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## Tacticity of Poly(o-methoxystyrene) Obtained by Cationic Polymerization

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### SUMMARY

o-Methoxystyrene was polymerized under various conditions with  $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ ,  $\text{SnCl}_4$ , or  $\text{Al}(\text{C}_2\text{H}_5)\text{Cl}_2$  catalyst. The effect of polymerization conditions on the steric structure of poly(o-methoxystyrene) was studied by NMR spectra of the methoxyl protons, and has been tentatively assigned to the triad tacticity of the polymer. Highly stereoregular polymers were not obtained by these catalysts. The tacticity of polymers was independent of the polarity of solvents, as observed in the cationic polymerization of  $\alpha$ -methylstyrene. This behavior was completely different from the cationic polymerization of vinyl ethers. It was found that the heterotactic fraction increased with decreasing polymerization temperature upon polymerization in toluene solution. The fraction of the triad tacticity calculated from Bovey's equation coincided with the experimental results. This fact shows that the steric structure of the addition monomer is determined only by the growing chain end unit and that there is no penultimate effect.

### INTRODUCTION

There exists a considerable literature on the stereoregular polymerization of alkyl vinyl ethers, but little work has been done to elucidate the stereospecific polymerization of styrene derivatives with a cationic catalyst. This may be due to the difficulty of crystallization of stereoregular polystyrene derivatives against the ease of crystallization of stereoregular poly(vinyl alkyl ethers).

Recently, however, high-resolution NMR has yielded quantitative information on the tacticity of polymer. NMR spectroscopy has

analyzed the tacticity of poly( $\alpha$ -methylstyrene) [1-3] and some poly(vinyl alkyl ethers) [4-6] obtained cationically.

Natta et al. [7] have studied the stereoregular polymerization of *o*-methoxystyrene (oMS) with homogeneous cationic catalysts. They found that poly(*o*-methoxy vinyl cyclohexane) formed by hydrogenation of poly(*o*-methoxystyrene) (PoMS) had a crystalline structure and assumed that it might have an isotactic structure. However, Kern and Braun [8] have pointed out that it may be a syndiotactic polymer.

In this paper we have tried to analyze NMR spectra of the methoxyl protons of PoMS. It was found that the methoxyl resonance was split into three components corresponding to triad tacticity as observed for poly(methyl vinyl ether) [4]. Although a highly stereoregular polymer was not produced in the cationic polymerization of oMS, the effect of polymerization conditions on the steric structure of polymer was studied from the viewpoint of the tacticity of polymer formed, in which the reaction mechanism was considered.

## EXPERIMENTAL

### Materials

*o*-Methoxystyrene was synthesized by the decarboxylation of *o*-methoxycinnamic acid as described previously [9]. *o*-Methoxycinnamic acid was obtained by hydrolysis of coumarin and succeeding methylation. The monomer was washed repeatedly with dilute alkali solution and water, then distilled twice just before use.  $n_D^{20}$ , 1.5563 (20°C); b.p., 97°C/17 mm Hg; purity (by gas chromatography), ca. 98%.

Toluene and methylene chloride were purified by the usual method, then distilled over calcium hydride before use.

Cationic catalysts,  $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ ,  $\text{SnCl}_4$ , and  $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$  (guaranteed reagents) were distilled just before use. Radical catalyst, azobisisobutyronitrile (guaranteed reagent) was purified by recrystallization from diethyl ether.

### Procedures

Cationic polymerization was carried out by adding catalyst to the monomer solution. Radical polymerization was carried out in sealed ampoules. Monomer, solvent, and catalyst were added in an ampoule, then degassed to  $10^{-4}$  mm Hg at low temperature. Monomer and catalyst concentrations were 20 vol. % and 20 mmoles/liter in the cationic polymerization and 10 vol. % and 30 mmoles/liter in radical polymerization, respectively.

At a specified time, polymerization was stopped by the addition of methanol containing ammonia, in cationic polymerization, and hy-

droquinone, in radical polymerization. The polymer was repeatedly washed with methanol and dried in vacuo at 40°C.

The intrinsic viscosity number  $[\eta]$  was measured in toluene solution at 30°C; the  $[\eta]$  of polymers obtained in these experiments was found to be relatively small (from 0.05 to 0.08). The NMR spectra of polymer were measured mainly at room temperature using 10% (w/v) solution in various solvents containing 2% tetramethylsilane as internal reference. A Varian A-60 spectrometer was employed.

