

The Effect of Counteranions on the Polymer Steric Structure in the Cationic Polymerization of α -Methylstyrene*

Yoshihiko MATSUGUMA and Toyoki KUNITAKE

Department of Organic Synthesis, Faculty of Engineering,
Kyushu University, Fukuoka, 812, Japan.

(Received November 16, 1970)

ABSTRACT: The cationic polymerization of α -methylstyrene was carried out at -78°C by using Lewis acids and triphenylmethyl salts as initiator. The polymerization with triphenylmethyl salts was much slower than that with Lewis acids. The triad tacticity data of the polymer determined by NMR spectroscopy fitted the theoretical curve of one parameter (Bovey's σ value). The σ value, though almost independent of the initiator used in CH_2Cl_2 — CH_3CN ($\sigma \cong 0.04$), increased with decreasing polarity of polymerization solvents and varied moderately (0.07—0.34) with the initiator in nonpolar solvents. In the case of triphenylmethyl salt initiators, the order of counteranions with increasing σ value ($\text{SnCl}_5^- \geq \text{SbCl}_6^- > \text{AlBr}_4^- > \text{AlCl}_4^- > \text{BF}_4^-$) was the same as that observed for the isotactic propagation of isobutyl vinyl ether. These results were interpreted within the framework of the cationic propagation scheme proposed by us earlier. The steric influence of counteranions was discussed, and the unusual effect of SnCl_5^- was considered in connection with its coordination state. The variation of the σ value with Lewis acids (SnCl_4 excluded) was much smaller than that with triphenylmethyl salts.

KEY WORDS Cationic Polymerization / Poly(α -methylstyrene) / Steric Structure / Triphenylmethyl Cation / Counteranion / Steric Course / Lewis Acid /

Poly(α -methylstyrene) is one of the few polymers the steric structure of which can be determined quantitatively. The variation of the steric structure of poly(α -methylstyrene) with polymerization conditions has been investigated and its implication discussed by Ohsumi, *et al.*¹ Previously we also investigated polymerizations of α -methylstyrene with several Lewis acids in connection with our proposal on the steric course of the cationic propagation, and found that the steric course of propagation was affected by the Lewis acid used.² In the case of the cationic polymerization of isobutyl vinyl ether with triphenylmethyl salts, the steric structure of the resulting polymer was correlated mainly with the size of the counteranion.³ We therefore became interested to learn how the counteranion would affect the steric structure of poly(α -methylstyrene). In this paper we

describe cationic polymerizations of α -methylstyrene with several triphenylmethyl salts and Lewis acids, and discuss the influence of the counteranion on the steric course of propagation.

EXPERIMENTAL

Materials

α -Methylstyrene was washed with dilute aqueous alkali and with water, dried over CaCl_2 , and distilled at reduced pressure under nitrogen with the use of a Vigreux column. The purity was confirmed by gas chromatography. The purified monomer was again distilled before use from CaH_2 . Solvents were purified by conventional methods. The preparation and characterization of triphenylmethyl salts were described previously.³ BF_3OEt_2 , SbCl_5 , and SnCl_4 were purified by distillation. AlCl_3 was sublimed under nitrogen from its mixture with NaCl and Al powders.

* This is contribution No. 227 from this department and Part III in the series "Mechanism of Cationic Polymerizations."

Polymerization

The polymerization with triphenylmethyl salts was conducted in glass-stoppered test tubes with side-arms for the nitrogen inlet. When polymerizations were carried out in CH_2Cl_2 —methylcyclohexane(MCH) mixtures, a given amount of initiator solution in CH_2Cl_2 was mixed with a necessary amount of MCH and cooled to -78°C . The total volume of solvents was usually 60 ml. Five ml of monomer were then added under nitrogen while stirring. In the case of polymerizations in CH_2Cl_2 solvent, 1 ml of an initiator solution in CH_2Cl_2 was added to a mixture of 5 ml of monomer and 49 ml of CH_2Cl_2 at -78°C . One ml of monomer, 1 ml of an initiator solution and 9 ml of solvent were used in polymerizations in CH_2Cl_2 — CH_3CN mixtures. The polymerization was terminated by adding methanol, and the mixture was poured into excess methanol. Upon centrifugation and washing, the polymer was dried *in vacuo* and weighed. The sample used for NMR

measurements was reprecipitated from benzene and methanol.

