

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

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

### Aqueous Polymerization of Methyl Methacrylate Initiated by the Potassium Bromate-Thiomalic Acid Redox System

J. S. Shukla<sup>a</sup>; S. K. Shukla<sup>a</sup>; G. K. Sharma<sup>a</sup>

<sup>a</sup> Department of Chemistry, University of Lucknow, Lucknow, India

**To cite this Article** Shukla, J. S. , Shukla, S. K. and Sharma, G. K.(1984) 'Aqueous Polymerization of Methyl Methacrylate Initiated by the Potassium Bromate-Thiomalic Acid Redox System', *Journal of Macromolecular Science, Part A*, 21: 2, 235 – 244

**To link to this Article:** DOI: 10.1080/00222338408056552

**URL:** <http://dx.doi.org/10.1080/00222338408056552>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

## Aqueous Polymerization of Methyl Methacrylate Initiated by the Potassium Bromate-Thiomalic Acid Redox System

J. S. SHUKLA, S. K. SHUKLA, and G. K. SHARMA

Department of Chemistry  
University of Lucknow  
Lucknow, India

### ABSTRACT

The redox system composed of potassium bromate and thiomalic acid was used to initiate the aqueous polymerization of methyl methacrylate under nitrogen atmosphere at  $35 \pm 0.2^\circ\text{C}$ . The initial rates of polymerization have been found to be approximately proportional to the first power of the initiator concentration in the range of  $2.5$  to  $6.0 \times 10^{-3}$  M and to the first power (1.15) of monomer concentration in the range of  $3.72$  to  $11.16 \times 10^{-2}$  M. The overall rate was independent of activator concentration, approaching a maximum at  $10 \times 10^{-3}$  M. The overall energy of activation was found to be  $8.80$  kcal/mol. The initial rate and the maximum conversion attained a maximum value at  $35^\circ\text{C}$  in the temperature range of  $20$  to  $45^\circ\text{C}$ .

### INTRODUCTION

Thio compounds coupled with such oxidants as potassium bromate and perdisulfate have been reported to be very useful redox pairs to initiate the free radical polymerization of various vinyl monomers in aqueous media [1-3].

The formation of free radicals by these redox pairs has been observed to initiate vinyl polymerization effectively. In this laboratory a research program to study the polymerization of various vinyl monomers by different redox pairs using thio compounds as activator has been carried out [4-9].

With a view to extend this work, we undertook a study of the aqueous polymerization of methyl methacrylate (MMA) initiated by the potassium bromate ( $\text{KBrO}_3$ )-thiomalic acid (TMA) redox pair at  $35 \pm 0.2^\circ\text{C}$  under a nitrogen atmosphere.

The advantage with  $\text{KBrO}_3$  is that most water-soluble monomers can be polymerized with a minimum induction period.

## EXPERIMENTAL

Methyl methacrylate was purified by a standard method [10]. Potassium bromate and thiomalic acid were of AnalaR grade. The polymerization procedure, estimation, etc. were the same as described earlier [9]. All experiments were carried out at  $35 \pm 0.2^\circ\text{C}$ , except as otherwise mentioned.

## RESULTS AND DISCUSSION

### Mechanism

A tentative mechanism for polymerization of MMA has been described earlier [9].

The organic free radical  $\dot{\text{S}}\text{CH}_2\text{CH}_2\text{COOH}$  produced by the interaction of bromate and thiomalic acid initiates the polymerization of MMA.

### Initiator Dependence

At fixed concentrations of activator TMA ( $10 \times 10^{-3} \text{ M}$ ) and monomer MMA ( $9.3 \times 10^{-2} \text{ M}$ ), the initial rate of polymerization is found to increase in the whole range of initiator concentration ( $2.5$  to  $30.0 \times 10^{-3} \text{ M}$ ) while the maximum conversion begins to decrease above an initiator concentration of  $4.0 \times 10^{-3} \text{ M}$  (Fig. 1). This can be explained as follows.

Since TMA alone is incapable of initiating the polymerization of MMA, any increase in an initiator concentration brings a corresponding increase in the number of primary free radicals from TMA due to its increased oxidation. This results in an increased rate of polymerization and maximum conversion [11]. At an initiator concentration above  $4.0 \times 10^{-3} \text{ M}$ , the maximum conversion experiences a falling trend, which means that termination takes place easily due to the number of growing polymer radicals.

