Grafting onto Cellulose. VII. Graft Copolymerization of Methyl Acrylate by Use of Metal Chelates as Initiators

B. N. Misra[a]; J. K. Jassal[a]; R. Dogra[a]

[a] Department of Chemistry, Himachal Pradesh University, Simla, India

PLEASE SCROLL DOWN FOR ARTICLE

Grafting onto Cellulose. VII. Graft Copolymerization of Methyl Acrylate by Use of Metal Chelates as Initiators

B. N. MISRA, J. K. JASSAL, and R. DOGRA

Department of Chemistry
Himachal Pradesh University
Simla 171005, India

ABSTRACT

Graft copolymerization of methyl acrylate (MA) onto cellulose has been studied in the presence of Fe(acac)$_3$, Al(acac)$_3$, and Zn(acac)$_2$ as initiators in aqueous medium. The percentage of grafting has been determined as a function of concentration of initiators and monomer, reaction time, and temperature. A plausible mechanism for grafting involving prior complex formation between metal chelates and monomers has been suggested. The free radical mechanism for grafting was confirmed by carrying out several experiments in the presence of chain transfer agents such as CCl$_4$, CHCl$_3$, CH$_3$CH$_2$CH$_2$SH, and Et$_3$N. All these additives, with the exception of Et$_3$N, were found to suppress grafting. The relative reactivity of different metal chelates toward grafting has been determined and was found to follow the order: Fe(acac)$_3$ > Zn(acac)$_2$ > Al(acac)$_3$.

INTRODUCTION

The modification of celluose by graft copolymerization has been extensively studied in recent years [1, 2]. Various initiation methods

1093

that have been successfully used for effecting grafting of a variety of
vinyl monomers onto cellulose include: (1) redox initiation [3, 4],
(2) initiation by chain transfer [5], (3) photochemical [6] and high
energy irradiation [7], (4) ring-opening reactions [8], and (5) mechan-
ical method [9]. All these methods essentially involve generation of
free radical sites onto a polymeric backbone where grafting can occur.
Grafting by the free radical method suffers from the serious limitation
that, simultaneously with grafting, considerable homopolymerization
occurs that leads to wastage of expensive monomer and separation of
homopolymer from the graft offers great difficulty. Hence a constant
search is being made to select a proper initiator system that would
selectively afford grafting or at least minimize the formation of homo-
polymer. In an attempt to find newer initiating systems, we have
studied the suitability of metal chelates as graft initiators. Metal
derivatives are capable of initiating vinyl polymerization. It was
observed by Bamford and co-workers [10] that many derivatives of
transition metals in their low oxidation states in association with
organic halides are active sources of free radicals which may initiate
vinyl polymerization. Initiation was believed to occur through elec-
tron transfer from metal to halide. Metal chelates were also found
capable of initiating vinyl polymerization.

The ability of certain metal chelates to produce free radicals when
heated was first pointed out by Arnett and Mendelsohn [11, 12] in the
course of an investigation on the oxidation of these compounds. They
observed that at $110°$ C some chelates are able to initiate the polym-
erization of styrene. They suggested the following order of reactivity
for the polymerization of styrene: $V^{III} > Cr^{III} > Al^{III} > Fe^{III} >$
$Co^{III} > Ce^{III} > Mn^{III}$. Kasting et al. [13] reported that of the simple
acetyl acetonates, those of Mn^{III} and Co^{III} are the most active initia-
tors. Indicator and Linder [14] reported that Co^{II}, Co^{III}, Cr^{III}, and
Fe^{III} acetyl acetonates in the presence of tertbutyl hydroperoxide can
be used as initiators for the polymerization of styrene. Recently,
Nandi et al. [15] were able to effect the polymerization of MMA by
using Fe(acac)$_3$ as the initiator.

