Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Spontaneous Polymerization of Maleic Anhydride by Imidazole Derivatives. I

Mikio Arakl[a]; Kazuo Kato[a]; Toru Koyanagi[a]; Seishi Machida[a]
[a] Chemical Laboratory of Textile Fibers Kyoto, University of Industrial Arts and Textile Fibers Sakyo-ku, Kyoto, Japan

To cite this Article Arakl, Mikio , Kato, Kazuo , Koyanagi, Toru and Machida, Seishi(1977) 'Spontaneous Polymerization of Maleic Anhydride by Imidazole Derivatives. I', Journal of Macromolecular Science, Part A, 11: 5, 1039 — 1052
To link to this Article: DOI: 10.1080/00222337708061306
URL: http://dx.doi.org/10.1080/00222337708061306

J. MACROMOL. SCI.–CHEM., A11(5), pp. 1039-1052 (1977)

Spontaneous Polymerization of Maleic Anhydride by Imidazole Derivatives. I

MIKIO ARAKI, KAZUO KATO, TORU KOYANAGI, and
SEISHI MACHIDA

Chemical Laboratory of Textile Fibers
Kyoto University of Industrial Arts and Textile Fibers
Sakyo-ku, Kyoto, Japan

ABSTRACT

Maleic anhydride was spontaneously polymerized and decarboxylated by imidazole derivatives. The polymerization was found to occur through formation of a charge-transfer complex, although its exact role in the mechanism is uncertain. When 1-vinyl-2-methylimidazole was used, the vinyl group did not participate in the polymerization. By fractionating the polymer by gel filtration, a polymer containing no imidazole group was separated. Both homopolymer and copolymer of the vinylimidazole also caused maleic anhydride to polymerize. The chemical structure of the polymer was investigated.

INTRODUCTION

Recently there has been interest in the spontaneous polymerization of maleic anhydride in the presence of organic base [1-3]. The mechanism of the polymerization and the structure of the polymer have not yet been elucidated.

As part of the investigation of imidazole polymers, our attention was called to the charge-transfer complex of the imidazole with maleic anhydride, for the complexation is presumed to take part in the spontaneous polymerization.

Maleic anhydride was found to be polymerized spontaneously by the imidazoles, and the polymerization was accompanied by decarboxylation.

The polymer obtained was fractionated by gel filtration and the chemical structure was investigated.

EXPERIMENTAL

Materials

Maleic anhydride (MAH) was purified by vacuum distillation. The imidazole derivatives used in this experiment are summarized in Table 1.

Methyl vinyl imidazol (MVI) was purified by vacuum distillation under nitrogen after drying with potassium carbonate; bp 46.5-48.0°C/0.15 Torr MI, EI, and PI were purified by recrystallization from chloroform. EMI was prepared by ethylation of MI with diethyl sulfate by the method of Balaban [4]. Homopolymer of MVI was prepared by the method reported previously [5]. Copolymer of MVI with styrene was obtained by the method of Murahashi [6].

Polymerization

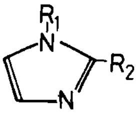
Polymerization was carried out in a three-necked flask equipped with a magnetic stirrer, Freidrich condenser with a calcium chloride guard tube, a gas inlet tube, and a thermometer. The solvent, MAH and a base were placed in the flask and deoxygenated by bubbling through nitrogen for 20 min with stirring before polymerization.

When MVZ, PI, and EMI were used, the copolymers were precipitated from chloroform. When MZ and EZ were used, the copolymers were precipitated from acetone.

Gel Filtration

A column consisting of a glass tube of 3 cm diameter and 21 cm length was packed with Sephadex G-10. A 100-mg portion of polymer

TABLE 1. Structure of Imidazole Derivatives



Imidazole derivatives	Substituent	
	R_1	R_2
MVI	$-CH=CH_2$	$-CH_3$
MI	H	$-CH_3$
EI	H	$-CH_2CH_3$
PI	H	$-C_6H_5$
EMI	$-CH_2CH_3$	$-CH_3$

was dissolved in 0.5 ml of water, and the solution was poured into the column. Eluant water was run through the column at a constant flow rate of 5.5 ml/hr and the eluates were collected in a fraction collector.

Characterization

Visible and ultraviolet spectra were obtained with a Hitachi-Perkin-Elmer Model 124 spectrophotometer.

