetrachloride in DMSO at 60°C . It was suggested by Latenberger et al. [11] that the polymerization was due to a charge-transfer complex formed between the electron donor compound and CCl_4 . Vofsi et al. [12] suggested that the polymerization was due to the charge-transfer complex formed between the electron donor compound and the monomer. Evidently both mechanisms could operate [5, 6]. So the polymerization was done with CPA and HA in the presence of CCl_4 to check the validity of the rate laws and mechanism already proposed.

EXPERIMENTAL

Materials

MMA [13], DMSO [14], and CCl_4 [1] were purified by published methods. Cyclopentylamine (Fluka) and heptylamine (Fluka AG) were distilled under reduced pressure before use.

Polymerization

The experiments were done in a three-limbed vessel. The first limb was filled with MMA in DMSO and the second with amine and CCl_4 in DMSO. The vessel was completely evacuated [15], and then the contents of the two limbs were thoroughly mixed and transferred to the third limb, the dilatometer. The sealed dilatometer was then immediately introduced into a thermostat at $60 \pm 0.01^\circ\text{C}$. The reaction was followed dilatometrically. The molecular weights were determined viscometrically using the relationship [16]

$$[\eta] = K \times \bar{M}_n^{\infty} = 4.35 \times 10^{-5} \bar{M}_n^{0.8}$$

RESULTS AND DISCUSSION

MMA can be polymerized even below 30°C by CPA and HA in the presence of CCl_4 in DMSO, DMF, or CHCl_3 . No polymerization takes place if amine or CCl_4 is missing from the system. The rate of polymerization, R_p , of MMA increased with an increase of $[\text{CCl}_4]$ and becomes independent of $[\text{CCl}_4]$ when $[\text{CCl}_4]/[\text{amine}] > 1$. The plot of R_p vs $[\text{CCl}_4]$ is shown in Fig. 1. When $[\text{CCl}_4]/[\text{amine}] \leq 1$, the rate of polymerization of MMA was first order with respect to $[\text{MMA}]$. A typical plot for CPA and HA with a fixed amount of CCl_4 is shown in

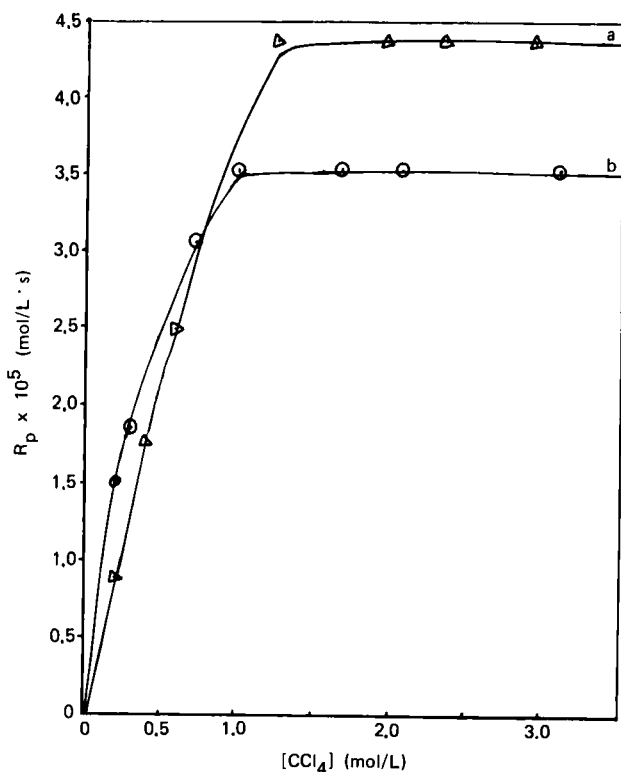


FIG. 1. Plot of R_p vs [carbon tetrachloride] at 60°C. (a) MMA; cyclopentylamine and CCl_4 system. (b) MMA; heptylamine and CCl_4 system. $[\text{MMA}] = 1.80 \text{ mol/L}$, $[\text{CPA}] = 0.99 \text{ mol/L}$, $[\text{HA}] = 0.59 \text{ mol/L}$.