The polymerization with Lewis acids was carried out in a similar manner. Catalyst solutions were added to mixtures of monomer and solvents at -78°C . The work-up was the same.

Miscellaneous

NMR spectra were obtained with a Varian A60 instrument in chlorobenzene at 120°C . The polymer concentration was 10% (w/v). The stereochemistry of the polymer was determined by the cut-and-weigh method of the relative area of the three methyl signals in the NMR spectrum. Viscosities were measured in benzene at 30°C .

RESULTS AND DISCUSSION**Polymerization**

The polymerization data of α -methylstyrene with triphenylmethyl salts are given in Table I.

Table I. Polymerization of α -methylstyrene with triphenylmethyl salts at -78°C

No.	Initiator ^a , mol/l $\times 10^3$	Monomer, mol/l	Solvent ^b	Polymeri- zation time, hr	Conversion, %	$[\eta]$, ^c dl/g	σ^d	
1	$\text{Ph}_3\text{C}^+\text{AlCl}_4^-$	4.8	0.60	I	20	46.4	0.532	0.233
2	$\text{Ph}_3\text{C}^+\text{SnCl}_5^-$	9.0	0.60	I	489	1.1	—	0.346
3	$\text{Ph}_3\text{C}^+\text{AlBr}_4^-$	8.3	0.65	II	67.5	12.4	0.983	0.099
4	$\text{Ph}_3\text{C}^+\text{AlCl}_4^-$	7.5	0.65	II	2	75.0	0.700	0.080
5	$\text{Ph}_3\text{C}^+\text{BF}_4^-$	5.5	0.71	II'	75	6.3	—	0.068
6	$\text{Ph}_3\text{C}^+\text{BF}_4^-$	6.2	0.65	II	336	3.9	0.216	0.074
7	$\text{Ph}_3\text{C}^+\text{SbCl}_6^-$	3.9	0.65	II	384	1.2	0.285	0.127
8	$\text{Ph}_3\text{C}^+\text{SnCl}_5^-$	6.5	0.71	II'	75	49.8	—	0.130
9	$\text{Ph}_3\text{C}^+\text{SnCl}_5^-$	9.0	0.65	II	190	27.2	0.516	0.135
10	$\text{Ph}_3\text{C}^+\text{AlBr}_4^-$	1.8	0.71	III	0.5	5.8	1.72	0.056
11	$\text{Ph}_3\text{C}^+\text{AlCl}_4^-$	1.8	0.71	III	0.3	7.4	2.39	0.056
12	$\text{Ph}_3\text{C}^+\text{BF}_4^-$	3.5	0.71	III	71	8.0	0.183	0.066
13	$\text{Ph}_3\text{C}^+\text{SbCl}_6^-$	1.8	0.71	III	18	12.8	0.618	0.084
14	$\text{Ph}_3\text{C}^+\text{SnCl}_5^-$	2.5	0.71	III	24	3.6	0.164	0.074
15	$\text{Ph}_3\text{C}^+\text{AlCl}_4^-$	10	0.71	IV	96	6.6	—	0.045
16	$\text{Ph}_3\text{C}^+\text{BF}_4^-$	1.9	0.71	IV	96	56.2	0.272	0.042
17	$\text{Ph}_3\text{C}^+\text{SbCl}_6^-$	4.9	0.71	IV	96	21.7	—	0.045
18	$\text{Ph}_3\text{C}^+\text{SnCl}_5^-$	12	0.71	IV	96	23.9	—	0.041

^a Initiator not completely soluble in solvents I and II.

^b Solvent I, methylcyclohexane (MCH)— CH_2Cl_2 (10:2 by volume); II, MCH— CH_2Cl_2 (8:3 by volume); II', MCH— CH_2Cl_2 (7:3 by volume); III, CH_2Cl_2 ; IV, CH_2Cl_2 — CH_3CN (7:3 by volume).

