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The Steric Course of the Cationic Polymerization of Vinyl and Related Monomers. The Counterion Effect

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ABSTRACT

Polymerization with many triphenylmethyl salts was conducted for α-methylstyrene, isobutyl vinyl ether, t-butyl vinyl ether, and spiro[2,4]hepta-4,6-diene (SHD). The variation of polymer structure (the isotactic unit content for the first three monomer systems and the amount of the 1,4-addition structure for SHD) showed fairly simple correlations with the counteranion size. The results can be interpreted in terms of the tightness of the propagating ion pair within the framework of a theory of the cationic propagation which had been proposed. When the counteranion radius was greater than 3.5 Å, the counteranion exerts a parallel influence on the tightness of the growing ion pair without regard to the monomer structure. However, in the case of smaller counterions, the tightness appears to be determined by the relative sizes of counteranion and monomer. The penta-coordinated counteranions gave rise to the polymer

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*Contribution No. 349.

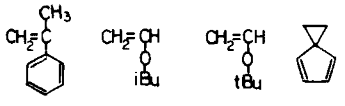
structure which would arise from tighter ion pairs than expected from their sizes alone. The polymer structure was also affected by the initiator concentration in these cases. These results are attributed to peculiar characteristics of penta-coordinated anions.

INTRODUCTION

Among the major unsolved problems in cationic polymerization is the role played by the counterion. The counteranion in the propagating ion pair is, in most cases, derived from the catalyst, and the so-called catalyst effect observed in the cationic propagation must be largely related to the behavior of the counteranion. Unfortunately, however, the structure of the growing ion pair is usually not well defined, and it is as yet difficult to interpret the propagation data in a unified way in terms of the nature of the growing species.

The stable carbocation salts have been used increasingly as initiators of cationic polymerization [1, 2]. They include triphenylmethyl, tropylium, and xanthylium ions in combination with several counteranions. Their use in vinyl polymerization is advantageous in that the anion becomes a part of the growing species without changing its structure.

In the present report we describe the systematic preparation of triphenylmethyl salts and their use for the cationic polymerization of the following representative vinyl and related monomers:


αMS IBVE tBVE SHD

Particular emphasis is placed on establishing the relation between the structures of counteranions and polymers, since the ambiguity which always accompanies the kinetic data is not present in this case.

RESULTS AND DISCUSSION

Initiation by Triphenylmethyl Salts

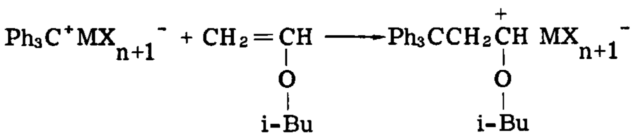
Triphenylmethyl salts may exist in the following forms which are in equilibrium:

$$Ph_3CX + MX_n \underset{}{\overset{K_1}{\rightleftharpoons}} Ph_3CX \cdot MX_n \overset{K_2}{\rightleftharpoons} Ph_3C^+MX_{n+1}^- \overset{K_3}{\rightleftharpoons} Ph_3C^+ + MX_{n+1}^- \quad (1)$$

contact and
agent-separated

There is a possibility that metal halides, MX_n, initiate polymerization by combination with H_2O and other contaminants. This possibility was denied from kinetic evidence in the $Ph_3C^+SnCl_5^-$-styrene-CH_2Cl_2 system [3]. Sambi et al. [4] and Ledwith [11] reached the same conclusion.

More direct evidence for initiation by the Ph_3C addition was obtained in the polymerization of isobutyl vinyl ether [5]. Table 1 shows the content of the triphenylmethyl group in the polymer as determined by UV spectroscopy. From a comparison with the number-average degree of polymerization, it is clear that 20 to 100% of the polymer chain is bonded to the triphenylmethyl group, depending on the polymerization condition. Therefore, the initiation is concluded to be the addition of the triphenylmethyl group by considering the facile chain transfer in the cationic polymerization:



$$Ph_3C^+MX_{n+1}^- + CH_2{=}\underset{\substack{| \\ O \\ | \\ i\text{-}Bu}}{CH} \longrightarrow Ph_3CCH_2\underset{\substack{| \\ O \\ | \\ i\text{-}Bu}}{\overset{+}{CH}}\ MX_{n+1}^- \quad (2)$$

NMR spectra of five triphenylmethyl salts ($Ph_3C^+MX_n^-$, $MX_n = BF_4$, $AlCl_4$, $AlBr_4$, $SnCl_5$, and $SbCl_6$) in ethylene dichloride or in acetonitrile showed a phenyl multiplet at around 8 ppm,

