Preparations of Triphenylmethyl Salts and Their Use in the Cationic Polymerization of α-Methylstyrene. Counteranion and Polymer Structure

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ABSTRACT: Triphenylmethyl salts which contain metal chlorides or bromides as the anion were prepared systematically, and employed as initiator for the cationic polymerization of α-methylstyrene. The isotactic unit content of the polymer was found to correlate with the anion size in a relatively simple way except for pentacoordinate anions. This was explicable by considering the steric effect of the counteranion and the coulombic interaction of the growing ion pair. Pentacoordinated counteranions gave rise to greater amounts of the isotactic unit than expected from their sizes, and, in the case of Ph_3SnCl_4Br, the polymer steric structure was dependent on the initiator concentration. These results were attributed to the peculiar structural characteristics of these anions.

The present paper is concerned with the use of various triphenylmethyl salts for the cationic polymerization of α-methylstyrene, with a hope to correlate the counteranion structure and the steric course of the cationic propagation.

Previously we investigated the cationic polymerization of isobutyl vinyl ether[1] and α-methylstyrene[2] by using some triphenylmethyl salts as initiator. The polymerization is initiated by addition of the triphenylmethyl cation in these systems. As a result, the anion of the initiator salt supposedly becomes the counteranion of the growing chain without structural modification. Therefore, straightforward discussions on the counteranion effect are possible.

The previous polymerization results suggested that the size and shape of the counteranion were important factors in controlling the steric structure. However, these studies were conducted with only five triphenylmethyl salts, and, therefore, the conclusion was necessarily of limited nature.

In the present study, new triphenylmethyl salts are prepared systematically, and they are used for the polymerization of α-methylstyrene in order to investigate the influence of the counteranion structure on the steric structure of poly(α-methylstyrene).

Experimental Section

1. Preparation of Triphenylmethyl Salts. Metal halides, commercially available and of highest grade, were used without further purification. However, $FeCl_3$ was prepared from Fe and Cl_2 and sublimed three times, and $TiCl_4$ and $SnCl_4$ were distilled two times.

The preparation and characterization of triphenylmethyl salts are summarized in Table I.

Most of the triphenylmethyl salts were synthesized from triphenylmethyl chloride, mp 111–112°C (lit.[3] 110.5–112°C), or triphenylmethyl bromide, mp 149–151.1°C (lit.[4] 153–154°C), and the corresponding metal halides; triphenylmethyl halide (10 mol% excess) was added to a solution of metal halides ($SnCl_4$, $SnBr_4$, $GaCl_3$, $FeCl_3$, BBr_3, BCl_3) with vigorous stirring under nitrogen in appropriate solvents. Yellow to orange precipitates which formed were filtered, washed with the preparation solvent and/or ether, and dried in vacuo.

When the solubility of the metal halides in organic solvents is low ($ZrCl_4$, $TaCl_4$, $NbCl_5$, $InBr_3$), CH_2Cl_2 was used as preparation solvent. Unreacted metal halides were removed by filtration and the solvent was evaporated. Orange yellow powders obtained by addition of CCl_4, followed by vigorous stirring, were washed and dried in vacuo.

$InCl_4 \cdot H_2O$ and $TlCl_3 \cdot 4H_2O$ were first stirred vigorously in propionic anhydride and acetic anhydride, respectively, and then equimolar amounts of triphenylmethyl chloride were added as CCl_4 solution. The precipitates formed were washed with CCl_4 and dried. Triphenylmethyl perchlorate was prepared from triphenylcarbinol and perchloric acid according to the method of Hoffmann et al.[5]

Generally, the formation of triphenylmethyl salts was confirmed by elemental analysis and ir and NMR spectroscopy. Melting points were measured in sealed capillaries. The analytical results are fairly satisfactory. Repeated purification attempts did not improve the discrepancies in the analysis for some triphenylmethyl salts given in Table I. Ph_3CBBr_4 was too sensitive to moisture to carry out elemental analysis, and its purity was confirmed from the yield of triphenylcarbinol formed upon hydrolysis.[6]

Ir spectra were measured as Nujol mulls. Except for the case of Ph_3CBCl_4 and Ph_3CBBr_4 (which decomposed very quickly in the air), all the spectra showed essentially the same pattern and possessed a peak at 1360 cm^{-1} which has been assigned to ν_{C-Ph} of the triphenylmethyl cation.[7] NMR spectra were obtained in ethylene dichloride. The measurement was difficult in several cases because of low solubility or facile decomposition; otherwise all the spectra coincided with that reported previously.[8]

The synthesis of triphenylmethyl salts was also attempted from the following metal halides: $HfCl_5$, $BiCl_4$, $BiBr_4$, $TeCl_5$, $SeCl_5$, $TiCl_4$, and ICl_3. Although yellow orange powders which undoubtedly contain triphenylmethyl salts were formed, the elemental analytical results were not satisfactory and, therefore, they were not used for polymerization.

