

Aqueous Polymerization on Clay Surfaces. IV. Effects of Hydrogen–Montmorillonite, Monomer Concentrations, and Temperature on the Polymerization of Methyl Methacrylate

J. BHATTACHARYA, S. TALAPATRA,* and S. K. SAHA,
*Department of Chemistry, University of North Bengal, Darjeeling-734
430, India, and S. C. GUHANIYOGI,† Institute of Polymer Science,
University of Akron, Akron, Ohio*

Synopsis

The polymerization of methyl methacrylate in aqueous montmorillonite suspension with thiourea was studied. The polymerization initiated on the montmorillonite surface following the adsorption of thiourea and the monomer. A 20% increase in the basal spacings of the clay mineral was observed. A large fraction of the polymer was nonextractable and was found to be thermally more stable than the extractables. The rate of the polymerization increased with increasing amounts of clay, thiourea, and followed one-half order on the latter. The apparent energy of activation (E_a) of the system was characteristic of redox free radical polymerization.

INTRODUCTION

In addition to preparing complex with organic compounds, clay minerals have been used as polymerizing initiators.¹⁻⁵ These clay-catalyzed polymerizations were aimed to enhance the catalytic activity of the free radical initiators. Certain monomers which do not undergo spontaneous polymerization in the presence of clays were polymerized radically following the decomposition of clay-initiator adduct with enhanced rates.^{6,7} We have already reported that clay minerals can be used in conjunction with organic substances like alcohol or thiourea to polymerize acrylates in an aqueous medium.^{8,9} Here, we present kinetic and thermodynamic evidence supporting free radical nature of hydrogen montmorillonite/thiourea-initiated aqueous polymerizations. Also included are the results of thermal and X-ray analyses of the polymers harvested.

EXPERIMENTAL

The preparation and purification of all the materials for polymerization, e.g., methyl methacrylate (MMA), thiourea (TU), and hydrogen–montmoril-

*Present address: Research Centre, Indian Petrochemicals Corporation Ltd., Baroda-391 346, India.

†Present address: Himont R & D Centre, 800 Green Bank Road, Wilmington, DE 19808.

lonite (HM), polymerization procedure, polymer purification, and extraction have already been reported.^{8,9} Number average molecular weights were determined by viscometric measurements at 30°C in benzene using the following equation:

$$[\eta] = 8.69 \times 10^{-5} \bar{M}_n^{0.76}$$

Free poly(methyl methacrylate) (PMMA) was separated from HM-PMMA adduct by extracting the blend (crude polymer) with boiling benzene and finally drying the separated polymers in vacuum oven at 60°C for 48 h. The concentration of HM has been expressed in % (weight/volume) throughout this study.

RESULTS AND DISCUSSION

Kinetics

The effects of variation in the clay concentration on the polymerizations of MMA at 60°C are presented in Figure 1. The rates of these polymerizations were determined from similar low conversion (10%) experiments and found to increase with [HM]. Thus, for systems of 0.376*M* MMA and 0.04*M* TU in 50 mL water, the rates were 1.96, 2.41, 2.94, and 3.36 × 10⁻⁵ mol L⁻¹ s⁻¹ with 0.12, 0.31, 0.62, and 1.25% HM, respectively. Figure 2 illustrates the dependence of rate on concentration of the lattice Fe³⁺ (estimated after complete digestion of HM with HF/HClO₄); the plot of log *R_p* against log[Fe³⁺] is linear with slope 0.24. However, the exact relationship between rate and clay concentration could not be ascertained due to MMA adsorption onto clay (an

