

Stereoregularity of Polystyrene Derivatives V. Poly(α -methylstyrene) Obtained by Cationic Catalysts

Tokiji KAWAMURA, Toshiyuki URYU, Toshiyuki SEKI,
and Kei MATSUZAKI

*Department of Industrial Chemistry, Faculty of Engineering,
University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113, Japan*

(Received June 17, 1982)

ABSTRACT: The stereoregularity of poly(α -methylstyrene)s prepared by cationic initiators was determined by ^1H NMR spectroscopy. Highly syndiotactic polymers were formed in methylene chloride (CH_2Cl_2) regardless of the sort of catalysts and polymerization temperature. The syndiotacticity of the polymers obtained in toluene decreased with increasing ionic radius of the catalysts. The polymers prepared by SbCl_5 in hexane had the lowest syndiotacticity, presumably due to the tightness of ion pairs and increasing interaction of counterions with the phenyl ring.

KEY WORDS α -Methylstyrene Polymer / Cationic Polymerization /
Stereoregularity NMR / Polymerization Mechanism /

It was found by the NMR spectroscopy of poly(α -methylstyrene)¹⁻⁸ that polymers having a syndiotactic structure predominately could be obtained by cationic polymerization at low temperatures. Ohsumi *et al.*⁴ investigated the effect of solvents and catalysts on the stereoregularity (syndiotacticity) of these polymers and found it to become greater with increasing solubility of the polymers in the polymerization solvents. That is, atactic polymers were obtained in hexane, a non-solvent (poor solvent) for poly(α -methylstyrene). The polarity of the solvents hardly affected the stereoregularity of the polymers. Kunitake and his co-workers⁵⁻⁸ reported that highly syndiotactic polymers were obtained in a homogeneous system of toluene-methylcyclohexane media. The isotacticity of the polymers increased on increasing the content of methylcyclohexane, as was found by Ohsumi *et al.*⁴ The effect of catalysts on stereoregularity was clearly noted in methylcyclohexane, a nonsolvent for the polymer. Kunitake *et al.* proposed a propagation mechanism of the cationic polymerization of α -methylstyrene accommodating that of vinyl ethers. These authors⁶⁻⁸ also studied the steric influence of counter anions, and mentioned that the size and shape of the counter

anions were important factors in controlling the steric structure of poly(α -methylstyrene).

Recently, we found that the introduction of methyl groups into the ortho and meta positions of the phenyl ring or into the α -position of styrene resulted in polymers with stereoregularities differing from those of styrene and *p*-methylstyrene^{9,10} in anionic polymerization in polar solvents such as tetrahydrofuran (THF) and dimethoxyethane (DME). In this article, we report on the stereoregularity of poly(α -methylstyrene) obtained by various cationic initiators. The effects of solvent and temperature on stereoregularity were investigated in detail. The polymerization mechanism is discussed and compared with previous results obtained on polystyrene,^{11,12} ring substituted polystyrenes,^{9,13,14} and poly(α -methylstyrene).¹⁰

EXPERIMENTAL

Purification and drying of the monomer and solvents were carried out as described in the previous paper.¹⁰

Boron trifluoride diethyl etherate ($\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$) and antimony pentachloride (SbCl_5) were purified by trap-to-trap distillation *in vacuo*. Phosphorus

Table I. Stereoregularity and P_r values of poly(α -methylstyrene)

Catalyst	CH ₂ Cl ₂			Toluene			Hexane			
	Temp °C	Stereoregularity (observed) ^a		I	Stereoregularity (observed) ^a		I	Stereoregularity (observed) ^a		P_r^b
		H	S		H	S		H	S	
BF ₃ O(C ₂ H ₅) ₂	0	0.21	0.77	0.02	0.21	0.77	0.02	0.21	0.77	0.88
	-70									0.88
	-78	0.19	0.79	0.02	0.18	0.81	0.01	0.18	0.81	0.90
PF ₅	0	0.19	0.79	0.02	0.19	0.79	0.03	0.18	0.79	0.89
	-78	0.16	0.82	0.02	0.16	0.82	0.05	0.21	0.74	0.86
	5	0.19	0.79	0.02	0.19	0.79	0.04	0.29	0.67	0.82
SbCl ₅	-70									0.82
	-78	0.16	0.82	0.02	0.16	0.82	0.03	0.28	0.69	0.83
										0.83

[monomer 2.5×10^{-2} mol], [catalyst 1 mol% to monomer], [solvent 10 ml].^a Determined from the peak area of α -methyl proton absorption.^b Proportion of racemic dyad calculated based on Bernoullian statistics.

pentafluoride (PF_5) was prepared by thermal decomposition of *p*-chlorobenzene-diazonium hexafluorophosphate (Ozark-Mahoning Co.) purified by recrystallization from water.

