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Kazuo Sugiyama[a]; Tadao Nakaya[a]; Minoru Imoto[a]
[a] Faculty of Engineering, Osaka City University, Sumiyoshi-ku, Osaka, Japan

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Vinyl Polymerization. 274. Polymerization of Acrylonitrile Initiated by the System Tetramethyl Tetrazene and Co(II) Chloride

KAZUO SUGIYAMA, TADAO NAKAYA, and MINORU IMOTO

Osaka City University
Faculty of Engineering
Sugimoto-cho, Sumiyoshi-ku
Osaka, Japan

SUMMARY

The binary system of tetramethyl tetrazene (TMT) and Co(II) chloride was used as initiator of acrylonitrile (AN) in dimethylformamide. The initial rate of polymerization (R_p) was found to be expressed by

$$R_p = k[\mathrm{TMT}]^{0.62}\,[\mathrm{Co(II)\ chloride}]^{0.57}\,[\mathrm{AN}]^{2.00}$$

The polymerization was confirmed to proceed via a radical mechanism. The over-all activation energy for the polymerization was estimated as 15.1 kcal/mole. On the basis of these results and the product analysis of the reaction between the catalyst components in the absence of monomer, the initiation mechanism of the polymerization is discussed.

INTRODUCTION

Previous papers [1-5] in this series have indicated that the polymerization of some vinyl monomers with tetramethyl tetrazene (TMT) is accelerated by the addition of the small quantities of the oxidizing agents, such as acetic anhydride [1], benzyl chloride [2], dimethyl maleate [3], bromoacetic acid [4], and 1-chloro-2,4-dinitrobenzene [5]. We have also demonstrated that the initiating species for the polymerization is the dimethylamino radical derived from the redox pair. Fetter et al. [6] and Bull et al. [7] have reported that the reactions of TMT with metal complexes, such as alkyl aluminium [6] and cadmium chloride [7] result in the formation of the corresponding unique chelate compounds. In this connection, our interests were mostly directed to the catalytic activities of metal salts in admixture with TMT for the polymerization of vinyl monomers. The metal salts used were Co(II) chloride, Fe(II) chloride, Fe(III) chloride, Cu(I) chloride, Cu(II) chloride, and Ni(II) chloride. The TMT-Co(II) chloride and TMT-Cu(I) chloride systems were found to be very effective for the initiation of AN. This paper is mainly concenred with a kinetic study of the radical polymerization of AN in dimethylformamide (DMF) initiated by the TMT-Co(II) chloride system. In order to elucidate the initiation mechanism, the reaction between TMT and Co(II) chloride in the absence of monomer was also investigated.

EXPERIMENTAL

Materials

The $CoCl_2 \cdot 6H_2O$, $FeCl_2 \cdot nH_2O$, $FeCl_3 \cdot 6H_2O$, $CuCl$, $CuCl_2 \cdot 2H_2O$, $NiCl_2 \cdot 6H_2O$, and 1,1-dimethyl hydrazine were commercial. TMT was prepared by the oxidation of the 1,1-dimethylhydrazine with mercuric oxide, according to Bull et al. [7]. The acrylonitrile (AN), methyl methacrylate (MMA), styrene (St), and DMF were purified in usual manner and redistilled under a stream of nitrogen before use.

Polymerization Procedure

The required amounts of monomer and initiator were placed in a tube, cooled in a Dry Ice-methanol bath, and sealed in vacuo. The sealed tube was shaken in a thermostat maintained at a definite temperature. After polymerization for a given time, the content of the tube was poured into a large amount of methanol to precipitate the polymer. The rate of conversion was calculated from the weight of the dry polymer obtained.

Characterization of the Polymer

The chemical composition of the resulting polymer was determined from elemental analysis. The intrinsic viscosities (dl/g) of the polyacrylonitrile