TABLE 1. Content of the Triphenylmethyl Group in Poly-IBVE

Initiator	Solvent	Number-average degree of polymerization[a] ($\overline{P}_n$)	Number of monomer unit per Ph_3C group incorporated	Number of chain transfer per initiation[b]
$Ph_3C^+AlCl_4^-$	MCH-CH_2Cl_2 8:3	227	530	1.3 ± 0.4
$Ph_3C^+BF_4^-$	MCH-CH_2Cl_2 8:3	240	326	0.4 ± 0.2
$Ph_3C^+SnCl_5^-$	MCH-CH_2Cl_2 8:3	134	237	0.8 ± 0.4
$Ph_3C^+AlCl_4^-$	CH_2Cl_2	167	396	1.4 ± 0.5
$Ph_3C^+BF_4^-$	CH_2Cl_2	175	410	1.3 ± 0.4
$Ph_3C^+SbCl_6^-$	CH_2Cl_2	154	420	1.7 ± 0.8
$Ph_3C^+SnCl_5^-$	CH_2Cl_2	130	170	0.4 ± 0.4
$Ph_3C^+AlCl_4^-$	CH_2Cl_2-CH_3CN 7:3	161	220	0.4 ± 0.3
$Ph_3C^+BF_4^-$	CH_2Cl_2-CH_3CN 7:3	142	320	1.3 ± 0.4
$Ph_3C^+SbCl_6^-$	CH_2Cl_2-CH_3CN 7:3	84	455	4.4 ± 0.8
$Ph_3C^+SnCl_5^-$	CH_2Cl_2-CH_3CN 7:3	57	57	0.1 ± 0.1

[a] Determined by vapor pressure osmometry.

[b] $\left\{\left[\frac{\text{Monomer unit}}{Ph_3C}\right] / \overline{P}_n\right\} - 1$. The error was estimated from the reliability of determinations of molecular weight and the triphenylmethyl content.

which was identical with the spectrum of the triphenylmethyl cation in chlorosulfonic acid [6]. The phenyl proton due to triphenylmethyl halides was not detected. A similar spectrum was observed for $Ph_3C^+AlBr_4^-$ in a 6:4 mixture of ethylene dichloride and n-hexane. Therefore, it is assured that the triphenylmethyl species exist mostly in the ionic form in the polymerization system. On the other hand, Higashimura et al. determined the equilibrium constant between the ionic and nonionic forms of Ph_3CSnCl_5 (K = 0.5 to 0.8 M) at the UV concentration (~10^{-4} M).

From the above discussion, the MX_{n+1}^- anion in the triphenylmethyl salts can be considered to become the counteranion of the growing chain without structural modification. This is a fundamental assumption in discussing the counterion effect in the propagation step. Direct evidence for this assumption is lacking. However, the fairly simple correlations described below provide strong circumstantial evidence.

Preparation of Triphenylmethyl Salts [7]

Although many triphenylmethyl salts have been reported in the literature, their systematic preparation has apparently not been attempted. Therefore, we carried out preparations of a number of the salts mostly from triphenylmethyl chloride or bromide and the corresponding metal halides by simply mixing and washing under nitrogen in appropriate solvents. The product was confirmed by elemental analysis and by IR and NMR spectroscopy.

The metal halides which have been successfully employed for the preparation for the first time include $GaCl_3$, $InCl_3$, $TlCl_3$, $ZrCl_4$, $TaCl_4$, $NbCl_5$, and $InBr_3$. Attempted preparations with the following metal halides were only partially successful: $HfCl_5$, $BiCl_4$, $BiBr_4$, $TeCl_5$, $SeCl_5$, $TiCl_4$, and ICl_3. In Table 2 the central metal atoms contained in the anion of triphenylmethyl salts ($Ph_3C^+MX_{n+1}^-$, X = F, Cl, and/or Br) are placed in their respective positions of the periodic table. The parentheses indicate isolation of impure salts, and underline indicates that pure triphenylmethyl salts were isolated when metal fluorides (but not chloride and bromide) are employed. It is clear from Table 2 that triphenylmethyl salts are most readily formed when the counteranion contains the IIIA group metal (B, Al, Ga, In, and Tl) and the 5th period metal (In, Sn, Zr, Sb, and Nb). The fluoride salts are more stable than their chloride and bromide counterparts, but the latter salts were usually employed in our study because of preparative convenience.

TABLE 2. 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 were isolated. The underlines indicate that pure triphenylmethyl salts were isolated when metal fluorides (but not chloride and bromide) were employed.

[b] F. Fairbrother, J. Chem. Soc., 1945, 503.