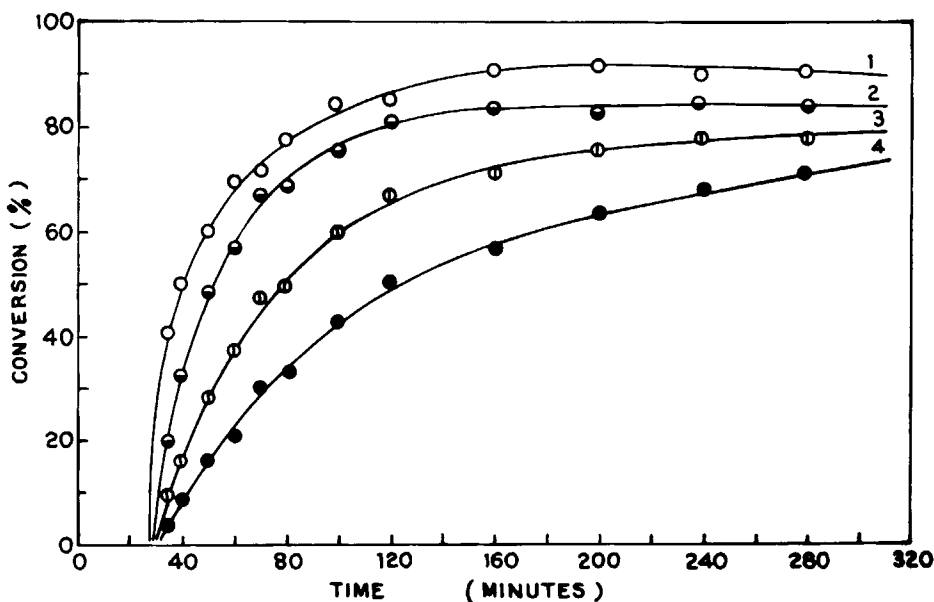


Fig. 1. Time-conversion plots for polymerization of MMA (0.376*M*) in the presence of 0.04*M* TU and 1.25% (1), 0.62% (2), 0.31% (3), and 0.12% (4) HM in 50 mL water at 60°C.

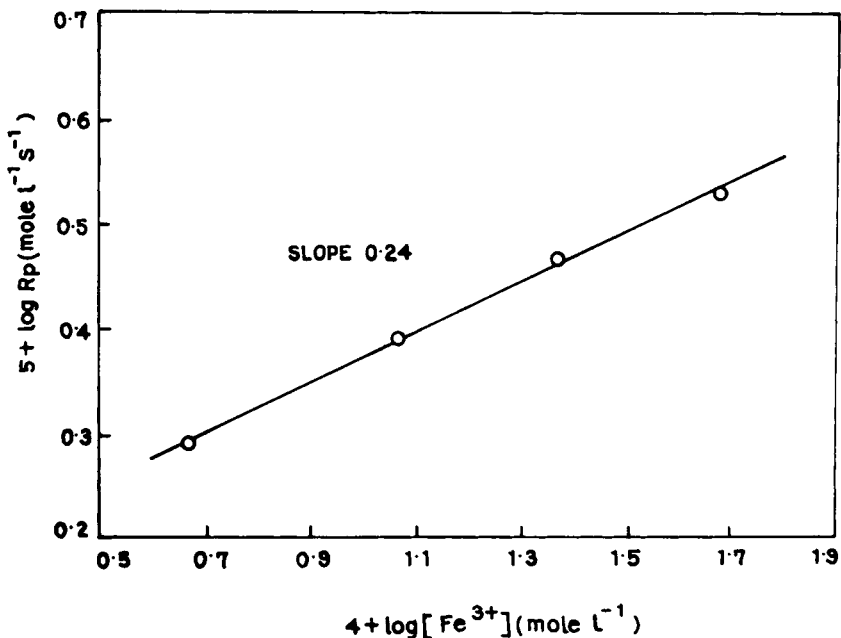


Fig. 2. Plot of $\log R_p$ as a function of $\log[\text{Fe}^{3+}]$ for the polymerization of 0.376M MMA with 0.04M TU in 50 mL at 60°C.

equilibrium process) and subsequent interaction of thiourea with free and MMA-adsorbed clay in aqueous suspension.

