

A Study of Graft Polymerization of Methacrylic Acid to Polycaproamide Using a Reversible Redox System Containing Cu^{2+} Ions

N. V. SMIRNOVA, G. A. GABRIELIAN,* and L. S. GAL'BRAIKH

Chair of Chemical Fibres Technology, Moscow Textile Academy Moscow, EUN (Russia)

SYNOPSIS

Graft polymerization of methacrylic acid to polycaproamide, initiated by the $\text{K}_2\text{S}_2\text{O}_8$ — $\text{Na}_2\text{S}_2\text{O}_3$ — Cu^{2+} reversible redox system, has been studied. Kinetic characteristics of graft polymerization have been investigated in a wide concentration range of every component of the initiating system. Cu^{2+} ions have been found to catalyze graft polymerization in the $1.0 \cdot 10^{-5}$ – $1.2 \cdot 10^{-4}$ M concentration range, whereas at concentrations higher than $1.2 \cdot 10^{-4}$ M, Cu^{2+} ions are involved in the kinetic chain termination. A mechanism of graft polymerization is proposed. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Graft polymerization is now widely used in modifying synthetic fibers and films to obtain new fibrous sorbents and membranes, as well as to improve the consumer properties of chemical fibers. Therefore, there is now a growing interest in the modification of fibers and films with acrylic and methacrylic acids used as the monomers. Of particular interest is the synthesis of graft polymers of polycaproamide (PCA) and polymethacrylic acid (PMAA).

Numerous publications are available, where various methods of initiating graft polymerization of methacrylic acid (MAA) have been proposed and comprehensively studied.^{1–7} Benzoyl peroxide– Cu^{2+} ,¹ potassium peroxydisulfate,² Ce^{4+} ions³ and Mn^{4+} ions,⁴ cumyl hydroxyperoxide–ascorbic acid,⁵ thiourea– KBrO_3 ,⁶ and Fe^{3+} — H_2O_2 (Ref. 7) have been used as initiators or initiating systems. These systems, however, are of low efficiency in graft polymerization, and, as a rule, grafting is accompanied by the formation of the homopolymer–PMAA in smaller or larger quantities.

Development of effective methods of synthesizing

PCA graft copolymers, making possible graft polymerization without the formation of a homopolymer, is, therefore, of significant scientific and practical interest. It has been shown^{8,9} that in the synthesis of PCA and PMAA graft copolymers the graft polymerization is most effectively initiated when redox reversible systems (RS) containing metal ions of variable oxidation states are used.

It was previously shown¹⁰ that for the graft polymerization of PMAA to PCA fiber the best results are obtained with divalent copper used as the third component of RS. The presence of Cu^{2+} ions in the system speeds up substantially the rate of graft polymerization and raises the amount of the polymer formed.¹¹

An important advantage of using RS with Cu^{2+} in the graft polymerization of MAA to PCA is the absence of homopolymer formation.^{10,11} However, the mechanism of the action of divalent copper ions and the other components of the initiating system, as well as the role of Cu^{2+} in initiating the graft polymerization, remained unresolved.

In some recent publications, Cu^{2+} ions have been shown¹² to play an important part in the mechanisms of chain initiation and termination when used for the polymerization of acrylates in the presence of three-component reversible initiating systems containing divalent copper ions. In this paper, we report the results of investigating the influence of

* To whom correspondence should be addressed.

the components of the $K_2S_2O_8$ — $Na_2S_2O_3$ — Cu^{2+} reversible redox system on the kinetics and the mechanism of MAA graft polymerization to PCA.

EXPERIMENTAL

Unelongated PCA fiber (0.68 tex) was used as the polymeric support, and the crystallinity degree was 40%. Freshly distilled MMA, $d_4^{20} = 1.0157$, $n_D^{20} = 1.4315$, and recrystallized $K_2S_2O_8$, $Na_2S_2O_3 \cdot 3H_2O$, and $CuSO_4 \cdot 5H_2O$ (reagent grade) were used for the grafting.