[c] Preparation of triphenylmethyl metal fluorides was reported for these metals in D. W. A. Sharp and N. Shepperd, J. Chem. Soc., 1957, 674.

Polymerization of α-Methylstyrene [7,8]

The polymerization of α-methylstyrene was carried out in several solvent systems at -76°C by using Friedel-Crafts catalysts and the triphenylmethyl initiators mentioned above. The polymerization was generally slow, the polymerization period being more than 100 hr in 8:1 methylcyclohexane (MCH)-CH_2Cl_2.

The steric structure of the polymer was determined from the relative peak area of the three methyl signals in the NMR spectrum according to Brownstein et al. [9]. The probability of isotactic propagation σ as defined by Bovey was calculated from the fraction of the sydiotactic triad P_{mm}:

$$P_{mm} = (1 - \sigma)^2 \tag{3}$$

The plot of σ vs the triad fraction closely fitted the theoretical curve of one parameter σ for all the polymer samples, as in the previous cationic polymerizations of this monomer. Therefore, the penultimate effect is absent.

Figure 1 shows the variation of the σ value with initiator and solvent. There are several important features included in this figure. One is the solvent effect. In the abscissa the solvent systems are arranged in the order of increasing polarity. The σ value decreases with increasing polarity of the medium. Furthermore, the σ variation with initiator is greatest in the least polar solvent, and the difference diminishes as the polarity of the medium increases. In fact, the σ value was independent of the counteranion in 3:7 CH_3CN-CH_2Cl_2, indicating that the growing ion pair is too loose for a counteranion to affect the steric course of propagation. A third feature is that Lewis acids give rise to σ values which are smaller than those obtained with the corresponding triphenylmethyl salt (e.g., $SnCl_4$ vs $Ph_3C^+SnCl_5^-$). It is possible that counteranions derived from Lewis acids possess structures quite different from what is expected by simple combinations of Lewis acid and cocatalyst. These results point to the danger of discussing the propagating ion pair based on the data obtained with Lewis acids.

Figure 2 shows the variation of the σ values with the counterion radius for poly-α-methylstyrene obtained at -76°C in 8:2 MCH-CH_2Cl_2. They fall in the range of 0.1 to 0.2, except for a high value (0.281) for $ZrCl_5^-$. The counteranion radius was estimated, where necessary, as the sum of the length of the metal-halogen bond and the van der Waals radius of the halogen atom [5]. The σ value increases with

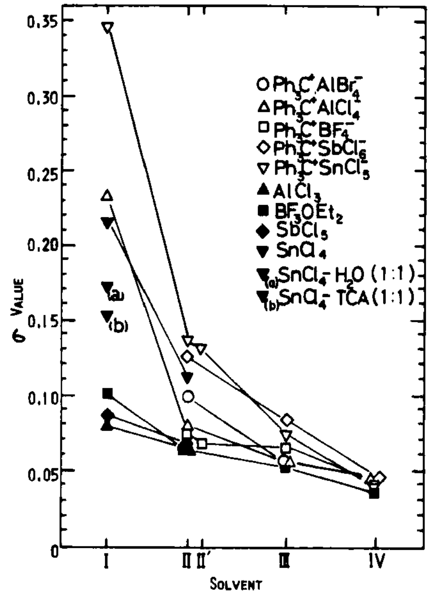


FIG. 1. Variation of the steric structure of poly-α-methylstyrene. Polymerization temperature: -76°C. Solvents: I, 10:2 MCH-CH_2Cl_2; II, 8:3 MCH-CH_2Cl_2; II′, 7:3 MCH-CH_2Cl_2; III, CH_2Cl_2; IV, 7:3 CH_2Cl_2-CH_3CN.

increasing anion size from BF_4^- to ClO_4^- to BCl_4^-, and then decreases to a fairly constant value for counteranions of greater size. The penta-coordinated anions ($ZrCl_5^-$, $SnCl_5^-$, $SnBr_5^-$) gave σ values greater than expected from their sizes, and they are excluded from the correlation.

The σ value may well be correlated with other properties of the counteranion such as the first ionization potential or the electronegativity of the central metal atom. Figure 3 shows plots of σ vs electronegativity for metal chloride counteranions. There does not seem to exist any meaningful trend.

