Heterogeneous Polymerization of Methyl Methacrylate in Absence and Presence of Surface Modified Cuprous Oxide

A. B. MOUSTAFA, *Department of Polymers and Pigments, National Research Center, Dokki, Cairo, Egypt,* and O. ABOUL-WAFA, F. M. RADWAN, and A. EMAM, *Department of Chemistry, Faculty of Science, Suez Canal University, Ismailia, Egypt*

Synopsis

The heterogenous polymerization of methyl methacrylate in the presence of cuprous oxide was studied. Adsorption measurements of stearic acid from benzene solution onto the surface of Cu_2O were carried out. The specific surface area of cuprous oxide as obtained from the extrapolation to the concentration of monolayer surface coverage in the adsorption isotherm was compared with that evaluated from the BET-equation. Sedimentation volume and sedimentation rate of the variably surface modified Cu_2O samples were determined. It was found that the surface modification of Cu_2O enhances its catalytic effect in the heterogenous polymerization of methyl methacrylate up to monolayer surface coverage. The viscosity average molecular weights $\bar{M}_v$ of the respective polymers as well as the apparent activation energy of the polymerization process were correlated with the reaction parameters.

INTRODUCTION

In recent years growing attention has been paid to methods in which organic and inorganic surfaces are chemically modified in order to increase their activity in catalytic processes. The influence of copper metal powder, copper oxides and salts on the heterogeneous polymerization of methyl methacrylate has been previously studied.[1-6]

The present investigation aims at studying the effect of surface modification of cuprous oxide with adsorbed stearic acid from benzene solution on the heterogeneous polymerization of methyl methacrylate. It is worth mentioning that the obtained polymer composites can be of considerable potential in antifouling paints as well as in the manufacture of semiconductors.

EXPERIMENTAL

All chemicals used throughout in the present work were of the A.R. grade. The polymerization runs were carried out at 40° and 50°C according to the method given by Moustafa et al.[7] The quantity of cuprous oxide whenever used was 0.05 g for a polymerization run. The initial rate of polymerization was calculated as the slope of the curve obtained from the plot of conversion vs. time up to 10% conversion. The apparent energy of activation between 40 and

Journal of Applied Polymer Science, Vol. 41, 2021–2030 (1990)
CCC 0021-8995/90/9-102021-10$04.00

50°C was calculated making use of the Arrhenius equation in its integrated form as

$$\log k_2/k_1 = E_a/2.303\, R[(T_2 - T_1)/T_2T_1]$$

where, k_1 and k_2 are the reaction rate constants at the temperatures T_1 and T_2 respectively, E_a is the apparent energy of activation and R is the universal gas constant. In the present investigation, k_1 and k_2 in the Arrhenius equation were substituted by the corresponding initial rates of polymerization R_1 and R_2 at the respective temperatures.[8-10]

The viscosity average molecular weights $\bar{M}_v$ of the obtained polymers were calculated from the viscosity measurements performed in benzene thiophene-free at 25°C,[11] after 4 h conversion time, by applying the following equation

