Section, this particular material is highly insoluble in C_6D_6. On the other hand, the trans polymer was made with an i-Bu_3Al–0.5·H_2O catalyst where a lower degree of enantiomorphic reflection was apparent.

^{13}C NMR data from crystalline poly(1,4-dichloro-2,3-epoxybutanes), together with the reduced hydrocarbon polymers, are summarized in Table III.

Only two signals were observed from the polymer derived from the *cis*-1,4-dichloro-2,3-epoxybutane, 79.34 and 43.69 ppm for the methine and methyl carbons, respectively. After reduction with $LiAlH_4$, this polymer gives two signals at 76.18 and 15.04 ppm, in very close agreement with those observed from the poly(*cis*-2,3-epoxybutane), shown as entry 1 in Table III. Therefore, poly(*cis*-1,4-dichloro-2,3-epoxybutane) has also the –RR–RR–RR– or –SS–SS–SS– microstructure.

It can also be seen from the data in Table III that the reduced poly(*trans*-1,4-dichloro-2,3-epoxybutane) has signals in almost exactly the same position as those from the poly(*trans*-2,3-epoxybutane), entry 2 in Table III. The intensity ratio of the two methine signals at 78.34 and 77.56 ppm was found also to be comparable to the ratio from the corresponding signals in poly(*trans*-2,3-epoxybutane). Therefore, these two polymers have similar microstructure, i.e., in stereoblocks with an average sequence of –RS–RS–RS–RS–RS–SR–SR–SR–SR–SR–.

Acknowledgment. The authors are indebted to Drs. W. J. Freeman and R. W. Harrell for many helpful discussions.

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Catalytic Difference between Oxo Acids and Metal Halides in the Cationic Oligomerization of Styrene

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ABSTRACT: The structure and molecular weight (distribution) of products in the cationic oligomerization of styrene were found to be controlled by the proper choice of counteranions. Oxo acids as catalysts ($AcClO_4$, CF_3·SO_3H, and p-$CH_3C_6H_4SO_3H$·H_2O) formed a linear unsaturated styrene dimer predominantly in benzene at 70 °C. On the other hand, metal halides yielded trimers (by BF_3·OEt_2 in C_6H_6) or tetramers (by BF_3·OEt_2 in $(CH_2Cl)_2$ and by $SnCl_4$ or $EtAlCl_2$ in C_6H_6) as the main product at 70 °C. Product distribution analysis showed that transfer constants (k_{tr}/k_p) for the oxo acids were larger than those for the metal halides and were independent of the chain length of the propagating species; in the case of the metal halides, transfer constants for short growing chains differed from those for long growing chains. The catalytic difference between the oxo acids and the metal halides was explained in terms of the interaction between a growing carbocation and a counteranion derived from a catalyst. The linear trimer or tetramer of styrene was produced in high yield by lowering initial monomer concentration and by using the metal halides as catalysts.

The acid-catalyzed cationic polymerization of vinyl compounds cannot generally give high polymers unless carried out at low temperature, and thus, at high temperature, it is a useful reaction for production of oligomers. For example, styrene treated with metal halides at room temperature readily yields oligomers with relatively high molecular weights (10^3–10^4),[1] and those with lower molecular weights $<10^3$ can be prepared by use of oxo acids such as sulfuric and phosphoric acids.[2] However, products in cationic oligomerization usually have complicated structures[3] that have hampered systematic investigations concerned with their chemical constitution, molecular weight, and molecular weight distribution under various reaction conditions. An exceptional case is our recent finding that a linear unsaturated dimer of styrene (1,3-diphenylbut-1-ene) has been selectively obtained in high yield with acetyl perchlorate ($AcClO_4$) or trifluoromethanesulfonic acid (CF_3SO_3H) in nonpolar solvents.[4]