These data can be comfortably accommodated in our proposal on the steric course of propagation of vinyl and related monomers [10]. In this scheme the most stable conformation of the last two monomer units is assumed to be that shown by I. The monomer attack at the frontside (less hindered site) of the carbenium ion results in a syndiotactic placement, and the monomer attack at the backside in an isotactic placement. The relative ease of

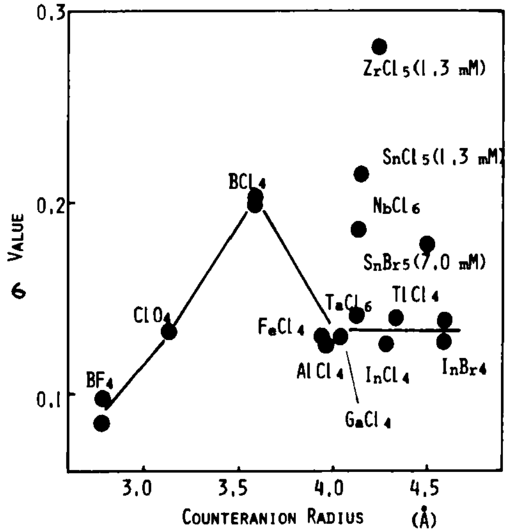


FIG. 2. Dependence of the steric structure of poly-α-methylstyrene on counteranion size. Temperature: -76°C. Solvent: 8:2 MCH-CH_2Cl_2.

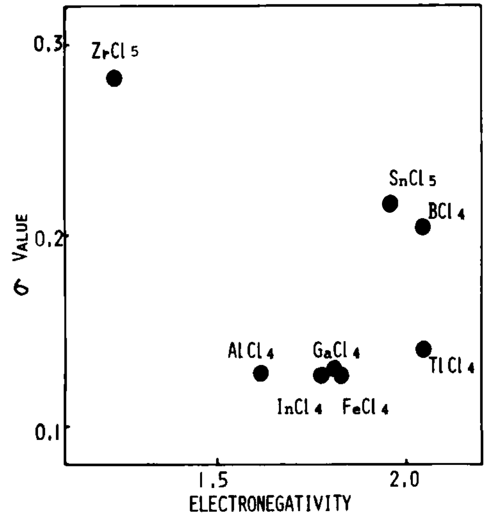
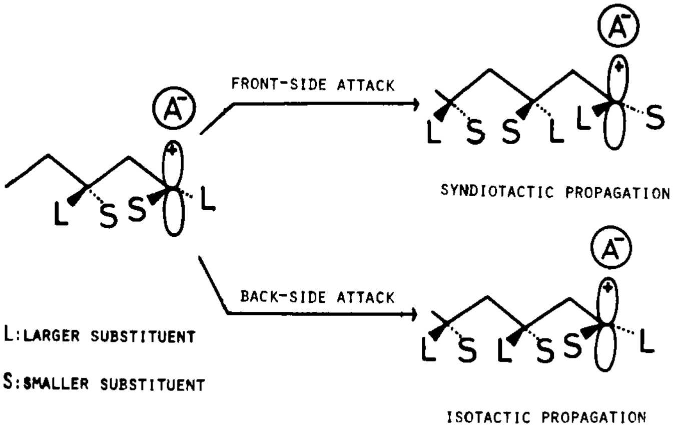


FIG. 3. Dependence of the steric structure of poly-α-methylstyrene on the electronegativity of the central metal of the counteranion. Polymerization condition: -76°C, 8:2 MCH-CH_2Cl_2.

monomer insertion at the frontside and the backside is influenced by the tightness of the propagating ion pair and the difference in the steric hindrance between the two modes of monomer attack. Therefore, the tightness is influenced only by counteranions for a given monomer under a given polymerization condition. The decrease of the σ value in polar media (Fig. 1) reflects a lowering of the tightness, i.e., an increased frontside attack.



(4)

The syndiotactic placement at the frontside is favored in the case of α-methylstyrene (small σ value) because the α-carbon is disubstituted and the backside attack is subject to the enhanced steric hindrance of the penultimate side chains.

Polymerizations of Isobutyl Vinyl Ether and t-Butyl Vinyl Ether

Vinyl ethers are one of the representative monomers in cationic polymerization, and the variation of the steric structure of these polymers has been studied to some extent. We selected two common vinyl ethers and investigated the variation of the steric structure.