$GeCl_4$ and $AsCl_3$ did not appear to react with triphenylmethyl chloride. No triphenylmethyl salts were recovered, when $MoCl_5$, WCl_6, and VCl_4 were used. An oily product was obtained from $ZnCl_2$ and triphenylmethyl chloride.

2. Miscellaneous. The polymerization procedure is the same as described previously.[1] The steric structure of poly(α-methylstyrene) was determined from the relative peak area of the three methyl signals in the NMR spectrum (chlorobenzene, 120°C).

Results and Discussion

1. Preparation of Triphenylmethyl Salts. In Table II, the central metals contained in the anion of triphenylmethyl salts are placed in the respective position of the periodic table. In the case of metals shown in parentheses, yellow products are obtained in oil or powder forms upon mixing of triphenylmethyl halides and metal halides. Although these products are undoubtedly triphenylmethyl salts, they could not be isolated in pure form. In the case of the metals which are in italic, triphenylmethyl salts have been obtained only as fluorides. In other cases, the triphenylmethyl salts were successfully prepared as bromide and/or chloride. These salts would be naturally obtainable as fluorides. Alkali and alkali-earth metals do not give the corresponding salts because of the highly ionic nature of the M–X bond. Chlorides or bromides of carbon, silicon, germanium, phosphorus, and arsenic do not form triphenylmethyl salts because their Lewis acidities are too weak. However, the phosphorus and arsenic salts have been formed when fluorides are used.[9]

It is immediately clear from this table that triphenylmethyl salts are most readily formed in the case of counteranions containing the IIIA group metals: B, Al, Ga, In, and Tl. The metals belonging to the V group similarly yield triphenylmethyl salts readily. Therefore, triphenylmethyl

Table I
Preparation of Triphenylmethyl Salts

$Ph_3C^+X^-$ X =	Preparative solvent	Yield, %	Mp dec, °C	Ir[e]	NMR[e]	Elemental Anal Found (calcd) C, %	H, %
BCl_4	Cyclohexane		162–169 (lit.[a] 187)			58.28 (57.63)	4.17 (3.82)
BBr_4	Cyclohexane	78	160–164 (lit.[b] 182)			46.62 (45.37) as Ph_3COH	
$GaCl_4$	CCl_4	95	167–169	○	○	49.61 (50.17)	3.40 (3.32)
$InCl_4$	$(C_2H_5CO)_2O-CCl_4$	70		○		45.17 (45.64)	3.23 (3.00)
$TlCl_4$	$(CH_3CO)_2O-CCl_4$	93	153–157	○	○	38.22 (38.72)	2.66 (2.54)
$SnBr_5$	C_6H_6	84	161–162 (lit.[c] 171)	○	○	30.13 (29.96)	2.13 (1.99)
$InBr_4$	CH_2Cl_2	92	164–167	○	○	33.77 (33.67)	2.33 (2.23)
$SnCl_4Br$	CCl_4	82	155–161	○	○	38.96 (39.10)	2.88 (2.59)
$SnClBr_4$	CCl_4	24	156–158	○	○	31.69 (31.82)	2.20 (2.10)
$ZrCl_5$	$CH_2Cl_2-CCl_4$	39	175–180	○		44.44 (44.59)	3.18 (2.95)
$NbCl_6$	$CH_2Cl_2-CCl_4$	82	160–166	○	○	41.78 (41.57)	3.06 (2.75)
$TaCl_6$	$CH_2Cl_2-CCl_4$	53	162–166	○		33.86 (35.80)	2.55 (2.36)
$FeCl_4$	CCl_4	83	166–169	○		51.31 (51.75)	3.72 (3.43)
ClO_4	Ac_2O	30	133–138 (lit.[d] 150)	○	○	66.79 (66.60)	4.52 (4.38)

[a] K. M. Harmon, A. B. Harmon, and F. E. Cummings, *J. Am. Chem. Soc.*, 83, 3913 (1961). [b] Reference 6. [c] F. Fairbrother and B. Wright, *J. Chem. Soc.*, 509 (1945). [d] Reference 5. [e] The circle indicates that ir and/or NMR spectra are satisfactory.