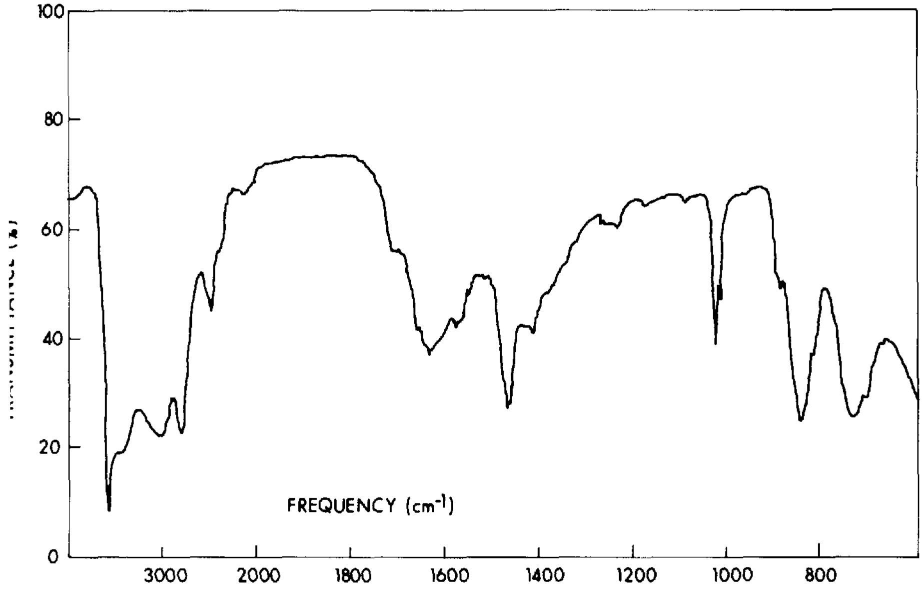


Fig. 1. Infrared spectrum of Co(II)dichloro-bis(N,N-dimethylamine).

were determined in DMF at 30°C, using an Ubbelohde viscometer. Following Houtz [8], the number-average molecular weights of polymers, M_n, were calculated from the intrinsic viscosity $[\eta]$ values.

$$[\eta]\ (\mathrm{dl/g}) = 1.75 \times 10^{-0.66} M_n$$

Reaction of TMT with Co(II)chloride

A mixture of 1.0 g of TMT and 1.0 g of $CoCl_2 \cdot 6H_2O$ in 10 ml of dry methanol was stirred at room temperature for 24 hr. The solvent was removed by distillation. The residue was filtered off and washed several times with dry methanol and dried to give 0.91 g of a dark green solid material which was very hygroscopic.

Analysis calculated for $CoCl_2 \cdot 4H_2O \cdot C_4H_{12}N_2$: N, 9.66, Found: N, 9.46.

The IR spectrum of the compound is shown in Fig. 1.

The typical absorption peaks for free OH group appeared at 2250 and 3550 cm^{-1}, and the characteristic absorption peaks for dimethylamino group appeared at 1020 and 2800 cm^{-1}. The band at 730 and 840 cm^{-1} were attributed to chlorine atom. Thus, this compound was identified as Co(II)dichlorobis(N,N-dimethylamine).

Furthermore, tetramethylhydrazine was also detected from the reaction mixture by gas chromatography.

RESULTS

Polymerization of AN Initiated by the Systems of TMT and Various Metal Chlorides

The results of the polymerization of AN by the systems of TMT and various metal chlorides are shown in Table 1. The value of conversion listed in Table 1 is free from that obtained by the polymerization initiated by TMT alone in the same conditions. Moreover, no evidence of polymerization was observed with the metal salt alone.

Table 1. Polymerization of AN Initiated by the Systems of TMT and Various Metal Chlorides in DMF at 80°C for 3 hr. [AN] = 4.56 moles/liter, [TMT] = [Metal Chloride] = 2.0 X 10^{-2} moles/liter

Metal chloride	Conversion (%)
$CuCl_2 \cdot 2H_2O$	None
$CuCl$	17.22
$FeCl_2 \cdot nH_2O$	None
$FeCl_3 \cdot 6H_2O$	None
$NiCl_2 \cdot 6H_2O$	0.97
$CoCl_2 \cdot 6H_2O$	16.72

As can be seen from Table 1, Co(II) chloride and Cu(I) chloride in admixture with TMT were very effective for the polymerization of AN, while Cu(II) chloride, Fe(II) chloride, Fe(III) chloride, and Ni(II) chloride lacked catalytic activities. Thus the polymerization of AN with the TMT-Co(II) chloride system was investigated in some detail.