Infrared spectra were taken on KBr disks with a Nippon Bunko Model 403G spectrophotometer.

Nuclear magnetic resonance spectra were taken with a Japan Electron Optics Model JNM-4H-100 spectrometer. The solvent used was either deuterium oxide or formic acid.

Number-average molecular weights were determined with a Hitachi-Perkin-Elmer Model 115 vapor-pressure osmometer.

RESULTS AND DISCUSSION

Visible Spectra of Mixture of MAH and Imidazole Derivative in Chloroform

Upon addition of a dilute chloroform solution of imidazole derivative such as MVI, MI, or EI to the MAH solution, the mixture became

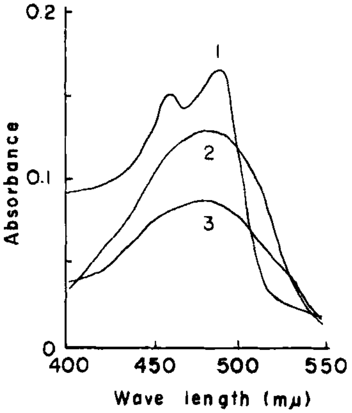


FIG. 1. Absorption spectra of imidazole derivative-MAH mixtures: (1) MVI-MAH; (2) MI-MAH; (3) EI-MAH.

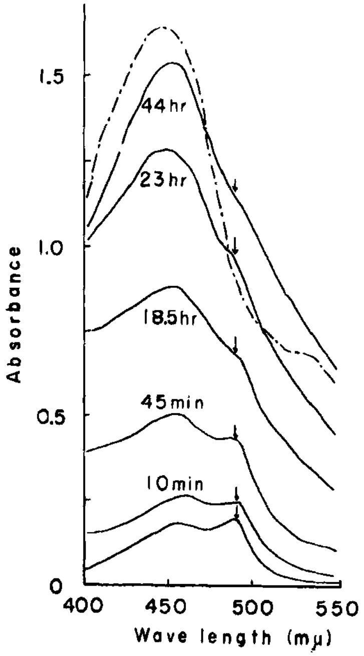


FIG. 2. Absorption spectra of MVI-MAH mixtures (spectrum change with time) and of the polymerization solution of MAH with AIBN: (—) MVI-MAH; (-·-) polymerization solution of MAH.

yellowish or reddish purple. The visible spectrum of the reaction solution showed absorbance at 460-490 nm. When the solution was allowed to stand, the absorbance changed as shown in Fig. 1. The increase in absorbance at 450-460 nm is larger than that at 489 nm, and after a long time the absorption at 489 nm became undistinguishable. The solution became turbid and the polymer precipitated after a period of time. The peak at 450 nm in the spectrum is assigned to the MAH unit, because a similar peak was given by poly(maleic anhydride) prepared by means of radical polymerization initiated with azobisisobutyronitrile, as shown in Fig. 2.

Spectra of chloroform solutions of MVI-MAH, MI-MAH, and EI-MAH systems were followed at 25°C by using the wavelengths at 489 and 480 nm. In each solution, a maximum absorbance was measured at approximately 1:1 molar ratio. In the chloroform solution of MVI-MAH system the equilibrium constant of the complex at 20°C was determined by the Benesi-Hildebrand equation as 1.5 l/mole.

MI and EI appeared to form complexes with MAH at a 1:1 molar ratio more readily than MVI, because their solutions became colored at lower concentrations. The MVI-MAH complex has, in other words, the smallest equilibrium constant under the conditions of our experiments.

The coloration mentioned above is considered attributable to the charge-transfer complex, though a formation of betaine has been proposed by some investigators [7, 8].

Polymerization

Upon mixing of the concentrated chloroform solutions of MVI and MAH, the colorless solution turned reddish violet and reddish brown, and carbon dioxide was generated violently for a few minutes at concentrations over a few mole per liter.

The reaction product is brown and soluble only in polar solvents. These phenomena are similar to those observed by Hallensleben [9] in whose experiment vinylpyridine was used in place of MVI as a catalyst. When 10 mole % of MVI was added to a MAH melt at about 100°C without solvent, the decarboxylation was explosive and the reaction went to completion instantaneously. The result of the reaction are summarized in Tables 2 and 3. It is shown in Table 2 that both yield and molecular weight of the reaction product are the highest when equimolar quantities of reactants are used. With increasing amounts of MVI reacted, the molecular weight decreases and the nitrogen content approaches 13.6%, the calculated value for the 1:1 complex.