In all polymerizations with HM/TU system an induction period was observed. The temperature dependency of the induction period, i.e., 58, 37, 27, 14, and 10 minutes at 40, 50, 60, 70, and 77°C, respectively, with 0.31% HM and 0.04M TU, may be attributed to the complex equilibrium between the HM, MMA, and TU, leading to the formation of initiating radicals and was found to be independent of MMA concentration. The rate of polymerizations increased with increasing concentration of MMA at all temperatures at constant $[\text{HM}]/[\text{TU}]$ and was found to obey first-order kinetics with respect to monomer concentration. Such data have been presented in Figure 3 for two different clay concentrations. The overall initial rate of these polymerizations was of the order of 0.5 with respect to TU (Fig. 4). The rate increased with increasing $[\text{TU}]$ in the range 1.0×10^{-3} to 0.1M for $[\text{MMA}] = 0.376\text{M}$, $[\text{HM}] = 0.31\%$ at 60°C. However, the molecular weights of the extractable polymers remained nearly constant at 7.3×10^5 g/mol. This cannot be explained only on the basis of absence of transfer to TU during the polymerizations and, moreover, the extractable polymer alone does not represent the picture of the polymerization mechanism. The amount of the nonextractable polymer (HM-PMMA adduct from which PMMA could not be separated even by extracting with boiling benzene) depended on the amounts of clay, monomer, and other experimental variables and is shown in Table I. It is, therefore, clear that the polymerization initiated primarily in the clay interlayers generating higher amounts of nonextractable clay-polymer adduct. This was corroborated by carrying out polymerizations in various solvent

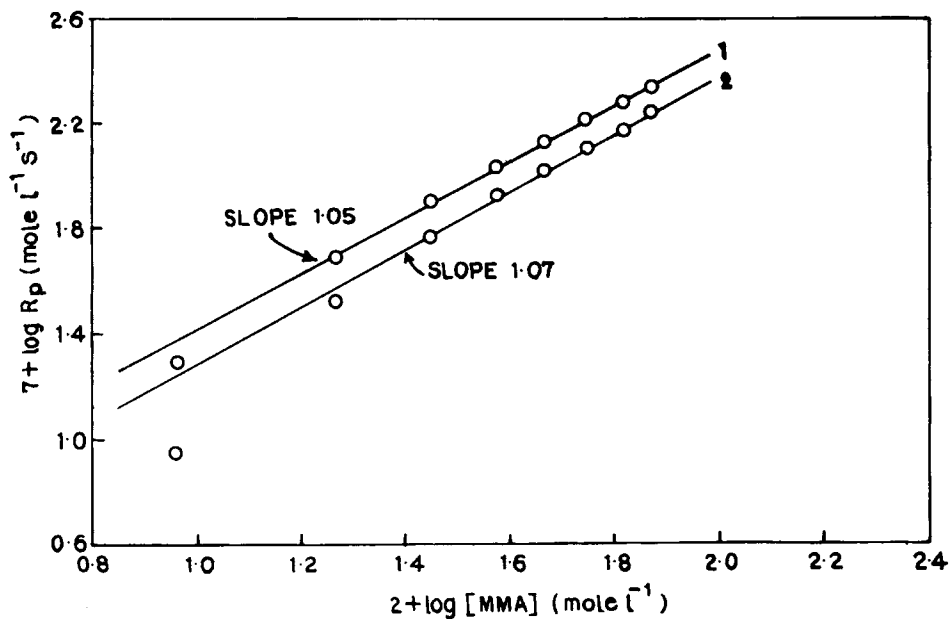


Fig. 3. Plots of $\log R_p$ vs. $\log[\text{MMA}]$ for polymerizations in 50 mL water with 0.04M TU and 0.62% (1) and 1.10% (2) HM at 60°C.

