

Stereospecific Polymerization of *o*-Methoxy- α -methylstyrene

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(Received February 28, 1970)

ABSTRACT: *o*-Methoxy- α -methylstyrene (*o*-MeO- α -MeSt) was polymerized under various conditions using BF_3OEt_2 , TiCl_4 , SnCl_4 , EtAlCl_2 , *n*-butyllithium (*n*-BuLi), or Na-naphthalene as catalysts, and methylene chloride, *n*-heptane, toluene, or tetrahydrofuran (THF) as solvents. Generally poly(*o*-MeO- α -MeSt) was formed below -30°C . The cationic polymerizations proceeded more rapidly than the anionic ones, which gave polymer only in a polar solvent such as THF. α -Methylstyrene (α -MeSt) was also polymerized for comparison with the tacticity of poly(*o*-MeO- α -MeSt). The stereoregularity of the polymer was investigated by NMR spectroscopy. Assignments of the α -methyl resonances of the polymers were made on the basis of the methylene resonances. In the NMR spectrum of poly(*o*-MeO- α -MeSt), the methyl groups showed three peaks at 4.45, 4.80, and 5.35 ppm on the high-field side from methylene chloride used as an internal standard; the peaks were assigned to isotactic (I), heterotactic (H), and syndiotactic (S) triad sequences with increasing magnetic field. The polymer obtained at -78°C from the anionic or cationic catalyst showed an S content higher than 74%, and the content decreased with an increasing polymerization temperature. The tacticities of the polymers formed in the cationic polymerizations depended only slightly on the catalyst and the solvent. The stereospecificity in the cationic polymerization was very similar to that of α -methylstyrene (α -MeSt) reported by Ohsumi, *et al.*,¹ whereas considerably different results were obtained in the anionic polymerization.

KEY WORDS Stereospecific Polymerization / *o*-Methoxy- α -methylstyrene / NMR / Boron Trifluoride / *n*-Butyllithium / α -Methylstyrene /

It has been reported that *o*-methoxystyrene (*o*-MeOSt) formed a crystalline isotactic polymer in a nonpolar solvent by *n*-BuLi,² and that the ether group of the monomer greatly affected the reactivity of the monomer.³ In the present study, *o*-MeO- α -MeSt was polymerized under various reaction conditions, and the stereoregularity of the polymer was determined by NMR spectroscopy in comparison with that of poly(α -MeSt). The results obtained were correlated with those of the stereospecific polymerization of α -MeSt which had been investigated by several groups.^{1,4-7} *o*-MeO- α -MeSt was copolymerized with styrene and isoprene by *n*-BuLi in order to determine the reactivity of this monomer in the anionic polymerization.

EXPERIMENTAL

Materials

o-MeO- α -MeSt was synthesized by dehydrating

dimethyl(2-methoxyphenyl)carbinol over acid potassium sulfate at $230-240^\circ\text{C}$. The carbinol was prepared by the reaction of *o*-methoxyphenylmagnesium bromide with acetone. The crude monomer obtained was fractionally distilled, and then the fraction of bp $62-63^\circ\text{C}$ (3 mm) was dried over lithium aluminum hydride, followed by redistillation. $n_D^{20}=1.5339$. No impurity was detected by gas chromatography and NMR spectroscopy.

Isoprene, styrene, and α -MeSt purified by the usual method were distilled from lithium aluminum hydride before use.

Methylene chloride, *n*-heptane, toluene, and THF were purified in the usual manner, and then the solvents were distilled in vacuo in the presence of appropriate drying agents such as *n*-BuLi, calcium hydride, or Na-naphthalene, just before use.

BF_3OEt_2 , EtAlCl_2 and SnCl_4 were used as

toluene solutions; TiCl_4 as an *n*-heptane solution.

n-BuLi was prepared from *n*-butyl chloride and metallic lithium in *n*-heptane.⁸ Na-naphthalene was prepared in THF.

Polymerization

The polymerization was carried out under dry nitrogen in a glass ampoule which had been dried by heating with a gas torch in vacuo. A purified solvent and a monomer were first transferred with syringes to the ampoule immersed in a thermostat. After the mixture reached thermal equilibrium, a catalyst was added with a syringe and then the ampoule was sealed. The polymerization was terminated by the addition of a small amount of methanol. The polymer was then precipitated in a large amount of methanol, filtrated, washed, and dried.

