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NOTE

POLYMERIZATION OF METHYL METHACRYLATE BY A CHARGE-TRANSFER MECHANISM

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INTRODUCTION

Charge-transfer polymerization of vinyl monomers like methyl methacrylate (MMA) and vinyl chloride has been widely investigated [1–7]. For MMA it can be initiated by charge-transfer complexes formed by the interaction 1) of aliphatic amines and MMA or 2) of aliphatic amines and carbon tetrachloride in nonaqueous solvents, such as *N,N*-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO). Polymerization of MMA by a compound containing a donor nitrogen atom in the presence of CCl_4 is now well established [5, 6]. Lautenberger et al. [8] established the existence of a charge-transfer complex between an aliphatic amine (donor) and CCl_4 (acceptor). Vofsi et al. [3] reported that the charge-transfer complex formed between an aliphatic amine and CCl_4 decomposes to produce free radicals, which initiate polymerization. According to Matsuda et al. [2], initiation is due to the donor-acceptor amine/monomer charge-transfer complex (1:1) in the presence of CCl_4 . Initiation through charge-transfer complexes involving Lewis acid, monomer, and CCl_4 has also been discussed [9–12]. The present communication deals with the polymerization of MMA in DMF initiated by ethanolamine (EA) and CCl_4 .

EXPERIMENTAL

MMA, DMF, and CCl_4 were purified by the standard methods. Ethanolamine (EA) was distilled under reduced pressure before use. The

polymerization was done in an atmosphere of positive pressure of oxygen-free nitrogen in a three-necked flask with DMF as solvent. The polymerization was not allowed to proceed beyond 25% to avoid gel effect [13]. After the reaction period, poly-MMA was precipitated by methanol containing trace quantities of hydroquinone. The amount of polymer formed was determined gravimetrically, and the rate of polymerization was determined.

Gel-permeation chromatography was performed at 25°C with purified tetrahydrofuran as eluent (1 mL/min) by a Waters Associates GPC unit. The sample concentration was 0.2% w/v, and the volume of polymer solution injected was 50 μ L. The GPC column combination was 10⁶, 10⁵, 10⁴, and 500 Å. A universal calibration curve, based on elution volumes of 9 narrow-MWD polystyrene samples from Waters Associates was used to compute the molecular weights of the polymer samples.

RESULTS AND DISCUSSION

It was found that an aliphatic amine (A) like methyl, ethyl, isopropyl, *n*-butyl, or cyclohexyl can act as donor, and CCl₄ and MMA can act as acceptor for the formation of charge-transfer complexes [14]. When aromatic amines and heterocyclic compounds, such as pyridine, β - or γ -picoline, are used in place of the aliphatic amine and CHCl₃ is used in place of CCl₄, no polymerization takes place under the experimental conditions [4].

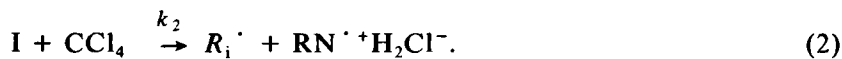
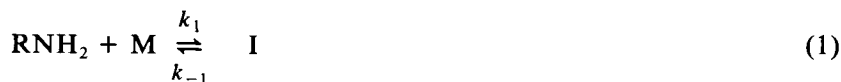
The relationship between the overall polymerization rate, R_p , and [MMA] at constant concentrations of amine and CCl₄ is shown in Fig. 1. R_p was proportional to [MMA]^{1.41}.

Figure 2 shows a linear relationship between log R_p and log [EA] at a constant concentration of MMA and CCl₄.

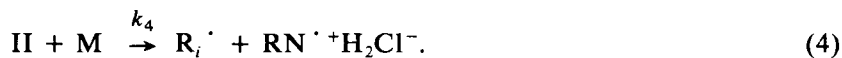
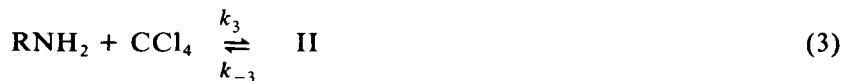
R_p is sensitive to [CCl₄] at low [CCl₄], but at higher concentrations (above 0.35 mol/L) it is independent of [CCl₄].

The reaction can be inhibited by oxygen and hydroquinone, suggesting a free-radical polymerization mechanism.

The mechanism for initiation of vinyl monomers (M) by charge-transfer complexes formed by interaction of amine and CCl₄ or by amine and vinyl monomer is not clear. According to Matsuda et al. [2], initiation is due to the amine/monomer charge-transfer complex (1:1), I, in the presence of CCl₄. Thus:



According to other schools [3, 7], initiation is due to the amine/ CCl_4 charge-transfer complex, II, which interacts with M and produces $\text{R}_i \cdot$. Thus



Presumably both mechanisms are possible [5, 10].