Confirmation of Radical Mechanism

Bulk copolymerization of MMA with St initiated by the TMT-Co(II)

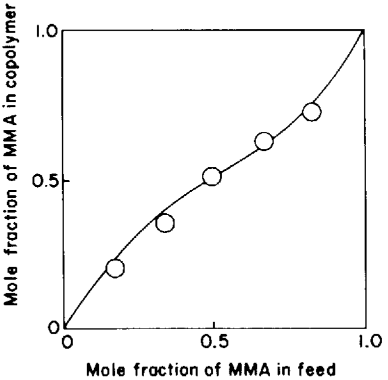


Fig. 2. Composition curve for the bulk copolymerization of MMA with styrene at 50°C for 4 hr. [TMT] = [Co(II) chloride] = 2.0 X 10^{-2} moles/liter.

chloride system was carried out at 50°C for 4 hr. Figure 2 shows the composition curve of the copolymer obtained, which is characteristic of a radical copolymerization. Hydroquinone was found to act as an inhibitor for the polymerization of AN initiated by the TMT-Co(II) chloride system, as shown in Fig. 3.

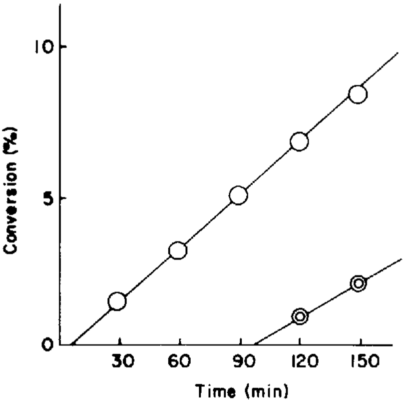


Fig. 3. Effect of hydroquinone on the polymerization of AN initiated by the TMT-Co(II) chloride system. [AN] = 4.56 moles/liter, [TMT] = [Co(II) chloride] = 2.0 X 10^{-2} moles/liter, at 75°C in DMF. (◎) [Hydroquinone] = 4.0 X 10^{-3} moles/liter; (○) without hydroquinone.

Table 2. Kinetic Data for the Polymerization of AN in DMF at 60°C for 3 hr

[AN] (moles/liter)	[TMT] × 10^2 (moles/liter)	[Co(II) chloride] × 10^2 ((moles/liter)	R_p × 10^5 (moles/liter · sec)	[η]	P_n
4.56	2.0	0.5	2.13	1.03	297
4.56	2.0	1.0	3.02	1.00	284
4.56	2.0	4.0	6.54	0.91	246
4.56	2.0	8.0	10.20	0.83	214
4.56	0.5	2.0	1.30	1.13	342
4.56	1.0	2.0	2.66	1.06	310
4.56	4.0	2.0	6.57	0.89	238
4.56	8.0	2.0	7.05	0.72	172
1.52	2.0	2.0	0.34	0.29	44
2.28	2.0	2.0	1.24	0.57	121
3.04	2.0	2.0	1.69	0.71	169
3.80	2.0	2.0	3.21	0.89	238
4.56	2.0	2.0	4.60	0.98	275

Based on the copolymerization of MMA with St and the inhibition effect of hydroquinone, the polymerization is undoubtedly a free radical process.

Kinetics of Polymerization

The homogeneous polymerization of AN initiated by the TMT-Co(II) chloride system was carried out in DMF at 60°C. The results are summarized in Table 2.

The kinetic data obtained in Table 2 are plotted in Figs. 4 and 5. Figure 4 shows that the initial rate of polymerization (R_p) was proportional to the 0.65 power of [TMT] and the 0.57 power of [Co(II) chloride], respectively.

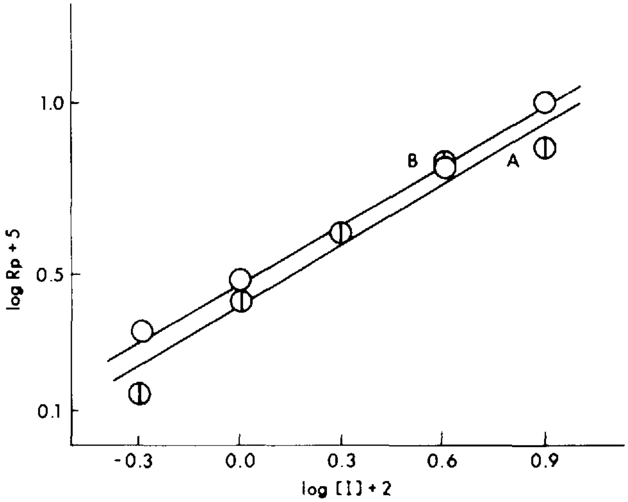


Fig. 4. Rate of polymerization (R_p) vs. concentration of the initiator system in the polymerization of AN with the TMT-Co(II) chloride system in DMF at 60°C. [AN] = 4.56 moles/liter. (A) [Co(II) chloride] = 2.0 × 10^{-2} moles/liter. [I] = [TMT] was varied. (B) [TMT] = 2.0 × 10^{-2} moles/liter. [I] = [Co(II) chloride] was varied.