Measurement

The NMR spectrum was measured with a JNM-4H-100 Spectrometer at 100 MHz in chloroform at 60°C. Methylene chloride was used as an internal standard, high field shifts being shown as positive values.

The solution viscosity of the polymer was determined in toluene at $30.00 \pm 0.03^\circ\text{C}$; the concentration was 0.50 g/dl.

The X-ray diffraction was taken with a Rigakudenki 4001 diffractometer using CuK_α radiation.

RESULTS

Assignments of NMR Spectra

The NMR spectra of poly(α -MeSt) are shown in Figure 1. Three different assignments of the methyl resonance of poly(α -MeSt) to the tactic triads have been reported,⁴⁻⁷ but no conclusion has yet been reached. A correct assignment may also be supported on the basis of the shape of the methylene resonance of poly(α -MeSt), when the meso (m) and racemic (r) protons are AB quartet and A_2 singlet respectively. This interpretation has already been made by Ramey, *et al.*,⁶ who assigned the methyl peaks to *H*, *I*, and *S* with increasing magnetic field. This assignment, however, appears to be incomplete, as stated in their recent paper.⁹ In the present paper, we also have tried to assign methyl resonances on the assumption that the methylene

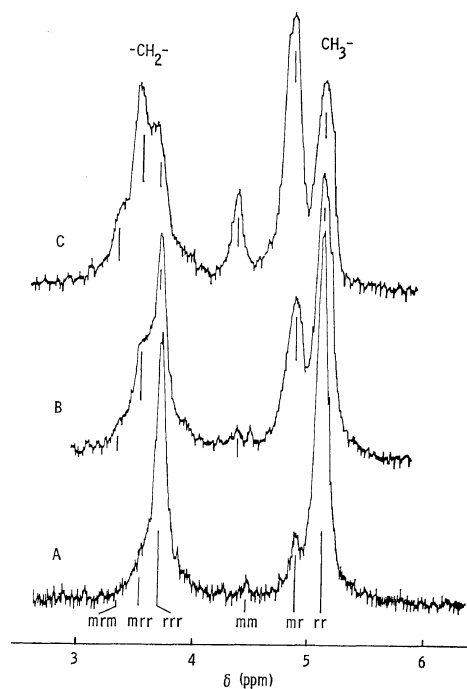


Figure 1. NMR spectra of poly(α -MeSt) (internal standard, CH_2Cl_2): (A) in toluene by EtAlCl_2 at -78°C , (B) in bulk by *n*-BuLi at 0°C , (C) in THF by Na-naphthalene at -78°C .

peaks show splitting by tetrad sequences. The intensities of the six tetrad sequences of the meso and racemic protons can be anticipated from those of the methyl resonances,^{10,11} since the usual cationic and anionic polymerizations of α -MeSt obeyed Bovey's "single σ " process.^{1,4} If the methyl peak at the highest field in Figure 1 A corresponds to *I*, the methylene resonance will be more complicated, because a greater part of the methylene proton should be meso. On the other hand, if the methyl peak corresponds to *S*, the shape of the methylene peak may resemble that of the methyl resonance as shown in Figure 1, because the portion of the meso methylene is small and the intensity ratio $\text{mrm} : \text{mrr} : \text{rrr}$ should be $\text{mm} : \text{mr} : \text{rr}$. The shape of the methylene resonance in Figure 1 A seems to be most reasonable, if the highest methyl peak is *S*. The methylene peaks in Figures 1B and 1C also seem to be interpreted as an overlap of a triplet of racemic protons and a multiplet of meso ones, which could not

