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# Catalytic Chain-Transfer in Polymerization of Methyl Methacrylate. I. Chain-Length Dependence of Chain-Transfer Coefficient

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# CATALYTIC CHAIN-TRANSFER IN POLYMERIZATION OF METHYL METHACRYLATE. I. CHAIN-LENGTH DEPENDENCE OF CHAIN-TRANSFER COEFFICIENT

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## ABSTRACT

Free-radical polymerization of methyl methacrylate has been conducted in the presence of a new catalytic chain-transfer agent at different temperatures. The new catalyst exhibits a strong chain transfer characteristic, and the chain-transfer coefficient varies from $2.8 \times 10^4$ to $6.6 \times 10^4$ and depends on chain length and temperature. The chain-transfer coefficients decrease with increasing chain length but reach a limiting value for chains more than 8 units in length. The activation energy for the chain transfer coefficient is -10.1 kJ/mol for this catalyst.

## INTRODUCTION

In recent years interest in making oligomers has been rising rapidly. Although much work has been devoted to the production of oligomers via free radical polymerization, very little kinetic information has been reported. Cobalt(II) complexes are extremely efficient catalytic chain transfer agents (CCTA) in free-radical polymerizations [1-3]. The new Co(II) catalyst which is the subject of this study is somewhat similar to reported Co(II) chelates [4]. The catalytic behavior of chain-transfer agents is simplified in the following sequence of reactions:

$$\text{Propagation:}\quad R_n{}^\circ + M \xrightarrow{k_p} R^\circ_{n+1}, \tag{1}$$

$$\text{Chain transfer:}\quad R_n{}^\circ + S \xrightarrow{k_{tr}} Q_n + SH^\circ, \tag{2}$$

$$\text{Reinitiation:}\quad SH^\circ + M \xrightarrow{k_{ri}} R_1{}^\circ + S. \tag{3}$$

CCTA acts as an intermediate reagent (S) to transfer the radical in the form of a hydrogen atom ($H^\circ$) from the propagating radical ($R_n{}^\circ$) to the monomer (M) to reinitiate a new chain ($R_1{}^\circ$). In the free-radical polymerization of methyl methacrylate (MMA), where initiation of chains is dominated by catalytic reinitiation reactions, the product polymer ($Q_n$) will have an $\omega$-unsaturated structure (Fig. 1); note that $Q_1$ is identical to the monomer.

In contrast to poly(methyl methacrylate), which shows a weak UV absorption, the $\omega$-unsaturated oligo(methyl methacrylate) exhibits a strong UV absorption due to the conjugated terminal double bond.

## EXPERIMENTAL

Cobaloxime boron fluoride (COBF) was made by a modification of the procedure of Bakac and Espenson [5]. The synthesis is illustrated by the following reaction sequence:

$$Co(CH_3COO)_2 \cdot 4H_2O + 2dmgH_2 \longrightarrow Co(dmgH)_2 \cdot 2H_2O + 2HCH_3COO + 2H_2O$$

$$Co(dmgH)_2 \cdot 2H_2O + 2BF_3 \cdot Et_2O \longrightarrow Co(dmgBF_2)_2 \cdot 2H_2O + 2HF + 2H_2O$$

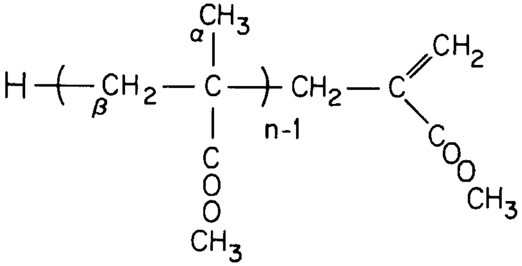

FIG. 1. Structure of oligomer of methyl methacrylate.

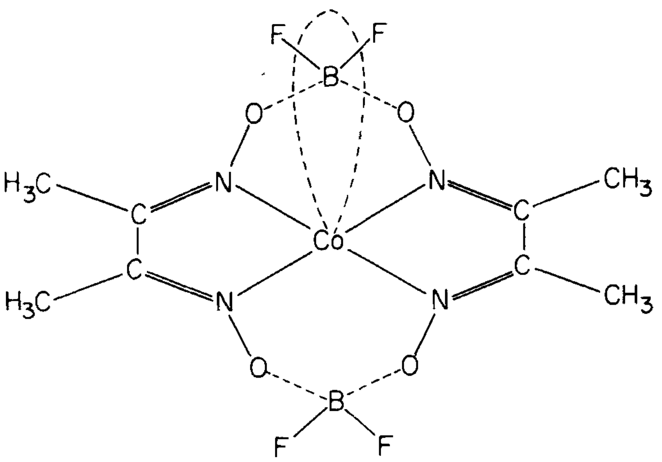

FIG. 2. Structure of cobaloxime boron fluoride.