Table II
Central Metals Contained in Triphenylmethyl Salts Prepared[a]

	II		III		IV		V		VI		VII	
	A	B	A	B	A	B	A	B	A	B	A	VIII
2	(Be)[b]		B									
3			Al				*P*[c]					
4		(Zn)	Ga			(Ti)	*As*[c]		(Se)			Fe
5		(Cd)	In	(Y)[b]	Sn	Zr	Sb[c]	Nb[c]	(Te)		(I)	
6		(Hg)	Tl	(Ce)[b]		(Hf)	(Bi)	Ta[c]				
7						(Th)[b]						

[a] The parentheses indicate that impure salts are isolated. The italics indicate that pure triphenylmethyl salts are isolated when metal fluorides (but not chloride and bromide) are employed. [b] F. Fairbrother, *J. Chem. Soc.*, 503 (1945). [c] Preparation of triphenylmethyl metal fluorides was reported for these metals: ref 9.

salts which contain these metals were mainly employed for the subsequent polymerization study. It is to be noted that metal halides consisting of the metals shown in Table II are effective, as such, for the cationic polymerization of vinyl monomers.[10]

It is also worthy of mentioning that the halogen exchange did not seem to occur during the preparations of $Ph_3CSnClBr_4$ and Ph_3CSnCl_4Br. On the other hand, Ph_3CAlCl_4 was recovered by the reaction of Ph_3CCl and $AlEtCl_2$.

2. Polymerization. The polymerizations of α-methylstyrene with triphenylmethyl initiators were conducted, as in the previous study, in the following media: (I) 7:3 (v/v) $CH_2Cl_2-CH_3CN$; (II) CH_2Cl_2; (III) 7:3 (v/v) methylcyclohexane-CH_2Cl_2; (IV) 8:2 (v/v) methylcyclohexane-CH_2Cl_2; (V) 10:2 (v/v) methylcyclohexane-CH_2Cl_2. In general, the rate of polymerization increases with the increasing medium polarity. The triphenylmethyl salts were only partially soluble in MCH-CH_2Cl_2 mixtures, and, therefore, the initiator concentrations in this medium are apparent values. Ph_3CFeCl_4 and Ph_3CGaCl_4 were efficient initiators compared with other triphenylmethyl salts. This is probably attributable to their greater solubilities in the polymerization medium. Table III is a summary of the polymerization results in 8:2 methylcyclohexane-CH_2Cl_2. The steric structure of the polymer was determined from the methyl peak area in the NMR spectrum.

Triphenylmethyl salt may dissociate into triphenylmethyl halide and metal halide under the polymerization condition, and there arises a possibility that metal halide initiates polymerization by combination with water and other contaminants. However, this possibility was denied from kinetic evidence in the $Ph_3C^+SnCl_5^-$-styrene-CH_2Cl_2 system.[11] Sambi et al.[12] and Bawn et al.[13] reached the same conclusion.

Table III
Polymerization in 8:2 Methylcyclohexane-CH_2Cl_2
(Monomer, 0.71 *M*; Polymerization Temperature, −78° C;
Solvent, CH_2Cl_2 (10 ml) and MCH (40 ml))

No.	Initiator Counteranion	10^3M	Polymerization time, hr	Conversion, %	σ[a]
1	$AlCl_4$	6.05	44.5	24	0.127
2	$FeCl_4$	3.10	161	63[b]	0.129
3	$GaCl_4$	4.02	161	46[b]	0.130
4	$SnBr_5$	7.04	785	0.7	0.179
5	ClO_4	4.52	785	0.6	0.132
6	$ZrCl_5$	1.33	106	10	0.281
7	$InCl_4$	8.44	106	4.2	0.127
8	$TlCl_4$	2.76	71	3.1	0.140
9	$TaCl_4$	6.60	218	9.1	0.141
10	$NbCl_6$	11.4	218	10	0.186
11	$SnCl_5$	13.1	218	63[b]	0.215
12	$SnBrCl_4$	10.9	163	6.3	0.208
13	$SnClBr_4$	7.11	378	32[b]	0.195
14	BCl_4	14.8	183	11	0.203 (0.198)[c]
15	$InBr_4$	12.2	354	8.7	0.128 (0.138)[d]
16	BF_4	22.6	354	11	0.085 (0.098)[e]

[a] The data in parentheses are obtained for the polymer prepared separately under similar conditions. [b] Polymer precipitated noticeably during polymerization. [c] Initiator concentration: 14.0 m*M*. [d] Initiator concentration: 5.42 m*M*. [e] Initiator concentration: 31 m*M*.