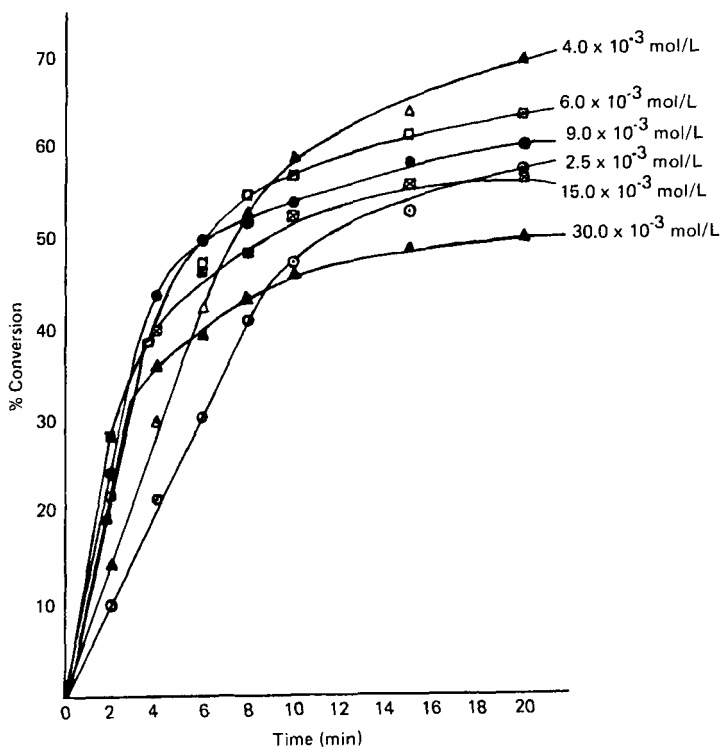


FIG. 1. Time vs conversion curves for the aqueous polymerization of MMA with varying initiator concentrations.  $[TMA] = 10.0 \times 10^{-3}$  mol/L,  $[MMA] = 9.3 \times 10^{-2}$  mol/L.

The initiator exponent is found to be nearly unity (0.964) in the range from  $2.5$  to  $6.0 \times 10^{-3}$  M, which indicates that termination of the growing polymer chain takes place unimolecularly [4, 9] (Fig. 2).

At an initiator concentration above  $6.0 \times 10^{-3}$  M, the rate of polymerization becomes almost independent of initiator concentration and hence of the termination. This means that either the rate of radical generation in this system becomes almost independent of initiator concentration or that the increased ionic strength of the medium leads to incipient coagulation which brings down the number of growing polymer particles, thereby affecting the rate of polymerization [8].

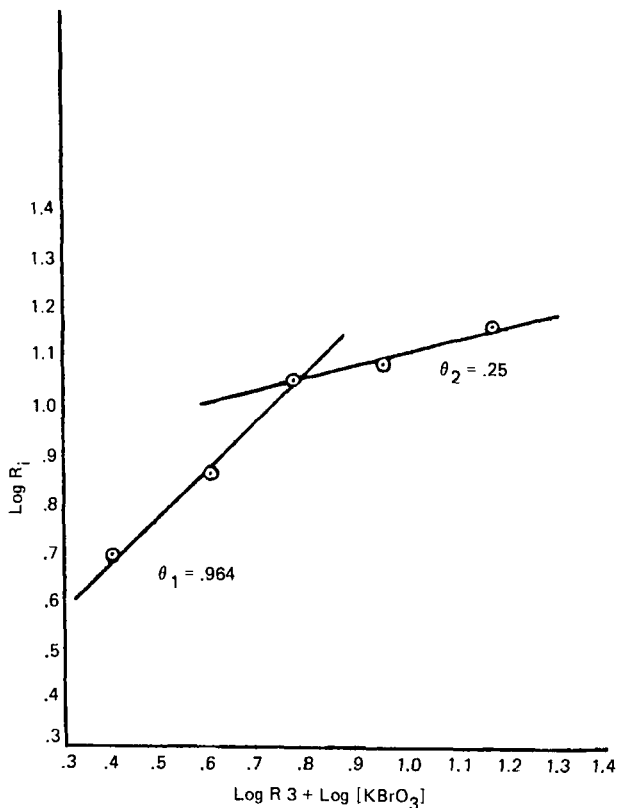


FIG. 2. Double logarithmic plot of the initial rates of polymerization  $R_i$  (%/min) vs the concentration of the initiator  $\text{KBrO}_3$  in mol/L.