A 250-mL round-bottomed flask, equipped with a magnetic stirring bar and condenser, is filled with 100 mL dry methanol. Dimethylglyoxime (1.9 g) ($dmgH_2$) is dissolved in the methanol and 2.0 g Co(II)acetate is added to the solution. The flask is closed and the solution stirred for 1.5 h. The orange-brown crystalline product is collected on a Buchner funnel and dried under a vacuum at room temperature. To the suspension of $Co(dmgH)_2 \cdot 2H_2O$ in 100 mL $Et_2O$ in the round-bottomed flask, 10 mL of $BF_3 \cdot Et_2O$ is added and is stirred for 20 h.

The resulting crystalline brownish powder is filtered, the solid is washed with ice-cold deionized water, and then recrystallized twice from 75 mL methanol. The final product is dried under a vacuum at room temperature. The COBF ligand structure is displayed in Fig. 2.

MMA was washed three times with 10% aqueous sodium hydroxide and three times with water to remove the inhibitor; it was stored at -10°C after drying over calcium chloride. It was freshly distilled under reduced pressure before use. AIBN was recrystallized twice from absolute methanol below 40°C.

Polymerizations were carried out in bulk monomer using AIBN as initiator and COBF (0.1 to 20 ppm) as CCTA at 60, 70, 80, and 90°C. All polymerizations were performed in sealed glass ampules after degassing the colutions by three successive freeze-pump-thaw cycles. After 4 half-lives of the initiator, the polymer was isolated by evaporation of the residual monomer under aspirator vacuum at 40°C.

Molecular weight distributions (MWD) were measured with a Waters 590-C GPC, equipped with a DRI detector and a UV detector with a 245-nm cut-off filter. Data acquisition was accomplished with an Apple-II microcomputer. Stabilized THF was used as the eluent through a set of PLgel columns (Polymer Laboratories, Shropshire, U.K.) with pore sizes of $10^4$, $10^3$, and $10^2$ Å. In this arrangement the elution times for monomer, dimer, trimer, tetramer, pentamer, and hexamer are distinct. Therefore, MWD's are precisely measureable for very low molecular weight polymers.

The NMR spectra were taken with a high-precision 250-MHz FT-NMR spectrometer at 130°C with *o*-dichlorobenzene-$d_4$ as solvent ($\approx$ 10% w/v solution) and 0.1% w/v tetramethylsilane as internal reference.

## RESULTS

The GPC is equipped with UV and DRI detectors. The DRI detects the MWD based on weight fraction of the oligomers, and the UV detects the MWD based on mole fraction (concentration) of the products. However, the result from either detector is convertible to that from the other (Table 1). A typical GPC trace is shown in Fig. 3, and results from both detectors are tabulated in Table 1. In Fig. 3, it should be noted that the right-hand peaks are due to low molecular weight impurities, perhaps CCTA fragments.

The $^1$H-NMR shifts of oligomers appear as shown in Fig. 4 at δ6.12 and 5.40 (olefinic $CH_2$), 3.55-3.63 (ester methyl $-OCH_3$), 2.54-2.64 (allylic $-CH_2$), 2.00-2.16 (β methylene $CH_2$), and 1.1-1.35 (α methyl $-CH_3$).

Each oligomer has one unsaturated double bond at the end. Therefore, $\bar{M}_n$ from the NMR spectrum is two-thirds of the ratio of the area under the ester methyl peak to the area under olefinic peaks. The resulting average molecular weights are in good agreement with GPC results, as can be seen in Table 1.