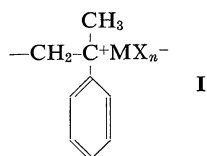
^c Determined in benzene at 30°C .

^d Calculated from eq 1.

Cationic Polymerization of α -methylstyrene

The polymerization was generally slow. It was particularly slow in methylcyclohexane (MCH)- CH_2Cl_2 (10:2 by volume) media and, therefore, the number of initiators used in this solvent was limited. The polymer precipitated during polymerization in CH_2Cl_2 - CH_3CN and MCH- CH_2Cl_2 solvents. In CH_2Cl_2 gel-like polymers precipitated partially. The triphenylmethyl salts used were only partially soluble in MCH- CH_2Cl_2 mixtures, and, therefore, the initiator concentrations given in Table I are not accurate for these solvents.

The polymerization of styrene and α -methylstyrene with triphenylmethyl cation as initiator has been studied by several groups,⁴⁻⁶ and it was generally agreed that the initiation step was the addition of the triphenylmethyl cation to monomer molecules. The salt anion would then become the counteranion in the growing species.



The polymerization with some Lewis acids is summarized in Table II. Except for AlCl_3 the

catalysts used were soluble in polymerization mixtures. The polymerization was much faster with Lewis acids, but SnCl_4 - H_2O was less effective.

The Steric Structure of the Polymer Obtained with Triphenylmethyl Initiators

The steric structure of poly(α -methylstyrene) can be determined from the relative area of the three methyl signals in the NMR spectrum. The assignment of these signals has been a subject of considerable controversy. Recently, Ramey, *et al.*,⁷ assigned the three methyl peaks to the isotactic, heterotactic and syndiotactic triads in the order of increasing magnetic fields, on the basis of the analysis of the methyl and methylene peaks of 220-MHz spectra. This assignment, being the one that we adopted in the previous study, appears most satisfactory and is, therefore, employed in the present study.

The reproducibility of tacticity determination (the fraction of the syndiotactic triad, T_s) can be considered to be within $\pm 0.5\%$. For instance, the syndiotactic fraction was 86.8 and 85.8% with $\text{Ph}_3\text{C}^+\text{BF}_4^-$ initiator in MCH- CH_2Cl_2 (Run no. 5 and 6, Table I), and 75.7 and 74.9% with $\text{Ph}_3\text{C}^+\text{SnCl}_5^-$ initiator in MCH- CH_2Cl_2 (Run no. 8 and 9, Table I). The signal-to-noise ratio of the spectrum was much

Table II. Polymerization of α -methylstyrene with Lewis acids at -78°C

No.	Catalyst $\times 10^3$, mol/l	Monomer, mol/l	Solvent ^a	Polymeri- zation time, min	Conversion, %	$[\eta]^b$	σ^c
1	AlCl_3^d ca. 3	0.60	I	10	77.6	—	0.080
2	BF_3OEt_2 3.8	0.60	I	18 hr	38.7	0.643	0.101
3	SbCl_5 1.8	0.60	I	10	41.7	—	0.086
4	SnCl_4 4.3	0.60	I	13	6.9	—	0.215
5	SnCl_4 -TCA (1:1) 2.0	0.60	I	20	11.4	—	0.153
6	SnCl_4 - H_2O (1:1) 2.0	0.60	I	76 hr	6.1	—	0.172
7	AlCl_3^d ca. 3	0.65	II	10	93.6	—	0.066
8	BF_3OEt_2 4.2	0.65	II	180	14.5	0.691	0.065
9	SbCl_5 1.9	0.65	II	10	56.8	—	0.069
10	SnCl_4 4.7	0.65	II	10	41.2	—	0.112
11	BF_3OEt_2 4.5	0.71	III	120	27.6	0.780	0.053
12	BF_3OEt_2 4.5	0.71	IV	18 hr	10.7	—	0.037

^a Solvent I, methylcyclohexane (MCH)- CH_2Cl_2 (10:2 by volume); II, MCH- CH_2Cl_2 (8:3 by volume); III, CH_2Cl_2 ; IV, CH_2Cl_2 - CH_3CN (7:3 by volume).