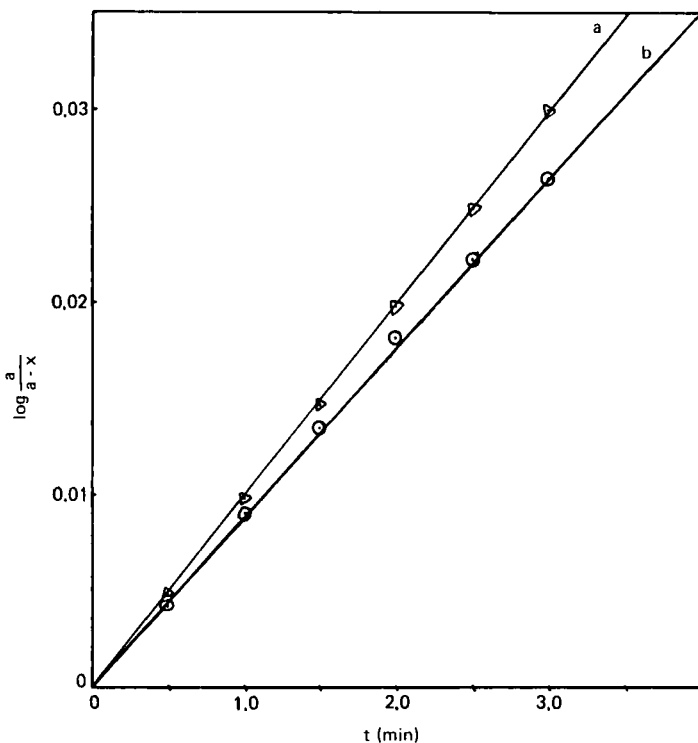


FIG. 2. Plot of $\log a/(a-x)$ vs time in minutes at 60°C , where "a" is the initial concentration of MMA and "x" is the concentration of MMA that disappeared with time. (a) MMA, CPA, and CCl_4 system. (b) MMA, HA, and CCl_4 system. $[\text{CPA}] = 0.99 \text{ mol/L}$, $[\text{CCl}_4] = 0.98 \text{ mol/L}$, $[\text{HA}] = 1.13 \text{ mol/L}$.

Fig. 2. The data for these plots are given in Tables 1 and 2. When $[\text{CCl}_4]/[\text{amine}] < 1$, the rate was proportional to $[\text{amine}]^{0.5}$ (Fig. 3) and $[\text{CCl}_4]^{0.5}$ (Fig. 4).

The order of reaction with respect to monomer was 1.40 when CPA was used as the donor and 1.46 when HA was used as the donor for $[\text{CCl}_4]/[\text{amine}] > 1$. The order of reaction with respect to amine was 0.5 for both systems. The relationship of R_p with MMA for a fixed composition of amine and CCl_4 is depicted in Fig. 5. Under these conditions

TABLE 1. Concentration of Monomer MMA (x) to Disappear after a Definite Interval of Time and the Average Rate Constant k (in s⁻¹). [CCl₄] = 0.98 mol/L, [CPA] = 0.99 mol/L, [DMSO] = 8.16 mol/L

Time (min)	Initial concentration of MMA (a)	Initial concentration (mol/L)	$\frac{a}{a-x}$	$\log \frac{a}{a-x}$	k (in s ⁻¹) from Fig. 2(a)
5	1.80		1.0115	0.0050	
10	1.80		1.0228	0.0098	
15	1.80		1.034	0.0147	
20	1.80		1.0468	0.0198	
25	1.80		1.0589	0.0248	
30	1.80		1.0719	0.0301	
35	1.80		1.0852	0.0355	
					1.66×10^{-5}

TABLE 2. Concentration of Monomer MMA (x) to Disappear after a Definite Interval of Time and the Average Rate Constant k (in s^{-1}). $[CCl_4] = 0.98$ mol/L, $[HA] = 1.13$ mol/L, $[DMSO] = 6.80$ mol/L

Time (min)	Initial concentration of MMA (a) (mol/L)	$\frac{a}{a-x}$	$\log \frac{a}{a-x}$	k (in s^{-1}) from Fig. 2(b)
5	1.80	1.01	0.0043	
10	1.80	1.02	0.0090	
15	1.80	1.03	0.0135	
20	1.80	1.04	0.0182	(1.46×10^{-5})
25	1.80	1.05	0.0226	
30	1.80	1.06	0.0264	