More direct evidence for initiation by the Ph_3C addition was obtained in the polymerization of isobutyl vinyl ether.[1] In this study, we determined the content of the triphenyl-

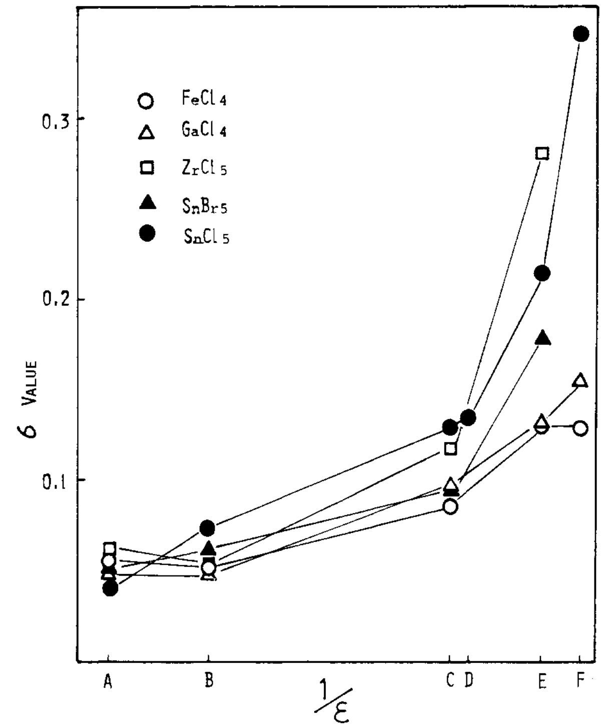


Figure 1. Variation of the σ value with the solvent polarity. The polymerization medium was placed in the order of decreasing polarity ($1/\epsilon$) in the abscissa: A, 3:7 CH_3CN-CH_2Cl_2; B, CH_2Cl_2; C, 7:3 MCH-CH_2Cl_2; D, 8:3 MCH-CH_2Cl_2; E, 8:2 MCH-CH_2Cl_2; F, 10:2 MCH-CH_2Cl_2.

methyl group by uv spectroscopy, and concluded from a comparison with the number-average molecular weight that 20–100% of the polymer chains are bonded to the triphenylmethyl group. Therefore, the polymerization must be initiated mostly by addition of the triphenylmethyl group if we take into account the facile chain transfer in the cationic polymerization.

These results strongly imply that the polymerization was initiated by the addition of the triphenylmethyl cation in the present system as well. The polymer was obtained only when the polymerization medium showed an orange yellow color of the triphenylmethyl cation.

It should be noted here that the conversions are greatly different, reflecting the change in the polymerization condition. Therefore, the correlation as described below would be meaningless, if the polymer structure is affected by the conversion. This problem was previously studied by Ohsumi et al.,[14] who found that the steric structure of poly(α-methylstyrene) was invariant over a wide range of conversion with BF_3OEt_2 in CH_2Cl_2. This conclusion would probably apply to the present catalytic system. In fact, the present data, though limited, clearly indicate that the steric structure is constant under a given polymerization condition.

3. Steric Structure of Polymer. The probability of the isotactic propagation σ as defined by Bovey was calculated from the fraction of the syndiotactic triad of the methyl signal P_{mm}.[2]

$$P_{mm} = (1 - \sigma)^2 \qquad (1)$$

The Bovey plot (triad fraction vs. σ) closely fitted the theoretical curve of one parameter σ for all the polymer samples, as in the previous cationic polymerizations of this monomer.[2,15,16] This means that the steric course of propagation can be described by the Bernoulli trial.[17]

The variation of σ with some initiators and polymerization solvents is shown in Figure 1. It is clearly seen that the σ value increases with the decreasing polarity of the polymerization medium. This tendency is the same with initiators having other anions: ClO_4^-, $TlCl_4^-$, $NbCl_6^-$, and $TaCl_6^-$. The counteranion effect on σ becomes more apparent in less polar media. A similar trend was observed previously for different initiators.[2] Thus, the influence of triphenylmethyl initiators on the steric structure was extensively studied in the 8:2 MCH-CH_2Cl_2 medium. Although the difference in the σ value becomes even greater in 10:2 MCH-CH_2Cl_2 media, the polymerization was too slow and it was difficult to obtain necessary amounts of the polymer in this solvent.