^b Determined in benzene at 30°C .

^c Calculated from eq 1.

^d Not completely soluble.

better in the present measurements than in those of the previous ones.² The experimental error in T_s was estimated to be $\pm 2\%$ in the latter case.

The probability of the isotactic propagation σ as defined by Bovey is calculated from T_s by the following equation

$$T_s = (1 - \sigma)^2 \quad (1)$$

Previously it was shown that the variation of the steric structure of poly(α -methylstyrene) could be described by a single parameter σ .^{8,9} This assumption is also valid for the tacticity data of the present investigation as shown in Figure 1. The Bovey plots closely fit the

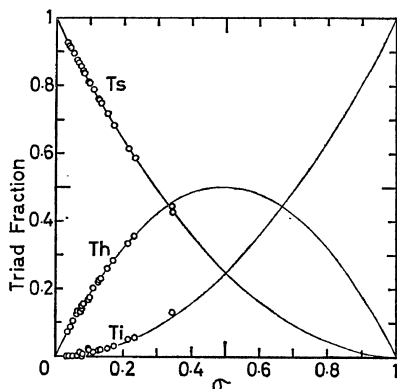


Figure 1. Bovey plots: T_s , syndiotactic; T_h , heterotactic; T_i , isotactic triad.

theoretical curve of one parameter σ , thus precluding the presence of the penultimate effect. The variation of σ with initiators and polymerization solvents is shown in Figure 2. The solvent systems are arranged in the order of increasing polarity in the abscissa. It is to be noted that the σ values are small. Therefore, syndiotactic propagation is predominant in all the systems. The σ value increased with decreasing polarity of the solvent. The variation of the σ value with counteranions was greatest in the least polar solvent and the difference diminished as the polarity of the polymerization medium increased. In CH_2Cl_2 — CH_3CN solvent the σ value was independent of the counteranion, indicating that the growing ion-pair was too loose for the counteranion to

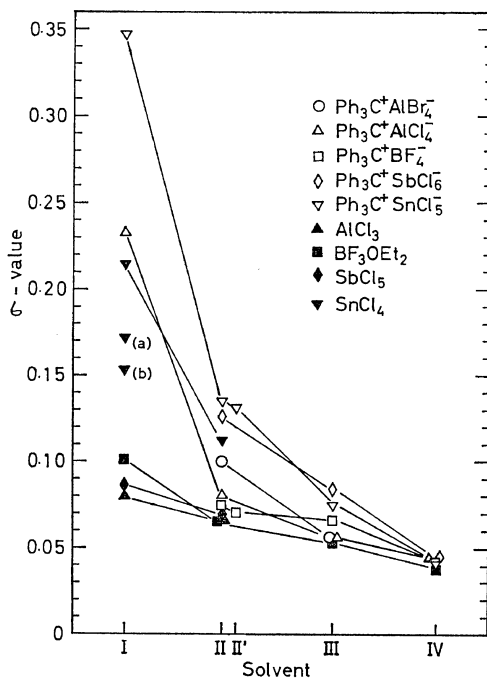
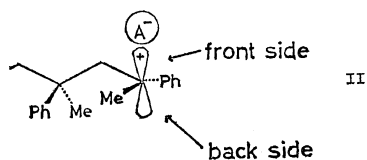


Figure 2. Variation of the σ value with polymerization conditions: solvent I, $\text{MCH}-\text{CH}_2\text{Cl}_2$ (10:2); solvent II, $\text{MCH}-\text{CH}_2\text{Cl}_2$ (8:3); solvent II', $\text{MCH}-\text{CH}_2\text{Cl}_2$ (7:3); solvent III, CH_2Cl_2 ; solvent IV, $\text{CH}_2\text{Cl}_2-\text{CH}_3\text{CN}$ (7:3); (a), $\text{SnCl}_4-\text{H}_2\text{O}$ catalyst; (b), SnCl_4 -trichloroacetic acid (TCA) catalyst.

affect the steric course of propagation.