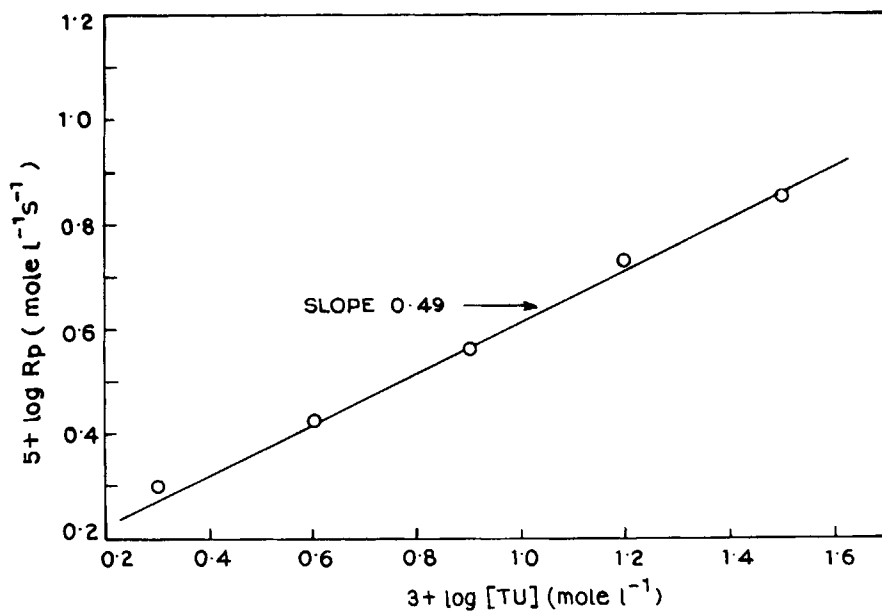


Fig. 4. Plot of $\log R_p$ as a function of $\log[\text{TU}]$ for the polymerization of 0.376M MMA with 0.31% HM in 50 mL water at 60°C.

TABLE I
 Nonextractable Polymer Obtained in the Polymerizations of 1.882 g MMA with
 0.625 g HM and 0.04M TU in 50 mL Water at Various Time and Temperatures

Temp. (°C)	Percent of nonextractable PMMA (of total) obtained during different lengths of polymerization (min)					
	30	40	50	70	90	120
40	—	—	—	100	78	56
50	—	100	100	67	51	—
60	100	94	68	50	47	—
70	77	63	51	46	—	—
77	68	57	45	46	—	—

mixtures. The results obtained are shown in Table II. Appreciable amounts of polymer formed only in aqueous *tert*-butanol system with 10% alcohol. With benzene and carbon tetrachloride, the monomer could not be adsorbed onto clay surface and was held by these solvents.

The chain transfer to either HM or TU being insignificant, a plot of $1/\bar{X}_n$ against $R_p/[MMA]^2$ would be linear for these polymerizations (where \bar{X}_n and R_p denote degree of polymerization and rate of polymerization, respectively). Such plots at three different temperatures are shown in Figure 5 and the values of the rate constants $k_{tr, M}/k_p$ and k_p^2/k_t calculated from these plots are presented in Table III (where k_p , k_t , $k_{tr, M}$ represent rate constants for propagation, termination, and transfer to monomer, respectively). k_p^2/k_t values are higher than those in homogeneous polymerizations.¹⁰ The increase in k_p^2/k_t is probably due to increase in k_p while k_t is relatively small because of the occlusion of the active chain ends inside the layers of clay material.^{11,12} An equilibrium of the type $MMA_{clay} \rightleftharpoons MMA_{aq}$ exists and is shifted when adsorbed monomer is consumed during the polymerization. The mineral adsorbs fresh monomer and polymer-clay gets solvated by the monomer. This, probably, explains high conversion and high molecular weights in the clay-catalyzed polymerizations.