In the present work, therefore, we studied extensively the factors controlling the structure and molecular weight (distribution) of products in the cationic oligomerization of styrene. Since the above-mentioned examples[1,2,4] suggest that these properties strongly depend on the type of catalysts, a variety of metal halides (BF_3·OEt_2, $SnCl_4$, and $EtAlCl_2$) and oxo acids or their derivatives ($AcClO_4$, CF_3SO_3H, and p-$CH_3C_6H_4SO_3H$·H_2O) were employed, and special attention was paid to the difference in catalytic behavior between the metal halides and the oxo acids. $AcClO_4$ should act as catalyst in the same way as perchloric acid, an oxo acid, because both should generate the same counteranion, ClO_4^-. Styrene was used as monomer, because its propagating carbocation scarcely undergoes side reactions such as rearrangement.

Selective preparation of linear styrene oligomers with low molecular weights (trimer–pentamer) was also examined.

Experimental Section

Materials. Styrene was washed with aqueous NaOH solution and then water, dried over anhydrous Na_2SO_4, and distilled twice

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Table I
Effect of Solvent and Initial Monomer Concentration on the Composition of Styrene Oligomers Formed by AcClO$_4$ at 50 °C

				product composition, wt %[a]			
$[M]_0$, M	solvent, (v/v)	$[C]_0$, mM	conv., %	dimer	trimer	tetramer	≥pentamer
0.10	C_6H_6	2.0	83	85.3	11.9	2.5	0.2
	$C_6H_6/(CH_2Cl)_2$ (1/1)	0.50	86	82.9	14.6	2.5	0.1
	$(CH_2Cl)_2$	0.50	95	38.2	17.5	12.0	32.3
0.50	C_6H_6	2.0	96	80.4	15.3	3.6	0.7
	$C_6H_6/(CH_2Cl)_2$ (1/1)	2.0	99	62.3	23.5	7.8	6.4
	$(CH_2Cl)_2$	1.0	100	23.0	17.4	8.5	51.1

[a] Determined by LC.

over CaH_2 under reduced pressure just before use. Solvents (benzene and 1,2-dichloroethane) were washed with aqueous H_2SO_4 and/or NaOH solutions and were freshly distilled twice over CaH_2 before use. AcClO$_4$ was synthesized as described elsewhere.[5] Commercial $BF_3 \cdot OEt_2$, $EtAlCl_2$, $SnCl_4$, and bromobenzene were used after distillation under reduced or atmospheric pressure. p-$CH_3C_6H_4SO_3H \cdot H_2O$, CF_3SO_3H, and transfer agents (n-propylamine (n-$PrNH_2$), pyridine, and *tert*-butyl alcohol (t-BuOH)) were all commercially obtained (guaranteed reagents) and used without further purification.

Procedure. Reaction was initiated by addition of a catalyst solution to a monomer solution under a dry nitrogen atmosphere. In this procedure, the concentration of water in the reaction mixture was smaller than 0.5 mM. For the reactions catalyzed by metal halides in benzene, water (half the molar quantity of the catalyst) was added as cocatalyst. After a certain interval the reaction was stopped by addition of methanol containing a small amount of aqueous ammonia. Conversion was determined from the residual monomer concentration measured by gas chromatography. Bromobenzene (the same quantity as the monomer) as internal standard was added to the reaction mixture prior to initiation. The reaction solution after quenching was washed with water to remove the catalyst residue, and the products were recovered from the organic layer by evaporation of the unreacted monomer and solvent under reduced pressure.

The composition of the products was measured by high-performance liquid chomatography (LC) on a JASCO-FLC-A700 chromatograph with a refractive index detector at room temperature. Two 50-cm columns packed with Shodex GPC A802 polystyrene gel were used and chloroform was the eluent. Weight fractions of oligomers were calculated from their LC peak areas. ^{1}H-NMR spectra (60 MHz) were recorded on a JEOL MH 60 spectrometer at room temperature in CCl_4.