Copper(II) ions were immobilized on the fiber (0.002%) after it had been treated in aqueous solutions of copper sulfate at 80°C (modulus 50) [modulus = the relations of monomer solution volume to the fiber weight (g)]. After the treatment, the fiber was washed with distilled water to remove the Cu^{2+} ions unbonded to PCA. This made possible introducing 0.002% Cu^{2+} into the fiber (measured photocolometrically¹³).

The graft polymerization was performed in an aqueous solution of MAA (0.696 mol/L). The fibers were immersed in the MAA solution and then $K_2S_2O_8$ (0.2% of monomer mass) and $Na_2S_2O_3$ (3 mol vs. $K_2S_2O_8$) were introduced. The grafting was performed at 70°C (modulus 30). During Cu^{2+} ion introduction in the course of the graft polymerization, the fiber not containing copper ions was used.

At first, the grafting process was carried out in the presence of binary RS $K_2S_2O_8$ — $Na_2S_2O_3$, and some time after the beginning of the reaction, $2 \cdot 10^{-5}$ – $2 \cdot 10^{-2}$ mol/L Cu^{2+} was introduced into the reaction mixture and MAA was added until its concentration in the solution reached 0.696 mol/L. The process was then continued, which was conventionally labeled as "post"-graft polymerization.

After the termination of graft polymerization, the samples were extracted with hot water to remove the unreacted monomer and dried to a constant mass. The quantity of grafted PMAA was determined gravimetrically and by titration (by the number of COOH groups).

RESULTS AND DISCUSSION

To ascertain the effects of individual components of the initiating system on the kinetics and the mechanism of graft polymerization of MAA to PCA, we studied the dependence of the graft polymerization kinetic characteristics on the concentrations of the initiating system components, as well as the de-

pendence between the kinetic orders of the graft polymerization reaction for the monomer and Cu^{2+} concentration.

As seen from Figure 1, at $K_2S_2O_8$ concentrations below $2.2 \cdot 10^{-4} M$, the reaction practically does not occur. This is evidently because at constant $Na_2S_2O_3$ concentration a decrease in the $K_2S_2O_8$ content leads to a large excess of $Na_2S_2O_3$ in the system. This, as will be shown below, as a result of interacting with the $SO_4^{\cdot -}$ ion radical, leads to the appearance of a low-reactivity radical incapable of initiating the graft polymerization.

The data in Figure 1 plotted as a lgV vs. $lgC_{K_2S_2O_8}$ function show the existence of two regions characterized by a different contribution of $K_2S_2O_8$ to the kinetics of graft polymerization (Fig. 2). At potassium peroxydisulfate concentrations exceeding $5.5 \cdot 10^{-4} M$, the reaction order with respect to $K_2S_2O_8$ is equal to zero, whereas at lower $K_2S_2O_8$ concentrations ($2.2 \cdot 10^{-4}$ – $5.5 \cdot 10^{-4} M$), the power at $K_2S_2O_8$ in the kinetic equation for the rate of MAA graft polymerization to PCA is equal to 1.2.

A marked deviation in the order of the graft polymerization reaction from that with respect to the initiator of the radical-chain polymerization (0.5) is indicative of the different chain initiation and termination mechanisms in graft polymerization.

The zero order of the reaction for $K_2S_2O_8$ at high peroxydisulfate concentrations demonstrates that the sulfate ion radicals, along with their participation in the initiation of graft polymerization, take