TABLE 2. Polymerization of MAH with MVI under Various Conditions

Expt.	Molar ratio MVI/MAH	Evolved CO_2 (%)[a]	Yield (%)[b]	MW of the product	Elementary analysis			Polymerization conditions[c]
					C (%)	H (%)	N (%)	
V-1	9:1	9.2	6.7	182	52.51	5.31	11.48	A
V-2	4:1	14.5	9.6	212	52.90	4.94	9.08	A
V-3	2:1	18.3	12.3	272	52.86	4.80	9.30	A
V-4	1:1	17.5	34.6	353	52.96	4.73	7.69	A
V-5	1:2	10.2	19.2	311	52.38	4.32	6.13	A
V-6	1:9	3.8	5.6	296	51.97	4.41	6.03	A
V-7	1:19	-	65.5	340	44.80	3.88	3.88	B
V-8	1:19	3.1	42.5	520	46.62	3.90	3.55	C
V-9	1:1	16.5	85.6	280	51.95	4.70	7.86	C
V-10	1:1	-	57.0	370	49.66	4.47	7.07	D

[a] Molar per cent based on MAH used.

[b] Weight per cent based on total reactants.

[c] Polymerization conditions: (A) solvent, $CHCl_3$, 50° C, 4 hr, total monomer 2.0 mole/liter, precipitant $CHCl_3$; (B) solvent $CHCl_3$, 60° C, 4 hr, total monomer 4.0 mole/liter, precipitant $CHCl_3$; (C) solvent DMF, 25° C, 24 hr, total monomer 4.01 mole/liter, precipitant $CHCl_3$; (D) solvent benzene, room temperature, 65 hr, total monomer 1.6 mole/liter, precipitant $CHCl_3$.

TABLE 3. Polymerization of MAH with Imidazole Derivatives

Expt.	Imidazole derivative	Molar ratio imidazole: MAH	Evolved CO_2 (mole %)[a]	Yield (%)[b]	MW of product	Elementary analysis			Polymerization conditions
						C (%)	H (%)	N (%)	
M-1	MI	9:1	6.8	-	137	51.37	5.78	19.85	A[c]
M-2		4:1	18.6	-	164	51.12	5.66	17.99	
M-3		1:1	20.3	86.6	198	50.81	5.88	14.58	
M-4		1:4	11.5	-	193	49.48	4.77	9.34	
M-5		1:9	23.6	23.6	180	48.05	4.56	7.57	
E-1	EI	9:1	9.8	-	158	50.34	5.75	19.85	A[c]
E-2		4:1	5.6	-	191	52.42	5.81	14.14	
E-3		1:1	22.5	-	201	54.76	6.01	14.38	
E-4		1:4	9.0	-	185	58.01	4.09	8.87	
E-5		1:9	5.7	-	181	51.08	5.04	9.23	
EM-1	EMI	1:19	12.1	42.4	490	-	-	-	d

[a] Based on moles MAH used.

[b] By weight, based on total reactants.

[c] See in Table 2.

[d] Solvent DMF, 50°C; 4 hr, total monomer, 2 mole/liter, precipitant chloroform.

Similar reactions were carried out by using MI and EI as the catalyst. The results obtained are shown in Table 3. It is shown in Table 3 that both the amount of carbon dioxide generated during the reaction and the molecular weight of the reaction product are maximum when equimolar quantities of reactants are used. When the MI or EI is reacted with MAH in a 1:1 molar ratio, the nitrogen content in each reaction product is near that calculated for the 1:1 complex.

The relation between molar ratio of MAH to imidazole derivatives in the reaction and molecular weight of the reaction product is shown in Fig. 3. In the reaction of MVI, the molecular weight of the product is higher than 206, the calculated value for the 1:1 complex of MVI and MAH. At a fraction of MAH higher than 0.5, the molecular weight of the product decreases. These facts suggest that MAH has been polymerized by the 1:1 complex. The results of the reactions of MVI with MAH under the various conditions shown in Table 2 also support this consideration.

The polymerization was not affected by radical inhibitors, as shown in Table 4.