Polymerization was performed using high vacuum technique as described.⁹⁻¹⁴ ^1H NMR spectroscopic measurements were carried out in 10% (wt/vol) polymer solutions of *o*-dichlorobenzene at 150°C . The stereoregularity of the polymers was determined from the peak area of α -methyl proton absorptions, based on assignment by Brownstein *et al.*¹

RESULTS

Poly(α -methylstyrene)s were prepared by $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$, PF_5 , and SbCl_5 as the catalyst in toluene, hexane, or methylene chloride (CH_2Cl_2). Since the monomer solution ($\sim 0.2\text{M}$) in hexane solidified at -78°C , the polymerization in hexane was carried out at -70°C . The polymers precipitated during polymerization. The polymerization conditions and the stereoregularity of the polymers are summarized in Table I. The observed triad tacticities of all the polymers prepared in this study agree well with the values calculated assuming Bernoullian statistics.

Polymerization in CH_2Cl_2

Highly syndiotactic poly(α -methylstyrene)s (fraction of racemic dyad (P_r) = $0.88 \sim 0.91$) were formed in CH_2Cl_2 regardless of the sort of catalysts. The stereoregularity was not dependent on the polymerization temperature.

Polymerization in Toluene

Although Kunitake and Aso⁵ reported that polymers with 100% syndiotactic structure were obtained by $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$, TiCl_4 , and AlCl_3 as catalyst in toluene, the syndiotacticity of the polymers prepared by $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$ at -78°C in this study was 88%. The polymers obtained by $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$ and PF_5 showed almost the same stereoregularity ($P_r = 0.86 \sim 0.90$). However, the syndiotacticity of the polymers prepared by SbCl_5 decreased to $0.82 \sim 0.83$. The stereoregularity, too, of the polymers prepared in toluene was not dependent on the polymerization temperature.

Polymerization in Hexane

The polymers prepared by $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$ in hexane had syndiotacticities (P_r values, $0.80 \sim 0.81$) lower than those of the polymers obtained in toluene. The syndiotacticity of the polymers prepared by SbCl_5 in hexane decreased with decreasing polymerization temperature ($P_r = 0.78$ at 0°C to 0.74 at -70°C).

DISCUSSION

Cationic polymerization of α -methylstyrene initiated by Lewis acids has been studied by several researchers.¹⁵⁻¹⁸ It is generally agreed that the initiation reaction is the addition of cations derived from initiators to the monomer. In the study of spectroscopic measurements,¹⁸⁻²³ the existence of carbonium ions was recognized in the propagation reaction. It is considered that cationic polymerization proceeds either by ion pairs or by free ions as in the case of anionic polymerization. Hence, the stereoregularity of the polymers is affected by the behavior of ion pairs and free ions.

Our study on the stereoregularity of polystyrene^{11,12} and its derivatives^{9,10,13,14} indicated that when a counterion (contact ion pairs) with a large ionic radius is used as a catalyst in nonpolar solvents, polymer isotacticity increases due to the strengthened interaction between the counterion and the phenyl ring of the growing chain end in the polymerization. For example, isotactic-rich polystyrene ($P_r = 0.28$) is obtained with cesium naphthalene (Cs naph.) in toluene at 30°C , whereas atactic polystyrene ($P_r = 0.53$) is prepared by butyllithium (BuLi) at 0°C .²⁴

The structure of poly(α -methylstyrene)s prepared in toluene was syndiotactic-rich, since the stereoregularity was determined primarily by steric repulsion between α -methyl groups. The tacticity did not vary with polymerization temperature. On increasing the radius of counterion²⁵⁻²⁷ ($\text{BF}_4^- < \text{PF}_6^- < \text{SbCl}_6^-$), the syndiotacticity of the polymers decreased; that is, the polymer prepared by SbCl_5 in toluene showed the lowest syndiotacticity, indicating that an interaction between the counter anion and the phenyl ring was strengthened.

Polymers with lower syndiotacticities were formed in hexane. Ohsumi *et al.*⁴ consider that the difference in the physical state of the polymerization

system (that is, homogeneous in toluene and heterogeneous in hexane) affects the stereoregularity of poly(α -methylstyrene).