Isobutyl vinyl ether(IBVE) polymerizes quite readily with various triphenylmethyl salts [5, 11, 12]. The steric structure of poly(isobutyl vinyl ether) can be determined from the CH_2 dyad by means of CMR spectroscopy [13]. Figure 4 shows examples of the FT-CMR spectrum of IBVE polymer. In addition to the change of the CH_2 doublet, the

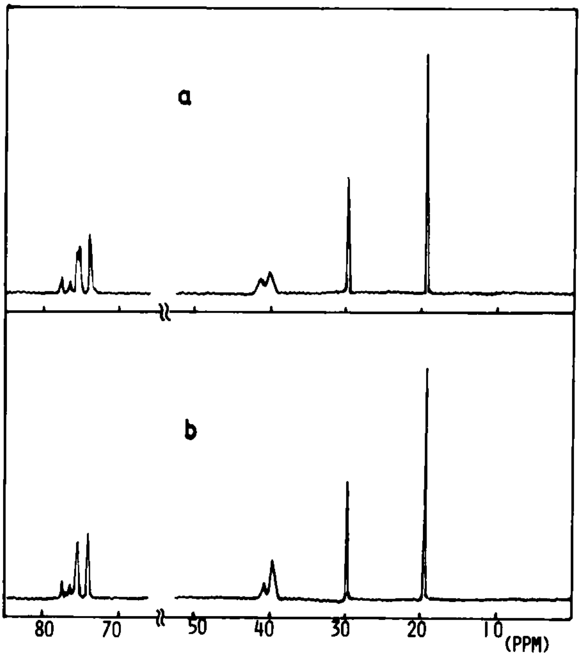


FIG. 4. ^{13}C NMR spectra of poly(isobutyl vinyl ether). (a) $CDCl_3$ solvent, 3600 scans, TMS reference. Polymerization conditions: -76°C, $Ph_3C^+ClO_4^-$, 5:5 C_6H_{14}-CH_2Cl_2. (b) $CDCl_3$ solvent, 5000 scans, TMS reference. Polymerization conditions: -76°C, $Ph_3C^+BCl_4^-$, 5:5 C_6H_{14}-CH_2Cl_2.

peaks of the methine and methylene carbons adjacent to oxygen are apparently affected by the steric structure. However, the assignment of the latter peaks has not been made.

The σ value was calculated from the relative peak area of the CH_2 dyad. It decreases with increasing polarity of the polymerization medium as in the polymerization of α-methylstyrene, reflecting loosening of the propagating ion pair. The variation of σ with counteranions is summarized in Fig. 5. The polymers were obtained at -76°C in 5:5 n-hexane—CH_2Cl_2. The σ value increases with increasing counterion sizes from BF_4^- to BCl_4^- via ClO_4^-, then decreases at $AlCl_4^-$, and again increases at $GaCl_4^-$ to $TlCl_4^-$. This trend is very similar to that of poly-α-methylstyrene, although it is less clear in the latter because of smaller changes of the σ value. Again the $SnCl_5^-$ counterion gave higher σ values.

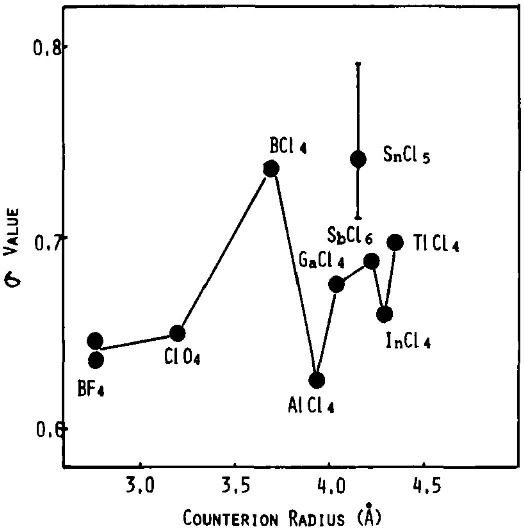
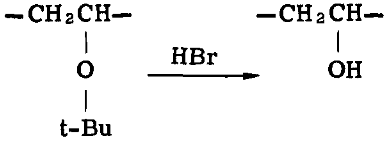


FIG. 5. Dependence of the steric structure of poly(isobutyl vinyl ether) on counteranion radii. Polymerization temperature: -76°C. Solvent: 5:5 C_6H_{14}-CH_2Cl_2.

Similarly, t-butyl vinyl ether (t-BVE) was polymerized with triphenylmethyl initiators [14]. Facile polymerization occurred. The polymer was converted to poly(vinyl alcohol) without separation [15], and the steric structure was determined from the splitting of the hydroxyl proton of poly(vinyl alcohol) in DMSO-d_6 [16].



$$\underset{\substack{|\\ \text{O}\\ |\\ \text{t-Bu}}}{-\text{CH}_2\text{CH}-} \xrightarrow{\text{HBr}} \underset{\substack{|\\ \text{OH}}}{-\text{CH}_2\text{CH}-} \qquad (5)$$

The trends in the σ variation are rather similar between the two poly(vinyl ethers) for counteranions with radii greater than 3.5 Å (Fig. 6). However, the σ values for BF_4^- and ClO_4^- are greater than that for BCl_4^- in the case of poly-t-BVE, and the reverse is true for polyIBVE. These results suggest that the counterion effect on σ is not always independent of the monomer structure.