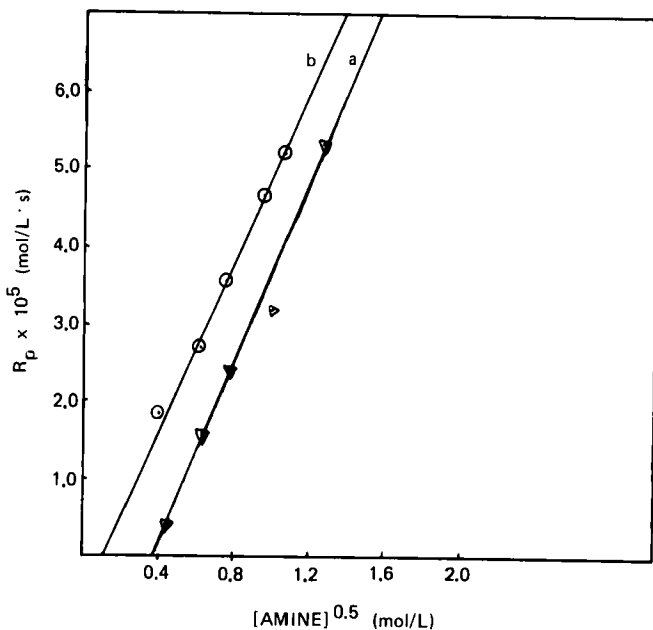


FIG. 3. Plot of R_p vs $[\text{amine}]^{1/2}$ at 60°C . (a) MMA, CPA, and CCl_4 system. (b) MMA, HA, and CCl_4 system. $[\text{MMA}] = 1.80 \text{ mol/L}$, $[\text{CCl}_4] = 0.98 \text{ mol/L}$.

the mean rate constant is $(1.16 \pm 0.04) \times 10^{-5} \text{ L/mol} \cdot \text{s}$ for the CPA and $(1.39 \pm 0.08) \times 10^{-5} \text{ L/mol} \cdot \text{s}$ for the HA systems, respectively. The linear plot of R_p vs $[\text{amine}]^{0.5}$ intercepted the axis of $[\text{amine}]^{0.5}$

at 0.36 mol/L for the CPA system and at 0.12 mol/L for the HA system, which were the limiting values for the concentration of amines, CPA, and HA for the formation of the associated complex with DMSO [17]. Thus the amines up to these limits were not free to initiate the polymerization of MMA. Above this concentration the free amine was available for the formation of a charge-transfer complex with MMA and CCl_4 , and so the initiation of polymerization was possible above 0.36 mol/L of CPA and 0.12 mol/L of HA (Tables 3 and 4).

As the reactions are inhibited by oxygen and hydroquinone, a radical mechanism is suggested. The radicals must be generated by decomposition of the charge-transfer complexes.

The mechanism for the initiation of MMA by the charge-transfer complex formed by the interaction of amine and CCl_4 , as well as of amine and vinyl monomer, is not very certain [18]. According to Vofsi et al.

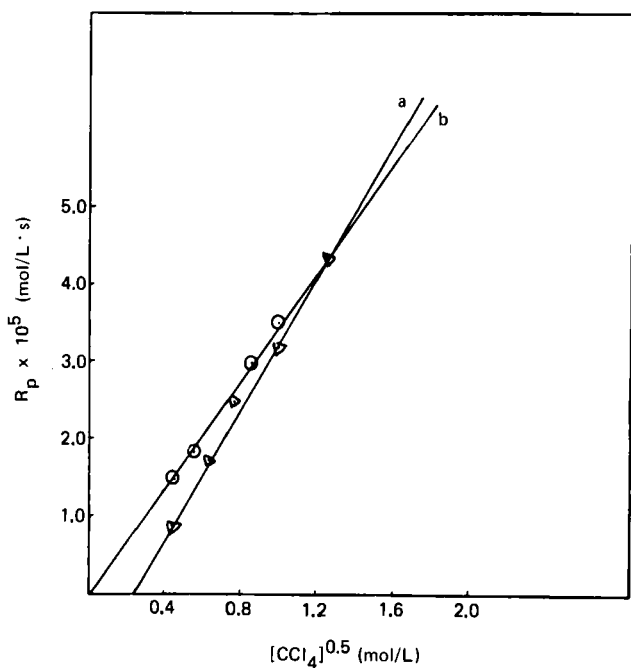
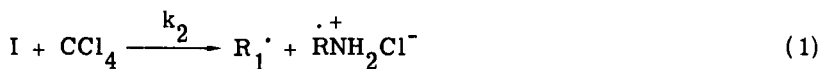
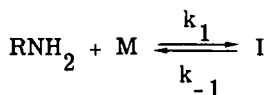