Results

Oligomerization by Oxo Acids and Their Derivative. Figure 1 shows LC traces of styrene oligomers obtained by AcClO$_4$ catalyst under various conditions. Higher molecular weight oligomers increased with an increase of solvent polarity at the same temperature and with lowering temperature in a polar solvent, $(CH_2Cl)_2$. In a nonpolar solvent, benzene, a dimer was always obtained exclusively. A preliminary qualitative description of these trends has been given in our previous paper.[4] ^{1}H-NMR and IR spectra of the products showed that they are mainly linear oligomers with terminal double bonds, although the presence of a cyclic (indanic) end structure to a minor extent was suggested by the small peaks (designated c) in Figure 1. Consequently, when AcClO$_4$ was used as catalyst, the fraction of the dimer was the highest in the product irrespective of reaction conditions.

Table I shows the effect of monomer concentration on the product composition in three solvents at 50 °C. Lower molecular weight oligomers increased with decreasing monomer concentration in all solvents.

The other oxo acids (CF_3SO_3H and p-$CH_3C_6H_4SO_3H \cdot H_2O$) gave similar results to those with AcClO$_4$ under the same conditions (Table II). In spite of their difference in acid strength and structure, all three catalysts formed the linear unsaturated dimer predominantly.

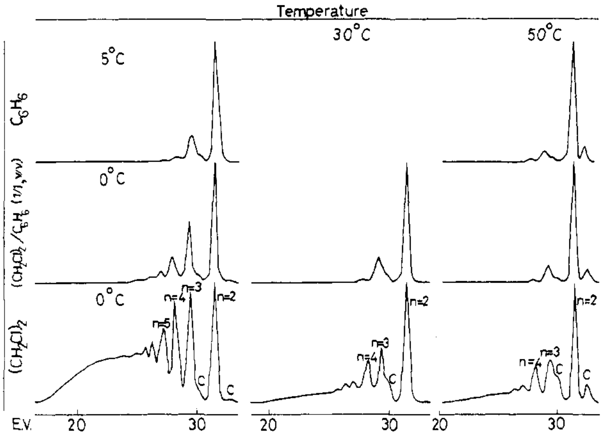


Figure 1. Effects of solvent and temperature on the product distribution in the oligomerization of styrene by AlClO$_4$: $[M]_0$ = 0.10 M; $[C]_0$ = 0.50–2.0 mM; conversion > 80%. n indicates the degree of polymerization. Peaks designated c correspond to oligomers with cyclic end structures.

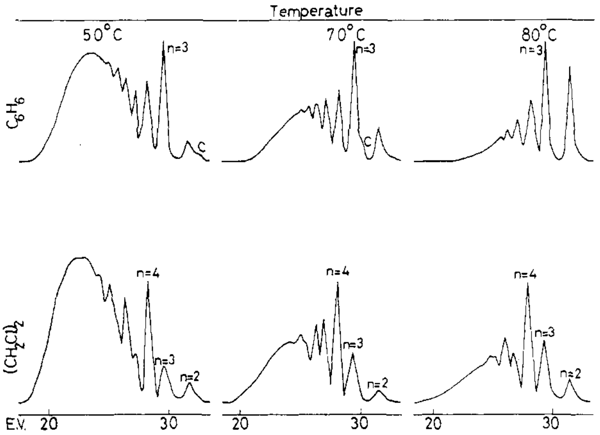


Figure 2. Effect of solvent and temperature on the product distribution in the oligomerization of styrene by $BF_3 \cdot OEt_2$: $[M]_0$ = 0.10 M; $[C]_0$ = 10–44 mM; conversion 40–70%. As to the meaning of n and c, see Figure 1.

Table II
Composition of Styrene Oligomers Formed by Oxo Acids and Their Derivative in Benzene at 70 °C ($[M]_0$ = 0.10 M)

			product composition, wt %[a]			
catalyst	$[C]_0$, mM	conv., %	dimer	trimer	tetramer	≥pentamer
AcClO$_4$	1.0	84	88.3	9.5	2.3	0
CF_3SO_3H	1.0	100	72.9	19.5	5.3	2.3
p-$CH_3C_6H_4SO_3H$	10.0	11	84.3	13.5	2.2	0

[a] Determined by LC.