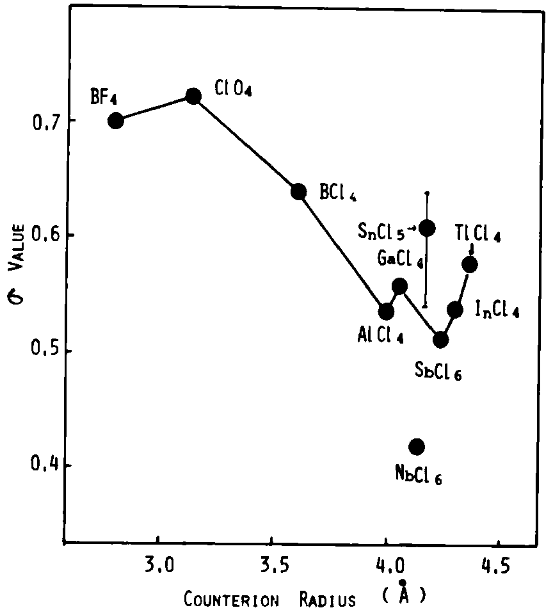
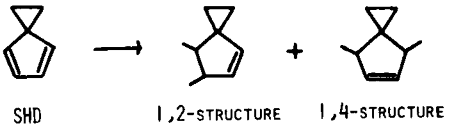


FIG. 6. Dependence of the steric structure of poly(t-butyl vinyl ether) on counteranion radii. Polymerization temperature: -76°C. Solvent: 7:3 CH_2Cl_2-toluene.

Polymerization of Spiro[2,4]hepta-4,6-diene

Cyclopentadiene polymerizes very readily with cationic initiators such as Lewis acids. Polycyclopentadiene formed under mild polymerization conditions is composed of the 1,2- and 1,4-addition structures. Their relative contents can be estimated by PMR spectroscopy [17]. Unfortunately, the structural variation with the polymerization condition was relatively small, and the counterion effect could not be studied in detail.

We recently found that spiro[2,4]hepta-4,6-diene (SHD) formed polymers very readily by cationic initiators [18]. This polymer is quite stable to autoxidation and heat compared with other cyclopentadiene polymers, and the polymer chain is presumed to be quite stiff from the viscometric data. On the other hand, spiro[4,4]nona-1,3-diene (SND) showed much less cationic reactivity [19].



(6)

The structure (1,2- and 1,4-structures) of polySHD can be accurately determined from the olefinic proton peak. There was no indication of opening of the cyclopropyl ring. The content of the 1,4-structure decreases with increasing solvent polarity for a given initiator. This means that the 1,4-structure content can be a measure of the tightness of the growing ion pair. Figure 7 shows the dependence of the 1,4-structure content on the counterion size [20]. The structural variation is remarkable, considering that

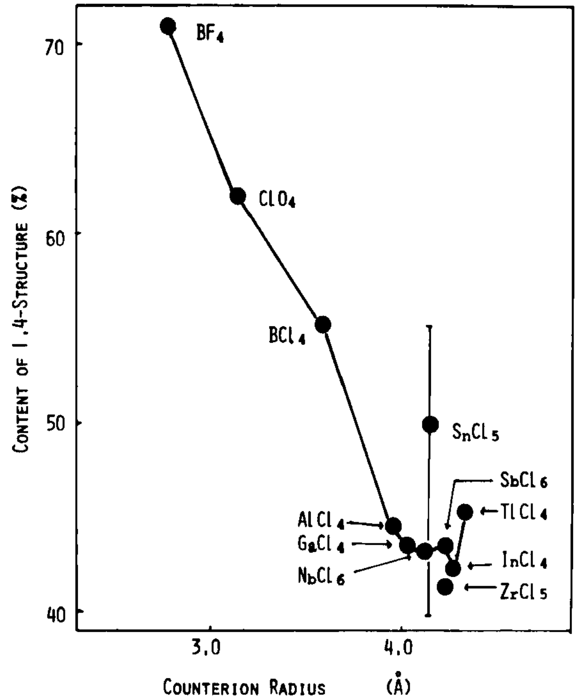
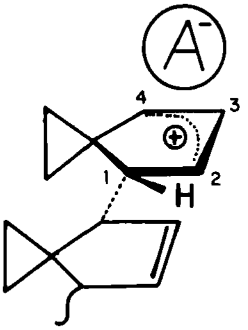


FIG. 7. Dependence of the structure of polyspiroheptadiene on counteranion radii. Polymerization temperature: -76°C. Solvent: 5:5 CH_2Cl_2-toluene.

the same polymerization medium is employed. The amount of the 1,4-structure decreases with increasing counterion radii from BF_4^- to $InCl_4^-$ and then increases at $TlCl_4^-$. It is noted that the structural change between $AlCl_4^-$ and $TlCl_4^-$ have some similarity to the variation of σ observed for other vinyl polymers. The penta-coordinated anions $SnCl_5^-$, $SnBr_5^-$, and $ZrCl_5^-$ again gave rise to the 1,4-structure contents, which are greater than expected from the correlation of Figure 7.