The use of metal chelates in graft copolymerization has not been
investigated. A comprehensive study on the utilization of a variety
of β-diketonates of transition metals as initiators for effecting graft-
ing onto a variety of natural polymeric backbones has been initiated
in our laboratory. It has been possible to effect grafting of MMA and
styrene onto cellulose and cellulose acetate by using Fe(acac)$_3$ and
Mn(acac)$_3$ as initiators [16]. We have recently reported [17] grafting
of MMA, AAc, and VAc onto wool protein by using VO(acac)$_2$ as the
graft initiator. In a previous paper we described studies on the graft-
ing of VAc [18], an electron-donating monomer, onto cellulose in the
presence of Fe(acac)$_3$, Al(acac)$_3$, and Zn(acac)$_2$ as initiators. In
this article we report on grafting of an acceptor monomer (MA) onto

cellulose by using $Fe(acac)_3$, $Al(acac)_3$, and $Zn(acac)_2$ as initiators. The relative reactivity of different metal chelates toward grafting of MA onto cellulose has been evaluated. The percentage of grafting and percent efficiency have been expressed as functions of different variables, and the results are presented in Tables 1a-d, 2a-d, and 3a-d.

TABLE 1a. Effect of Concentration of MA on Percent Grafting[a]

Sample	$[MA] \times 10^2$ mol/L	% grafting	% efficiency
1	22	12.40	6.499
2	44	21.69	5.683
3	84	10.90	1.904
4	110	8.07	0.846
5	160	8.00	0.559

[a]$[Fe(acac)_3]$ = 0.249×10^{-2} mol/L; cellulose = 1 g; time = 180 min; H_2O = 100 mL; temperature = $60 \pm 1°C$.

TABLE 1b. Effect of Concentration of $Fe(acac)_3$ on Percent Add-on[a]

Sample	$[Fe(acac)_3]$ $\times 10^2$ mol/L	% grafting	% efficiency
1	0.0623	6.40	1.68
2	0.1246	10.78	2.824
3	0.2493	21.69	5.633
4	0.4986	15.60	4.088
5	0.7479	10.75	2.817
6	0.8725	10.60	-
7	0.9971	10.62	-

[a]$[MA]$ = 44×10^{-2} mol/L; cellulose = 1 g; time = 180 min; H_2O = 100 mL; temperature = $60 \pm 1°C$.

TABLE 1c. Effect of Time on Percent Grafting[a]

Sample	Time (min)	% grafting	% efficiency
1	30	8.80	2.30
2	60	15.15	3.97
3	90	18.40	4.82
4	120	21.69	5.68
5	180	22.00	5.76
6	210	21.90	5.76
7	240	21.10	5.70
8	270	21.82	

[a] $[Fe(acac)_3]$ = 0.249 × 10^{-2} mol/L; cellulose = 1 g; $[MA]$ = 44 × 10^{-2} mol/L; H_2O = 100 mL; temperature = 60 ± 1°C.

EXPERIMENTAL

Materials and Methods

Pure cellulose powder (Carl Schleicher & Schüll, Selecta) has been used in all experiments. Methyl acrylate (BDH) was washed with 5% sodium hydroxide solution followed by washing with water and drying over anhydrous sodium sulfate. The dried methyl acrylate was distilled and the middle fraction was used. Carbon tetrachloride, chloroform, and triethylamine were freshly distilled. Propane-1-thiol (BDH) was of reagent grade and used without further purification.

Acetyl acetonates of Fe(III) and Al(III) were prepared by the methods previously described [19, 20]. Zn(acac)₂ was obtained as a gift from Acira Akimoto (Central Research Lab., Toyosoda Manufacturing Co., Japan).

Nitrogen gas was purified by passage through a freshly prepared alkaline pyrogallol solution.