Polymerization of *o*-Methoxy- α -methylstyrene

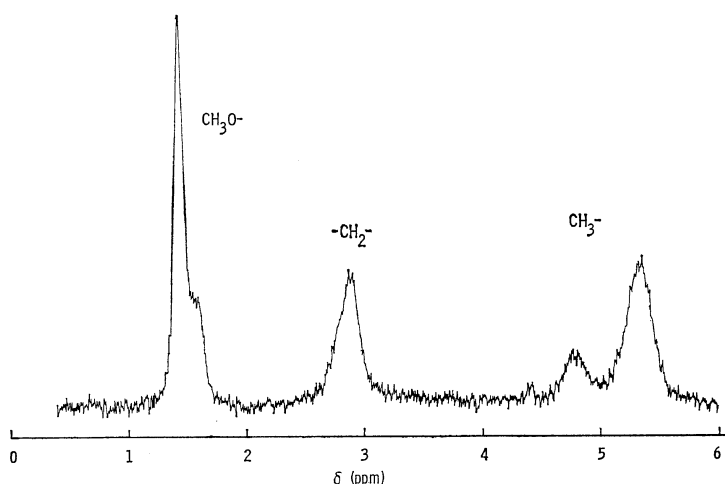


Figure 2. NMR spectrum of poly(*o*-MeO- α -MeSt); internal standard, CH₂Cl₂.

be assigned because of their complexity. Then, we assigned the methyl peaks to *I*, *H*, and *S*, with increasing magnetic field, as first reported by Brownstein, Bywater, and Worsfold.⁴ Ramey, *et al.*,⁹ assigned the tetrad sequences on the basis of the NMR spectrum measured at 220 MHz. Their assignment seems to be a little different from that shown in Figure 1, but the assignment of the methyl resonance was in the same order as that shown in the present paper.

The NMR spectrum of poly(*o*-MeO- α -MeSt) prepared by means of Na-naphthalene in THF at -30°C is shown in Figure 2. From the chemical shifts and the intensity ratio of the peaks, the methoxy, methylene, and methyl resonances were assigned to the peaks at 1.45, 2.9, and 4.45–5.35 ppm, respectively, on the high-field side from methylene chloride. (The peak of methylene chloride appeared at δ 5.27 ppm from tetramethylsilane in chloroform.) The methyl resonance was also split into three groups at 4.45, 4.80, and 5.35 ppm, as in the NMR spectrum of poly(α -MeSt) (Figure 1), in which the methyl were observed at 4.35, 4.84, and 5.10 ppm. Similar positions of these methyl splittings may indicate that the corresponding peaks of poly(*o*-MeO- α -MeSt) and poly(α -MeSt), for example, the ones at 5.35 and 5.10 ppm respectively, have the same triad sequences. However, the methoxy resonance was not split so clearly as that of poly(*o*-MeOSt),² but two peaks

were always observed at 1.42 and 1.55 ppm. The fraction of the former in the two peaks was nearly consistent with that of the peak at 5.35 ppm in the above three peaks. One of the three methoxy resonances may overlap that at 1.55 ppm. The relationship between the α -methyl and methylene resonances was also similar to that of poly(α -MeSt) described in Figure 1. In consequence the same assignment was given to this polymer.

Polymerization

The results of the polymerizations by BF₃OEt₂ in methylene chloride and toluene are shown in Tables I and II, respectively. Although no polymer insoluble in methanol was formed at 0°C , it was below -30°C that the polymer was

Table I. Cationic polymerization of *o*-MeO- α -MeSt in methylene chloride by BF₃OEt₂^a

Temp, $^{\circ}\text{C}$	Time, hr	Yield, %	Tacticity, %			$[\eta]$, dl/g
			<i>I</i>	<i>H</i>	<i>S</i>	
0	24.0	0	—	—	—	—
-30	24.0	28.2	30 ^c	—	70 ^c	0.04
-45	48.0	71.0	3	13	84	0.14
-78	24.0	92.2	1	9	90	0.51
-95^b	6.0	98.8	0	8	92	—

^a Monomer, 1.0 ml; solvent, 3.0 ml; catalyst, 0.05 mmol.

^b Catalyst, EtAlCl₂, 0.05 mmol.

^c Determined from the methoxy resonance.

obtained. The polymer yield, the fraction of *S*, and the intrinsic viscosity of the polymer were increased by decreasing the polymerization tem-

perature, except for the yield in toluene at -78°C . Although the tacticities of the polymers formed at -30°C were determined from the methoxy resonance, they could not be determined from the peaks of the methyl resonances, because these peaks overlapped on other peaks which may be due to the end group of a low-molecular-weight polymer. In the polymerization in *n*-heptane the polymer was precipitated during the reaction. All of the polymers obtained were softened at $230\text{--}280^{\circ}\text{C}$; and it was found the higher the degree of tacticity the higher was the softening point.