FIG. 4. Plot of R_p vs $[\text{carbon tetrachloride}]^{1/2}$ at 60°C . (a) MMA, CPA, and CCl_4 system. (b) MMA, HA, and CCl_4 system. $[\text{MMA}] = 1.80$ mol/L, $[\text{CPA}] = 0.99$ mol/L, $[\text{HA}] = 0.59$ mol/L.

[12], the charge-transfer complex I formed between amine as the donor and vinyl monomer as the acceptor in the presence of CCl_4 initiates the polymerization:



where $\text{M} = \text{MMA}$

$\text{R} = \text{C}_5\text{H}_{11}$ and C_7H_{15}

$\text{R}_1^\cdot = \text{MCCl}_3$

$\text{I} = \text{charge-transfer complex}$

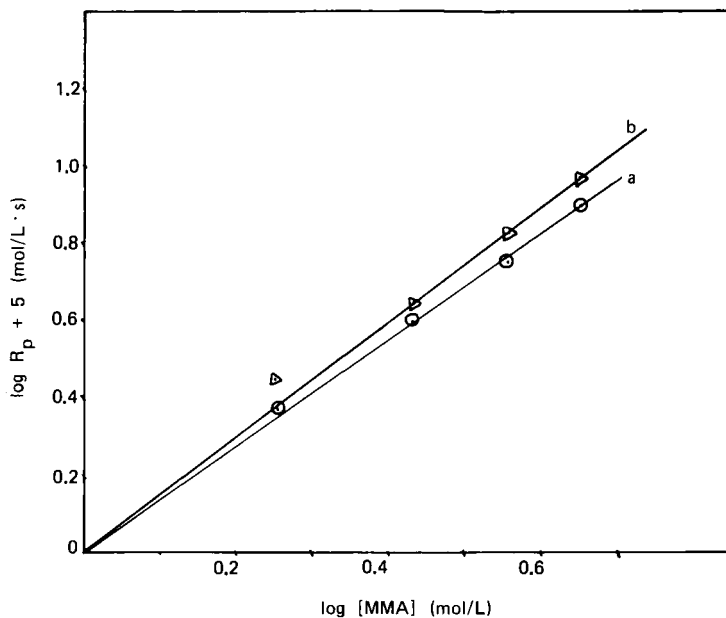
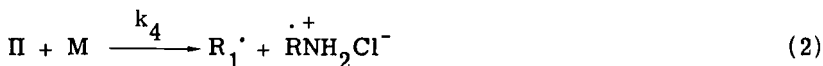
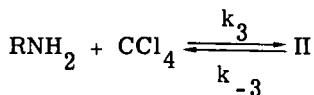


FIG. 5. Relationship between $\log R_p$ and $\log [\text{MMA}]$ at 60°C . (a) MMA, CPA, and CCl_4 system. (b) MMA, HA, and CCl_4 system. (a) $[\text{CPA}] = 0.59 \text{ mol/L}$, $[\text{CCl}_4] = 0.98 \text{ mol/L}$. (b) $[\text{HA}] = 0.56 \text{ mol/L}$, $[\text{CCl}_4] = 1.25 \text{ mol/L}$.