Graft Copolymerization

Pure cellulose powder (1.0 g) was dispersed in 100 mL of deaerated water (40°) in a three-necked flask. The flask was purged with purified nitrogen for about 30 min. A weighed amount of metal chelates dissolved in a minimum amount of appropriate solvents was added to the reaction mixture. The temperature of the water was raised to

TABLE 1d. Effect of Additives on Percent Grafting[a]

Sample	Additive (mL)	% grafting	% efficiency
CCl_4			
1	2	11.48	3.0
2	4	0	0
3	6	0	0
$CHCl_3$			
4	2	2.1	0.55
5	4	1.47	0.38
6	6	0	0
$CH_3CH_2CH_2SH$			
7	1	0	0
8	2	0	0
9	3	0	0
$(C_2H_5)_3N$			
10	2	15.56	4.09
11	4	10.06	2.64
12	6	6.17	1.62

[a] $[Fe(acac)_3] = 0.249 \times 10^{-2}$ mol/L; $[MA] = 44 \times 10^{-2}$ mol/L; time = 180 min; temperature = $60 \pm 1°C$.

$60 \pm 1°C$. A measured amount of methyl acrylate (MA) was added dropwise, and graft copolymerization was carried out under nitrogen atmosphere for various reaction periods. The separation and purification of graft were performed by the method described. The percentage of grafting and percent efficiency were determined from the weight increase of cellulose after grafting in the following manner:

$$\% \text{ grafting} = \frac{W_1 - W_0}{W_0}$$

$$\% \text{ efficiency} = \frac{W_1 - W_0}{W_2}$$

TABLE 2a. Effect of Concentration of MA on Percent Grafting[a]

Sample	$[MA] \times 10^2$ mol/L	% grafting	% efficiency
1	33	14.73	5.146
2	44	12.20	2.841
3	66	10.19	1.710
4	100	10.48	1.098
5	166	10.40	0.72

[a]$[Al(acac)_3]$ = 2.14×10^{-3} mol/L; temperature = 60 ± 1°C; time = 90 min; cellulose = 1 g; H_2O = 100 mL.

TABLE 2b. Effect of Concentration of Al(acac)$_3$ on Percent Grafting[a]

Sample	$[Al(acac)_3] \times 10^3$ mol/L	% grafting	% efficiency
1	1.07	4.82	1.684
2	2.14	14.80	5.146
3	3.21	10.12	3.50
4	4.28	7.00	2.445
5	5.35	6.90	2.444
6	6.42	6.40	2.236
7	7.49	6.50	-

[a]$[MA]$ = 33×10^{-2} mol/L; time = 90 min; temperature = 60 ± 1°C; cellulose = 1 g; H_2O = 100 mL.

where W_0, W_1, and W_2 denote the weight of cellulose, grafted cellulose, and monomer added, respectively.

The percentage grafting has been expressed as function of the concentration of metal chelates, the concentration of monomer, and the reaction time. Several experiments were carried out in the presence of additives, and the results are presented in Tables 1a-d, 2a-d, and 3a-d.

TABLE 2c. Effect of Time on Percent Grafting[a]

Sample	Time (min)	% grafting	% efficiency
1	30	3.10	0.104
2	60	7.00	0.244
3	90	14.72	5.146
4	120	9.12	3.18
5	150	3.97	1.387
6	180	4.12	0.144

[a] $[Al(acac)_3]$ = 2.14×10^{-3} mol/L; temperature = $60 \pm 1°C$; $[MA]$ = 33×10^{-2} mol/L; cellulose = 1 g; H_2O = 100 mL.
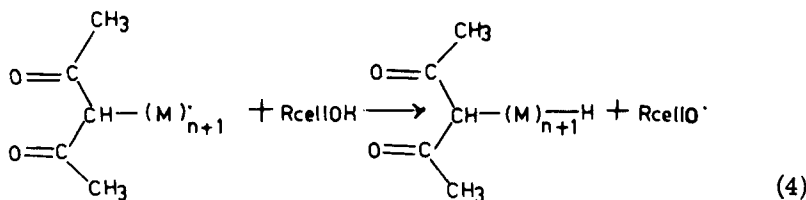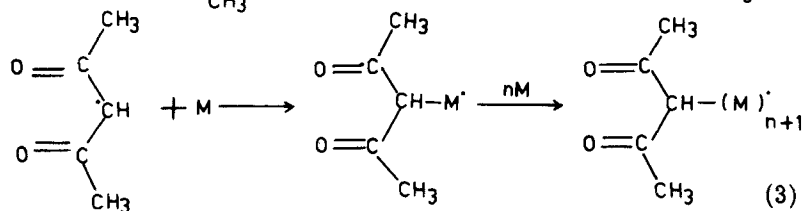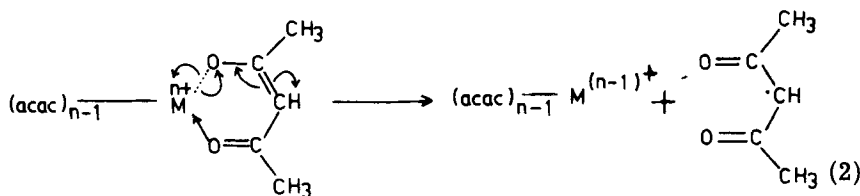
Evidence of Grafting