The average chain-transfer coefficients $\bar{C}_s$ ($= k_{tr}/k_p$) were estimated by the Mayo equation for individual runs and tabulated on the assumption that $1/P_n{}^\circ$ was negligible ($P_n{}^\circ \approx 10^4$). The plot of the Mayo equation is shown in Fig. 5.

$$\frac{1}{\bar{P}_n} - \frac{1}{\bar{P}_n{}^\circ} = \bar{C}_s \frac{[S]}{[M]}. \tag{4}$$

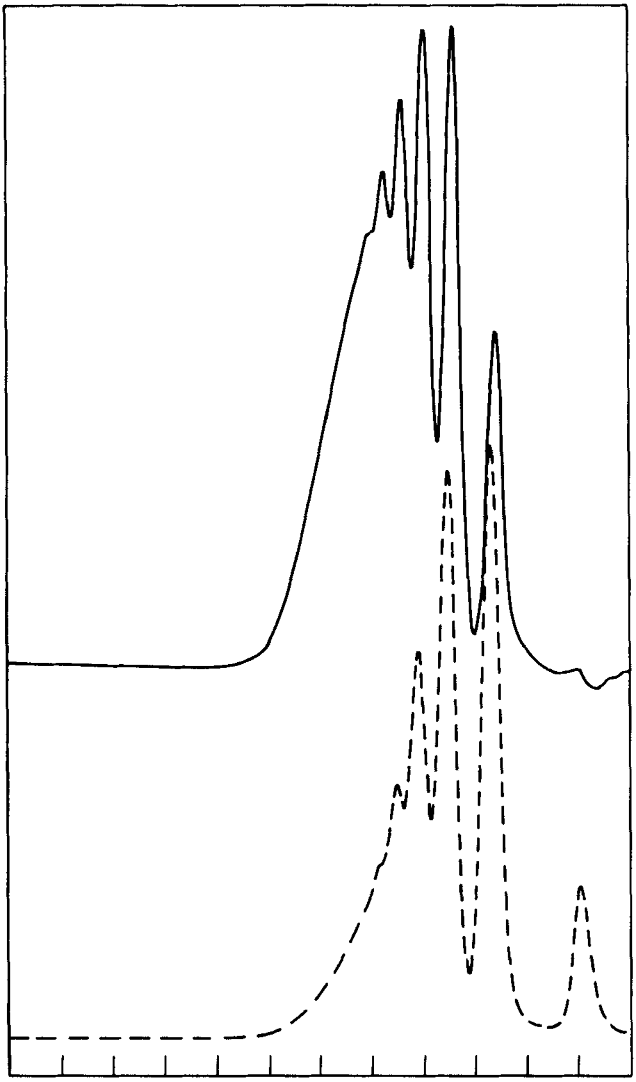

FIG. 3. GPC traces: (—) DRI detector and (- -) UV detector.

TABLE 1. Effect of COBF Concentration and Temperature on Molecular Weight

| $\frac{[S]}{[M]} \times 10^6$ | Conversion | $\bar{M}_{n(\mathrm{UV})}$ | $\bar{M}_{n(\mathrm{DRI})}$ | $\bar{M}_{n(\mathrm{NMR})}$ | $\frac{\bar{M}_w}{\bar{M}_n}$ (DRI) | $\bar{C}_s \times 10^{-4}$ |
|---|---|---|---|---|---|---|
| Temperature = 60°C and $[I^\circ]$ = 6.15 μmol/L | | | | | | |
| 0.178 | 13.22 | | 14081 | | 1.91 | 4.003 |
| 0.355 | 13.38 | | 7054 | | 1.92 | 3.995 |
| 1.065 | 12.09 | | 2314 | | 1.95 | 4.060 |
| 1.774 | 12.17 | 1455 | 1668 | 1454 | 1.91 | 3.379 |
| 3.548 | 6.10 | 716 | 882 | 894 | 1.65 | 3.195 |
| 10.654 | 5.30 | 344 | 352 | 355 | 1.45 | 2.669 |
| 13.306 | 5.04 | 312 | 310 | 334 | 1.33 | 2.424 |
| Temperature = 70°C and $[I^\circ]$ = 9.47 μmol/L | | | | | | |
| 0.178 | 10.90 | | 15455 | | 1.94 | 3.647 |
| 0.355 | 8.78 | | 7377 | | 1.94 | 3.820 |
| 1.065 | 7.38 | | 2675 | | 1.88 | 3.152 |
| 1.774 | 6.85 | 1573 | 1682 | 1580 | 1.84 | 3.351 |
| 3.548 | 7.39 | 1172 | 945 | 1105 | 1.79 | 2.982 |
| 10.654 | 4.84 | 419 | 401 | 472 | 1.46 | 2.343 |
| 13.306 | 2.96 | 341 | 332 | 408 | 1.35 | 2.264 |