TABLE II
 Effect of Organic Solvents on the Aqueous Polymerization of MMA^a

Organic solvent (vol %)	Percent conversion in			
	Benzene	CCl ₄	<i>tert</i> -Butanol	Water
0	—	—	—	81.5
2	1.9	1.8	54.7	—
5	1.8	1.6	51.5	—
10	0	0	45.2	—
20	0	0	0	—

^a[MMA] = 0.376M, [TU] = 0.04M, [HM] = 0.31% in 50 mL total volume at 60°C for 6 h. Transfer constants ($C_s \times 10^4$) for benzene, CCl₄, and *tert*-butanol are 0.04, 0.925, and 0.085, respectively (*Polymer Handbook*, 2nd ed., J. Brandrup and E. H. Immergut, Eds., Wiley-Interscience, New York, 1975).

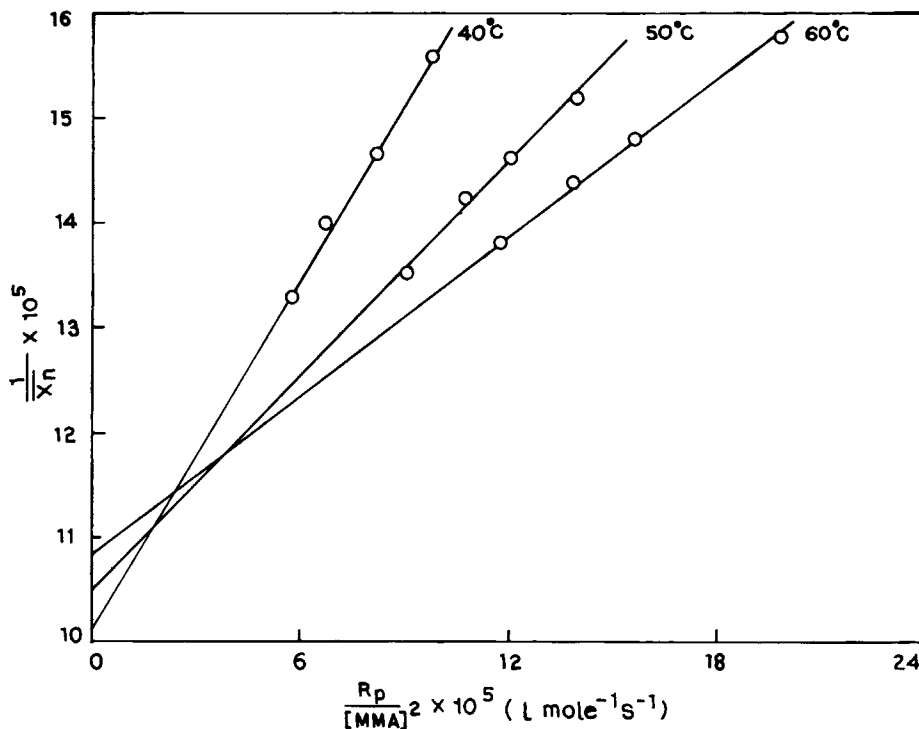


Fig. 5. Plots of $1/\bar{X}_n$ vs. $R_p/[\text{MMA}]^2$ at 40, 50, and 60°C for the aqueous polymerization with HM/TU system.

Apparent Activation Energy

The rate of polymerization increased with increasing temperatures. The overall initial rates of polymerizations at 40, 50, 60, 70, and 77°C were 1.11, 1.68, 2.19, 3.61, and $5.88 \times 10^{-5} \text{ mol L}^{-1} \text{ s}^{-1}$, respectively. The overall apparent activation energy E_a , calculated from plots of R_p against $1/T$ with 0.188, 0.376, and 0.564M MMA, along with E_p and E_t (calculated from k_p^2/k_t at 40, 50, and 60°C) are presented in Table III. The overall activation energy of 38.5 kJ mol^{-1} for the polymerization is characteristic of aqueous redox polymerization of MMA.¹³ However, the overall activation energy for the degree of polymerization $E_{\bar{X}_n} = -1.3 \text{ kJ mol}^{-1}$ and suggests an almost transfer free system.