The IR spectrum of grafted samples showed an absorption band at 1730 cm^{-1} (C=O) which was attributed to grafted poly(methyl acrylate). No such band was present in cellulose.

An intimate physical mixture of cellulose (1.0 g) and poly(methyl acrylate) (0.5 g) in benzene was stirred at room temperature for 3 h. The mixture was filtered and the residue was extracted with benzene for 24 h. The quantitative recovery of cellulose (0.99 g) indicated that all poly(methyl acrylate) was removed by benzene extraction from the physical mixture. The increase in weight of cellulose after grafting followed by extraction with benzene is due to the presence of poly(methyl acrylate) covalently bonded to cellulose.

RESULTS AND DISCUSSION

Metal chelates are known to decompose upon heating to generate free radicals that can initiate vinyl polymerization. The growing polymeric radical can abstract a hydrogen atom from cellulose to generate an active site where grafting can occur. Since the amount of metal chelates used is very small, generation of an active site by the free radical species arising from decomposition of metal chelates is unlikely. The following tentative mechanism (Eqs. 1-6) is therefore suggested to explain grafting of PMA onto cellulose in the presence of metal chelates:

$$(acac)_{\overline{n-1}} - M \overset{n+}{\underset{}{}} \rightleftharpoons (acac)_{\overline{n-1}} - M \overset{n+}{\underset{}{}} \tag{1}$$

$$(acac)_{\overline{n-1}} - M \overset{n+}{\underset{}{}} \longrightarrow (acac)_{\overline{n-1}} M^{(n-1)+} + \cdot \tag{2}$$

$$O = C \overset{CH_3}{\underset{}{}} \cdots \dot{C}H \cdots O = C \overset{CH_3}{\underset{}{}} + M \longrightarrow O = C \overset{CH_3}{\underset{}{}} \dot{C}H - M^{\cdot} \overset{nM}{\longrightarrow} O = C \overset{CH_3}{\underset{}{}} \dot{C}H - (M)_{n+1}^{\cdot} \tag{3}$$

$$O = C \overset{CH_3}{\underset{}{}} \dot{C}H - (M)_{n+1}^{\cdot} + RcellOH \longrightarrow \dot{C}H - (M)_{\overline{n+1}}H + RcellO^{\cdot} \tag{4}$$

$$RcellO^{\cdot} + M \longrightarrow RcellO \ M^{\cdot} \overset{nM}{\longrightarrow} RcellO - (M)_{n+1}^{\cdot} \tag{5}$$