$$[\eta] = 0.94 \times 10^{-4} \bar{M}_v^{0.76}$$

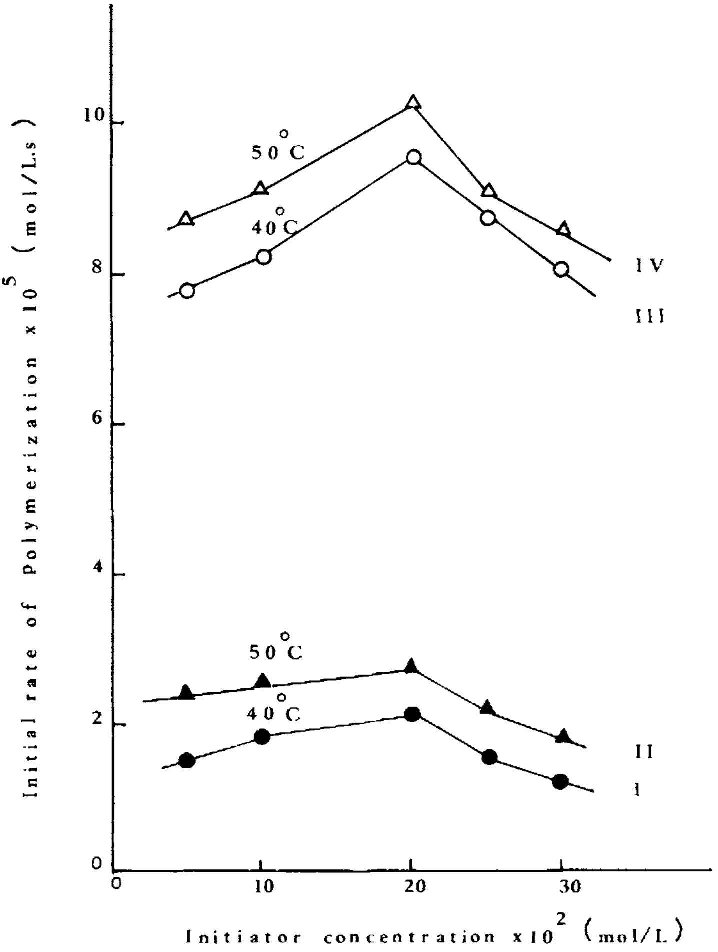


Fig. 1. Polymerization of methyl methacrylate in absence (I, II) and in presence (III, IV) of unmodified cuprous oxide at different initiator concentrations in ambient air.

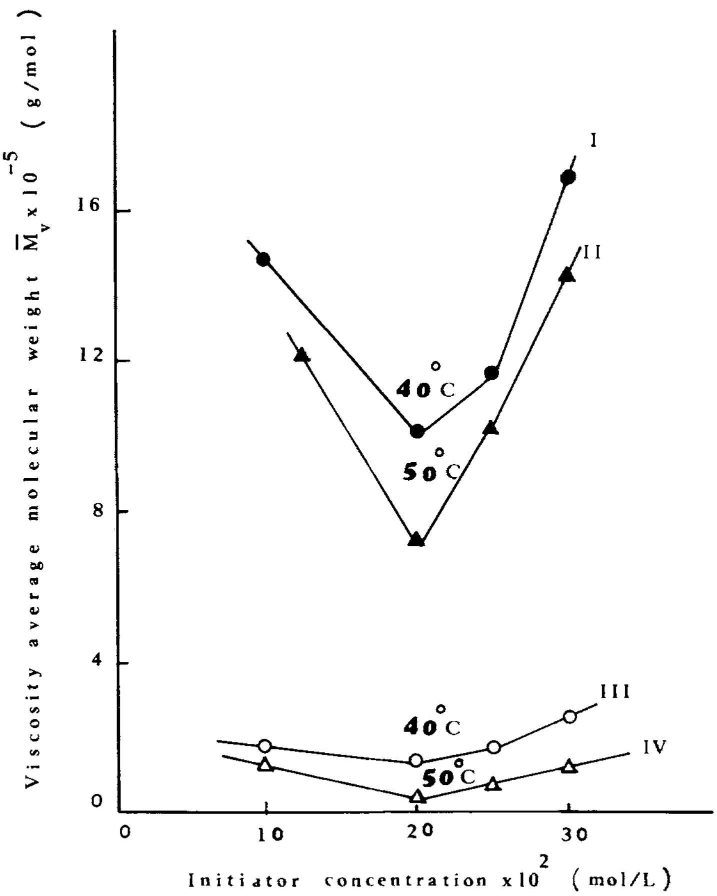


Fig. 2. Dependence of the viscosity-average molecular weights of poly(methyl methacrylate) after 4 h. conversion time on the initiator concentration in absence (I, II) and in presence (III, IV) of unmodified cuprous oxide in ambient air.

The adsorption measurements of stearic acid from benzene solution onto the surface of cuprous oxide were carried out.[12] Surface area assessment was undertaken through the concentration corresponding to monolayer surface coverage and also through nitrogen adsorption at liquid nitrogen temperature (−196°C) according to the BET-equation.[13]

Sedimentation volume and sedimentation rate of the variably modified Cu_2O samples have been determined.[12] The results presented hereafter have been obtained in ambient air.