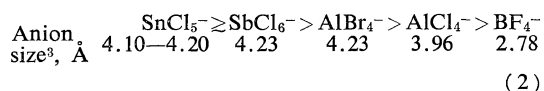
According to the model of the steric course of propagation proposed earlier,² the most stable conformation of the growing α -methylstyrene segment is assumed to be the one shown by II. Insertion of a monomer molecule at the front side gives rise to a syndiotactic placement and insertion at the back side an isotactic placement.



As explained previously, a syndiotactic placement at the front side is favored for α -methylstyrene, because the α -carbon is disubstituted and the back-side attack is less favorable due to enhanced steric hindrance of the penultimate side chains. Nevertheless, the

back-side attack to give an isotactic placement will be facilitated when a tightly bound counteranion interferes with the front-side attack.

The σ value increased in MCH—CH₂Cl₂ (8/3) solvent in the following order of the counteranion.



Thus isotacticity of poly(α -methylstyrene) increased mainly with increasing sizes of the counteranion in this solvent, except for SnCl₅⁻. Interestingly, this order is the same as that of increasing isotacticity in the cationic polymerization of isobutyl vinyl ether.³ Therefore, the role of the counteranion in affecting the steric course appears to be the same with these two monomers in spite of their different side chains. This is consistent with our proposed scheme, since none of the specific interactions of monomer substituents with counteranions was required for determining the steric course in this scheme. The steric hindrance of the counteranion is seemingly more influential than the coulombic interaction of the ions in determining the site of monomer attack in both systems.

The SnCl₅⁻ anion gave a larger amount of the isotactic unit than would be expected from its size. The coordination number of this anion is five, in contrast with the coordination numbers of four and six in other anions which correspond to the tetrahedral and octahedral structures, respectively.

It is known that the structure of pentacoordinate compounds is generally nonrigid,¹⁰ and one of the possible configurations—trigonal bipyramid—may readily convert to the other configuration—tetragonal pyramid. This structural characteristics can give rise to an asymmetrical SnCl₅⁻ anion, and its effect could be different from what is expected from its size alone.

The Steric Structure of the Polymer Obtained with Lewis Acids

The variation of the σ values of the polymer obtained with several Lewis acids is also shown in Figure 2. Except for SnCl₄ polymers, the σ values were much smaller than those of the polymers obtained with triphenylmethyl initia-

tors. The order of Lewis acids with increasing σ values (in 10:2 MCH—CH₂Cl₂) was



This order agrees with that previously observed in MCH—toluene solvents: SnCl₄ > BF₃OEt₂ ≥ TiCl₄ > AlCl₃.²

It is evident from Figure 2 that the influence of Lewis acid catalysts on σ is small. In fact, almost the same value was obtained for BF₃OEt₂, SbCl₅, and AlCl₃ in 8:3 MCH—CH₂Cl₂. Thus it is suggested that the interaction of the counteranions derived from these Lewis acids with the propagating cation is weak, so far as the steric course is concerned.

The different effects of triphenylmethyl salts and the corresponding Lewis acids are noteworthy. The structure of the counteranions derived from Lewis acids may be more complex than expected from simple coordination of cocatalysts.

The peculiarity of SnCl₄ compared with other Lewis acids is evident in Figure 2. An explanation similar to that given for SnCl₅⁻ may again be applicable. Interestingly, addition of equimolar amounts of cocatalysts (H₂O or trichloroacetic acid) to SnCl₄ resulted in decreased σ values.

It is probable that, among many facets of the counteranion effect, the steric effect is especially important in determining the steric course of propagation. The reactivity of growing ion-pairs may be influenced more strongly by other facets of the counteranion effect. In this connection we are now carrying out copolymerization, and other reactions related to polymerization, using triphenylmethyl salts.

Acknowledgement. We are deeply grateful to Prof. Chuji Aso head of our research group, for his constant encouragement and advice.

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