In general, isotactic vinyl polymers are obtained by ionic polymerizations in nonpolar solvents at low temperatures. The tightness of the growing ion pair, that is, the contact ion pair, is one of the main factors bringing about the formation of the isotactic structure. Hexane is a less polar solvent than toluene. Therefore, the solvation of growing chain end of α -methylstyrene by hexane may possibly be less than by toluene. Thus, the tightness of the ion pair between the counter anion and the growing chain end increases in hexane and also the interaction between the phenyl ring and counter anion increases with increase in the size of the anions, so that the polymers with the lowest syndiotacticity are formed in hexane by SbCl_6^- as the catalyst.

The stereoregularity was found to be independent of the polymerization temperature and kind of catalysts for polymers prepared in polar solvents such as CH_2Cl_2 . It may be supposed that in CH_2Cl_2 , highly syndiotactic polymers are formed by solvent-separated ion pairs or free ions of the anions.

In conclusion, it may be said that the mechanism of the cationic polymerization of α -methylstyrene by Lewis acids is essentially the same as that of the anionic polymerization of styrene and its derivatives.

REFERENCES

- S. Brownstein, S. Bywater, and D. J. Worsfold, *Makromol. Chem.*, **48**, 128 (1961).
- Y. Sakurada, M. Matsumoto, K. Imai, A. Nishioka, and Y. Kato, *J. Polym. Sci., B*, **1**, 633 (1963).
- D. Braun, G. Heufer, U. Johnsen, and K. Kolbe, *Ber. Bunsenges Physik. Chem.*, **68**, 959 (1964); *Chem. Abstr.*, **62**, 5339g (1965).
- Y. Ohsumi, T. Higashimura, and S. Okamura, *J. Polym. Sci., A*, **3**, 3729 (1965).
- T. Kunitake and C. Aso, *J. Polym. Sci., A-1*, **8**, 665 (1970).
- Y. Matsuguma and T. Kunitake, *Polym. J.*, **2**, 353 (1971).
- T. Kunitake and S. Tsugawa, *Macromolecules*, **8**, 709 (1975).
- T. Kunitake, *J. Macromol. Sci., Chem.*, **A9**, 797 (1975).
- T. Kawamura, T. Uryu, and K. Matsuzaki, *Makromol. Chem.*, **183**, 153 (1982), (Part 3 of this series).
- T. Kawamura, T. Uryu, T. Seki, and K. Matsuzaki, *Makromol. Chem.*, **183**, 1647 (1982), (Part 4 of this series).
- T. Uryu, T. Seki, T. Kawamura, A. Funamoto, and K. Matsuzaki, *J. Polym. Sci., Polym. Chem. Ed.*, **14**, 3035 (1976).
- T. Uryu, T. Kawamura, and K. Matsuzaki, *J. Polym. Sci., Polym. Chem. Ed.*, **17**, 2029 (1979).
- T. Kawamura, T. Uryu, and K. Matsuzaki, *Makromol. Chem.*, **183**, 125 (1982), (Part 1 of this series).
- T. Kawamura, T. Uryu, and K. Matsuzaki, *Makromol. Chem.*, **183**, 143 (1982), (Part 2 of this series).
- D. O. Jordan and A. R. Mathieson, *J. Chem. Soc.*, 2354, 2358, 2363 (1952).
- F. S. Dainton and R. H. Tomlinson, *J. Chem. Soc.*, 151 (1953).
- D. J. Worsfold and S. Bywater, *J. Am. Chem. Soc.*, **79**, 4917 (1957).
- S. Okamura, T. Higashimura, and Y. Imanishi, *Kobunshi Kagaku*, **16**, 129, 165 (1959).
- G. A. Olah and C. U. Pittman, Jr., *Adv. Phys. Org. Chem.*, **4**, 305 (1966).
- S. Bywater and D. J. Worsfold, *Can. J. Chem.*, **44**, 1671 (1966).
- G. A. Olah, C. U. Pittman, Jr., R. Waack, and M. Doran, *J. Am. Chem. Soc.*, **88**, 1488 (1966).
- V. Bertoli and P. H. Plesch, *Spectrochimica Acta*, **25A**, 447 (1968).
- V. Bertoli and P. H. Plesch, *J. Chem. Soc., B*, 1500 (1968).
- T. Kawamura, T. Uryu, and K. Matsuzaki, *Makromol. Chem., Rapid Commun.*, **3**, 661 (1982).
- H. L. Yeager and B. Kratochvil, *J. Phys. Chem.*, **73**, 1963 (1969).
- T. Kunitake, T. Matsuguma, and C. Aso, *Polym. J.*, **2**, 345 (1971).
- A. Ledwith and D. C. Scherrington, *Adv. Polym. Sci.*, **19**, 1 (1975).