According to Latenberger et al. [11], charge-transfer complex (II), formed between amine and CCl_4 , produces the radical $\dot{\text{C}}\text{Cl}_3$.



where $\text{M} = \text{MMA}$

$\text{R} = \text{C}_5\text{H}_{11}$ and C_7H_{15}

$\text{R}_1\dot{\text{C}} = \text{M}\dot{\text{C}}\text{Cl}_3$

II = charge-transfer complex

TABLE 3. Concentration of MMA, CPA, Rate of Polymerization (R_p), and Average Rate Constant (k):
Reaction Time, 30 min. $[CCl_4] = 0.98$ mol/L, $[CPA] = 0.59$ mol/L

[MMA] (mol/L)	$[MMA]^{1.5}[CPA]^{0.5}$	$R_p \times 10^5$ mol/L·s	$k \times 10^5$ L/mol·s	Mean of k
1.80	1.839	2.39	1.30	
2.69	3.388	3.99	1.17	
3.59	5.224	5.69	1.09	$(1.16 \pm 0.04) \times 10^{-5}$
4.49	7.302	7.99	1.09	

TABLE 4. Concentration of MMA, HA, Rate of Polymerization (R_p), and Average Rate Constant (k):
Reaction Time, 25 min. $[CCl_4] = 1.25$ mol/L, $[HA] = 0.56$ mol/L

[MMA] (mol/L)	$[MMA]^{1.5}[HA]^{0.5}$	$R_p \times 10^5$ mol/L·s	$k \times 10^5$ L/mol·s	Mean of k
1.80	1.800	2.83	1.570	
2.69	3.316	4.46	1.345	
3.59	5.112	6.78	1.326	$(1.39 \pm 0.08) \times 10^{-5}$
4.48	7.146	9.47	1.325	

It is presumed that both mechanisms are possible [5, 6]. If $[A]_0$ is the concentration of added amine and $[A]_t$ is the concentration of unreacted free amine, at equilibrium the concentration of the amine reacted would be $[A_0 - A_t]$. For Mechanism (1):

$$\frac{dR_1}{dt} = k_2[I][CCl_4] = k_2[A_0 - A_t][CCl_4]$$

Again

$$\frac{d[A_0 - A_t]}{dt} = k_1[A_0][M] = k_{-1}[A_0 - A_t] - k_2[A_0 - A_t][CCl_4] = 0$$

$$[A_0 - A_t] = \frac{k_1[A_0][M]}{k_{-1} + k_2[CCl_4]}$$

$$[I] = \frac{k_1[A_0][M]}{k_{-1} + k_2[CCl_4]} \quad (3)$$

For Mechanism (2):

$$\frac{dR_1}{dt} = k_4[II][M] = k_4[A_0 - A_t][M]$$

The charge-transfer Complex II can be detected by UV spectroscopy [11]. The charge-transfer Complexes I and II could not be detected in the polymerization system. Apparently the complex became too reactive to be detected in the presence of monomer, and this justified the application of the steady-state principle.

Again,

$$\frac{d[A_0 - A_t]}{dt} = k_3[A_0][CCl_4] - k_{-3}[A_0 - A_t] - k_4[A_0 - A_t][M] = 0$$

$$[A_0 - A_t] = \frac{k_3[A_0][CCl_4]}{k_{-3} + k_4[M]}$$

$$[\text{II}] = \frac{k_3[A_0][\text{CCl}_4]}{k_{-3} + k_4[\text{M}]} \quad (4)$$

If a fraction α of the reacted amine is used for the formation of I and the fraction $(1 - \alpha)$ for II, then the rate of initiation R_i will be

$$R_i = \frac{dR_i}{dt} = \frac{\alpha k_1 k_2 [A_0] [M] [\text{CCl}_4]}{k_{-1} + k_2 [\text{CCl}_4]} + \frac{(1 - \alpha) k_3 k_4 [A_0] [M] [\text{CCl}_4]}{k_{-3} + k_4 [M]} \quad (5)$$

Assuming bimolecular termination

$$R_i = \frac{1}{k_t^{1/2}} \left[\frac{\alpha k_1 k_2 [A_0] [M] [\text{CCl}_4]}{k_{-1} + k_2 [\text{CCl}_4]} + \frac{(1 - \alpha) k_3 k_4 [A_0] [M] [\text{CCl}_4]}{k_{-3} + k_4 [M]} \right]^{1/2} \quad (6)$$