$$RcellO \quad -(M)_{n+1}^{\cdot} + \cdot(M)_{\overline{n+1}} - CH \overset{CH_3}{\underset{CH_3}{}} \longrightarrow Graft \tag{6}$$
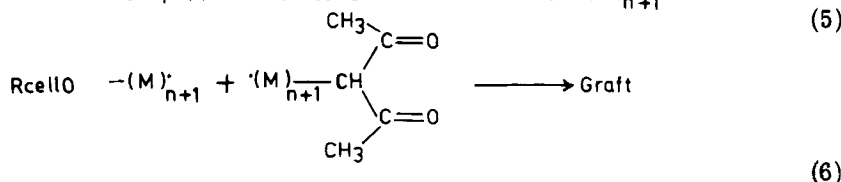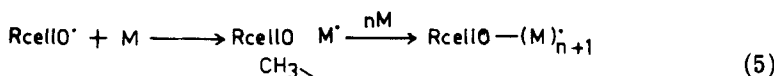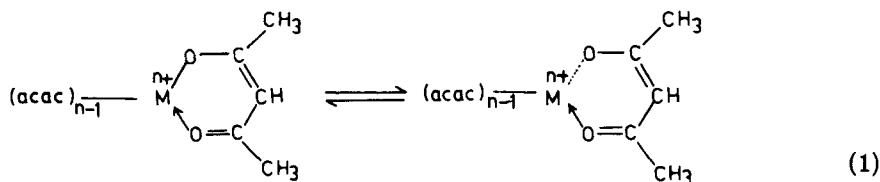
In the above mechanism it is proposed that the metal chelates upon heating first loosen the metal-oxygen bond followed by decomposition into a free radical species by a one-electron transfer process. The free radical species thus formed is responsible for grafting as well as for homopolymerization. However, this appears unlikely since all grafting experiments were carried out at $60°C$, much below the decomposition temperature of the metal chelates. It is observed from

TABLE 2d. Effect of Additives on Percent Grafting[a]

Sample	Additive (mL)	% grafting	% efficiency
CCl_4			
1	2	10.01	3.51
2	4	5.49	1.92
3	6	1.20	0.42
$CHCl_3$			
4	2	10.68	3.74
5	4	5.00	1.75
6	6	1.30	0.45
$CH_3CH_2CH_2SH$			
7	1	0	0
8	2	0	0
9	3	0	0
$(C_2H_5)_3N$			
10	2	22.49	7.85
11	4	13.12	4.60
12	6	7.50	2.63

[a]$[Al(acac)_3]$ = 2.14×10^{-3} mol/L; $[MA]$ = 33×10^{-2} mol/L; time = 90 min; temperature = $60 \pm 1°C$.

Tables 1b, 2b, and 3b that chelates vary in their abilities to produce graft. Fe(acac)₃ under optimum conditions produces maximum grafting of MA to the extent of 21.69%, while Al(acac)₃ and Zn (acac)₂ under optimum conditions afforded maximum grafting of 14.80 and 17.63%, respectively. This may indicate that grafting of MA is highly dependent upon the nature of the central metal atom in the chelates. Further, it is observed from Tables 1a, 2a, and 3a that an increase in monomer concentration leads to an increase in percent grafting. This effect is pronounced with Fe(acac)₃, and with Al(acac)₃ and Zn(acac)₂, an increase in monomer concentration does not produce significant graft formation. Since graft formation with all chelates occurred at 60°, much below the decomposition temperature of the chelates, it is assumed that the chelates undergo monomer-assisted decomposition at low temperature. In view of these facts, the earlier mechanism (Eqs. 1-6) proposed for grafting requires modification. It is presumed

TABLE 3a. Effect of Concentration of MA on Percent Grafting[a]

Sample	$[MA] \times 10^2$ mol/L	% grafting	% efficiency
1	33.0	4.73	1.652
2	55.0	6.52	1.378
3	110.0	8.30	0.87
4	165.0	8.50	0.59

[a]$[Zn(acac)_2] = 2.5 \times 10^{-2}$ mol/L; cellulose = 1 g; time = 120 min; H_2O = 100 mL; temperature = 60 ± 1°C.