## RESULTS AND DISCUSSION

### NMR Spectrum of Poly(*o*-methoxystyrene)

Figure 1 shows the NMR spectra of PoMS dissolved in deuteriochloroform. The spectra consisted of four main resonances, 3.0-3.5, 6.7, 7.5, and 8.5  $\tau$ , corresponding to the phenyl, methoxyl, chain methine, and chain methylene protons, respectively. The area ratios of the four resonances, 4:3:1:2, show that the abovementioned assignment is reasonable. The ratios also show that the polymers were constructed only by vinyl polymers.

The NMR spectra of phenyl and methoxyl protons of polymer cationically obtained was slightly different from that radically obtained, as shown in Fig. 1. The intensity of absorption near 3.5  $\tau$  in phenyl protons of polymer radically obtained was stronger than that cationically obtained. The methoxyl resonances in both polymers were split into three components, corresponding to 6.64, 6.76, and 6.93  $\tau$ . The intensities of the three peaks were slightly different in the two polymers. This behavior is very similar to that found by Brownstein et al. [1] for poly( $\alpha$ -methylstyrene); they ascribed the shifts of the phenyl and methyl groups to the differences in chain configurations.

Three components of methoxyl resonance may represent triad tacticity, i.e., isotactic, syndiotactic, and heterotactic forms, as observed in poly(methyl vinyl ether) [4]. It was observed that the peak separation of the methoxyl group depended on the kind of solvent for the case in which the methoxyl spectrum shows the tacticity of the polymer [4, 10, 11]. Figure 2 shows the effect of solvent in the methoxyl resonance of PoMS obtained by  $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$  in toluene at -78°C. An aromatic solvent, *o*-dichlorobenzene, broadened the lines in the spectrum of this polymer by which the resolution was decreased. On the other hand, it was possible to distinguish the three peaks in a nonaromatic solvent such as chloroform. In other nonaromatic solvents, such as deuteriochloroform and methylene chloride, the resolution of methoxyl protons was almost the same as that observed in chloroform. In this paper, the spectra of polymers

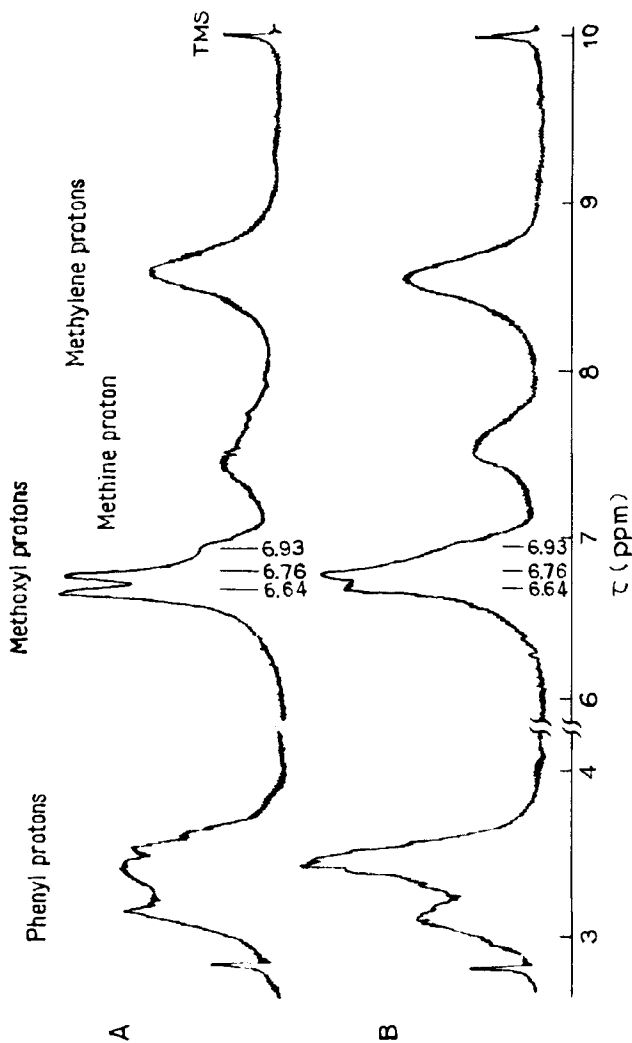


Fig. 1. NMR spectra of poly(o-methoxystyrene) obtained by  $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$  in toluene at  $-78^\circ\text{C}$  (A) and by AIBN in toluene at  $80^\circ\text{C}$  (B).

were measured in chloroform solution because of the requirement for discussion of only the methoxyl resonance.