RESULTS AND DISCUSSION

Polymerization of Methyl Methacrylate in the Absence and Presence of Unmodified Cuprous Oxide

The results of the heterogenous polymerization of methyl methacrylate in absence and presence of unmodified cuprous oxide are shown in Figures 1, 2, and Table I.

TABLE I
Apparent Activation Energy of the Heterogeneous Polymerization of Methyl Methacrylate at Different Initiator Concentrations in Absence and Presence of Unmodified Cu_2O

	Apparent activation energy (kJ/mol)	
[Initiator] × 10^2 (mol/L)	In absence of unmodified Cu_2O	In presence of unmodified Cu_2O
5	39.7	9.2
10	27.8	8.8
20	21.2	6.0
25	32.4	2.9
30	34.3	5.1

It was found that increasing the initiator concentration up to 0.2 mol/L resulted in an increase of the initial rate of polymerization accompanied by a corresponding decrease in the apparent activation energy and viscosity average molecular weights of the polymers. This is in accordance with data found in literature.[2-6,14-20]

With further increase of the initiator concentration, a decrease in the initial rate of polymerization and an increase in both of apparent activation energy and the viscosity average molecular weights was observed. This could be explained in terms of the reduction of the number of polymerization initiating species in the reaction medium due to a lower degree of ionization when higher concentrations of the initiator are used.[1]

A comparison of the initial rate of the polymerization process, apparent activation energy and the viscosity average molecular weights of the polymers obtained in the absence and presence of unmodified cuprous oxide shows that this oxide has a marked catalytic influence on the polymerization of methyl methacrylate. This could be attributed to the reaction between the acidic solution of the initiator and cuprous oxide producing Cu^{1+}-ions which would lead through a disproportionation reaction, for which the equilibrium constant at 25°C is 1.2×10^6, to the formation of Cu^{2+}-ions and copper metal.[21-23]

$$Cu_2O + 2HSO_3^- \rightarrow 2Cu^{1+} + 2SO_3^{2-} + H_2O$$

$$2Cu^{1+} \rightarrow Cu^{2+} + Cu$$

TABLE II
Comparison of the Polymerization of Methyl Methacrylate Initiated by Sodium Bisulphite (0.2 mol/L) in Presence of Cu_2O (0.05/100 mL Reaction Mixture) with that in Presence of Al_2O_3 (0.5 g/100 mL Reaction Mixture)

	In the presence of:	
	Cu_2O	Al_2O_3
Initial rate of polymerization ($\times 10^5$ mol/L s)	9.5	2.1
Apparent energy of activation (kJ/mol)	6.0	17.0
Viscosity average molecular weight ($M_v \times 10^{-5}$ g/mol)	1.6	7.7