| | | | | | | |
|---|---|---|---|---|---|---|
| Temperature = 80°C and $[I^{\circ}]$ = 24.65 μmol/L | | | | | | |
| 0.210 | 10.87 | | 12182 | | 1.88 | 3.901 |
| 0.421 | 9.45 | | 5661 | | 1.92 | 4.200 |
| 1.051 | 8.88 | | 2745 | | 1.81 | 3.465 |
| 2.103 | 8.81 | 1262 | 1317 | 1404 | 1.86 | 3.511 |
| 4.205 | 9.11 | 758 | 757 | 818 | 1.76 | 4.141 |
| 15.771 | | 331 | 336 | 386 | 1.38 | 1.887 |
| Temperature = 90°C and $[I^{\circ}]$ = 49.31 μmol/L | | | | | | |
| 0.210 | 10.94 | | 17240 | | 2.03 | 2.759 |
| 0.421 | 9.08 | | 8271 | | 1.85 | 2.875 |
| 1.051 | 8.13 | | 3284 | | 1.87 | 2.986 |
| 2.103 | 8.20 | 1565 | 1485 | 1502 | 1.94 | 3.202 |
| 4.205 | 8.21 | 988 | 883 | 881 | 1.85 | 2.693 |
| 10.654 | 8.55 | 469 | 448 | 469 | 1.56 | 2.123 |
| 15.771 | 8.55 | 343 | 351 | 425 | 1.42 | 1.807 |

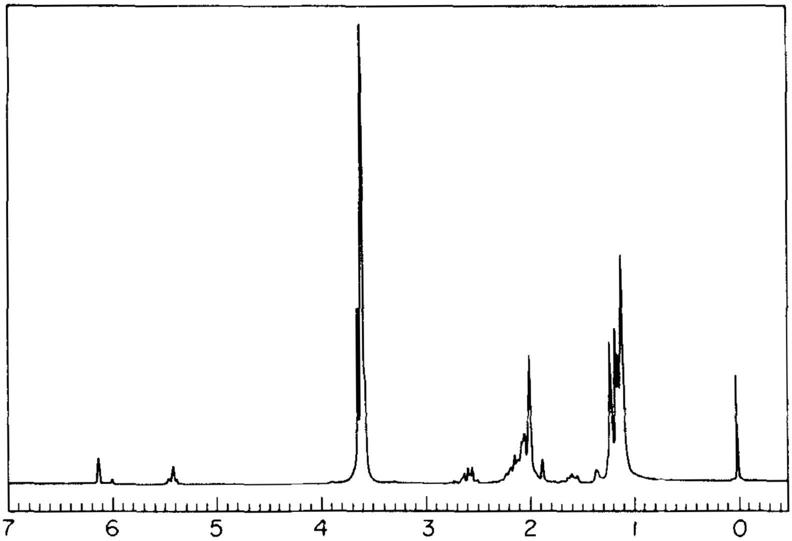

FIG. 4. NMR spectrum of sample with 2.103 ppm COBF at 90°C.

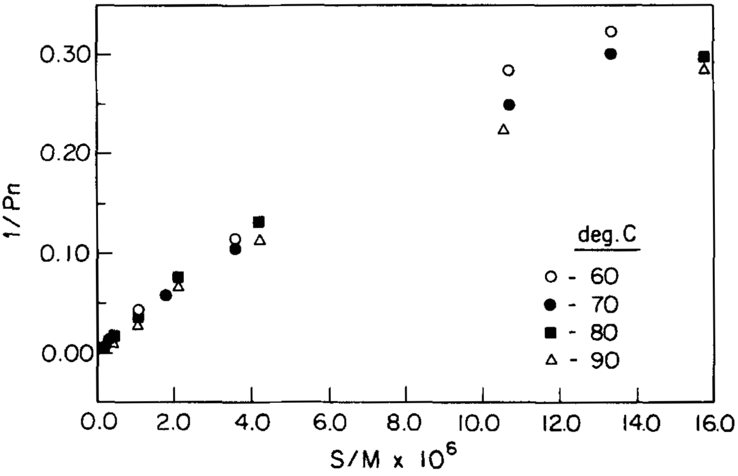

FIG. 5. Plot of $1/\bar{P}_n$ against [S]/[M] for different temperatures.