The influence of the polymerization conditions on the mode of propagation of SHD may be discussed using a propagation model related to the above-mentioned proposal. The structure of the propagating ion pair of SHD may be assumed to be



The counterion A^- is supposedly placed on the face of the five-membered ring which is remote from the penultimate unit. When the counteranion is only loosely associated with the growing cation, monomer molecule may react with the cation at the 2- and 4-positions from the less hindered side of the five-membered ring, avoiding the steric crowding of the penultimate unit. The formation of the 1,2-structure may be favored in this case because of the steric hindrance of the cyclopropyl group toward monomer attack at the 4-position. The difference in stability may also favor formation of the 1,2-structure.

As the tightness of the propagating ion pair increases, the reaction of the incoming monomer at the face of the five-membered ring opposite to the counterion (backside attack) will occur more readily. In this case the reaction at the 4-position is preferred because of the steric influence of the penultimate unit.

Influence of Initiator Concentration

In the previous sections the structural data obtained with penta-coordinated counteranions were omitted from the correlation because of their peculiar behavior. For example, in the polymerization of α-methylstyrene using $Ph_3C^+SnClBr_4^-$, the σ value was greater than expected from the counteranion size and, in addition, showed dependency on the initiator concentration [7].

Similar results are obtained with polySHD. When $Ph_3C^+SnCl_5^-$ was used as initiator, the content of the 1,4-structure decreased from 58 to 40% with an increase in the initiator concentration from 0.5 to 10 mM (-76°C, n-hexane—CH_2Cl_2). The polymer structure was independent of the initiator concentration (1,4-structure: 42%), when $Ph_3C^+InCl_4^-$ was used [20].

Figure 8 shows the structure changes of poly(vinyl ethers) with initiator concentrations. In the case of polyIBVE the same initiator dependence as mentioned above was observed: the σ value decreased with increasing concentrations of $Ph_3C^+SnCl_5^-$ initiator, and the concentration changes of $Ph_3C^+InCl_4^-$ and $Ph_3C^+SbCl_6^-$ did not affect the σ value. On the other hand, a somewhat different situation was found for poly-t-BVE. The σ value for this polymer increases with increasing concentrations of $Ph_3C^+SnCl_5^-$ and reaches a constant value. Again, the concentration change of $Ph_3C^+InCl_4^-$ did not affect the σ value. Interestingly, the σ value increased when t-BVE was polymerized by $Ph_3C^+SnCl_5^-$ (1 mM) in the presence of 7 mM of $(n\text{-}Bu)_4N^+SnCl_5^-$.

Except for poly-t-BVE, the structures of polymers obtained with higher concentrations of $Ph_3C^+MX_5^-$ (saturation value) are quite close to those obtained with other initiators where no concentration effects are observed.

Counteranion Effects on Polymer Structure

According to the propagation scheme mentioned above, the counteranion effect is, in the main, related to the tightness of the propagating ion pair. Two major findings are obtained from the present research. One is the relatively simple correlation of the polymer structure with counteranion sizes. The other is the peculiarity of penta-coordinated counteranions.

The counteranions may be characterized by various properties in relation to the tightness of the propagating ion pair. When a counteranion is symmetrical or fully-coordinated, electrostatic

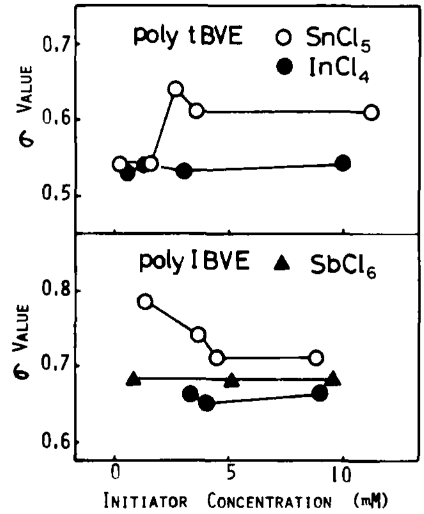


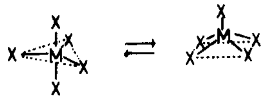
FIG. 8. Influence of the initiator concentration on the steric structure of poly(vinyl ethers). Polymerization conditions: for polytBVE, -76°C, 7:3 CH_2Cl_2-toluene; for polyIBVE, -76°C, 5:5 $CH_2Cl_2C_6H_{14}$.