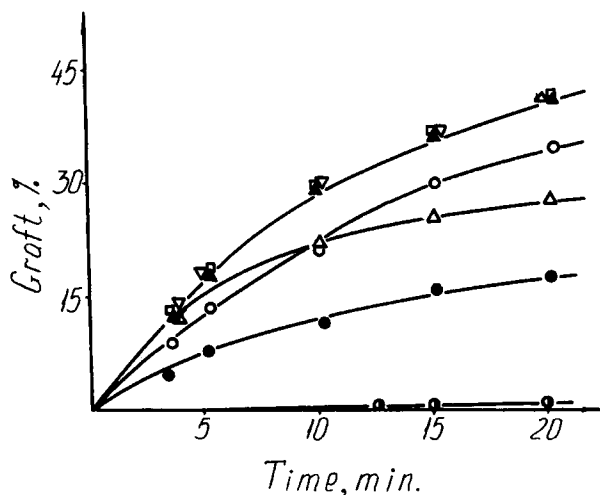


Figure 1 The amount of grafted PMAA vs. the reaction time. $K_2S_2O_8$, mol/L: (●) $2.2 \cdot 10^{-4}$; (●) $3.3 \cdot 10^{-4}$; (○) $4.4 \cdot 10^{-4}$; (▲) $5.5 \cdot 10^{-4}$; (□) $6.7 \cdot 10^{-4}$; (▽) $7.8 \cdot 10^{-4}$; (△) $8.9 \cdot 10^{-4}$. MAA = 0.696 mol/L; $Na_2S_2O_3 = 1.3 \cdot 10^{-3}$ mol/L; modulus 30, temperature 70°C.

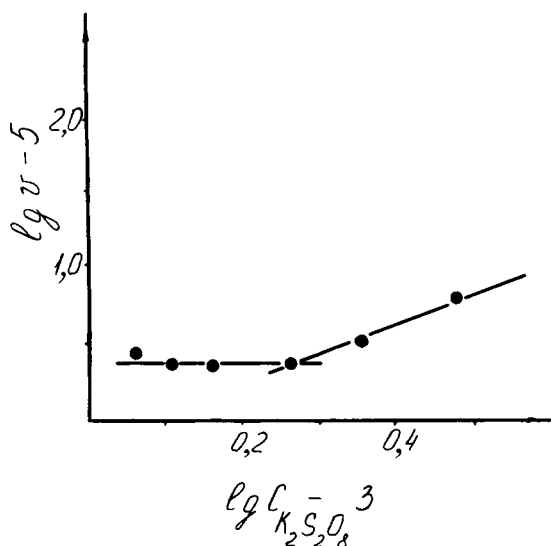


Figure 2 The $\lg v$ vs. $\lg C_{K_2S_2O_8}$ plot.

an active part in chain termination at the initial stages of grafting.

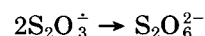
Similar kinetic features of graft polymerization induced by active oxidants are typical of the graft polymerization of other vinyl monomers.¹² The reaction order for these monomers, established to be close to zero with respect to the oxidant, is explained¹² by the decay of the primary growing radicals as a result of their interaction with the oxidant radicals.

The fact that the reaction order for $K_2S_2O_8$ in graft polymerization at low concentrations, on the contrary, becomes higher than that corresponding to the ideal radical polymerization is indicative of peroxydisulfate taking part in the side reactions. It can be assumed that one of such reactions involves $SO_4^{\cdot-}$ interaction with $S_2O_3^{2-}$, yielding $SO_4 \cdot S_2O_3^{2-}$,¹⁴ the latter being unable to induce polymerization.¹⁵ Naturally, these species cannot initiate graft polymerization either. As a possible side reaction, one could consider the termination of the growing macroradical of the grafted chain by the sulfate ion radicals. However, this reaction seems to be rather improbable with a large excess of $Na_2S_2O_3$.

The dependence of the rate of MAA graft polymerization to PCA on the sodium thiosulfate concentration was studied in the $2.2 \cdot 10^{-4}$ – $17.2 \cdot 10^{-4} M$ concentration range, at constant $K_2S_2O_8$, MAA, and Cu^{2+} concentration. The data obtained, shown in the $\lg v$ – $\lg C_{Na_2S_2O_3}$ coordinates in Figure 3, reflect the existence of three different concentration regions where the relative contributions of various types of radical reactions between $K_2S_2O_8$ and $Na_2S_2O_3$ at the initiation step are substantially different.¹⁴

At the ratio of $K_2S_2O_8 : Na_2S_2O_3 = 1 : (0.5-1.9)$,¹⁰ when, because of the rather low thiosulfate concentration, the probability of $SO_3^{\cdot-}$ involvement in the suppression of the homopolymerization in solution, initiated by $SO_4^{\cdot-}$ and $\cdot OH$ radicals, is sharply decreased, the reaction order with respect to $Na_2S_2O_3$ is 0.58. Low rates of the graft polymerization of MAA are typical of this thiosulfate concentration region.