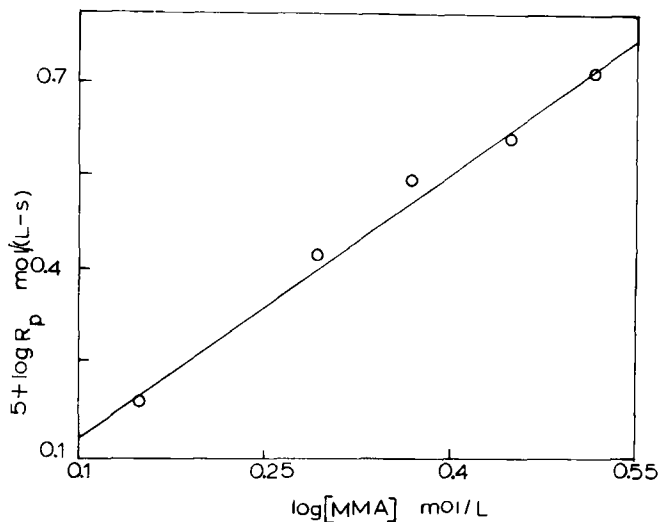


FIG. 1. Relationship between $\log R_p$ and $\log [\text{MMA}]$ at 30°C . $[\text{CCl}_4] = 2.00 \text{ mol/L}$, $[\text{EA}] = 1.96 \text{ mol/L}$.

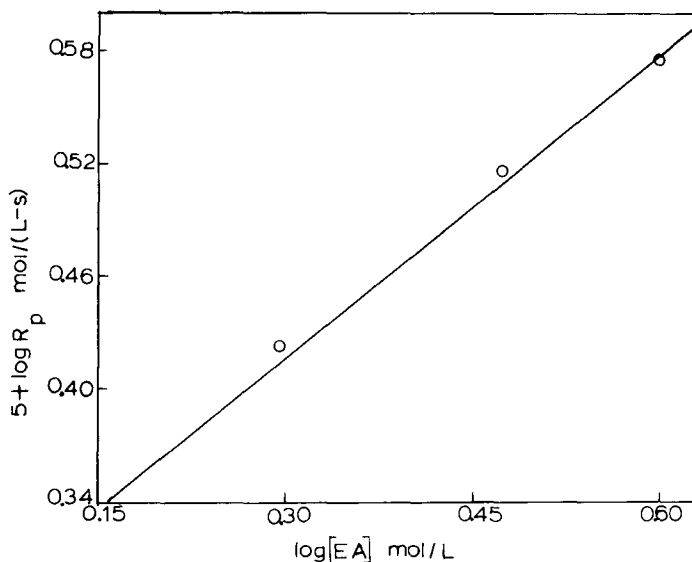


FIG. 2. Plot of $\log R_p$ vs $\log [EA]$ at 30°C . $[MMA] = 2.90 \text{ mol/L}$, $[CCl_4] = 2.00 \text{ mol/L}$.

Investigation of the polymerization of MMA with IPA [5] and *n*-butylamine [6] established that the rate can be given by

$$R_p = k_p/k_t^{1/2}(k_3)^{1/2}[MMA][A]^{1/2}[CCl_4]^{1/2} \quad (5)$$

when $[CCl_4]/[A] < 1$.

Again, when $[CCl_4]/[A] \gg 1$, R_p becomes independent of $[CCl_4]$, and the rate expression becomes

$$R_p = k_p/k_t^{1/2}(k_1)^{1/2}[MMA]^{3/2}[A]^{1/2}. \quad (6)$$

The experimental results with ethanolamine agree with Eqs. (5) and (6), i.e., R_p was found to be independent of CCl_4 for $[CCl_4] > 0.35 \text{ mol/L}$ and to vary as $[M]^{1.41}$ and $[EA]^{0.53}$ when $[CCl_4] \gg [EA]$. The average rate constant, k , is $7.1 \times 10^{-6} \text{ L}/(\text{mol} \cdot \text{s})$ at 30°C . Since some monomer was used up in in-