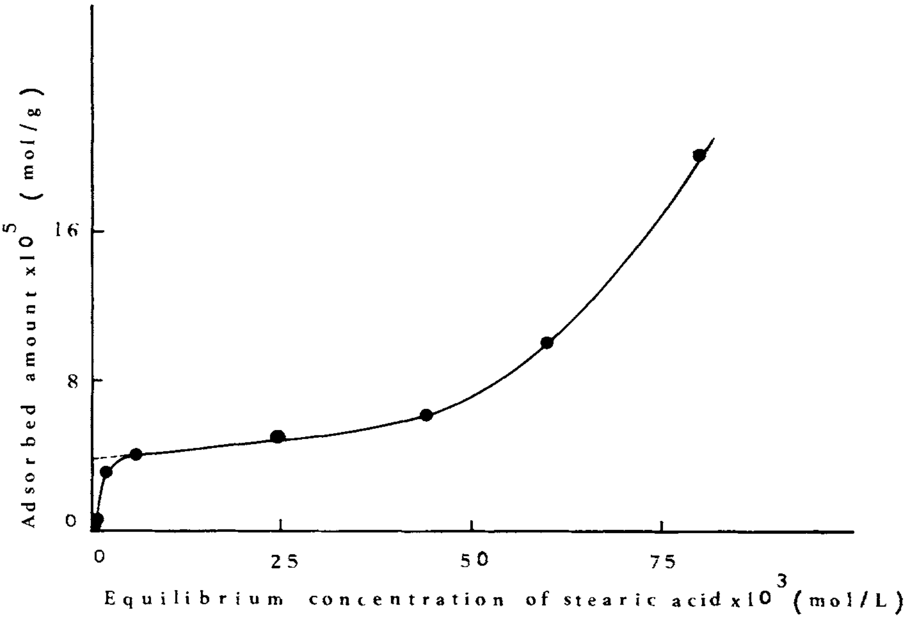
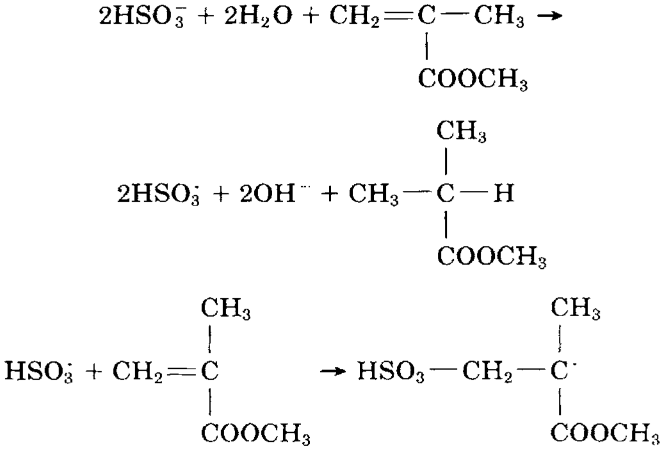


Fig. 3. Adsorption isotherm of stearic acid from benzene solution onto the surface of cuprous oxide.

Both of the species, Cu^{2+} and copper metal, especially the former, have proved to catalyze the polymerization of methyl methacrylate.[3] Possibly, the Cu^{2+}-ions would accelerate the ionization of the initiator leading to the formation of more polymerization initiating entities.[12]

$$NaHSO_3 \rightleftharpoons Na^+ + HSO_3^-$$



$$2HSO_3^- + 2H_2O + CH_2{=}\underset{\displaystyle COOCH_3}{\underset{|}{C}}-CH_3 \rightarrow$$

$$2HSO_3^{\cdot} + 2OH^- + CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle COOCH_3}{\underset{|}{C}}}}-H$$

$$HSO_3^{\cdot} + CH_2{=}\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle COOCH_3}{\underset{|}{C}}}} \rightarrow HSO_3-CH_2-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle COOCH_3}{\underset{|}{C^{\cdot}}}}}$$

The observed lowering of the viscosity average molecular weights of the polymethyl methacrylate obtained in presence of unmodified cuprous oxide is in accordance with the data of the literature.[2,3,6] Actually, this lowering of the average molecular weights coincides with the increase of the number of the initiating species due to the catalytic role of Cu_2O.

Comparing the results of the polymerization of methyl methacrylate in presence of surface unmodified Cu_2O with those of previous studies that dealt with the polymerization of methyl methacrylate in the presence of other metal oxides such as Al_2O_3,[24] it was found that Cu_2O present in a quantity which is only one-tenth that of Al_2O_3 exhibited considerably higher catalytic activity as indicated by the higher initial rate of polymerization, the lower apparent energy of activation and the *lower* values of the viscosity average molecular weights $\bar{M}_v$ of the respective polymer samples (Table II).

Adsorption Measurements and Surface Modification of Cuprous Oxide

The adsorption of stearic acid from benzene solution on the surface of cuprous oxide is illustrated by the adsorption isotherm shown in Figure 3. The concentration of adsorbate corresponding to monolayer coverage onto the surface of cuprous oxide is found to be 3.7×10^{-5} mol/g.

The specific surface area of Cu_2O as calculated on the basis that the cross-sectional area of stearic acid molecule amounts to 20.5 A^2 was found to be 4.6 m^2/g. Also the specific surface area of the oxide applying the BET-equation[13] was evaluated as 1.5 m^2/g.