Figure 5 shows that R_p is proportional to the 2.0 power of [AN]. Thus we obtain

$$R_p = k[\mathrm{TMT}]^{0.62}[\mathrm{Co(II)\ chloride}]^{0.57}[\mathrm{AN}]^{2.00} \tag{2}$$

where k is the rate constant.

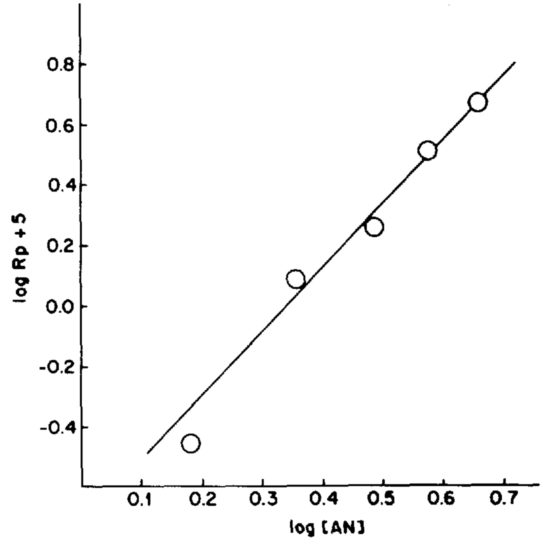


Fig. 5. Rate of polymerization (R_p) vs. concentration of AN in the polymerization of AN with the TMT-Co(II) chloride system in DMF at 60°C. [TMT] = [Co(II) chloride] = 2.0×10^{-2} moles/liter. [AN] was varied.

Estimation of Over-all Activation Energy

In order to estimate the over-all activation energy in the polymerization of AN initiated by the TMT-Co(II) chloride system, homogeneous polymerizations of AN were carried out in DMF, changing the temperature in the range 50 to 65°C.

By an Arrhenius plot of R_p vs. $1/T$, the over-all activation energy was estimated as 15.1 kcal/mole, as shown in Fig. 6.

Degree of Polymerization of the Polymers

The degree of polymerization of the resulting polymers was generally low, as shown in Fig. 7. As can be seen from the figure, the reciprocal of the number-average degree of polymerization, which was calculated from the intrinsic viscosity as described in the Experimental section, depends on the square root of the concentration of TMT and Co(II) chloride, respectively.

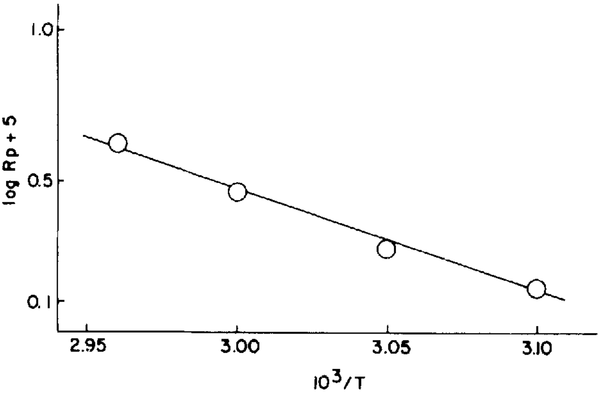


Fig. 6. Arrhenius plot of log R_p vs. $1/T$.