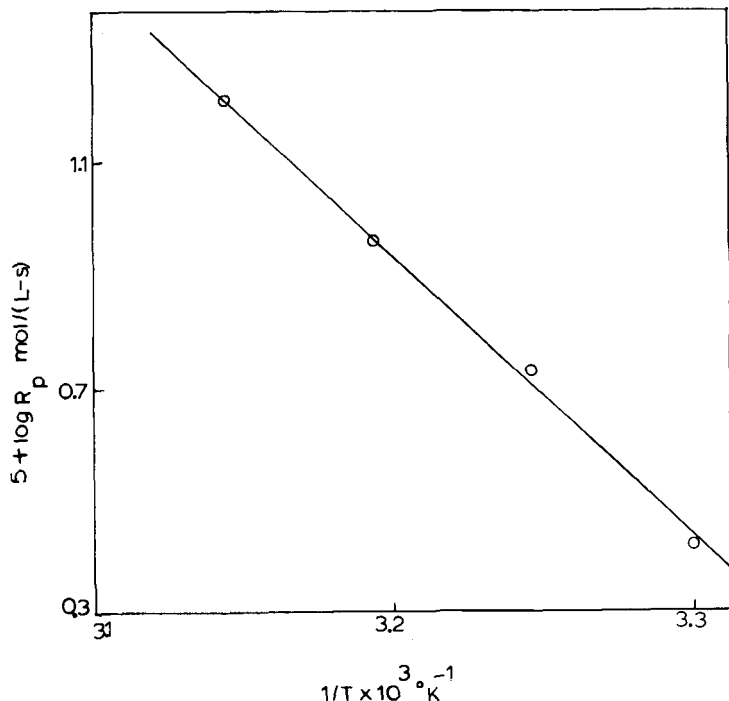


FIG. 3. Arrhenius plot of polymerization rate (30–50°C). [MMA] = 2.90 mol/L, [CCl₄] = 2.00 mol/L, [DMF] = 4.90 mol/L, [EA] = 1.96 mol/L.

itation, the order of reaction with respect to [M] is less than the theoretical value.

From the slope of the Arrhenius plot in Fig. 3, the overall activation energy was calculated to be 9.7 kcal/mol.

The degree of polymerization, \overline{DP} , of poly-MMA obtained with the ethanolamine-CCl₄ system increased with increasing monomer concentration and decreased with increasing amine concentration, presumably due to the termination by ethanolamine also. The plot of $1/\overline{DP}$ against R_p was also linear (Fig. 4).

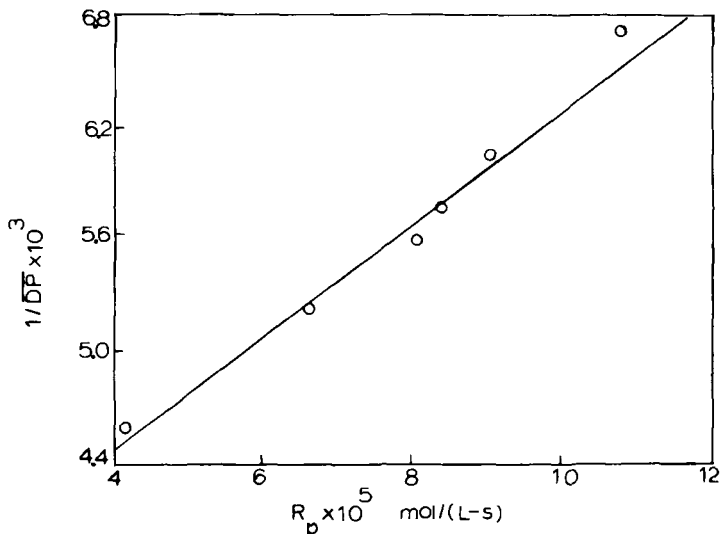


FIG. 4. Plot of $1/\overline{DP}$ as a function of R_p in N_2 atmosphere at $30^\circ C$ in DMF. $[EA] = 1.96$ mol/L, $[CCl_4] = 2.00$ mol/L, $[MMA]$ variable.

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REFERENCES

- [1] M. Matsuda and Y. Ishiroshi, *J. Polym. Sci., Part A-1*, **8**, 387 (1970).
- [2] M. Matsuda, Y. Ishiroshi, and K. Seki, *J. Polym. Sci., Polym. Chem. Ed.*, **14**, 1337 (1976).
- [3] H. Rosin, S. L. J. Daren, M. Asscher, and D. Vofsi, *J. Appl. Polym. Sci.*, **16**, 1687 (1972).
- [4] S. Hussain, S. D. Baruah, and N. N. Dass, *J. Polym. Sci., Polym. Lett. Ed.*, **16**, 167 (1978).
- [5] S. D. Baruah and N. N. Dass, *Eur. Polym. J.*, **16**, 11 (1980).
- [6] S. R. Sen and N. N. Dass, *Ibid.*, **18**, 477 (1982).

- [7] K. Dodgson and J. R. Ebdon, *Ibid.*, 13, 791 (1977).
- [8] W. J. Lautenberger, E. N. Jones, and J. G. Miller, *J. Am. Chem. Soc.*, 90, 1110 (1960)
- [9] S. D. Baruah and N. N. Dass, *Makromol. Chem.*, 180, 1351 (1979).
- [10] S. S. Begum and N. N. Dass, *Eur. Polym. J.*, 18, 1033 (1982).
- [11] S. K. Saha and A. K. Choudhury, *J. Polym. Sci., Polym. Chem. Ed.*, 25, 519 (1987).
- [12] S. K. Saha and A. K. Choudhury, *J. Polym. Sci., Polym. Chem. Ed.*, 26, 901 (1988).
- [13] F. W. Billmeyer, *Textbook of Polymer Science*, Wiley-Interscience, New York, 1971, p. 277.
- [14] N. N. Dass, *Prog. Polym. Sci.*, 10, 51 (1984).
- [15] G. C. Pimentel and A. L. McClellan, *The Hydrogen Bond*, Reinhold, New York, 1960, p. 373.

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