The conversion in the solution polymerization increases with increasing dielectric constant of the solvent, as shown in Table 5. The electroconductivity was found to increase with initiation of the

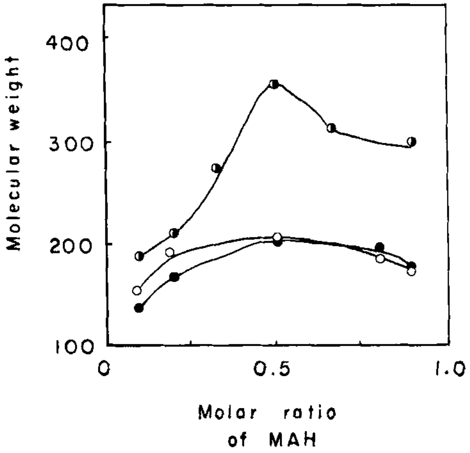


FIG. 3. Relation between molar ratio of MAH: imidazole derivatives and molecular weight of the polymerization products: (◑) MVI/MAH; (●) MI/MAH; (○) EI/MAH.

TABLE 4. Effect of Radical Inhibitors on the Polymerization of MAH with MVI[a]

Expt.	Additive	Yield (%)	MW of the product
2-1	None	55.3	350
2-2	DPPH[b]	57.2	370
2-3	Hydroquinone	59.2	400

[a] Polymerization conditions: 40° C, 26 hr, total monomer, 0.8 mole/liter, molar ratio MVI/MAH = 1:1.

[b] 1,1-Diphenyl-2-picrylhydrazyl.

TABLE 5. Effect of the Solvent on the Polymerization of MAH with MVI[a]

Expt.	Solvent	Dielectric constant	Yield (%)	MW of the product	Elementary analysis C (%)	H (%)	N (%)
3-1	Chloroform	4.6	27.0	290	-	-	-
3-2	Acetone	21.3	40.3	340	51.08	4.18	6.57
3-3	Nitrobenzene	34.8	69.4	410	48.86	4.06	6.87
3-4	Acetonitrile	36.7	68.8	330	50.81	4.71	9.04
3-5	Dimethyl sulfoxide	45.0	74.6	410	50.75	4.34	7.20

[a] Polymerization conditions: 30° C, 3 hr, total monomer 1.5 mole/liter, molar ratio MVI/MAH = 1:2.

polymerization. These facts show that the polymerization is ionic. The polymerization of MAH with homopolymer of MVI and copolymer of MVI with styrene were also investigated. The results obtained are shown in Table 6. It was calculated from the weight increase that two to three molecules of MAH were polymerized by each MVI unit in the homopolymer, and four molecules of MAH were polymerized by that in the copolymer. The resulting polymer is light yellow and is insoluble in water, as opposed to the polymer produced by the reaction of MAH with monomer MVI. The insolubility is perhaps due

TABLE 6. Polymerization of MAH with MVI Polymers[a]

Expt.	Polymer	Weight of added polymer (g)	Temp (°C)	Time (hr)	Yield (g)	Weight increase (%)[b]
PV-1	MVI-homopolymer	0.55	25	24	1.35	250
PV-2	MVI-homopolymer	0.10	60	4	0.35	310
PV-3	MVI-styrene copolymer[c]	0.10	60	4	0.22	220

[a] MAH 9.4 g; solvent DMF (25 ml).
[b] By weight based on used polymer.
[c] Containing 47.6 mole % of styrene units.

to the crosslinking between carboxyl and imidazole group by salt formation, which is supported by the data of IR spectrophotometry.

Structure of Polymer

The IR spectrum of the reaction product of MAH with MVI (expt. V-2~3 in Table 3) is given in Fig. 4a. The absorptions at 1845 and 1775 cm^{-1} are assigned to the carbonyl stretching of the five-membered anhydride ring, and the absorptions at 1240 and 1720 cm^{-1} are assigned to the ether and carbonyl stretching, respectively. The spectrum shows the presence of a band due to the vinyl group. As the vinyl group is also detected in the NMR spectrum, the polymerization proved to be independent of the vinyl group of MVI. The polymer obtained from the reaction of MAH with MVI (expt. V-9) was fractionated by the gel-filtration method. The polymer was separated into three fractions. The analytical data of the fractions are shown in Table 7, and the IR spectra of fractions B and C are shown in Fig. 4b and 4c, respectively. Fractions A and B contain few MVI units, for their nitrogen contents are less than 0.51%. The spectra show that the anhydride rings have been hydrolyzed to give carboxyl groups. Both absorptions at 1630 cm^{-1} in curve 4b and 1590 cm^{-1} in curve 4c are assigned to the conjugated C=C bond conjugated with a C=O bond. This means that a longer chain of the polymer (fraction C) has longer conjugation and causes a shift in the absorption towards lower wavenumber.