The higher value of the specific surface area found from the adsorption of stearic acid onto the surface of Cu_2O would suggest that the molecules of the adsorbate are perpendicularly oriented and attached to the surface of the cuprous oxide by the carboxylic group. This is in agreement with the findings of other workers for the adsorption of stearic acid on the surface of metal oxides.[25-28]

The effects of the adsorbed amount of stearic acid on the sedimentation properties of the surface modified cuprous oxide using benzene as a dispersion medium are manifested in Figures 4 and 5. The plot of the sedimentation volume vs. the adsorbed amount of stearic acid (Fig. 4) indicates no special change in sedimentation volume around the adsorbed amount corresponding to the monolayer surface coverage. Actually the adsorption of stearic acid lowers the adhesion forces between the solid particles of Cu_2O.

The relationship between the sedimentation rate of the suspension and the adsorbed amount of stearic acid is seen in Figure 5. A rapid decrease of the sedimentation rate with increasing the adsorbed amount of stearic acid could be observed up to about 4×10^{-5} mol/g, which approximately represents the monolayer surface coverage. Afterwards, the decrease is slow until about 5 $\times 10^{-5}$ mol/g with the start of formation of a second stage. This region of slow change in the sedimentation rate with the adsorbed amount of stearic acid, in which practically a monolayer coverage on the surface of the adsorbant is formed, an orientation of the polar group of stearic acid toward the surface of the metal oxide and the hydrocarbon chain towards the medium would take place. This orientation results in a higher stability of the suspension.

When the amount of the adsorbed stearic acid increases appreciably more than monolayer surface coverage, a second layer would start to form, in which, the molecules of the adsorbate are oriented on the opposite direction. This would effectively decrease the stability of the suspension as shown in Figure 5.

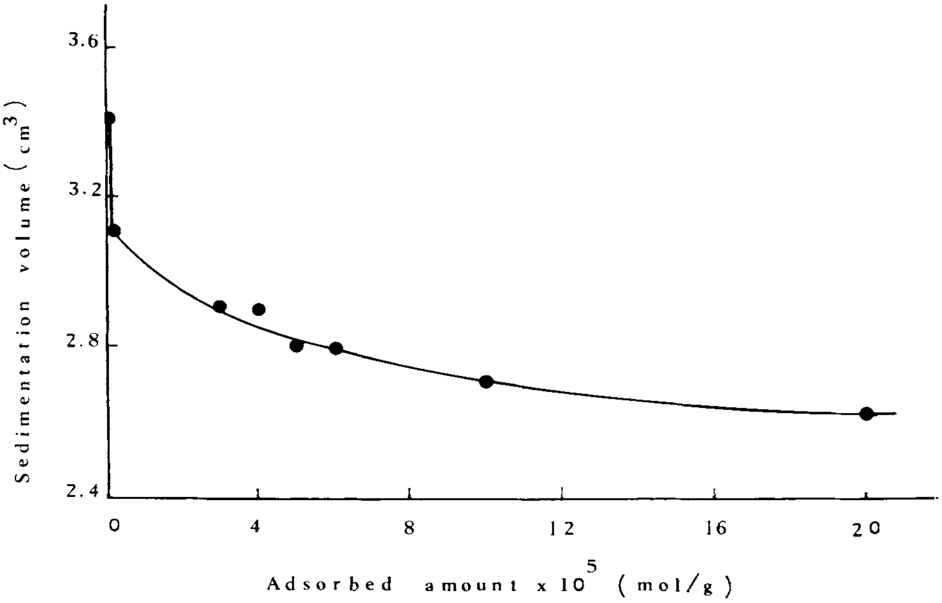


Fig. 4. Sedimentation volume vs. adsorbed amount of stearic acid onto the surface of cuprous oxide.