TABLE III
Kinetic and Energy Parameters for the Aqueous Polymerization
of MMA with 0.04M TU and 0.62% HM at Various Temperatures

Temp (°C)	k_p^2/k_t ($\text{L mol}^{-1} \text{ s}^{-1}$)	$k_{tr,M}/k_p$ ($\times 10^4$)	E_a (kJ mol^{-1})	$E_p - E_t/2$ (kJ mol^{-1})	$E_{\bar{X}_n}$ (kJ mol^{-1})
40	3.30	1.02			
50	5.44	1.05	38.5	19.3	-1.3
60	7.44	1.09			

X-Ray and Thermogravimetric Analysis

The X-ray data indicated an increase in the basal spacing of HM from 14.0 to 15.8 and 16.8 Å for thiourea-treated HM and HM-PMMA adduct, respectively. This increase is due to accommodating thiourea in the interlamellar space in TU adsorbed HM, and, in the latter case, to the interlayer PMMA formed via the polymerization of intercalated MMA.

The thermograms of (1) HM, (2) benzene extracted PMMA, and (3) nonextractable PMMA, i.e., HM-PMMA adduct are shown in Figure 6. Hydrogen-montmorillonite loses water during heating up to 250°C. PMMA was decomposed completely around 375°C, while HM-PMMA adduct retained nearly 15% PMMA at this stage (correction was made for HM). This suggests that nearly 85% of PMMA in the adduct was bound to the external surface for the clay mineral through weak interaction whereas 15% was strongly intercalated in the phyllosilicate.

Mechanism

Neither HM nor TU alone could initiate the aqueous polymerization of MMA even when the system was kept equilibrated at 100°C for 48 h under N₂ blanket. However, a mixture of both in any concentration polymerized MMA to high conversion and high molecular weights. The transition metal (Fe³⁺) in

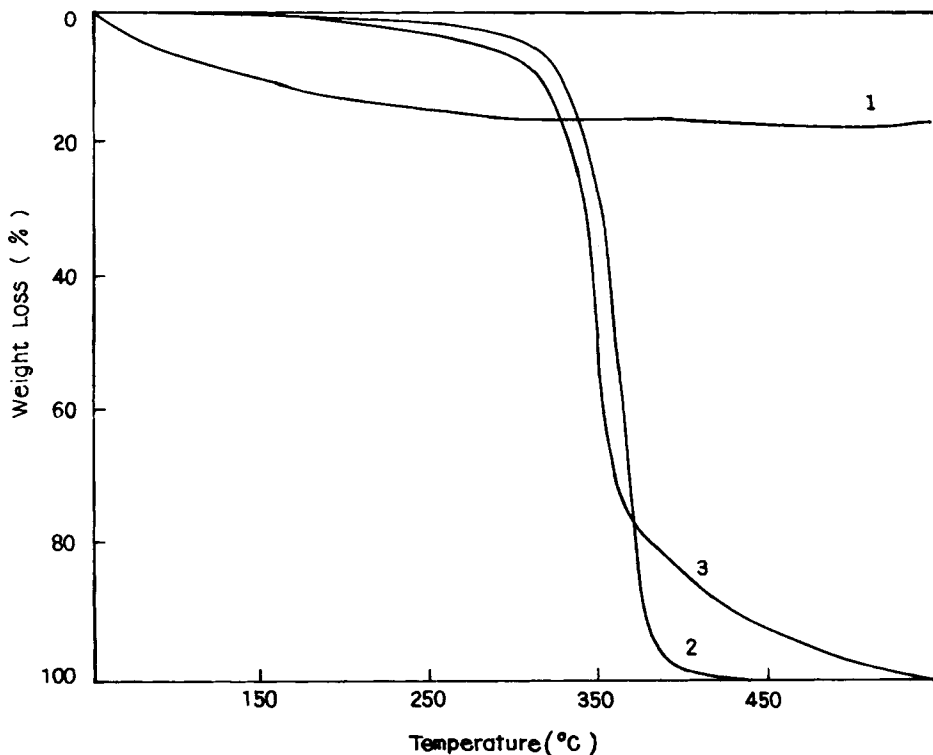
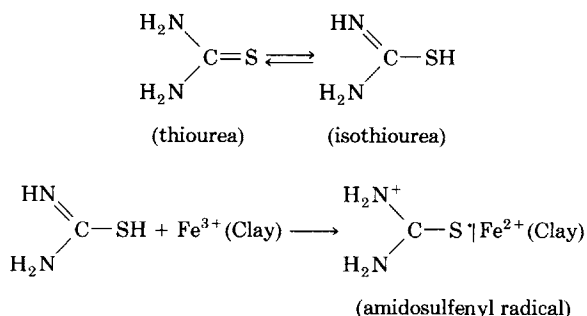