### Activator Dependence

Figure 3 shows the results of having a variation in activator (TMA) at fixed concentrations of initiator ( $6.0 \times 10^{-3}$  M) and of monomer MMA ( $9.3 \times 10^{-2}$  M).

The striking feature is that the rate of conversion of monomer into polymer is practically independent of activator concentration and falls only above  $10 \times 10^{-3}$  M in the range from  $4.0$  to  $40.0 \times 10^{-3}$  M. Such a trend is analogous to the reports of Shukla et al. [6, 7], Misra et al. [12], Palit et al. [13], and others [14, 15] in other redox polymerizations. Actually, beyond an optimum concentration of activator, the growing polymer chain radicals are ruptured and thus the overall rate

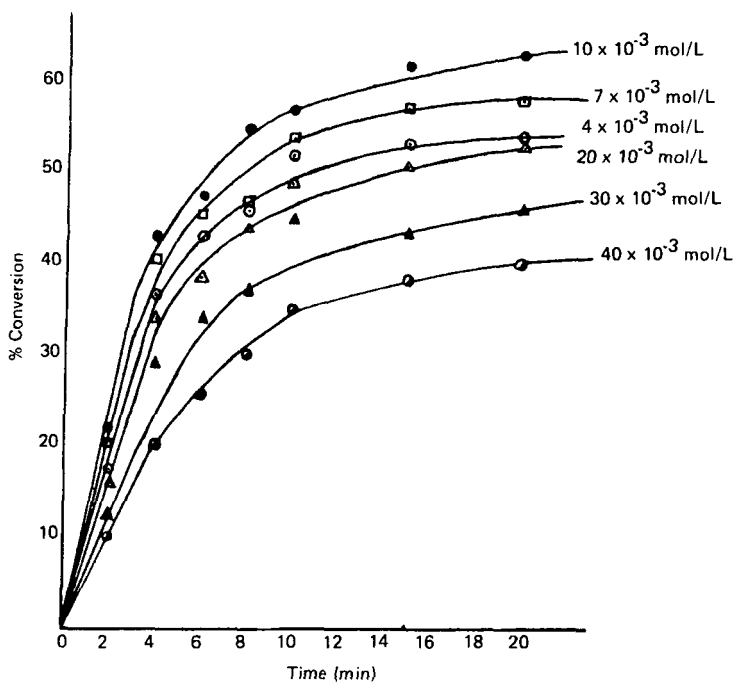


FIG. 3. Time vs conversion curves for the aqueous polymerization of MMA with varying activator concentrations.  $[\text{KBrO}_3] = 6.0 \times 10^{-3}$  mol/L,  $[\text{MMA}] = 9.3 \times 10^{-2}$  mol/L.

of polymerization is suppressed [7]. In our case this takes place at an activator concentration above  $10 \times 10^{-3}$  M. Also, chain transfer reaction due to a growing polymer chain cannot be ruled out as observed by Cohen and Sparrow [16].

### Monomer Dependence

It was seen that the initial rate of polymerization varied somewhat linearly with increasing monomer concentration from 3.72 to  $11.16 \times 10^{-2}$  M.

However, a deviation is observed at higher monomer concentration, say at  $11.16 \times 10^{-2}$  M, where the maximum conversion begins to decrease. Similar observations have been made by previous workers in other redox systems [4, 6, 17-20]. (Fig. 4). This can be explained on the basis of an explanation advanced by Norrish and Smith [21].