## OLIGOMER CHAIN-TRANSFER COEFFICIENT

When the oligomer products cannot reenter the growth step, the product distribution is determined by the rate of chain transfer relative to chain growth. In other words, the radical $R_n{}^\circ$, may either undergo chain transfer to catalyst to yield $Q_n$ or react with M to give $R^\circ_{n+1}$ (Eqs. 2 and 3). The mole fraction of dimer in the product is given by [6]

$$F_2 = \frac{\text{rate of formation of dimer}}{\text{rate of formation of all oligomers}} \tag{5}$$

$$= \frac{k_{tr2}[\mathrm{S}]\,[\mathrm{R}_2{}^\circ]}{k_{tr2}[\mathrm{S}]\,[\mathrm{R}_2{}^\circ] + k_{p2}[\mathrm{M}]\,[\mathrm{R}_2{}^\circ]} \tag{6}$$

$$= \frac{C_{s2}\dfrac{[\mathrm{S}]}{[\mathrm{M}]}}{1 + C_{s2}\dfrac{[\mathrm{S}]}{[\mathrm{M}]}} . \tag{7}$$

The mole fraction of $Q_n$ has the same relation to all higher oligomers as the mole fraction of dimer to all higher oligomers. Therefore, a new fraction distribution is calculated for each chain-transfer coefficient by successively leaving out lower oligomer populations:

$$F_n{}' = \frac{[\mathrm{Q}_n]}{[\mathrm{Q}_n] + \sum\limits_{i=n+1}^{\infty} [\mathrm{Q}_i]} \tag{8}$$

$$= \frac{C_{sn}\dfrac{[\mathrm{S}]}{[\mathrm{M}]}}{1 + C_{sn}\dfrac{[\mathrm{S}]}{[\mathrm{M}]}} . \tag{9}$$

Figure 6 shows variation of $C_{sn}$ with chain length; $C_{s_\infty}$ is the limiting value for $C_{sn}$ when $n > 10$. $C_{s_\infty}$ is estimated from Eq. (4) by linear regression on the assumption that $1/\bar{P}_n{}^\circ = 0$ and $n > 10$.

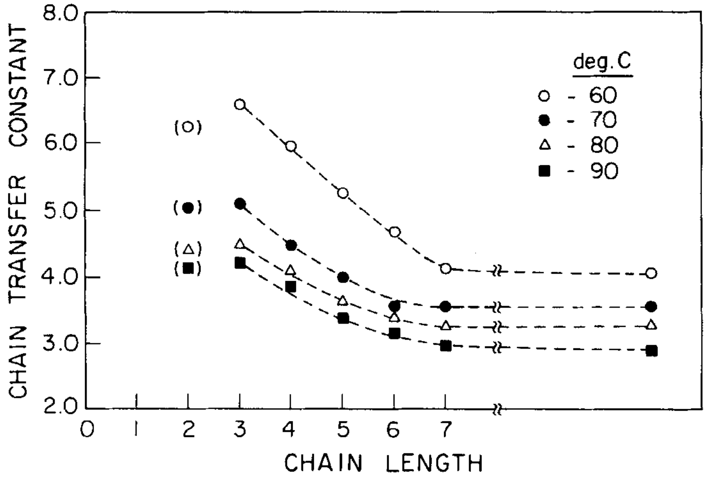

FIG. 6. Plot of chain-transfer coefficient versus chain length.

## DISCUSSION

In free-radical polymerization, if the termination step is dominated by chain transfer or by disproportionation, the polydispersity ($\bar{M}_w/\bar{M}_n$) for the ideal case is 2, and when termination is purely by combination polydispersity, it is 1.5. In the presence of CCTA, the polydispersity is expected to be two, but the results in Table 1 show the polydispersity of the products (particularly for shorter polymers) is significantly less than two. This deviation is the result of two effects:

1) The Schulz-Flory distribution [7] describes the polydispersity as

$$\text{polydispersity} = \frac{\bar{M}_w}{\bar{M}_n} = 1 + \nu, \tag{10}$$

where $\nu$ is the probability of growth by addition of monomer to the growing chain,

$$\nu = \frac{R_p}{R_p + R_{tr} + R_t}, \tag{11}$$

and $R_p$, $R_{tr}$, and $R_t$, the rates of propagation, chain transfer, and termination, respectively, and defined as

$$R_p = k_p[M][R^\circ] \tag{12}$$

$$R_{tr} = k_{tr}[S][R^\circ] \tag{13}$$

$$R_t = k_t[R^\circ][R^\circ]. \tag{14}$$

In our case $R_p + R_{tr} >> R_t$, thus,

$$\nu = \frac{1}{1 + C_s\frac{[S]}{[M]}}. \tag{15}$$

Therefore, increasing the CCTA concentration will decrease the polydispersity, e.g., to a limiting value of 1.66 (when $P_n = 2$).