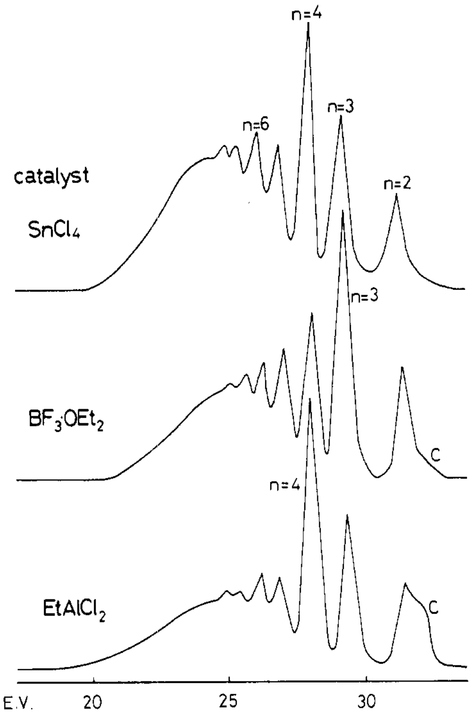


Figure 3. Distribution of the styrene oligomers formed by metal halides in benzene at 70 °C: $[M]_0 = 0.10$ M. $[C]_0$ and conversion: $SnCl_4$, 1.0 mM, 9.8%; BF_3OEt_2, 10 mM, 52%; $EtAlCl_2$, 1.0 mM, 100%. As to the meaning of *n* and c, see Figure 1.

Oligomerization by Metal Halides. Figure 2 shows LC traces of styrene oligomers produced by $BF_3·OEt_2$ under various conditions. Higher temperatures (50–80 °C) than those for the oxo acids were employed because polymers having molecular weights more than several thousand were yielded below 30 °C. The molecular weight distribution of oligomers obtained by $BF_3·OEt_2$ was apparently different from that of the products formed by the oxo acids. In both polar and nonpolar solvents, the product contained a large amount of higher oligomers than decamer, and these components increased with lowering temperature. It should also be noted that, among low molecular weight oligomers, $BF_3·OEt_2$ yielded trimer (in benzene) or tetramer (in $(CH_2Cl)_2$) as the main product at high tmperature, whereas the oxo acids produced dimer as the main product irrespective of reaction conditions.

The other metal halides ($SnCl_4$ and $EtAlCl_2$) gave products similar to those formed by $BF_3·OEt_2$ in benzene at 70 °C (Figure 3). Trimer or tetramer, rather than dimer, was also of the highest content among low molecular weight oligomers. Oligomers higher than pentamer were produced to a large extent, as in the $BF_3·OEt_2$ catalysis, and their content decreased in the following order: $SnCl_4 > BF_3·OEt_2 > EtAlCl_2$. A paper[6] states that $EtAlCl_2$ gave a cyclic dimer of some styrene derivatives in high yield. With this catalyst under the conditions described in Figure 3, the cyclic dimer was produced, but its amount was less than that of the linear one, and tetramer was the main product (22.4 wt %).

Thus, a remarkable difference in catalytic behavior was found between the oxo acids and the metal halides. This will be discussed later more quantitatively.

Synthesis of Styrene Trimer or Tetramer. There has been no study concerning the selective preparation of trimer or tetramer of styrene in high yield by a cationic mechanism, although our present and previous[4] work has provided a convenient method for the selective dimerization of styrene using oxo acid catalysts. It is expected that the trimer or tetramer will be obtained in high yield if polymer formation is suppressed in the oligomerization by metal halides, e.g., $BF_3·OEt_2$, because they yielded these two oligomers more preferably than dimer, as described above. The following two factors were considered here to suppress the polymer formation: (a) lowering initial monomer concentration ($[M]_0$) in a nonpolar solvent; (b) addition of transfer agents.