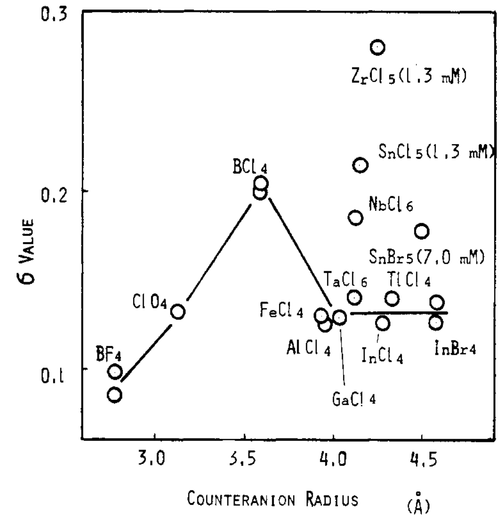


Figure 2. Dependence of the σ value on the counteranion radius. The initiator concentration is given in parentheses for the pentacoordinate anion.

4. Counteranion Effect on Steric Structure. The σ values for the polymers obtained in the 8:2 MCH-CH_2Cl_2 solvents are given in Table III. They fall in the range of 0.1 to 0.2, except for a high value (0.281) for $ZrCl_5^-$. The difference in the σ value between duplicate polymer samples appears to be 0.01 or less.

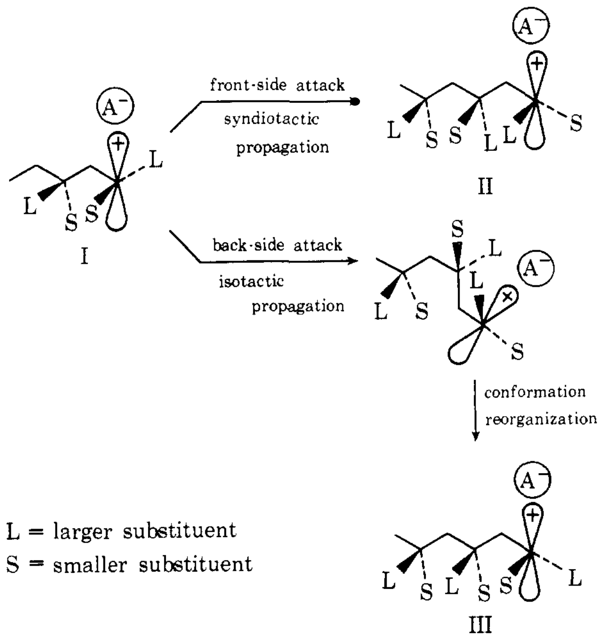
The σ values obtained were plotted against the radius of counteranions (Figure 2). The anion radius was estimated, where necessary, from the length of the metal-halogen bond and the van der Waals radius of the halogen atom involved, as mentioned previously.[1]

It is possible that the effective size of counterions is greater due to solvation. However, this is not likely since Szwarc showed that the conductivity data of $(C_6H_5)_3C^+SbCl_5^-$ in CH_2Cl_2 were explained without considering specific solvation.[18] The counteranions employed appear to be too large for specific solvation.

Figure 2 suggests that there exists a fairly simple correlation between the counteranion size and the σ value. Excluding the plots of $ZrCl_5$, $SnCl_5$, $SnBr_5$, and $NbCl_6$, the σ value increases with increasing anion size from BF_4^- to ClO_4^- and to BCl_4^-, and then decreases to a fairly constant value for counteranions of greater size. The peculiarity of the pentacoordinated anion was noted before, and is further discussed below. Observation of a greater σ value for $NbCl_6^-$ than expected from its size is difficult to rationalize at the moment. In the cationic polymerization of spiro[2.4]hepta-4,6-diene, $NbCl_6^-$ showed a counterion effect which is comparable to those of $GaCl_4^-$ and $InCl_4^-$.[19] Further experiments may be required to confirm the validity of these data.