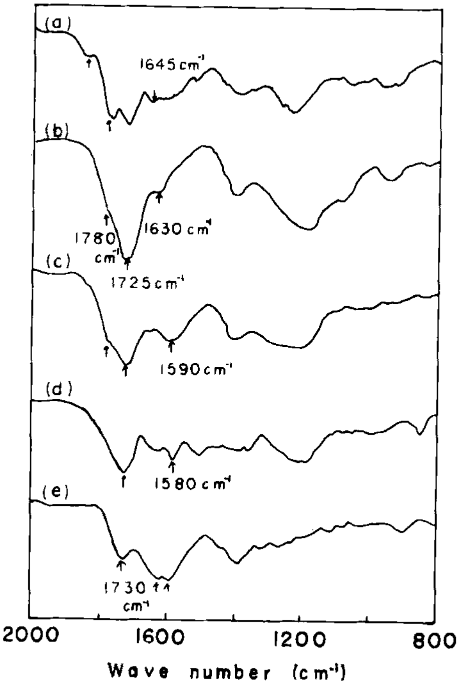


FIG. 4. Infrared spectra of the polymerization products: (a) expt. 3-2; (b) expt. V8 fractionated polymer (MW 450); (c) expt. V8 fractionated polymer (MW 860); (d) expt. PV-2; (e) expt. M3.

TABLE 7. Gel Filtration of the Product (Expt. V-9)

Fraction	Molecular weight	Elementary analysis		
		C (%)	H (%)	N (%)
A	300	52.30	5.43	11.97
B	450	41.35	3.43	0.51
C	860	42.35	3.76	0.32

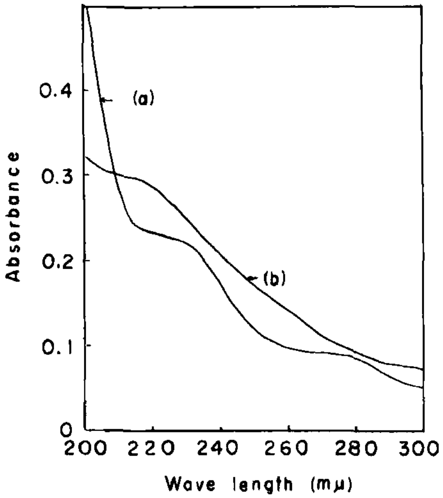


FIG. 5. UV spectra of the fractionated polymers (expt. V-9): (a) MW 860; (b) MW 450.

The UV spectra of fractions B and C are shown in Fig. 5. The absorbance at 210-230 nm assigned to the conjugated enone group is shifted towards long wavelength with increasing molecular weight.

In the NMR spectrum, a peak at 1.2 ppm assigned to the methylenic protons of cyclopentanone structure was found in the fraction B, as shown in Fig. 6. The spectrum showed a peak assigned to methine protons of the main chain at 3.6 ppm, but no conjugated olefinic protons were not distinguished.

The IR spectrum of the reaction product of MAH with poly-MVI (expt. PV-2) is shown in Fig. 4d. The absorption at 1580 cm^{-1} is assigned to carboxylate ion, for it appears in the spectra of the salt composed of MVI and maleic acid. Figure 4e shows the IR spectrum of the reaction product of MAH with MI (expt. M-3). The absorption at 1620 and 1580 cm^{-1} assigned to the conjugated structure between carbonyl and ethylenic group is stronger than that at 1730 cm^{-1} assigned to the carbonyl group. The cyclic anhydride structure is not found in the absorption curve. It is considered from the spectrometry that the MAH unit in the molecular chain of the reaction product of MAH with MI or EI is opened to a linear structure, rather than being cyclic.

As to the molecular structure of the polymer prepared by the spontaneous polymerization of MAH catalyzed by organic bases, the following types shown as I-III have been proposed previously [1-3].