With increasing $Na_2S_2O_3$ concentration ($8.4 \cdot 10^{-4}$ – $1.3 \cdot 10^{-3} M$), the rate of graft polymerization in the initiating system increases substantially, obviously because of a rise in the concentration of $SO_4^{\cdot-}$ ion radicals formed by the interaction of $K_2S_2O_8$ with $Na_2S_2O_3$. Correspondingly, the concentration of PCA macroradicals increases due to the chain transfer from $SO_4^{\cdot-}$ to PCA. The reaction order with respect to the reductant increases up to 2.3 in this region. Such a high value can be explained by the fact that $Na_2S_2O_3$ or $S_2O_3^{2-}$ ions are also consumed in the interaction with $SO_4^{\cdot-}$ and $\cdot OH$ radicals in solution. Thiosulfate consumption may be also caused by the recombination of thiosulfate ion radicals to give dithionite¹⁶:



With a sufficiently large excess of $Na_2S_2O_3$ (more than 3 mol of $Na_2S_2O_3$ per 1 mol of $K_2S_2O_8$; $1.3 \cdot 10^{-3}$ – $1.7 \cdot 10^{-3} M$), the order of graft polymerization, as seen from Figure 3, becomes equal to zero. This indicates, therefore, that $Na_2S_2O_3$ is not only

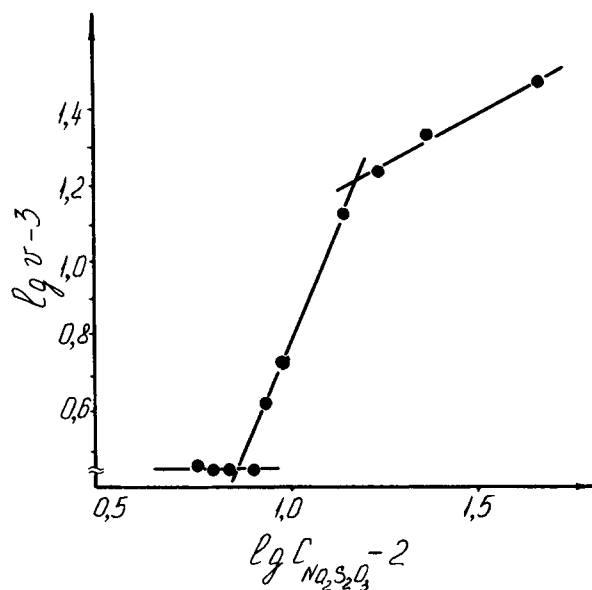


Figure 3 The $\lg v$ vs. $\lg C_{Na_2S_2O_3}$ plot.

a component of the initiating RS but is also actively involved in kinetic chain termination. At $\text{Na}_2\text{S}_2\text{O}_3$ concentration higher than $2.6 \cdot 10^{-3} M$, the graft polymerization was found not to be taking place.

It has been previously demonstrated^{10,11} that the presence of divalent copper ions in this system markedly increases both the graft polymerization rate and the monomer conversion. It was of interest therefore to find out how this reversible initiating system would behave in the graft polymerization of MAA to PCA at low and relatively high concentrations of copper (II) ions.