An assignment of three components in the methoxyl resonance to triad tacticity is not possible on the basis of spectral data alone and recourse must be taken to a method such as X-ray diffraction. The spectra of PoMS did not yield an unambiguous assignment of the triad tacticity, because not all the polymers obtained in this study were crystalline.

We found in PoMS obtained by a radical process that the relative intensities of the methoxyl triplet changed slightly with polymerization temperature. Usually, the syndiotactic structure of polymer increases with decreasing polymerization temperature in a radical process in which the steric configurations of polymers are decided only by the repulsive interaction between the substituents [12-15]. Therefore, a peak in methoxyl triplet which increased with decreasing polymerization temperature was expected to be caused by the syndiotactic triad. The intensities of peaks and polymerization temperature are shown in Table 1. As the peaks were insufficiently resolved to measure these areas, the intensities of the methoxyl triplet were estimated using the Lorenz function.

**Table 1.** Observed and Calculated Intensities of Methoxyl Protons in PoMS Obtained by AIBN in Toluene at Various Temperatures

Temp., °C	Observed fractions, %			Calculated fractions		
	6.64 $\tau$	6.76 $\tau$	6.93 $\tau$	$\sigma$	H, %	I, %
80	35	47	18	0.41	48	17
60	39	48	13	0.38	47	14
30	40	46	14	0.37	46	14

The intensity at 6.64 $\tau$  slightly increased and that at 6.93 $\tau$  slightly decreased with decreasing temperature. Such slight changes of the intensity with polymerization temperature do not yield an unambiguous assignment in the methoxyl triplet. However, the peak at 6.64 $\tau$  was assigned tentatively to the syndiotactic triad. In the NMR spectra of polymers assigned clearly triad tacticities, the line ordering of triplet was syndiotactic, heterotactic, and isotactic triads—or the reverse with increasing field strength [16]. Therefore, if the peak at 6.64 $\tau$  was due to the syndiotactic triad, those at 6.76 and 6.93 $\tau$  might be due to the heterotactic and isotactic triads, respectively.

As Bovey and Tiers [17] found for poly(methyl methacrylate), the following relationship is usually given in the polymer radically obtained:

$$I = \sigma^2 \quad (1)$$

$$H = 2\sigma(1 - \sigma) \quad (2)$$

$$S = (1 - \sigma)^2 \quad (3)$$

where I, H, and S are a fraction of the triad for the isotactic, heterotactic, and syndiotactic forms, and  $\sigma$  is defined as the probability that an addition monomer gives the same configuration as that of the last unit at its growing end.

In radically prepared PoMS, we obtained the probability  $\sigma$  from the fraction at  $6.64\tau$ . Using the value of  $\sigma$ , the isotactic and heterotactic fractions can be calculated from Eqs. (1) and (2). As shown in Table 1, the observed fractions at  $6.76$  and  $6.93\tau$  were in good agreement with the calculated heterotactic and isotactic fractions, respectively.

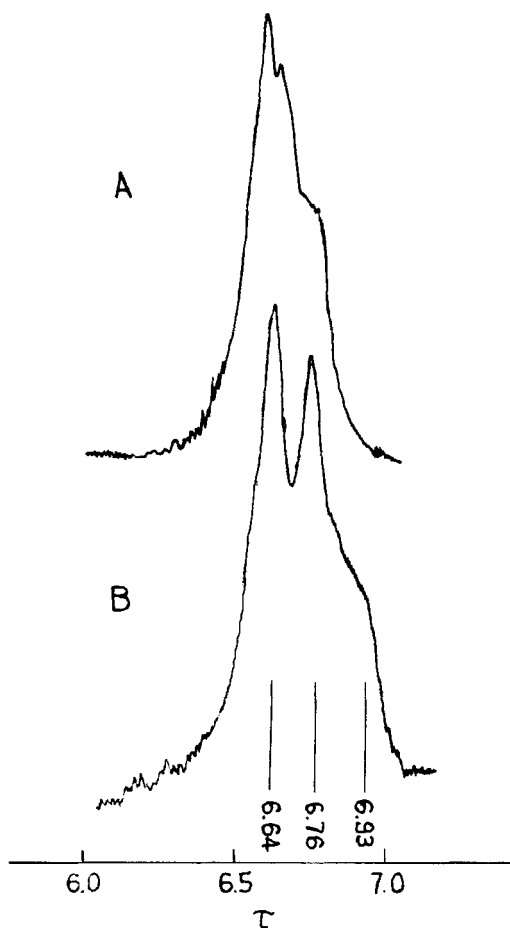
In this assignment, the line ordering of the methoxy triplet was syndiotactic, heterotactic, and isotactic triads with increasing field strength. This ordering was the same as that of the methoxyl triplet of poly(methyl vinyl ether). However, the assignment mentioned above may be tentative, as the crystalline PoMS was not produced in our experiments. Also, the reverse assignment of methoxyl resonance, i.e., isotactic, heterotactic, and syndiotactic triad with increasing field strength, cannot be rejected, because Bovey's relationship was also established in the latter assignment.