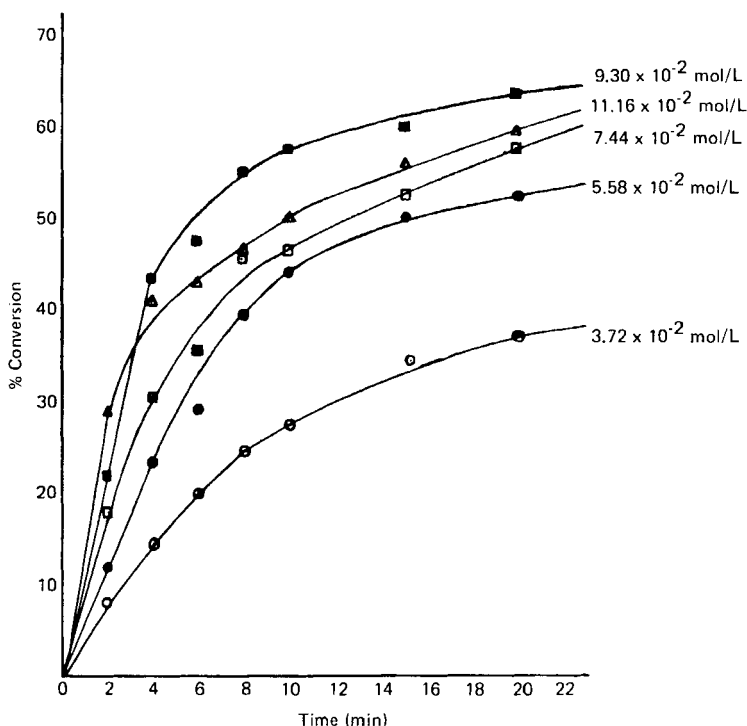


FIG. 4. Time vs conversion curves for the aqueous polymerization of MMA with varying monomer concentrations.  $[\text{KBrO}_3] = 6.0 \times 10^{-3}$  mol/L,  $[\text{TMA}] = 10.0 \times 10^{-3}$  mol/L.

According to them, the excess monomer acts as a good solvent for the polymer formed during the course of reaction, and a good solvent increases the mobility of the growing polymer chain, thereby increasing the chances of early termination and thus decreasing the polymerization rate.

The linear relationship of monomer conversion into polymer suggested that the termination rate was unimolecular (Fig. 5). For a monomer like MMA which has a higher affinity for its insoluble polymer than for water, the general observation is of first-order dependence of the rate on the initial monomer concentration [22].

### Temperature Dependence

The overall rate of polymerization increases as the temperature is raised from 20 to 35°C and then decreases up to 45°C. This is in line

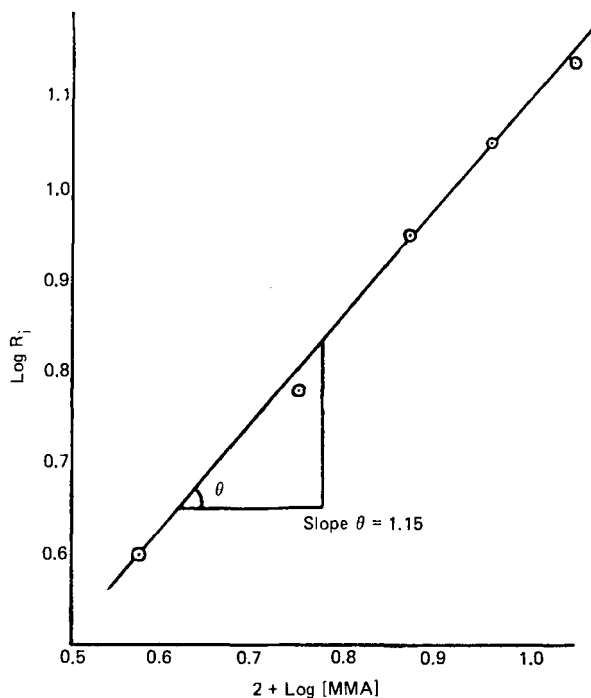


FIG. 5. Double logarithmic plot of the initial rates of polymerization (%/min) vs concentration of monomer MMA in mol/L.

with the observations of Shukla et al. [6, 7] (Fig. 6). Actually, above 35°C, a visible change in the physical nature of the aqueous polymerization media from a colloidal to a precipitative phase takes place, which probably affects the overall rate of polymerization [22]. Several workers have reported that the coagulating effect of heat is likely to decrease the overall rate of polymerization and is due to more facile mutual termination of growing macroradical chains [22, 23]. Also, the chain transfer reaction of thio compounds becomes faster than the production of primary free radicals at higher temperatures, with the result that easy termination takes place and decreases the overall rate of polymerization.