The effects of the catalysts were studied in toluene at -78°C . The results are collected in Table III. The order of the catalytic activity was $\text{TiCl}_4 > \text{SnCl}_4 > \text{EtAlCl}_2 > \text{BF}_3\text{OEt}_2$, and the fraction of *S* seemed to increase in the reverse order. In the initial stage of the reaction a red color appeared, the order of the intensity being the same as that of the catalytic activity. It was found that the tacticity of poly(α -MeSt) prepared under the same reaction conditions was nearly equal to that of poly(*o*-MeO- α -MeSt).

Table IV shows the results of the anionic polymerizations in THF by means of *n*-BuLi and Na-naphthalene. The rate of polymerization was very slow in comparison with that of α -MeSt; the polymer was obtained only at low temperature and at a high concentration of the monomer. The stereoregularity was slightly lower than that in the cationic polymerization. The tacticity of poly(α -MeSt) prepared under the same conditions was much lower than that of the corresponding poly(*o*-MeO- α -MeSt). The anionic polymerization in bulk or in toluene

Table II. Cationic polymerization of *o*-MeO- α -MeSt in toluene by $\text{BF}_3\text{OEt}_2^a$

Temp, $^{\circ}\text{C}$	Time, hr	Yield, %	Tacticity, %			$[\eta]$, dl/g
			<i>I</i>	<i>H</i>	<i>S</i>	
0	19.5	0	—	—	—	—
-30	39.0	41.4	23 ^c	—	77 ^c	0.04
-45	48.0	68.3	1	10	89	0.10
-78	24.0	42.3	1	7	92	0.29
-30^b	72.5	36.7	0	14	86	0.06
-78^b	72.5	7.5	2	20	78	0.12

^a Monomer, 1.0 ml; solvent, 3.0 ml; catalyst, 0.05 mmol.

^b Solvent, *n*-heptane.

^c Determined from the methoxy resonance.

Table III. Cationic polymerization of *o*-MeO- α -MeSt in toluene by various catalysts^a

Catalyst	mmol	Yield, %	Tacticity, %			$[\eta]$, dl/g
			<i>I</i>	<i>H</i>	<i>S</i>	
TiCl_4	0.050	80.9	4	16	80	0.21
SnCl_4	0.049	64.1	3	14	83	0.32
AlEtCl_2	0.050	55.0	2	14	84 ^c	0.37
BF_3OEt_2	0.053	0.4	—	—	—	—
$\text{BF}_3\text{OEt}_2^b$	0.053	42.3	1	7	92	0.29

^a Monomer, 1.0 ml; solvent 3.0 ml; time, 1.0 hr; temp, 78°C .

^b Time, 24.0 hr.

^c Tacticity of poly(α -MeSt) prepared under the same reaction conditions was *I* (3%), *H* (14%), and *S* (83%).

Table IV. Anionic polymerization of *o*-MeO- α -MeSt in THF^a

Catalyst	mmol	Temp, $^{\circ}\text{C}$	Time, day	Yield, %	Tacticity, %			$[\eta]$, dl/g
					<i>I</i>	<i>H</i>	<i>S</i>	
<i>n</i> -BuLi	0.038	0	11	0	—	—	—	—
<i>n</i> -BuLi	0.038	-30	4	4.6	4	28	68	—
<i>n</i> -BuLi	0.042	-78	23	17.7	5	21	74	0.04
Na-naphthalene	0.046	0	2	0	—	—	—	—
Na-naphthalene	0.046	-30	16	23.9	2	22	76	0.12
Na-naphthalene	0.046	-78	16	38.2	2	20	78 ^b	0.29

^a Monomer, 0.8 ml; solvent, 0.8 ml.

^b Tacticity of poly(α -MeSt) prepared under the same reaction conditions was *I* (11%), *H* (48%), and *S* (41%).

Polymerization of *o*-Methoxy- α -methylstyrene

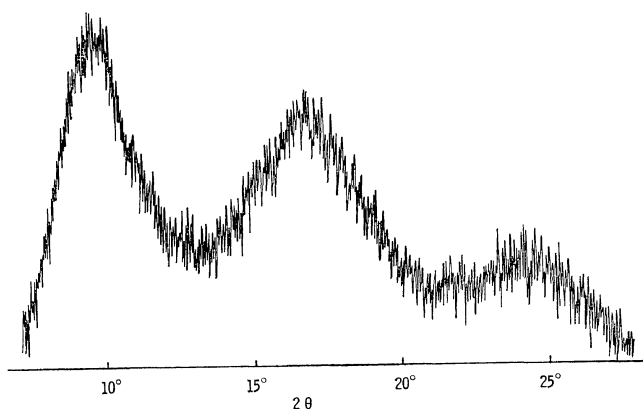


Figure 3. X-ray pattern of poly(*o*-MeO- α -MeSt).