Effect of Surface Modification of Cuprous Oxide on the Heterogenous Polymerization of Methyl Methacrylate

The dependence of the initial rate and the apparent activation energy of polymerization as well as the viscosity average molecular weights of the obtained polymers on the extent of surface modification of cuprous oxide are shown in

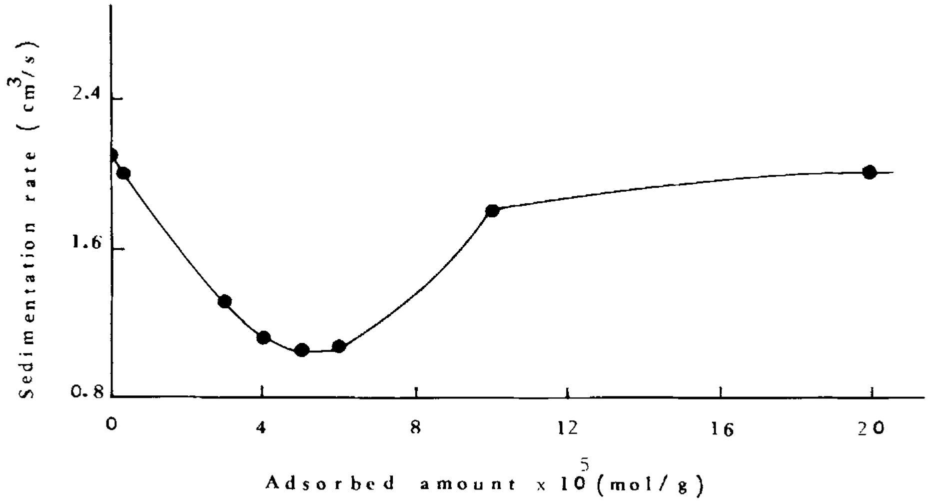


Fig. 5. Sedimentation rate vs. adsorbed amount of stearic acid onto the surface of cuprous oxide.

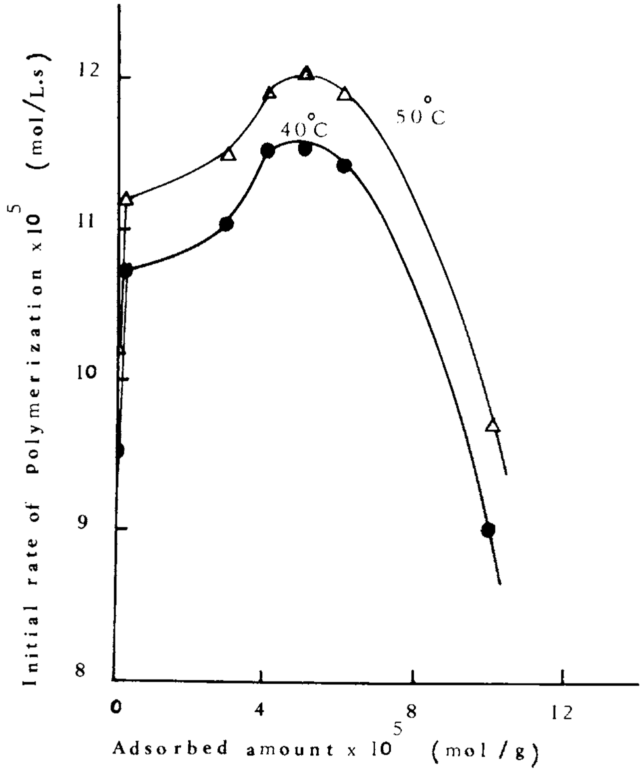


Fig. 6. Dependence of initial rate of polymerization on the extent of surface modification of cuprous oxide at an initiator concentration of 0.2 mol/L in ambient air.

Figure 6, Table III, and Figure 7 respectively. It is clear that the surface modification of Cu_2O enhanced its catalytic effect on the heterogeneous polymerization of methyl methacrylate and increased the viscosity average molecular weights of the respective polymers up to approximately monolayer surface coverage. In fact, the surface modification with adsorbed stearic acid is an organ-

TABLE III

Dependence of the Apparent Activation Energy of the Polymerization of Methyl Methacrylate at Initiator Concentration of 0.2 mol/L on the Extent of Surface Modification of Cu_2O