Comparing the kinetic curves in Figure 4, one can observe that at low Cu^{2+} concentrations ($1.1 \cdot 10^{-5}$ – $3.0 \cdot 10^{-5} M$) there is a noticeable induction period after which the grafting proceeds at very high rates. It is possible that the induction period corresponds to the time needed for the required amount of the intermediate Cu^{2+} complex with $\text{Na}_2\text{S}_2\text{O}_3$ to be formed,¹⁷ which then participates in the redox decomposition of $\text{K}_2\text{S}_2\text{O}_8$. An increase in Cu^{2+} concentration (curves 4–10, Fig. 4) eliminates the induction period. However, comparing the graft polymerization rates at the initial stages, one can notice that, despite the absence of an induction period, the initial rate proves to be lower ($2.1 \cdot 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$) than that at low Cu^{2+} concentrations ($2.9 \cdot 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$).

For the Cu^{2+} ion concentration region ($1.0 \cdot 10^{-5}$ –

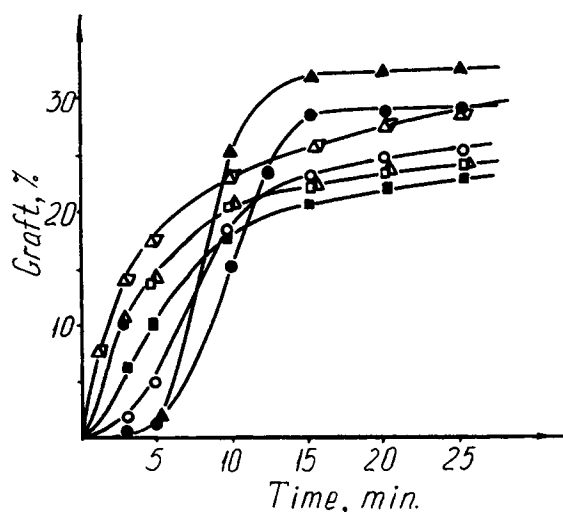


Figure 4 The yield of grafted PMAA vs. the reaction time. Cu^{2+} , mol/L: (●) 10^{-5} , (▲) $2 \cdot 10^{-5}$, (○) $4 \cdot 10^{-5}$; (□) $8 \cdot 10^{-5}$, (△) 10^{-4} ; (▽) $4 \cdot 10^{-4}$; (■) $6 \cdot 10^{-4}$. MAA = 0.696 mol/L ; $\text{K}_2\text{S}_2\text{O}_8 = 4.4 \cdot 10^{-4} \text{ mol/L}$; $\text{Na}_2\text{S}_2\text{O}_3 = 1.3 \cdot 10^{-3} \text{ mol/L}$; modulus 30; temperature 70°C .

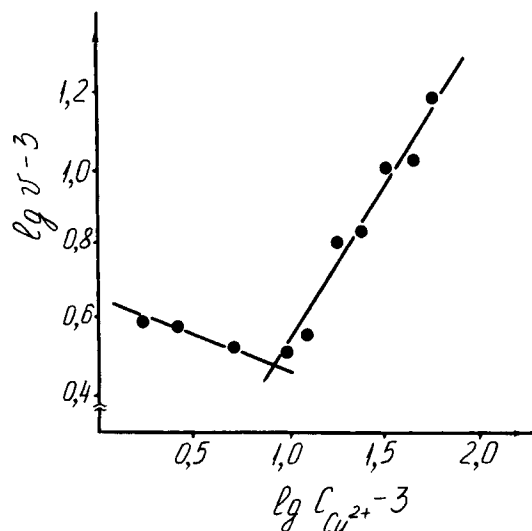


Figure 5 The $\lg V$ vs. $\lg C_{\text{Cu}^{2+}}$ plot.

$12.0 \cdot 10^{-5} M$), the order of the reaction of graft polymerization of MAA to PCA with respect to the Cu^{2+} ion, calculated from the $\lg V$ – $\lg C_{\text{Cu}^{2+}}$ plot, presented in Figure 5, is equal to 0.6. This means that at such Cu^{2+} concentrations in the system the metal ions are predominantly involved in the decomposition of $\text{K}_2\text{S}_2\text{O}_8$ and, probably, do not take part in the termination of the growing polymeric chain.