Table V. Anionic copolymerizations of *o*-MeO- α -MeSt with styrene and isoprene in toluene by *n*-BuLi^a

M ₁	[M ₂] ₀ , mmol	[M ₁] ₀ /[M ₂] ₀ , mol/mol	Time, hr	Yield, %	[m ₁]/[m ₂] ^b , mol/mol
Styrene	4.81	1.06	25.0	43.1	5.8
Styrene	6.21	0.82	69.0	54.1	4.8
Styrene	7.77	0.66	69.0	35.1	3.4
Isoprene	4.60	0.40	72.0	15.4	2.6

^a Solvent, 15 ml; catalyst, 0.09 mmol; temp, 0°C.

^b Copolymer composition was determined by elementary analysis.

by *n*-BuLi gave no polymer in spite of the presence of a red carbanion. The thermal polymerization at 60°C also yield no polymer.

Poly(*o*-MeO- α -MeSt) (*S*=89%) showed no polarization under a polarized microscope, although isotactic poly(*o*-MeOSt) (*I*=90%) showed it very clearly.² The X-ray pattern of the powder sample of poly(*o*-MeO- α -MeSt) obtained in methylene chloride by BF₃OEt₂ at -78°C is shown in Figure 3. Three peaks were observed at 9.5, 16.9, and 24.3°, but the fiber identity period could not be determined.

Anionic copolymerizations of *o*-MeO- α -MeSt (M₂) with styrene and isoprene (M₁) were carried out in toluene and THF by means of *n*-BuLi at 0°C in order to determine the reactivity of *o*-MeO- α -MeSt. At this temperature, no homopolymerization of *o*-MeO- α -MeSt occurred. In toluene, copolymers were obtained, whereas in THF only the homopolymers of the M₁ monomers were formed. The results in toluene are shown in Table V. It was found that *o*-MeO-

α -MeSt was relatively less reactive than the M₁ monomers.

DISCUSSION

o-MeO- α -MeSt showed a rather greater rate of polymerization with cationic catalysts at low temperature, but with anionic catalysts the reactivity was very low in comparison with α -MeSt. In THF the polymer was produced by the anionic catalyst only below -30°C. In hydrocarbon solvent the rate of the anionic polymerization of *o*-MeO- α -MeSt was extremely slow and gave no polymer even at low temperature. These results may indicate that the reactivity in the anionic polymerization was lowered by the steric and inductive effects of the *o*-methoxy group, and that in the cationic polymerization the effects compensate one another. The ceiling temperature seems to be lower than that of α -MeSt¹² because lower temperature and higher concentration of the

monomer were required to form the polymer.

The results of the anionic copolymerizations with styrene and isoprene show that copolymerization can proceed in toluene even at 0°C. The relative reactivity of *o*-MeO- α -MeSt in toluene was higher than that in THF, and *o*-MeOSt also had relatively higher reactivity in the anionic copolymerization in hydrocarbon than in THF.³ These observations suggest that the *o*-methoxy group may raise the relative reactivities of the monomers by the coordination to lithium cation in hydrocarbon. However, the relative reactivity in THF was much lower than those of styrene and isoprene. It is probable that THF may prevent such a coordination as found in hydrocarbon. After the consumption of the M₁ monomer, the living polymer anion may add to *o*-MeO- α -MeSt, but the propagation by the latter monomer can not proceed at 0°C, and even the block copolymer of M₁ and M₂ could not be formed in the copolymerization.