In the previous paper we showed for a limited number of the counteranions that the isotacticity of poly(α-methylstyrene) increased with increasing size of the counteranion. It was suggested from these results that the steric effect of the counteranion possessed a predominant influence on the steric course of propagation. A fairly simple correlation observed in Figure 2 again indicates that the anion size is a major factor to determine the steric course for the majority of counteranions.

We have proposed the following scheme for the steric course of the cationic propagation.[20]



In this scheme, the most stable conformation of the last two units is assumed to be such as shown by I, and the front-side (less-hindered site) attack to the carbonium ion gives rise to a syndiotactic placement and the backside attack an isotactic placement. The relative ease of these modes of monomer attack is decided by the tightness of the growing ion pair for a given monomer; isotactic propagation is preferred with a tight ion pair.

The coulombic attraction of the oppositely charged ions descreases with increasing ion sizes, whereas the steric hindrance of the counteranion toward monomer attack may simply increase with its size. The observed tendency is explicable by a combination of these two effects.

The front-side attack becomes relatively less favorable as the anion size increases from BF_4^- to BCl_4^- because of their increasing steric hindrance. Further increase in the anion size may decrease the tightness of the ion pair due to decreased electrostatic attraction, provided that the steric influence levels off. Independent support of this interpretation may be obtained by the investigation of the steric course of β-substituted monomers which is being studied at present in these laboratories.

The *conformation* of the growing chain end will change with different counterions and solvents. However, the conformation change cannot affect the relative arrangement of the penultimate and terminal substituents and the counterion in the above scheme.[20]

In the cationic polymerization of isobutyl vinyl ether, considerable difference in the steric structure was caused by the use of different IIIA group metal chlorides as counteranion.[1] The corresponding change in the σ value of poly(α-methylstyrene) is barely beyond the experimental error except for BCl_4^-, although the trends in these two systems are the same.

Table IV
Initiator Concentration and Polymer Structure
(Monomer, 0.71 *M*; Polymerization Temperature, −78° C; Solvent, CH_2Cl_2 (10 ml) and MCH (40 ml))

No.	Initiator: Counterion	Initiator: 10^3M	Polymerization time, hr	Conversion, %	σ
1	$SnBrCl_4^-$	4.83	183	4.2	0.208
2	$SnBrCl_4^-$	10.9	163	6.3	0.188
3	$SnBrCl_4^-$	13.0	378	82.0	0.137,[a] 0.143[b]

[a] Fraction which remained in solution during polymerization. [b] Fraction which precipitated during polymerization.

The character of counteranions may also be influenced by the nature of the metal–halogen bond involved. Therefore, the ionization potential or electronegativity of the metal involved may be utilized as indices of the counteranion character. Unfortunately, the variation of the σ value was relatively small, if we exclude the pentacoordinate anions. Therefore, these correlations will be discussed in other polymerization systems where the difference in the steric structure is more pronounced.

5. Pentacoordinated Counteranions. It was indicated in the previous papers that the use of Ph_3CSnCl_5 as initiator gave rise to much greater amounts of the isotactic unit than expected from its counterion size.[1,2] Analogous results were obtained for $SnClBr_4$, $SnCl_4Br$, $SnBr_5$, and $ZrCl_5$, as seen from Figure 2. As mentioned before, these data are most satisfactorily explained by considering the peculiar structure of these counteranions. Pentacoordinate compounds generally assume non-rigid structures with facile interconversion between trigonal bipyramid and tetragonal pyramid structures.[21] The conceivably asymmetrical nature of these pentacoordinate counteranions may lead to tighter ion pairs than expected otherwise.

An interesting observation related to this discussion is the dependency of the steric structure on the initiator concentration shown in Table IV. The σ value decreased from 0.208 to 0.14 with increasing initiator concentrations. This σ variation cannot be attributed to precipitation of the polymer during polymerization, since the two fractions in run No. 3 gave the identical σ values within the experimental error.

Pentacoordinate anions are capable of association by using the vacant coordination site, unlike tetra- and hexacoordinated compounds. Therefore, it is possible that the structure of pentacoordinate counteranions varies by changing their concentrations. The results given in Table IV seem to support this view. The decreasing σ value with increasing Ph_3CSnCl_4Br may indicate that the nature of this pentacoordinate anion approaches those of fully coordinated counteranions. In fact, the σ value obtained with the highest Ph_3CSnCl_4Br concentration is 0.14 and this value is in the same range as those obtained with fully coordinated counteranions of comparable size. The change in the initiator concentration did not appear to affect the σ value in the case of BF_4, BCl_4, and $InBr_4$ counteranions (see Table III), in accordance with the above theory.