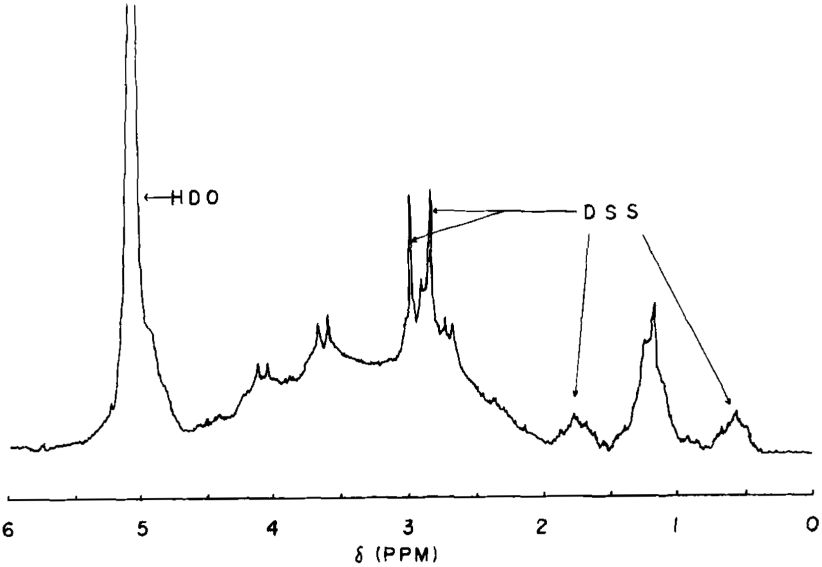
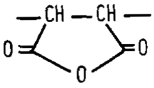
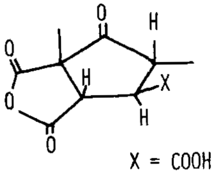


FIG. 6. NMR spectrum of the fractionated polymer (expt. V-9), MW 450.



I



II

$$\text{-CO-CH=CH-CO-O-CO-CH=CH-CO-O-} \xrightarrow{-CO_2} \text{-CO-CH=CH-CO-CH=CH-CO-O-}$$

III

Structure III has been already confirmed [9]. The polymer obtained in the present experiment is considered to have these three structures in the molecular chain, and the presence of a structure other than those may be presumed.

The mechanism of the catalytic action of imidazole derivatives for the spontaneous polymerization of MAH is not yet clear in detail. But the nitrogen atom of 3-position in the imidazole ring is at least presumed to participate in the reaction on the basis of the following facts. EMI reacts with MAH in a similar manner as MVI, and the catalytic effect is scarcely shown by PI, perhaps as a result of steric hindrance of the phenyl group to the nitrogen atom at the 3 positions in the imidazole ring. It is thought that the imidazole derivatives first forms a 1:1 complex with MAH and then the complex initiates the polymerization of MAH, while the complexes react with each other. This consideration is strongly supported by the fact that the product which is considered to be produced from each reaction is separated by the gel-filtration of the reaction mixture.

The stoichiometry of the complex and the polymerization of MAH by the copolymer-containing imidazole derivatives are still under investigation.

REFERENCES

[1] D. Braun, I. A. Aziz El Sayey, and J. Pomakis, Makromol. Chem., 142, 249 (1969).

[2] I. Schopov, Makromol. Chem., 137, 293 (1970).

[3] H. Zweifel, J. Lälinger, and T. Völker, Makromol. Chem., 153, 125 (1972).

[4] I. E. Balaban and F. L. Pyman, J. Chem. Soc., 125, 156 (1924).

[5] S. Shimada and K. Hattori, Yuki Gosei Kyokai Shi, 25, 324 (1967).

[6] S. Murahashi, S. Nozakura, A. Umehara, and K. Obata, Kobunshi Kagaku, 21, 625 (1964).

[7] A. Shönberg and F. A. Lsmail, J. Chem. Soc., 1940, 1374.

[8] E. Rucinschi, A. Caraculacu, and I. Zugravescu, Rev. Roum., 1968, 13 (5), 637; Chem. Abstr., 70, 1978, (1969).

[9] M. L. Hallensleben, Makromol. Chem., 142, 303 (1971).

Accepted by editor December 25, 1976
Received for publication December 31, 1976