In the NMR spectrum of poly(*o*-MeOSt), the methoxy peak was observed at δ 3.05–3.40 ppm from tetramethylsilane in CDCl₃, while poly(*o*-MeO- α -MeSt) and many other derivatives of anisole¹³ showed the peak at δ 3.60–3.90 ppm from tetramethylsilane in the same solvent. This may mean not only that the conformation of poly(*o*-MeOSt) is greatly different from that of poly(*o*-MeO- α -MeSt), but that poly(*o*-MeOSt) has a conformation in which the methoxy resonance shifts to a higher magnetic field by the anisotropic effect of benzene rings. On the other hand, the α -methyl resonance of poly(*o*-

MeO- α -MeSt) resembled that of poly(α -MeSt), probably indicating that both the polymers have similar conformations in chloroform.

Bovey's plots taken for the results of the cationic and anionic polymerizations in Tables I–IV, are shown in Figure 4. As in the case of poly(α -MeSt),^{1,4} the plots seem rather to fit the theoretical curves, showing that the process of the polymerization may be a Bernoulli-trial.

The tacticities of the cationically obtained poly(α -MeSt) and poly(*o*-MeO- α -MeSt) agreed with one another, although those of the anionically obtained polymer were rather different. These results demonstrate that the stereochemical processes in the cationic polymerizations of α -MeSt and *o*-MeO- α -MeSt may be alike, regardless of the presence of *o*-methoxy groups, and that those of the anionic polymerizations may differ because of the groups. The effects of the polymerization temperature, solvent, and catalyst on the tacticity bore a resemblance to those found in the polymerization of α -MeSt reported by Ohsumi, *et al.*,¹ also suggesting similar transition states in the homogeneous cationic polymerizations of α -MeSt and *o*-MeO- α -MeSt. Unexpectedly *o*-MeO- α -MeSt gave a syndiotactic polymer even in a hydrocarbon solvent, while *o*-MeOSt can give an isotactic polymer by *n*-BuLi in toluene at low temperature. The steric effect of the α -methyl group may overcome the effect of the *o*-methoxy group found in the stereospecific polymerization of *o*-MeOSt.

The authors wish to thank Dr. Koichi Hataeda for discussing the contents of this paper, and Mr. Yoshio Terawaki for the measurements of the NMR spectra.

REFERENCES

1. Y. Ohsumi, T. Higashimura, and S. Okamura, *J. Polym. Sci., Part A-1*, **6**, 923 (1966).
2. H. Yuki, Y. Okamoto, Y. Kuwae, and K. Hatada, *J. Polym. Sci., Part A-1*, **7**, 1933 (1969).
3. H. Yuki and Y. Okamoto, *Polymer J.*, **1**, 13 (1970).
4. S. Brownstein, S. Bywater, and D. J. Worsfold, *Makromol. Chem.*, **48**, 127 (1961).
5. Y. Sakurada, M. Matsumoto, K. Imai, A. Nishioka and Y. Kato, *J. Polym. Sci., Part B*, **1**, 633 (1963).

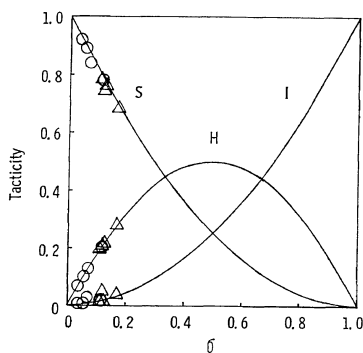


Figure 4. Bovey's plots for cationic and anionic polymerizations of *o*-MeO- α -MeSt: \circ , cationic polymerization; \triangle , anionic polymerization.

Polymerization of *o*-Methoxy- α -methylstyrene

6. K. C. Rammy and G. L. Statton, *Makromol. Chem.*, **85**, 287 (1965).
7. K. Fujii, D. J. Worsfold, and S. Bywater, *ibid.*, **117**, 275 (1968).
8. K. Ziegler and A. Colonijs, *Ann.*, **479**, 135 (1930).
9. K. C. Ramey, G. L. Statton, and W. C. Jankowski, *J. Polym. Sci., Part B*, **7**, 693 (1969).
10. H. L. Frisch, C. L. Mallows, and F. A. Bovey, *J. Chem. Phys.*, **45**, 1565 (1966).
11. H. L. Frisch, F. Heatley, and F. A. Bovey, *Macromolecules*, **1**, 533 (1968).
12. H. W. McCormick, *J. Polym. Sci.*, **25**, 488 (1957).
13. F. A. Bovey, "NMR Data Tables for Organic Compounds," Vol. 1, Interscience Publishers, New York, N. Y., 1967.