The overall rate of polymerization, R_p , can be expressed by

$$R_p = k_4 [M] [R_i] \\ = \frac{k_p}{k_t^{1/2}} [M] \left[\frac{\alpha k_1 k_2 [A_0] [M] [\text{CCl}_4]}{k_{-1} + k_2 [\text{CCl}_4]} + \frac{(1 - \alpha) k_3 k_4 [A_0] [M] [\text{CCl}_4]}{k_{-3} + k_4 [M]} \right]^{1/2} \quad (7)$$

When the concentration of CCl_4 is less than that of the amine, i.e., $[\text{CCl}_4]/[A_0] \leq 1$, Mechanism (2) predominates. Under that condition, $\alpha = 0$, and R_p may be written as

$$R_p = \frac{k_p}{k_t^{1/2}} [M] \left[\frac{k_3 k_4 [A_0] [M] [\text{CCl}_4]}{k_{-3} + k_4 [M]} \right]^{1/2} \quad (8)$$

If $k_4 [M] \gg k_{-3}$, then

$$R_p = \frac{k_p k_3^{1/2}}{k_t^{1/2}} [M]^{1.0} [A_0]^{0.5} [\text{CCl}_4]^{0.5} \quad (9)$$

The relation between R_p and $[\text{CCl}_4]$ as shown by Eq. (9) is in good agreement with the experimental results (Figs. 2, 3, and 4). When $[\text{CCl}_4]/[\text{amine}]$ exceeds unity, Mechanism (1) predominates. Under this condition, $\alpha = 1$ and the rate may be expressed as [6]

$$R_p = \frac{k_p}{k_t^{1/2}} [M] \left[\frac{k_1 k_2 [A_0] [M] [CCl_4]}{k_{-1} + k_2 [CCl_4]} \right]^{1/2} \quad (10)$$

If $k_2 [CCl_4] \gg k_{-1}$,

$$R_p = \frac{k_p k_1}{k_t^{1/2}} [M]^{3/2} [A_0]^{1/2} \quad (11)$$

Experimentally, R_p varies as $[M]^{1.40}$ for the CPA system and as $[M]^{1.46}$ for the HA system as shown in Fig. 5 (a,b) and R_p varies as $[A_0]^{0.5}$ for both the systems as shown in Fig. 3(a,b).

As some of the monomer is used up in the initiation and termination steps, the order is slightly less than the theoretical value. For other conditions, Eq. (7) is applicable where k_t is the termination rate constant.

Since the polymerization is initiated by free radicals produced from the charge transfer complex, Eq. (12) should be valid (data in Tables 5 and 6):

$$- DP \left[\frac{d[M]}{dt} \right] = \left[\frac{k_p^2}{k_t} \right] [M]^2 \quad (12)$$

where k_p and k_t represent the rate constants of propagation and termination, respectively. The values of $(k_p/k_t^{1/2})$ are 0.134 (L/mol·s)^{1/2} for the CPA system and 0.109 (L/mol·s)^{1/2} for the HA system. Some of the

TABLE 5. Value of $k_p/k_t^{1/2}$ Obtained for Various Polymerization Conditions at 60°C. $[CCl_4] = 0.98$ mol/L, $[CPA] = 0.59$ mol/L

$[MMA]_0$ (mol/L)	\overline{DP}	$-10^5 \left[\frac{d[M]}{dt} \right]$	$k_p/k_t^{1/2}$ (L/mol·s) ^{1/2}
1.80	2196	2.39	
2.69	3258	3.99	
3.59	4042	5.69	0.134
4.48	4505	7.99	

TABLE 6. Value of $k_p/k_t^{1/2}$ Obtained for Various Polymerization Conditions at 60°C. $[CCl_4] = 1.25 \text{ mol/L}$, $[HA] = 0.56 \text{ mol/L}$

$[MMA]_0$ (mol/L)	\overline{DP}	$-10^5 \left[\frac{d[M]}{dt} \right]$	$k_p/k_t^{1/2}$ (L/mol·s) ^{1/2}
1.80	1272	2.83	
2.69	2015	4.46	
3.59	2273	6.78	0.109
4.48	2464	9.74	

typical constant values for such systems are reported to be 0.160 [1] and 0.125 (L/mol·s)^{1/2} [19]. Therefore, the initiation must be by the free radical produced by the decomposition of the charge-transfer complex.

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