TABLE 3b. Effect of Concentration of $Zn(acac)_2$ on Percent Grafting[a]

Sample	$[Zn(acac)_2] \times 10^2$ mol/L	% grafting	% efficiency
1	0.250	2.90	0.976
2	0.50	4.73	1.652
3	1.0	10.19	3.560
4	1.5	10.20	3.560
5	2.0	10.25	3.560
6	2.5	10.32	3.570

[a]$[MA] = 165 \times 10^{-2}$ mol/L; cellulose = 1 g; H_2O = 100 mL; time = 120 min; temperature = 60 ± 1°C.

that the chelates, instead of undergoing spontaneous decomposition, prefer to combine with monomer to form Complex I which decomposes at low temperature.
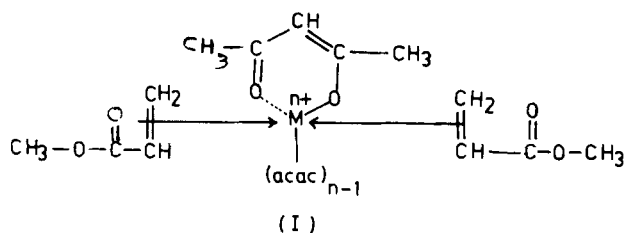

(I)

TABLE 3c. Effect of Time on Percent Grafting[a]

Sample	Time (min)	% grafting	% efficiency
1	30	3.75	1.310
2	60	7.1	2.480
3	90	12.75	4.50
4	120	17.63	6.16
5	150	17.0	5.94
6	180	16.36	5.72

[a][$Zn(acac)_2$] = 2.5×10^{-2} mol/L; [MA] = 165×10^{-2} mol/L; temperature = $60 \pm 1°C$; cellulose = 1 g; H_2O = 100 mL.

Evidence for Monomer-Metal Chelate Complex Formation

1. The ability to form Complex I depends upon the nature of the central metal atom. Since the amount of graft produced by $Fe(acac)_3$ is more than that produced by $Al(acac)_3$ and $Zn(acac)_2$, it is assumed that Fe(III) is more efficient than Al(III) and Zn(II) in entering into complex formation with vinyl monomer.

2. An attempt was made to isolate Complex I. Upon treatment of MA with $Fe(acac)_3$, a solid residue was obtained which was extracted with benzene to remove poly(methyl acrylate). The IR spectrum of this residue showed an absorption band at 430 cm^{-1} which was not present in the IR spectrum of $Fe(acac)_3$. The new band at 430 cm^{-1} was attributed to the Fe–C bond. The complex of MA and $Zn(acac)_2$ $Al(acac)_3$ also showed the presence of a metal carbon bond in the IR spectrum.

The complex of MA and $Fe(acac)_3$ was dissolved in benzene and the percent transmission of benzene solution was determined in a UV spectrophotometer as a function of wavelength. The UV spectrum of $Fe(acac)_3$ was compared with that of the $Fe(acac)_3$-MA complex. The band at 278 nm of $Fe(acac)_3$ was shifted to 319 nm in the $Fe(acac)_3$-MA complex, indicating that complex formation occurs between $Fe(acac)_3$ and MA.

The effect of time upon percent grafting was studied, and it is observed from Tables 1c, 2c, and 3c that $Fe(acac)_3$ affords maximum grafting in 180 min, while $Al(acac)_3$ and $Zn(acac)_2$ afford maximum grafting within 90 and 120 min, respectively. A further increase in time has no effect on percent grafting with all the chelates.

Several grafting experiments were carried out in the presence of

TABLE 3d. Effect of Additives on Percent Grafting[a]

Sample	Additive (mL)	% grafting	% efficiency
CCl_4			
1	2	12.28	4.23
2	4	0	0
3	6	0	0
$CHCl_3$			
4	2	12.77	4.48
5	4	3.51	1.26
6	6	0	0
$CH_2CH_2CH_2SH$			
7	1	0	0 .
8	2	0	0
9	3	0	0
$(C_2H_5)_3N$			
10	2	22.51	7.9
11	4	11.68	4.09
12	6	4.03	1.41

[a]$[Zn(acac)_2] = 2.5 \times 10^{-2}$ mol/L; time = 120 min; temperature = $60 \pm 1°C$; $[MA] = 165.0 \times 10^{-2}$ mol/L.