Thus no final interpretation has been obtained in PoMS, as well as poly( $\alpha$ -methylstyrene).

#### Effect of Polymerization Conditions on the Steric Structure of PoMS Formed in Cationic Polymerization

oMS was polymerized in toluene by  $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$  at  $-20^\circ\text{C}$ . As shown in Fig. 3, the tacticity of resultant polymers was independent of the conversion. The stereoregularity of PoMS was found to be not good, but the amount of syndiotactic fraction was always much more than those of heterotactic and isotactic ones.

Figure 4 shows the relationship between the triad tacticity of PoMS and the composition of solvent at the polymerization by  $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$  in the toluene-methylene chloride mixed solvent. Figures 5 and 6 show the effect of polymerization temperature on the steric structure of PoMS obtained by  $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$  in toluene and in methylene chloride, respectively. The solvent hardly affects the steric structure of the polymer.



**Fig. 2.** Solvent effect on the methoxyl protons of poly(*o*-methoxystyrene) obtained by  $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$  in toluene at  $-20^\circ\text{C}$ . A, in *o*-dichlorobenzene solution at  $120^\circ\text{C}$ ; B, in chloroform solution at  $25^\circ\text{C}$ .

It has been found that the steric structure of poly(alkyl vinyl ethers) was remarkably affected by the polarity of solvent in cationic polymerization, and an isotactic polymer was obtained only in a nonpolar solvent [5, 18]. On the other hand, the steric structure of poly( $\alpha$ -methylstyrene) was remarkably affected by the solubility of solvent for a polymer in cationic polymerization, and highly stereoregular polymer was obtained in a good solvent for polymer [19].



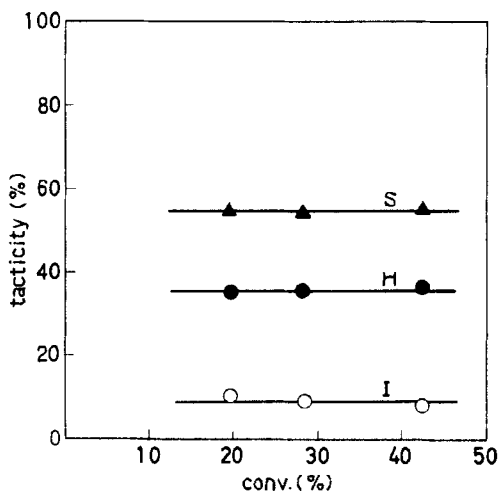


Fig. 3. Relationship between tacticity and conversion of poly(*o*-methoxystyrene) obtained by  $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$  in toluene at  $-20^\circ\text{C}$ .

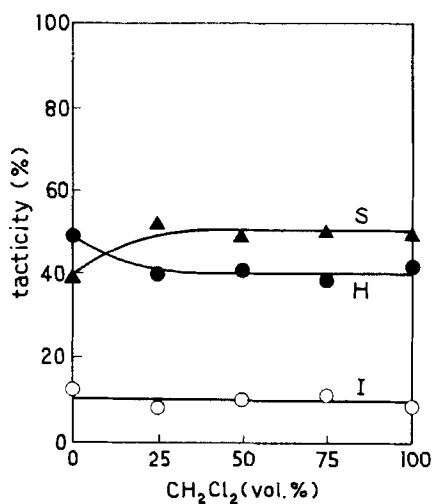


Fig. 4. Effect of polarity of solvent on the tacticity of poly(*o*-methoxystyrene) obtained in toluene-methylene chloride at  $-78^\circ\text{C}$ .