When determining the monomer reaction order for the initiating system with a low Cu^{2+} content

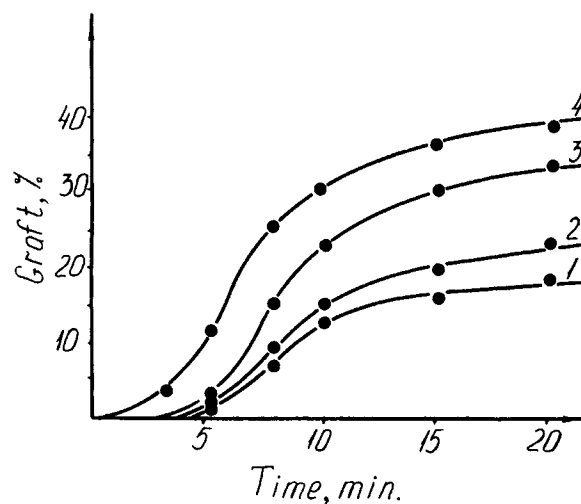


Figure 6 The yield of grafted PMAA vs. the reaction time. MAA, mol/L: (1) 0.464; (2) 0.580; (3) 0.696; (4) 0.929. $\text{Na}_2\text{S}_2\text{O}_3 = 1.3 \cdot 10^{-3} \text{ mol/L}$; $\text{K}_2\text{S}_2\text{O}_8 = 4.4 \cdot 10^{-4} \text{ mol/L}$; $\text{Cu}^{2+} = 2 \cdot 10^{-5} \text{ mol/L}$; modulus 30; temperature 70°C .

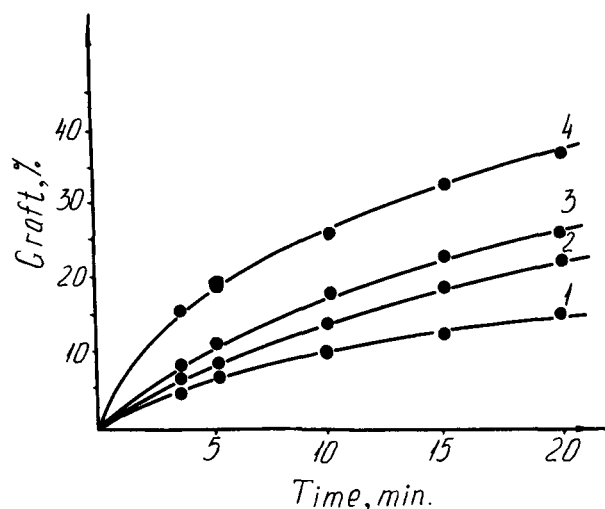


Figure 7 The yield of grafted PMAA vs. the reaction time. MAA, mol/L: (1) 0.464; (2) 0.580; (3) 0.696; (4) 0.929. $\text{Na}_2\text{S}_2\text{O}_3 = 1.3 \cdot 10^{-3}$ mol/L; $\text{K}_2\text{S}_2\text{O}_8 = 4.4 \cdot 10^{-4}$ mol/L; $\text{Cu}^{2+} = 2 \cdot 10^{-5}$ mol/L; modulus 30; temperature 70°C .

from the kinetic curves in Figure 6, the order of the reaction with respect to the monomer was found to be equal to 2.3. According to Ref. 18, the reaction order for the monomer, equal to 2, is indicative of the participation of the monomer as a dimer at the stage of polymerization initiation. It can be assumed that in the course of grafting, when the local concentration of MAA on the fiber sharply increases due to sorption, the possibility of the formation of dimeric forms and associates of MAA also increases. This creates favorable conditions for their complexing with Cu^{2+} ions. This may be the reason why the reaction order with respect to the monomer becomes higher than 2, and with respect to Cu^{2+} , higher than 0.5.

At Cu^{2+} concentrations higher than $1.2 \cdot 10^{-5} \text{M}$, the shape of the $\lg V - \lg C_{\text{Cu}^{2+}}$ plot changes sharply (Fig. 5); the reaction order for Cu^{2+} becomes negative (-0.13). This fact indicates that in this case the Cu^{2+} ions are involved both in the decay of primary radicals capable of initiating the graft polymerization and in the termination of the polymeric chain.