Fig. 6. Thermogravimetric analysis of HM (1), extractable PMMA (2), and HM-PMMA adduct (3).

montmorillonite lattice reacted with isothiurea, tautomeric form of thiourea, generating amidosulfenyl radical to initiate the polymerization:



(amidosulfenyl radical) The free radical nature of the polymerization has been established from the kinetic and energetic parameter. These polymerizations were completely inhibited by the presence of 2,2-diphenyl-1-picryl hydrazyl or hydroquinone. The presence of amine end groups in harvested polymers, determined by the dye partition technique with water soluble disulfine blue VN-150,^{14,15} was further supportive evidence to the proposed mechanism.

One of the authors (J. B.) wishes to thank the University of North Bengal for financial support. We are thankful to the National Physical Laboratory, Pune, India for X-ray analysis.

References

1. J. A. Bittles, A. K. Chaudhury, and S. W. Benson, *J. Polym. Sci. A*, **2**, 1221 (1964).
2. D. H. Solomon and M. J. Rosser, *J. Appl. Polym. Sci.*, **9**, 1261 (1965).
3. I. Icho and K. C. Joung, *Polymer (Korea)*, **3**(1), 51, (1979).
4. D. H. Solomon and B. C. Loft, *J. Appl. Polym. Sci.*, **12**, 1253 (1968).
5. H. Z. Friedlander and C. R. Frink, *J. Polym. Sci. B*, **2**, 475 (1964).
6. H. G. G. Dekking, *J. Appl. Polym. Sci.*, **9**, 1641 (1965).
7. H. G. G. Dekking, *J. Appl. Polym. Sci.*, **11**, 23 (1967).
8. S. Talapatra, S. K. Saha, S. K. Chakravarti, and S. C. Guhaniyogi, *Polym. Bull.*, **10**, 21 (1983).
9. J. Bhattacharya, S. K. Chakravarti, S. Talapatra, S. K. Saha, and S. C. Guhaniyogi, *J. Polym. Sci. Polym. Chem. Ed.*, to appear.
10. M. S. Matheson, E. E. Auer, E. V. Bevilacqua, and E. J. Hart, *J. Am. Chem. Soc.*, **71**, 497 (1949); **73**, 1700 (1951).
11. C. H. Bamford, A. D. Jenkins, M. C. R. Simons, and M. G. Townsend, *J. Polym. Sci.*, **34**, 181 (1959).
12. C. H. Bamford and A. D. Jenkins, *Proc. Roy. Soc. London*, **A216**, 515 (1953); **A228**, 220 (1955).
13. M. A. Abd-El-Ghaffar, A. A. Abd-El-Hakim, A. S. Badran, and A. B. Moustafa, *Angew. Makromol. Chemie*, **155**, 21 (1987).
14. B. M. Mandal, U. S. Nandi, and S. R. Palit, *J. Polym. Sci. A-1*, **4**, 3115 (1966).
15. A. R. Mukherjee, R. Pal, A. M. Biswas, and S. Maiti, *J. Polym. Sci. A-1*, **5**, 135 (1967).

Received August 1, 1989

Accepted September 1, 1989