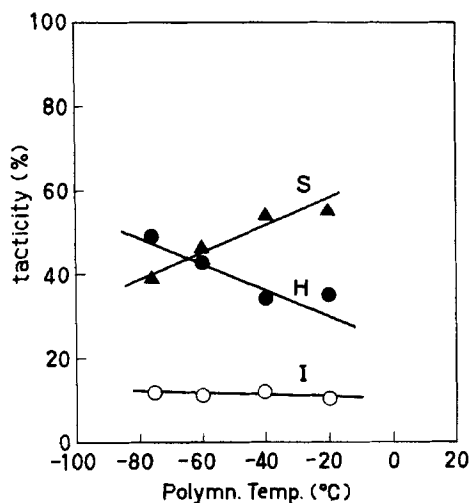


Fig. 5. Effect of polymerization temperature on tacticity of poly(*o*-methoxystyrene) obtained by  $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$  in toluene.

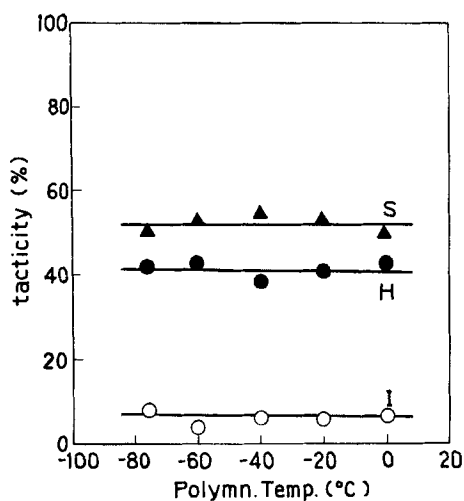


Fig. 6. Effect of polymerization temperature on tacticity of poly(*o*-methoxystyrene) obtained by  $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$  in methylene chloride.

Nevertheless, highly stereoregular polymers were not obtained, and the steric structure of polymer was hardly affected by the polarity of solvent in the cationic polymerization of oMS. Atactic PoMS was obtained in toluene with decreasing polymerization temperature, whereas the temperature hardly affected the steric structure in methylene chloride. It is an unusual phenomenon that the heterotactic fraction increases with decreasing temperature in toluene.

The type of catalyst affected the steric structure of polymers obtained in toluene. As shown in Table 2, the polymers obtained by

**Table 2.** Effect of the Kind of Catalyst on Tacticity of PoMS Obtained in Toluene at  $-78^{\circ}\text{C}$

Catalyst	S, %	H, %	I, %
$\text{BF}_3\text{OEt}_2$	39	49	12
$\text{SnCl}_4$	49	41	10
$\text{AlEtCl}_2$	40	50	10

$\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$  and  $\text{Al}(\text{C}_2\text{H}_5)\text{Cl}_2$  have almost the identical steric structure. However, the polymer obtained by  $\text{SnCl}_4$  contained a high syndiotactic fraction. In the cationic polymerization of alkyl vinyl ethers, the stereoregularity of the polymer obtained by  $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$  has been found to be higher than that obtained by  $\text{SnCl}_4$  [18, 20]. On the other hand, in the cationic polymerization of  $\alpha$ -methylstyrene, the nature of the catalyst has hardly affected the stereoregularity of polymer [19].

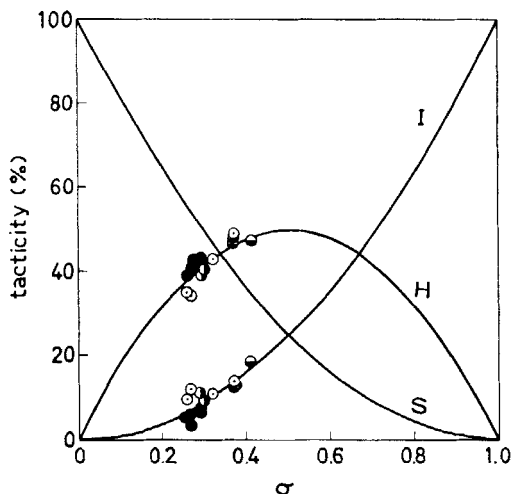
In the cationic polymerization of oMS, no variation of tacticity by the change of the polarity of the solvent was observed as being similar to that found in the case of  $\alpha$ -methylstyrene. However, the effects of polymerization temperature and the catalysts on the steric structure were characteristic of polymerization of oMS. Particularly, it was found that the heterotactic fraction increases with decreasing polymerization temperature in toluene.