An increase in the reaction order for the monomer from 2.3 to 2.6 at comparatively high Cu^{2+} concentration (Fig. 7) can be obviously explained in terms of the increasing probability of a complex formation between Cu^{2+} and MAA at the initiation stage.

The data obtained have thus made it possible to describe the influence of each component of the ini-

tiating RS on the kinetics of MAA graft polymerization to PCA.

REFERENCES

1. I. F. Osipenko and V. I. Martinovitch, *Vysokomol. Soed.*, **29A**, 2316 (1987).
2. V. A. Kuznetsova, Yu. G. Kryazhev, Z. A. Rogovin, and N. A. Toropseva, *Zhur. Prikl. Khim.*, **37**, 1334 (1964).
3. S. Haworth and J. R. Holker, *J. Soc. Dyers Colour.*, **82**, 257 (1966).
4. M. J. Khalil, S. H. Abdel-Tattan, and A. J. Nantouch, *Appl. Polym. Sci.*, **19**, 2699 (1975).
5. K. Koszi, H. Tsussi, and N. Noboru, *Sanyi Gakkasi*, **34**, 55 (1978).
6. A. Hebeish, M. H. El-Rafie, and A. I. Waly, *J. Polym. Sci. Polym. Chem. Ed.*, **14**, 2895 (1976).
7. T. V. Druzhinina, F. A. Goldshtein, B. P. Morin, and B. A. Mukhin, USSR Pat. 361,179 (Published in B.I., 1973, No. 26).
8. N. P. Lits, A. B. Korzhevsky, Zh. V. Radugina, A. I. Bykov, and A. E. Kylysov, USSR Pat. 1,032,051 (Published in B.I., 1983, No. 28).
9. G. Bogoeva-Gatseva, G. A. Gabrielyan, and L. S. Gal'braikh, *Khim. Volokna*, **2**, 24 (1987).
10. N. B. Smirnova and G. A. Gabrielyan, in *Razrabotka Vysokoeffektivnykh Tekhnologicheskikh Protsessov 1 Oborudovaniya, System Upravleniya 1 Avtomatizatsionnogo Proektirovaniya v Textilnoy Promyshlennosti (Development of High-Efficiency Technological Processes and Equipment, Control Systems and Automated Design in Textile Industry)*, MTI, Moscow, 1987, p. 53.
11. G. Bogoeva-Gatseva, G. A. Gabrielyan, and L. S. Gal'braikh, *Vysokomol. Soed.*, **29A**, 406 (1987).
12. G. G. Reddy, I. Nagabhushanam, K. V. Rao, and M. Santappa, *Br. Polym. J.*, **3**, 89 (1982).
13. A. S. Chegoli and N. M. Kvasha, Eds., *Analitichesky Kontrol Proizvodstva Sinteticheskikh Volokon (Analytical Control of Synthetic Fiber Production)*, Khimia, Moscow, 1982, p. 256.
14. B. A. Dolgoplosk and E. I. Tenyakova, *Okislitel'no-vosstanovitelnye Systemy Kak Istochniki Svobodnykh Radikalov (Redox Systems as Sources of Free Radicals)*, Nayka, Moscow, 1972, p. 240.
15. J. P. Riggs and F. Rodriguez, *J. Polym. Sci. Part A-I*, **5**, 3167 (1967).
16. D. Bunn, *Trans. Faraday Soc.*, **42**, 169 (1946).
17. Yu. S. Paikachev, L. N. Mizerovsky, A. N. Bykov, and B. F. Borodkin, *Izv. Vuzov. Khim. Khim. Tekhnol.*, **11**, 716 (1958).
18. D. N. Marjit, V. Kalpagam, and U. S. Nandi, *J. Polym. Sci. Polym. Chem. Ed.*, **21**, 803 (1983).

Received June 23, 1991

Accepted April 3, 1992