and steric factors would suffice to describe its effect, provided that there are no specific interactions operating between counteranion and monomer. These two factors are primarily determined by the size of counteranions. The nature of the metal-halogen bond is influenced by the electronegativity or ionization potential. However, they are probably of secondary importance. In fact, the experimental results could not be correlated with these properties in any simple way. The specific solvation may alter the effective size of counteranions. This is again considered to be of minor importance. In anionic polymerization with alkali metals as countercations, Cs^+ is not specifically solvated in THF because of its size (radius, 1.69 Å) [21]. The counteranions employed in the present study are much larger than Cs^+, and the specific solvation is probably unimportant.

The trends shown in Figs. 2, 5, 6, and 7 are generally similar for counteranions larger than BCl_4^- in that general decreases of the σ values and the 1,4-structure are observed with increasing counteranion sizes. The variations between $AlCl_4^-$ and $InCl_4^-$ are fairly small, and detailed comparisons among counteranions and among polymers are not desirable. These data may be interpreted as showing that the tightness decreases due to weakened coulombic interaction for larger counteranions. The unmistakable increase in the tightness at $TlCl_4^-$ might be a reflection of the large ionization potential of Tl metal. It is of particular import that the common counterion effects were observed in this region.

On the other hand, the polymer structures depend on the counteranion size quite differently among polymers in the region of BF_4^-, ClO_4^-, and BCl_4^-. The monomer structure must affect the tightness (the relative ease of the frontside and backside attack) when counterions are small. This is readily seen by comparing the relative influences of these counteranions on the polymer structure. The σ value increases in the order of $BF_4^- < ClO_4^- < BCl_4^-$ for poly-α-methylstyrene and for polyIBVE. The order is $BF_4^- \lesssim ClO_4^- > BCl_4^-$ for poly-t-BVE, and the 1,4-structure of polySHD decreases in the order of $BF_4^- > ClO_4^- > BCl_4^-$. Steric crowding of the propagating terminal is apparently associated with the varying influences of these small counteranions. It may be postulated that the tightness of the ion pair decreases with increasing counterion sizes because of steric interference of counterion and side chain when the propagating end is crowded. The tightness increases with the increasing size of counteranions when crowding of the propagating chain end is reduced. In essence, the frontside attack is hindered most effectively when either (but not both) the counteranion or the side chain is bulky. However, this does not hold true if the counteranion size is greater than 3.5 to 4.0 Å. In this region the tightness becomes fairly insensitive to the sizes of counteranion and side chain.

The peculiar behavior of penta-coordinated anions may be attributed to their characteristic structures. It is known that the structure of penta-coordinated species (MX_5) is generally nonrigid, and one of the possible conformation—trigonal bipyramid—may readily convert to the other conformation—tetragonal pyramid [22].



(7)

This structural characteristic can give rise to an asymmetrical MX_5^- anion, and its effect could be different from what is expected from its size alone.

The tetragonal-pyramid conformation of the penta-coordinated anion possesses a vacant coordination site, in contrast to the fully coordinated tetra- and hexa-halide anions. The observed dependency of the polymer structure on the initiator concentration suggests the occurrence of aggregation of the penta-coordinated counteranions at high concentrations. The lack of the concentration effect for other anions is consistent with this view. The tightness (that is, the σ value and the 1,4-structure) in the penta-coordinated anion system was considerably greater than that of other anions at low initiator concentrations. The tetragonal-pyramid counteranion could yield an ion pair tighter than expected from other conformations. The tightness approaches a normal value with increasing initiator concentrations because of aggregation of counterion. The poly-t-BVE system is an exception, and the σ value increases with increasing concentrations of the $SnCl_5^-$ anion. This fact is hard to interpret.

CONCLUSION

Representative vinyl-type monomers for cationic polymerization were selected and subjected to polymerization by various triphenylmethyl initiators. A fairly simple picture emerged concerning the counteranion effect on the steric (and geometrical) course of propagation, in spite of differences in the monomer structure.

The present study was limited to the structural change of polymers. It should be interesting to examine the implications of the present study on other polymerization characteristics. Further efforts must be directed to confirming the propagation model and to designing counteranions with desired characteristics.

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