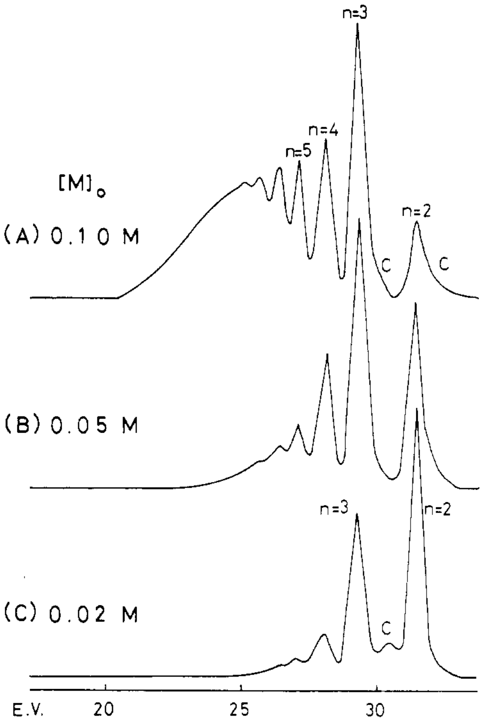


Figure 4. Effect of initial monomer concentration on the distribution of styrene oligomers formed by $BF_3·OEt_2$ in benzene at 70 °C. $[C]_0$ and conversion: (A) 10.0 mM, 52% (from Figure 2); (B) 5.0 mM, 40%; (C) 2.0 mM, 4.6%. As to the meaning of *n* and c, see Figure 1.

Table III
Effect of Amines on the Oligomerization of Styrene by $BF_3·OEt_2$ in Benzene at 70 °C ($[M]_0 = 0.10$ M, $[C]_0 = 10$ mM, [amine] = 2.0 mM, 24 h)

		product composition, wt %[a]			
amine	conv., %	dimer	trimer	tetramer	≥pentamer
none	72	18.0	26.3	14.5	41.2
n-$PrNH_2$	27	24.0	29.9	15.8	30.4
pyridine	47	25.1	30.5	12.8	31.7

[a] Determined by LC.

Figure 4 shows the effect of lowering $[M]_0$ on the products formed by $BF_3·OEt_2$ in benzene at 70 °C. The dimer, trimer, and tetramer comprised 80.5 wt % of the whole product at $[M]_0 = 0.05$ M, the trimer content (36.5 wt %) being the highest. Oligomers higher than hexamer were only 11.4 wt % in total. Moreover, at $[M]_0 = 0.02$ M the content of dimer and trimer reached 85 wt % with little contamination of higher oligomers. Thus, improvement for the selective formation of trimer was achieved on lowering $[M]_0$, though the selectivity was not very high.

As transfer agents two amines (*n*-$PrNH_2$ and pyridine) and an alcohol (*t*-BuOH) were added to the reaction system catalyzed by $BF_3·OEt_2$. As shown in Table III, the addition of *n*-$PrNH_2$ and pyridine (1/5 the molar quantity of the catalyst) did not sufficiently suppress high molecular weight oligomers, although it reduced the reaction rate considerably. In contrast to this, *t*-BuOH (half the molar

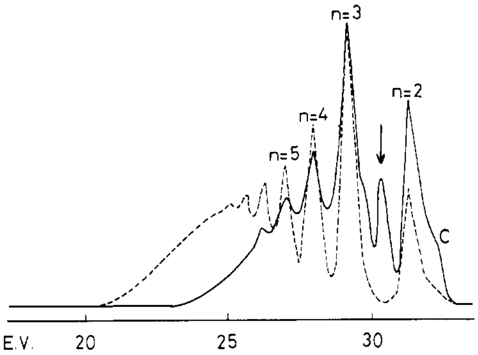
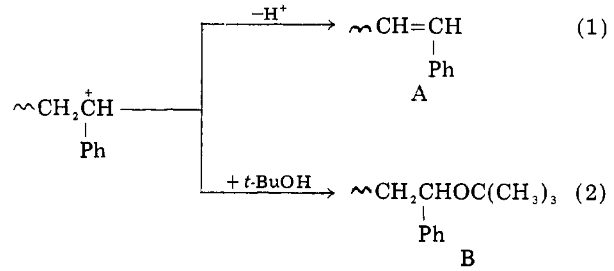