#### Probability Treatment on the Polymerization of oMS

The factors which controlled the steric structure of an addition monomer were studied from tacticity data. When the configuration of an addition monomer is determined in homogeneous cationic polymerization, there are two cases in which the steric configuration is determined only by the chain end unit, and the penultimate effect exists. It has been found that the polymerization of  $\alpha$ -methylstyrene [19] belongs to the former case and that of alkyl vinyl ethers [18, 21]

belongs to the latter case. It is very important to know the factors controlling steric structures of oMS, because oMS is a styrene derivative with a polar substituent.

The triad tacticities of PoMS cationically obtained were analyzed by Bovey's treatment.  $\sigma$  was calculated from the observed syndiotactic fraction. In Fig. 7 the theoretical curves and experimental results of heterotactic and isotactic fractions were plotted for  $\sigma$ . Experimental points fell satisfactorily on the theoretical curves within experimental errors. Therefore, in the cationic polymerization of oMS, there was no penultimate effect and the configuration of an addition monomer was determined only by an end unit of the growing chain.



**Fig. 7.** Relationship between  $\sigma$  and tacticity of poly(*o*-methoxystyrene) obtained under various conditions.  $\circ$ ,  $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$  in toluene;  $\bullet$ ,  $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$  in  $\text{CH}_2\text{Cl}_2$ ;  $\bullet$ ,  $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$  in toluene +  $\text{CH}_2\text{Cl}_2$ ;  $\bullet$ , AIBN in toluene.

In the cationic polymerization of oMS with the same polar methoxyl substituent as methyl vinyl ether, it is very interesting to note that the configuration of an addition monomer is determined only by an end unit independent of the type of solvent. It seems to be characteristic in the cationic polymerization of styrene derivatives that the configuration of an addition monomer is controlled only by the end unit.

## REFERENCES

- [1] S. Brownstein, S. Bywater, and D. J. Worsfold, *Makromol. Chem.*, **48**, 127 (1961).
- [2] Y. Sakurada, M. Matsumoto, E. Imai, and A. Nishioka, *J. Polymer Sci.*, **B1**, 633 (1963).
- [3] K. C. Ramey and G. L. Statton, *Makromol. Chem.*, **85**, 287 (1965).
- [4] S. Brownstein and D. M. Wiles, *J. Polymer Sci.*, **A2**, 1901 (1964).
- [5] K. C. Ramey, N. D. Field, and A. E. Borchert, *J. Polymer Sci.*, **A3**, 2885 (1965).
- [6] S. Murahashi, S. Nozaruka, M. Sumi, H. Yuki, and K. Hatada, *J. Polymer Sci.*, **B4**, 65 (1966); K. Fujii, Y. Fujiwara, and S. Fujiwara, *Makromol. Chem.*, **89**, 278 (1965).
- [7] G. Natta, G. Dall'Asta, G. Mazzanti, and A. Casale, *Makromol. Chem.*, **58**, 217 (1962).
- [8] W. Kern and D. Braun, *J. Polymer Sci.*, **C4**, 1529 (1965).
- [9] Y. Imanishi, T. Higashimura, and S. Okamura, *Makromol. Chem.*, **70**, 68 (1964).
- [10] K. C. Ramey, N. D. Field, and T. Hasegawa, *J. Polymer Sci.*, **B2**, 865 (1964).
- [11] K. C. Ramey and J. Messick, *J. Polymer Sci.*, **A2**, 155 (1966).
- [12] J. W. L. Fordham, *J. Polymer Sci.*, **39**, 321 (1959).
- [13] F. A. Bovey, *J. Polymer Sci.*, **46**, 59 (1960).
- [14] F. A. Bovey, F. P. Hood, E. W. Anderson, and R. L. Kornegay, *J. Phys. Chem.*, **71**, 312 (1967).
- [15] J. Bargon, K. H. Hellwege, and U. Johnson, *Makromol. Chem.*, **95**, 187 (1966).
- [16] W. M. Ritchey and F. J. Knoll, *J. Polymer Sci.*, **B4**, 853 (1966).
- [17] F. A. Bovey and G. V. D. Tiers, *J. Polymer Sci.*, **44**, 173 (1960).
- [18] Y. Ohsumi, T. Higashimura, and S. Okamura, *J. Polymer Sci.*, **(A1)5**, 849 (1967).
- [19] Y. Ohsumi, T. Higashimura, and S. Okamura, *J. Polymer Sci.*, **A4**, 923 (1966).
- [20] T. Higashimura, K. Suzuoki, and S. Okamura, *Makromol. Chem.*, **86**, 259 (1965).
- [21] M. Sumi, S. Nozakura, and S. Murahashi, *Kobunshi Kagaku*, **24** 424 (1967).

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