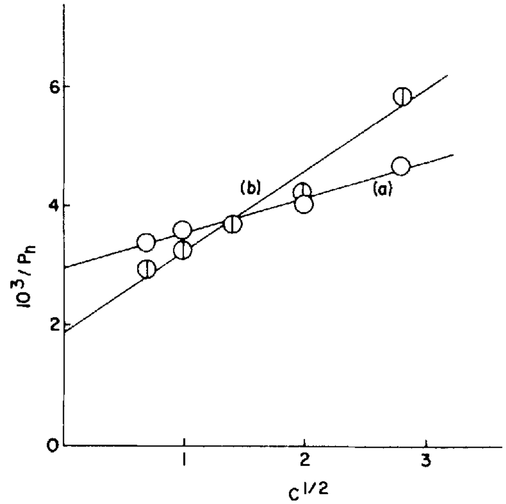


Fig. 7. Relationship between $1/P_n$ vs. $[TMT]^{1/2}$ or $[Co(II)\ chloride]^{1/2}$. (a): [AN] = 4.56 moles/liter, [TMT] = 2.0×10^{-2} moles/liter, C = [Co(II) chloride] was varied. (b): [AN] = 4.56 moles/liter, [Co(II) chloride] = 2.0×10^{-2} moles/liter, C = [TMT] was varied.

Chain Transfer Constant

The chain transfer constants for the initiator (I), monomer (M), and solvent (S) in the polymerization of AN initiated by the TMT-Co(II) chloride system were estimated by [9]

$$1/P_n = C_M + C_I[Cat]/[M] + C_S[S]/[M] + AR_p$$

The data for the polymerization of AN are summarized in Table 2. The value of A was estimated as 25.0 from the slope of the 1/P vs. R_p line. A linear relationship between the reciprocal of P_n and R_p is shown in Fig. 8.

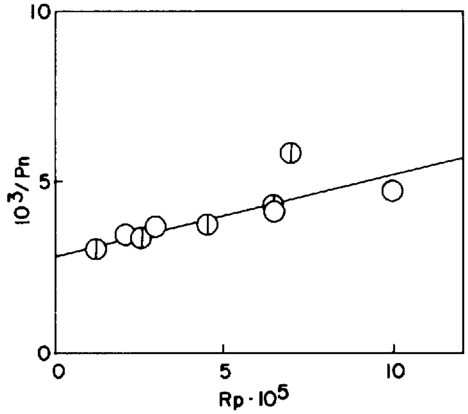


Fig. 8. Relationship between $1/P_n$ and R_p.

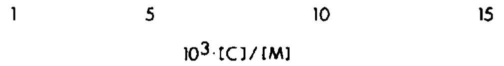


Fig. 9. Relationship between $1/P_n$ - AR_p and [Cat]/[M].

The chain transfer constant of the initiator was evaluated as 0.0 from the slope of the ($1/P_n$ - AR_p) vs. ([Cat]/[M]) plot, as shown in Fig. 9.

In a previous paper [4], the chain transfer constant of DMF, C_{DMF}, was reported as 1.28×10^{-3}.

Using this value, the chain transfer constant of AN, C_M, was calculated as 0.3×10^{-4}: [AN] = 4.56 moles/liter, [DMF] = 9.09 moles/liter.

Detection of Nitrogen in the Polymer

In order to obtain information regarding the active catalyst species in vinyl polymerization with the TMT-Co(II) chloride system, the bulk polymerization of MMA was carried out at 70°C, in which [MMA], [TMT], and [Co(II) chloride] were 5.6, 8.0×10^{-2}, and 8.0×10^{-2} moles/liter, respectively.

By elemental analysis of the resulting polymer, 0.34% nitrogen was detected.

Attempted Polymerization of AN Initiated by Co(II)dichlorobis(N,N-dimethylamine)

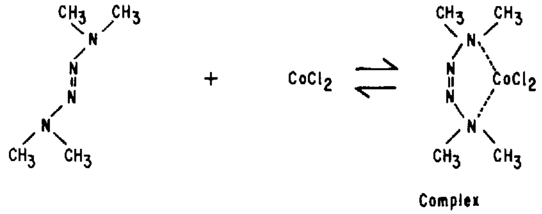
An attempt to polymerize AN by Co(II)dichlorobis(N,N-dimethylamine) at 75°C for 3 hr was completely unsuccessful. The finding indicates that Co(II)chlorobis(N,N-dimethylamine) has no catalytic activity for the polymerization of AN.