The overall activation energy ( $E_a$ ) was found to be about 8.80 kcal/mol as calculated from the Arrhenius plot (Fig. 7), a value well within the range observed by others in aqueous systems [24-26]. Some of the values for  $E_a$  given by others are:  $E_a = 8.90$  kcal/



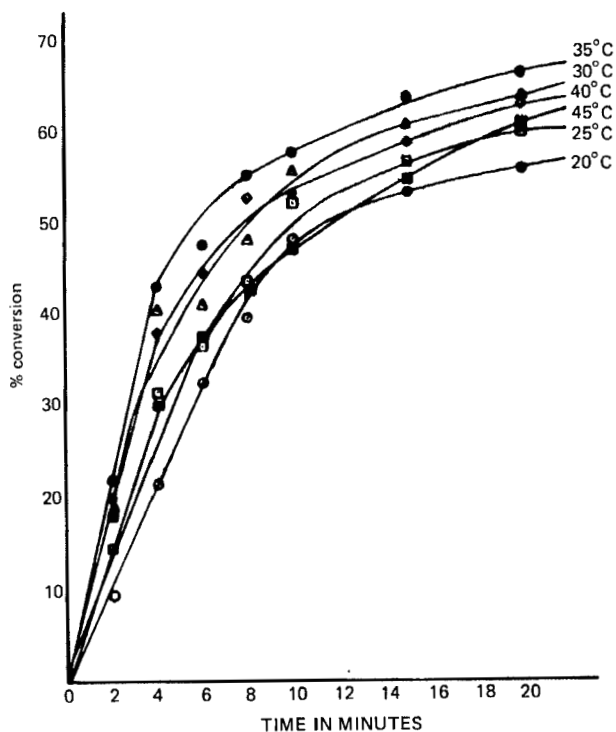


FIG. 6. Effect of temperature on the rate of polymerization of MMA in aqueous media.  $[\text{KBrO}_3] = 6.0 \times 10^{-3}$  mol/L,  $[\text{TMA}] = 10.0 \times 10^{-3}$  mol/L,  $[\text{MMA}] = 9.3 \times 10^{-2}$  mol/L.

mol for MMA by  $\text{KMnO}_4$ -oxalic acid (Palit and Konar [20]),  $E_a = 8.34$  kcal/mol for MMA by  $\text{K}_2\text{S}_2\text{O}_8$ -thioglycolic acid (Shukla and Tiwari [27]), and  $E_a = 8.34$  kcal/mol for acrylamide by  $\text{K}_2\text{S}_2\text{O}_8$ -TMA (Misra and Dubey [28]).

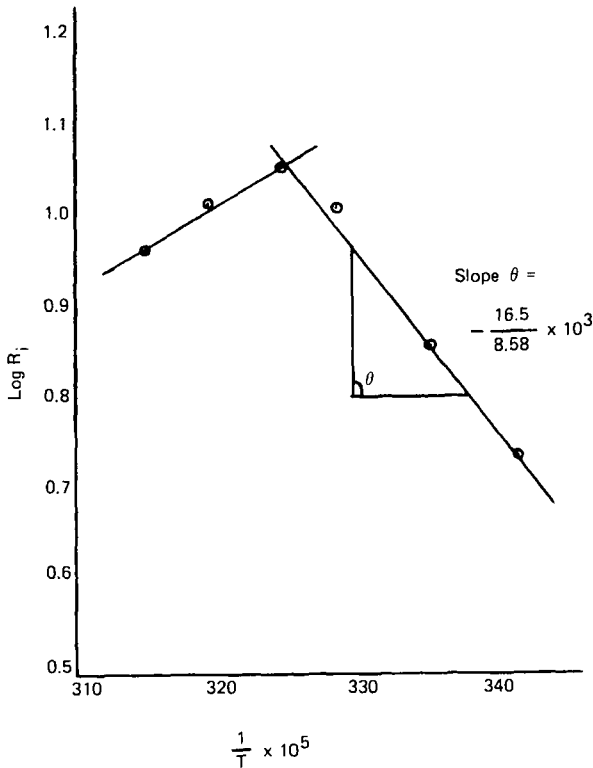


FIG. 7. Arrhenius plot of the initial rates of polymerization  $R_i$  (%/min) vs the reciprocal absolute temperature of polymerization.