The present polymerization system is not advantageous for the elucidation of this problem, since the variation of the steric structure is not necessarily great. More definite discussions may be done in the cationic polymerization of vinyl ethers in later publications.

Acknowledgment. We are grateful to Mr. K. Takarabe for carrying out a part of the experimental work.

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Mechanism of Radical Copolymerizations of *N*-Vinylcarbazole with Diethyl and Dimethyl Maleate

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Received July 18, 1975

ABSTRACT: Free-radical initiated copolymerizations of *N*-vinylcarbazole (VCZ) (M_1) with diethyl maleate (M_2) or dimethyl maleate (M_2') have been studied in connection with the 1:1 alternating radical copolymerization of VCZ with the isomeric diethyl fumarate. The compositions of the copolymers vary from 1:1 alternation to increasingly VCZ rich with the increase of VCZ in the monomer feed (Table I). Results are strongly in favor of the mechanism involving the participation of free monomers in the alternating copolymerization (eq 2–5). Copolymer composition is well reproduced with $r_1 = 0.27$ (M_2), 0.26 (M_2'); $r_2 = 0$. This mechanism leads to the copolymerization rate eq 14, which fits well the experimental data (Figure 2).

The mechanism for the alternating radical copolymerization has recently attracted a great deal of attention, and is still controversial. Some propose the charge-transfer model to explain the alternation, that is, the charge-transfer complex formed between monomer pairs (the charge-transfer complexed monomer) homopolymerizes to yield the 1:1 alternating copolymer.[1] Others insist that the cross-propagation of free monomers, the transition state of which is stabilized, is operative.[2]

We have been investigating free-radical initiated copolymerizations of *N*-vinylcarbazole (VCZ), a typical electron-donating monomer which has recently received great attention in the field of the so called charge-transfer polymerization, with a series of electron-accepting monomers with a hope of elucidating the mechanism of the alternating radical copolymerization.

In the previous paper,[3] we reported the first known examples of the 1:1 alternating radical copolymerization of VCZ with diethyl fumarate or fumaronitrile, and proposed a new model for the alternating radical copolymerization. The generalized mechanism which we have proposed involves the participation of both free monomers and the charge-transfer complexed monomer (CT-complexed monomer) in the propagation step of the polymerization with a varying degree of their contributions to the polymerization which depends on the reaction system. Our model stands on the basis that the alternation can be brought about by the stabilization of the transition state of the cross-reaction of both free monomers and the CT-complexed monomer, and that the participation of the CT-complexed monomer in the polymerization makes contribution to the enhancement of the polymerization rate due to its higher reactivity than the free monomer.

Our continued interest in this field has led us to extend the study to the copolymerization of VCZ with the isomeric electron-accepting monomer of diethyl fumarate and diethyl and dimethyl maleate. The present results are consistent with our model and seem to provide the experimental evidence for the participation of the free monomer in the alternating radical copolymerization.

Experimental Section

Materials. *N*-Vinylcarbazole (VCZ) and 2,2′-azobisisobutyronitrile (AIBN) were purified and dried as described in the previous paper.[4] Diethyl maleate and dimethyl maleate which were obtained commercially (WAKO Pure Chemical Ind. Ltd.) as pure grade reagents were dried over calcium chloride, and distilled twice from calcium hydride in vacuo under a nitrogen stream, bp 71.5°C (2 mm) and 60.5°C (2 mm), respectively. The purity of the material was checked by means of GLC.

Polymerization Procedure. All copolymerizations were carried out in a benzene solution using AIBN as an initiator. The total monomer concentration was fixed as 1.0 *M*, the monomer feed ratio being varied widely. The initiator concentration was 1.0×10^{-3} *M*. The polymerization solution contained in a glass tube, ca. 1.5 cm in diameter, was evacuated at 2×10^{-2} Torr by means of several freeze–pump–thaw cycles, sealed off and then allowed to stand for an appropriate time in a thermostat maintained at 80 ± 0.1°C. The polymerization was stopped at low conversions. The polymerization solution was chilled and poured into a large volume of MeOH to precipitate the polymer. The polymers were collected by filtration with a glass filter, washed with MeOH repeatedly, dried in vacuo, and weighed. The polymers were reprecipitated twice from benzene with MeOH and submitted to analyses.