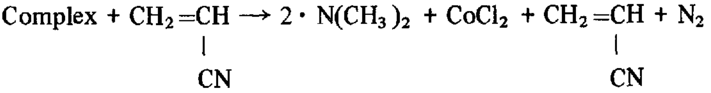
DISCUSSION

As mentioned above, Co(II) chloride and Cu(I) chloride were effective in promoting the polymerization of AN when used in conjunction with TMT, while no effect was observed when Cu(II) chloride, Fe(II) chloride, Fe(III) chloride, and Ni(II) chloride were used as promoters. The 15.1 kcal/mole for the over-all activation energy for the polymerization with TMT-Co(II) chloride system was lower than that by TMT alone (25.4 kcal/mole) as initiator and close to those for ordinary redox systems containing metal salts [10]. The polymerization was confirmed to proceed through a radical mechanism. The initial rate of polymerization of AN in DMF was proportional to $[\mathrm{TMT}]^{0.62}$, to $[\mathrm{Co(II)\ chloride}]^{0.57}$, and to $[\mathrm{AN}]^{2.00}$. The second-order dependence on monomer concentration may be attributed to a combination of the monomer participation in the initiation step and the participation of the relatively unreactive radical derived from the solvent (DMF) by chain transfer, as described in a former paper [3]. The rate of polymerization was proportional to nearly the same order of concentration of TMT and Co(II) chloride. The reaction of TMT with Co(II) chloride in the absence of AN resulted in the formation of Co(II)dichlorobis(N,N-dimethylamine). Moreover, the metal salt had no initiating activity to polymerize AN. These results suggest that TMT and Co(II) chloride react to form an unstable coordinate complex with the molar ratio 1:1 and then the minor part of the complex collides with AN to produce dimethyamino radical and the major part of the complex decomposes to form a Co(II)dichlorobis(N,N-dimethylamine).

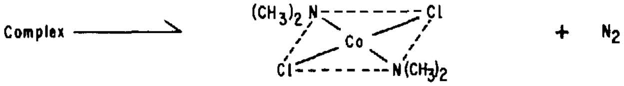
As described above, the evidence that the resulting polymer obtained by the polymerization of MMA in bulk using a large amount of TMT and Co(II) chloride involves the dimethylamino group on the end group of the polymer reflects that the initiating species is the dimethylamino radical. In the absence of monomer, the major part of the dimethylamino radical dimerises to form tetramethylhydrazine.

We propose the following set of reactions to account for our findings:

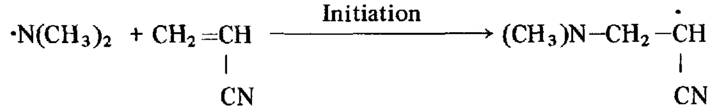




$$\text{Complex} + \underset{\substack{| \\ \text{CN}}}{\text{CH}_2{=}\text{CH}} \longrightarrow 2\cdot\text{N(CH}_3)_2 + \text{CoCl}_2 + \underset{\substack{| \\ \text{CN}}}{\text{CH}_2{=}\text{CH}} + \text{N}_2$$



$$2\ \cdot\text{N(CH}_3)_2 \longrightarrow (\text{CH}_3)_2\text{N{-}N(CH}_3)_2$$



$$\cdot\text{N(CH}_3)_2 + \underset{\substack{| \\ \text{CN}}}{\text{CH}_2{=}\text{CH}} \xrightarrow{\text{Initiation}} (\text{CH}_3)\text{N}{-}\text{CH}_2{-}\underset{\substack{| \\ \text{CN}}}{\overset{\bullet}{\text{CH}}}$$

REFERENCES

[1] T. Nakaya, Y. Maki, and M. Imoto, *Makromol. Chem.*, **113**, 131 (1968).

[2] T. Nakaya, Y. Maki, and M. Imoto, *Makromol. Chem.*, **125**, 161 (1969).

[3] K. Sugiyama, T. Nakaya, and M. Imoto, *Polym. J.*, **2**, 50 (1971).
[4] K. Sugiyama, T. Nakaya, and M. Imoto, *J. Polym. Sci.*, In Press.
[5] K. Sugiyama, T. Nakaya, and M. Imoto, *Polym. J.*, In Press.
[6] N. R. Fetter, F. E. Brinckman, Jr., and D. W. Moore, *Can. J. Chem.*, **40**, 2184 (1962).
[7] W. E. Bull, J. A. Seaton, and L. F. Audrieth, *J. Amer. Chem. Soc.*, **80**, 2516 (1958).
[8] R. C. Houtz, *Text. Res. J.*, **20**, 786 (1950).
[9] B. Baysal and A. V. Tobolsky, *J. Polym. Sci.*, **8**, 529 (1952).
[10] J. Barton and M. Lazar, *Makromol. Chem.*, **124**, 38 (1969).

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