additives such as CCl_4, $CHCl_3$, $CH_3CH_2CH_2SH$, and Et_3N. It is observed from Tables 1d, 2d, and 3d that all the additives with the exception of Et_3N decrease the percent grafting. The decrease was maximum with propane-1-thiol, which is a good transfer agent and promotes homopolymerization. No grafting was observed in the presence of propane-1-thiol with the chelates studied. CCl_4 and $CHCl_3$ at small concentration afforded some grafting. At higher concentration, the percentage of grafting decreased considerably. Triethylamine promoted grafting of MA in the presence of $Al(acac)_3$ and $Zn(acac)_2$. With $Fe(acac)_3$, 15.56% grafting was obtained in the presence of 2.0 mL of Et_3N. With a further increase in Et_3N concentration, the percent grafting decreases. This indicates that Et_3N assists in the decomposition of metal chelates at lower concentration, and at higher concentration it acts as a chain transfer agent that causes a decrease in the percent grafting. This behavior of Et_3N is in agreement with

the findings of Bamford et al. [21] who observed that certain amines are capable of promoting metal chelate-initiated vinyl polymerization.

ACKNOWLEDGMENTS

REFERENCES

[1] E. H. Immergut, in Encyclopedia of Polymer Science and Technology, Vol. 3 (H. F. Mark, N. G. Gaylord, and N. M. Bikales, eds.), Wiley-Interscience, New York, 1965, p. 242.

[2] J. J. Hermans, Pure Appl. Chem., 15, 147 (1962).

[3] B. N. Misra, R. Dogra, I. K. Mehta, and J. K. Jassal, J. Polym. Sci., Polym. Chem. Ed., 17, 1861 (1979).

[4] G. N. Richards, J. Appl. Polym. Sci., 5, 545 (1961).

[5] B. N. Misra, C. S. Pande, and J. K. Jassal, J. Polym. Sci., Polym. Chem. Ed., 16, 295 (1978).

[6] N. Geacintov, V. Stannett, and E. W. Abrahamson, Makromol. Chem., 36, 52 (1960).

[7] V. Stannett, Chem. Eng. News, 40(25), 57 (1962).

[8] S. G. Cohen and H. C. Haas, J. Am. Chem. Soc., 72, 3954 (1950).

[9] W. Deters and D. Huang, Faserforsch. Textiltech., 14(5), 183 (1963).

[10] C. H. Bamford and D. J. Lind, Proc. R. Soc. London, Ser. A, 302, 145 (1968).

[11] E. M. Arnett and M. A. Mendelsohn, J. Am. Chem. Soc., 84, 3821 (1962).

[12] E. M. Arnett and M. A. Mendelsohn, Ibid., 84, 3824 (1962).

[13] E. G. Kasting, H. Naarmann, H. Reis, and C. Berding, Angew. Chem. Int. Ed., 4, 322 (1965).

[14] N. Indicator and C. Linder, J. Polym. Sci., Part A-1, 5, 1083 (1967).

[15] R. Prabha and U. S. Nandi, J. Polym. Sci., Polym. Lett. Ed., 14, 19 (1976).

[16] B. N. Misra and C. S. Pande, J. Polym. Sci., Polym. Chem. Ed., 11, 2369 (1973).

[17] B. N. Misra, I. K. Mehta, and D. S. Sood, J. Macromol. Sci.-Chem., A14, 1255-1268 (1980).

[18] B. N. Misra, J. K. Jassal, R. Dogra, and D. S. Sood, Ibid., A14, 1061-1070 (1980).

[19] Krauze, Z. Anorg. Allg. Chem., 169, 286 (1928); R. Weinland and E. Gussmann, Ber. Dtsch. Chem. Ger., 42, 3888 (1909); Z. Anorg. Chem., 61, 157 (1960).

[20]   T. Morgan and H. D. Drew, J. Chem. Soc., 119, 1060 (1921).
[21]   C. H. Bamford and A. N. Ferrar, Proc. R. Soc. London, Ser. A,
       321, 425 (1971).