Adsorbed amount × 10^6 of stearic acid (mol/g)	Apparent activation energy (kJ/mol)
0.0	6.0
0.2	3.8
3.0	3.8
4.0	3.7
5.0	3.6
6.0	3.6
10.0	6.0

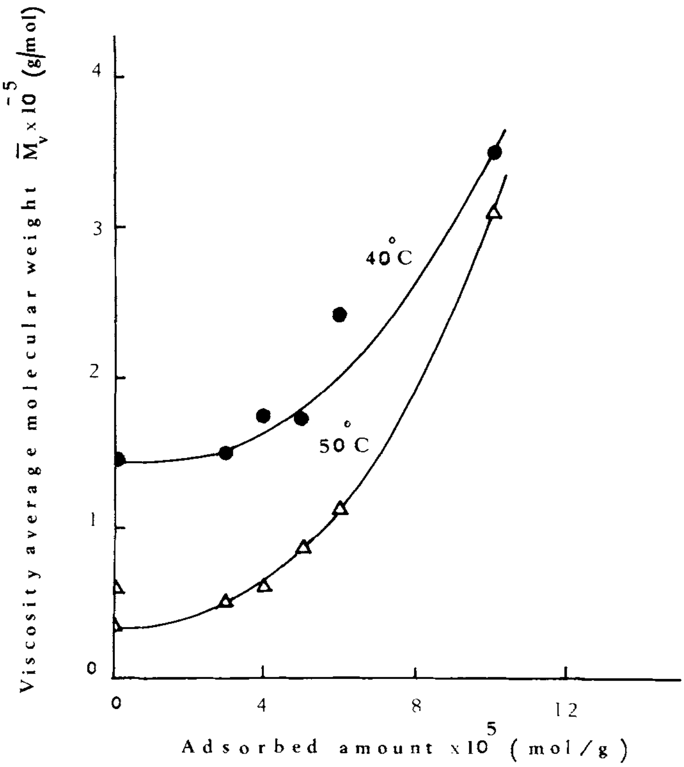


Fig. 7. Dependence of the viscosity-average molecular weights of poly(methyl methacrylate) after 4 h. conversion time on the extent of surface modification of cuprous oxide at an initiator concentration of 0.2 mol/L in ambient air.

ophilization process which would increase the compatibility of the monomer with the surface of Cu_2O resulting in an increase of the monomer concentration involved in the polymerization process per unit time. This would consequently increase the rate of polymerization and the viscosity average molecular weights of the resulting polymers.

The further increase in the amount of adsorbed stearic acid more than monolayer surface coverage caused a decrease in the rate of polymerization. Meanwhile the viscosity average molecular weights of polymers continuously increased. This would suggest a decrease in the number of the polymerization initiating species in addition to the contribution of the compatibility of the monomer with the adsorbed stearic acid. A possible explanation of the decrease in the number of polymerization-initiating species could be given in terms of the multilayer formation of adsorbed stearic acid on the surface of Cu_2O particles. This would hinder the formation of Cu^{2+}-ions in solution that is possibly responsible for the catalytic role of Cu_2O in the heterogeneous polymerization of methyl methacrylate.

CONCLUSIONS

The surface modification of Cu_2O with adsorbed stearic acid from benzene solution accelerated the heterogeneous polymerization of methyl methacrylate and increased the viscosity average molecular weights of the resulting polymers up to monolayer surface coverage. This could be attributed to the compatibility of the monomer with the organophilized Cu_2O. In case of multilayer formation of stearic acid onto the surface of Cu_2O particles, a decrease in the rate of polymerization accompanied by an increase in the viscosity average molecular weights of the obtained polymers was observed. This might be explained as a result of lesser formation of Cu^{2+}-ions in the reaction medium which possibly catalyze the production of the polymerization-initiating species, in addition to the contribution of the compatibility of the monomer with the surface modified Cu_2O.