ACKNOWLEDGMENTS

The authors are thankful to the Head, Department of Chemistry, for departmental facilities. One of the authors (S.K.S.) is thankful to the University Grants Commission, New Delhi, for the award of a Teacher Research Fellowship.

REFERENCES

[1] B. Nilamber, N. C. Pati, and P. L. Nayak, J. Macromol. Sci.-Chem., A18(4), 545 (1982).

- [2] N. C. Pati, S. Lenka, P. L. Nayak, and T. R. Mohanty, J. Polym. Sci., Polym. Chem. Ed., **16**, 343 (1978).
- [3] G. S. Misra and S. L. Dubey, Colloid Polym. Sci., **257**, 156 (1979).
- [4] J. S. Shukla and D. C. Misra, Makromol. Chem., **158**, 9 (1972).
- [5] J. S. Shukla and R. K. Tiwari, J. Polym. Sci., Polym. Chem. Ed., **19**, 1517 (1981).
- [6] J. S. Shukla and K. Singh, Ibid., **17**, 531 (1979).
- [7] J. S. Shukla and R. K. Tiwari, J. Makromol. Sci.-Chem., **A16**(5), 1047 (1981).
- [8] J. S. Shukla, R. K. Tiwari, G. K. Sharma, and S. K. Shukla, J. Polym. Sci., Polym. Chem. Ed., **21**, 2665 (1983).
- [9] J. S. Shukla, S. K. Shukla, R. K. Tiwari, and G. K. Sharma, J. Macromol. Sci.-Chem., **A20**(1), 13 (1983).
- [10] S. R. Palit and R. S. Konar, J. Polym. Sci., **57**, 609 (1962).
- [11] G. S. Misra and J. J. Rebello, Makromol. Chem., **176**, 2203 (1975).
- [12] G. S. Misra and H. Narain, Ibid., **119**, 74 (1968).
- [13] S. R. Palit and R. S. Konar, J. Polym. Sci., **A2**, 1731 (1964).
- [14] L. B. Morgan, Trans. Faraday Soc., **42**, 169 (1946).
- [15] G. S. Whitby, M. D. Gross, J. R. Miller, and A. J. Costanza, J. Polym. Sci., **16**, 549 (1955).
- [16] S. G. Cohen and D. B. Sparrow, Ibid., **3**, 693 (1948).
- [17] F. A. Bovey, I. M. Kolthoff, A. I. Medalia, and E. J. Meehan, Emulsion Polymerization, Interscience, New York, 1955, p. 167.
- [18] J. Abere, G. Goldfinger, H. Naidus, and H. Mark, J. Phys. Chem., **49**, 211 (1945).
- [19] A. Chapiro, J. Chim. Phys., **47**, 747 (1950).
- [20] S. R. Palit and R. S. Konar, J. Polym. Sci., **58**, 85 (1962).
- [21] R. G. W. Norrish and R. R. Smith, Nature, **150**, 336 (1942).
- [22] S. R. Palit, T. Guha, R. Das, and R. S. Konar, in Encyclopedia of Polymer Science and Technology, Vol. 2, 1965, p. 229.
- [23] D. Pramanick and S. R. Palit, Kolloid-Z. Z. Polym., **229**, 24 (1969).
- [24] W. M. Thomas, E. H. Gleason, and G. Mino, J. Polym. Sci., **24**, 43 (1957).
- [25] J. H. Baxendale, M. G. Evans, and J. K. Kilhan, Trans. Faraday Soc., **42**, 668 (1946).
- [26] A. Kačhalsky and G. Blauer, Ibid., **47**, 1360 (1951).
- [27] J. S. Shukla and R. K. Tiwari, J. Makromol. Sci.-Chem., **A18**(5), 759 (1982).
- [28] G. S. Misra and S. L. Dubey, J. Polym. Sci., Polym. Chem. Ed., **17**, 1393 (1979).

Accepted by editor June 11, 1983

Received for publication July 9, 1983