2) In the chain-transfer step (Eq. 2), when $n = 1$, the polymer product is identical to the monomer, as can be seen in Fig. 1. Thus, the fraction of product with a chain length of one is excluded from MWD. Since the MWD does not include the fraction of $Q_1$ in the product, the polydispersity will be less than two. An increase in the concentration of CCTA leads to an increase in the production of $Q_1$, which reduces the polydispersity.

Since the UV detector of the GPC shows the MWD based on mole fraction, the individual mole fraction of each oligomer is proportional to the area under the corresponding peak. Chain-transfer constants are calculated for dimer, trimer, tetramer, pentamer, and hexamer by Eq. (8) and the GP chromatograms. The estimated chain-transfer coefficient for dimer is slightly lower than that for the other oligomers, possibly because some dimer was lost in the isolation of the products.

As shown in Fig. 6, the chain-transfer coefficients decrease with chain length but reach a limiting value. Since the chain-transfer coefficient is the ratio of the chain transfer rate constant to the propagation rate constant, the factors which affect either rate constant may change its value, and it is not presently possible to explain the observed chain length dependence.

If the rate constants for chain transfer and growth were written in terms of Arrhenius parameters, the limiting chain-transfer coefficient may be expressed as a function of temperature:

$$C_s = \frac{k_{tr}}{k_p} = \frac{A_{tr}}{A_p} \exp\left[-\frac{(E_{tr} - E_p)}{RT}\right], \tag{16}$$

where $A_{tr}$ and $A_p$ are frequency factors, and $E_{tr}$ and $E_p$ are activation energies for chain transfer and chain growth, respectively. Through a nonlinear regression, $A_{tr}/A_p$, and $(E_{tr} - E_p)$ were estimated as $1.054 \times 10^3$ and -10.10 kJ/mol, respectively. Although the Arrhenius plot (Fig. 7) of the limiting values for the chain-transfer coefficients shows some scatter, it may be represented by

$$C_s = (1.054 \pm 0.3) \times 10^3 \times \exp\left[-\frac{-(10.10 \pm 1.08)}{RT}\right], \tag{17}$$

where $RT$ is in kJ/mol. For MMA, the temperature dependence of the propagation rate constant can be represented [8] by

$$k_p = 4.92 \times 10^5 \times \exp\left[-\frac{(18.21)}{RT}\right]. \tag{18}$$

Therefore, the catalytic transfer rate constant is given by

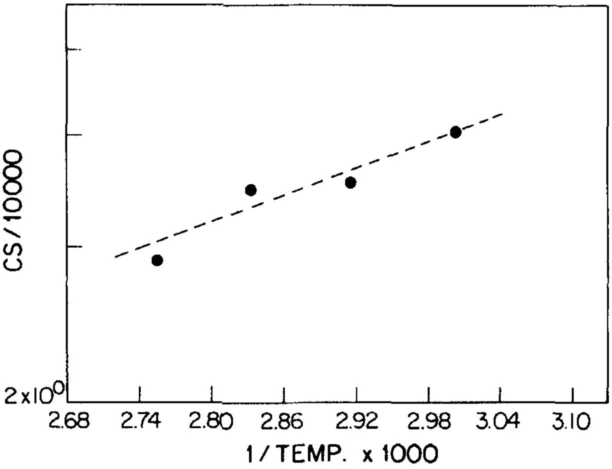

FIG. 7. Arrhenius plot for chain-transfer coefficients.

$$k_{tr,s} = (5.188 \pm 0.2) \times 10^8 \times \exp\left[-\frac{(8.11 \pm 1.08)}{RT}\right]. \qquad (19)$$

At 60°C, for example, $k_{tr,s} = 2.77 \times 10^7$, which may be compared with the termination rate constant, $k_t$, for MMA, which at 60°C is $3.4 \times 10^7$ [8] and is known to be diffusion controlled. Perhaps the chain-transfer process is also diffusion controlled for COBF.

## ACKNOWLEDGMENT

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