References

1. A. R. Mukherjee, P. Ghosh, S. C. Chadha, and S. R. Palit, *Makromol. Chem.*, **80**, 208 (1967).
2. A. B. Moustafa and A. A. Abdel-Hakim, *J. Appl. Polym. Sci.*, **21**, 905 (1977).
3. A. B. Moustafa, M. A. Abdel-Ghaffar, A. S. Badran, and A. M. Rabie, *J. Polym. Sci. Polym. Chem. Ed.*, **19**, 719 (1981).
4. A. B. Moustafa and A. S. Badran, *Angew. Makromol. Chem.*, **103**, 153, Nr. 1605 (1982).
5. A. B. Moustafa, M. A. Abdel-Ghaffar, and A. S. Badran, *Acta Polymerica*, **34**, Heft 4, 236 (1983).
6. A. B. Moustafa, M. A. Abdel-Ghaffar, and A. S. Badran, *Acta Polymerica*, **35**, Nr. 1, 68 (1984).
7. A. B. Moustafa, Z. H. Abdel-Latif, and L. I. Amer, *J. Polym. Sci. Polym. Chem. Ed.*, **26**, 1587 (1988).
8. A. B. Moustafa and M. Abd-El-Maboud Sakr, *Angew. Makromol. Chem.*, **55**, 11 (1976).
9. A. B. Moustafa and A. S. Badran, *J. Polym. Sci. Polym. Chem. Ed.*, **17**, 603 (1979).
10. M. A. A. El-Ghaffar, A. A. A. El-Hakim, A. S. Badran, and A. B. Moustafa, *Angew. Makromol. Chem.*, **155**, 21 (1987).
11. A. I. Goldberg, W. P. Hohenstein, and H. Mark, *J. Polym. Sci.*, **2**, 502 (1947).
12. A. B. Moustafa, A. A. Abdel-Hakim, A. S. Badran, M. A. Abdel-Ghaffar, and M. A. I. E. Sakr, *J. Appl. Polym. Sci.*, **31**, 1403 (1986).
13. S. Brunauer, P. H. Emmett, and E. Teller, *J. Am. Chem. Soc.*, **60**, 309 (1938).
14. A. B. Moustafa and A. A. Abdel-Hakim, *J. Polym. Sci. Polym. Chem. Ed.*, **14**, 433 (1976).
15. A. B. Moustafa, M. H. Nosseir, and N. E. Nashed, *Angew. Makromol. Chem.*, **52**, 71 (1976).
16. A. B. Moustafa, N. A. Ghanem, and A. A. Abdel-Hakim, *J. Appl. Polym. Sci.*, **20**, 2643 (1976).
17. A. B. Moustafa, A. M. Rabie, and A. S. Badran, *Angew. Makromol. Chem.*, **103**, 87 (1982).
18. A. B. Moustafa and M. A. Diab, *Angew. Makromol. Chem.*, **45**, 41 (1975).
19. A. B. Moustafa and M. A. Diab, *J. Appl. Polym. Sci.*, **19**, 1585 (1975).
20. A. B. Moustafa, N. A. Ghanem, and M. A. Diab, *J. Polym. Sci. Polym. Chem. Ed.*, **13**, 1987 (1975).
21. P. J. Durrant and B. Durrant, *Introduction to Advanced Inorganic Chemistry*, Longman, New York, 1977, p. 1107.
22. J. C. Bailer Jr., H. J. Emeleus, R. Nyholm, and A. F. Trotman-Dickenson, *Comprehensive Inorganic Chemistry*, Pergamon Press, New York, 1973, p. 32.
23. F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Wiley Eastern Private Ltd., New Delhi, 1972, p. 895.
24. A. B. Moustafa, Z. H. Abdel-Latif, and L. I. Amer, *J. Polym. Sci. Polym. Chem. Ed.*, **24**, 3049 (1986).
25. J. H. de Boer, G. M. M. Houben, B. C. Lippens, W. H. Meijs, and W. K. A. Walrave, *J. Catal.*, **1**, 1 (1962).
26. J. J. Kipling and E. H. M. Wright, *J. Chem. Soc.*, 3535 (1964).
27. A. S. Russel and N. Cochran, *Ind. Eng. Chem.*, **42**, 1332 (1950).
28. C. G. Inks and R. B. Hahn, *Anal. Chem.*, **39**, 925 (1967).

Received May 22, 1989
Accepted December 13, 1989