Figure 5. Effect of t-BuOH on the distribution of styrene oligomers formed by $BF_3 \cdot OEt_2$ in benzene at 70 °C: (—) [t-BuOH] = 10 mM; (---) none. $[M]_0$ = 0.10 M; $[C]_0$ = 20 mM. The peak indicated by the arrow was not identified. As to the meaning of n and c, see Figure 1.

quantity of the catalyst) markedly reduced production of high molecular weight oligomers (higher than hexamer) as shown in Figure 5. The main product was trimer as intended, but the selectivity for it was unsatisfactory. A ^{1}H-NMR spectrum of the product obtained in the presence of t-BuOH showed a peak at δ 0.9 ppm due to the terminal *tert*-butoxy group.[7] Comparison of its peak intensity with that of the olefinic protons (δ 6.3 ppm) indicated that unsaturated (A in eq 1) and *tert*-butoxy-capped (B in eq 2) end structures are present in about 1:1 molar ratio in the product.



$$\sim CH_2\overset{+}{C}H(Ph) \xrightarrow{-H^+} \sim CH{=}CH(Ph) \quad \text{A} \qquad (1)$$

$$\sim CH_2\overset{+}{C}H(Ph) \xrightarrow{+t\text{-BuOH}} \sim CH_2CH(Ph)OC(CH_3)_3 \quad \text{B} \qquad (2)$$

Discussion

Difference between Oxo Acids and Metal Halides. In the oligomerization of styrene catalyzed by oxo acids and their derivative in a nonpolar solvent, benzene, at 50 °C, the linear unsaturated dimer was obtained in more than 80 wt % yield at initial monomer concentrations less than 0.50 M, and the dimer and trimer comprised 95 wt % of the product (especially more than 98 wt % at 0.10 M). Although high molecular weight oligomers gradually increased with an increase of solvent polarity, the main product was still the dimer, and products having a high trimer (or tetramer) content could not be obtained with the oxo acids. The products formed by metal halides clearly differed from those by the oxo acids. They were composed of a large amount of high molecular weight oligomers irrespective of solvent polarity at temperatures below 50 °C. Their molecular weight distribution depended strongly on reaction temperature, rather than on solvent polarity (see Figure 2).

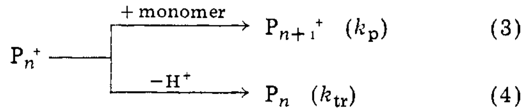
The high selectivity for the linear dimer exhibited by the oxo acids may result from the fact that the oxygen atoms of counteranions derived from them interact strongly with the β-hydrogen of the propagating end to promote its elimination, as discussed in our previous paper.[4] This is supported by the large transfer constants for the oxo acid catalyzed oligomerizations shown below. On the other hand, counteranions derived from the metal halides should be reluctant to interact with the β-hydrogen because of their bulkiness and lack of nucleophilic oxygen atoms. This may promote propagation relative to (spontaneous) transfer. High molecular weight oligomers were thus preferably produced at lower temperature; trimer or tetramer, rather than dimer, was the main product at higher temperature. Therefore, the clear difference between the oxo acids and the metal halides can be attributed to the different nature of counteranions derived from the two classes of catalyst.

Selective Synthesis of Styrene Oligomers. In this work, it was attempted to produce selectively styrene trimer or tetramer by suppressing the formation of higher oligomers. Although the selectivity was not satisfactory, the proper choice of conditions allowed these components to be obtained as the main products. For example, the reaction catalyzed by $BF_3 \cdot OEt_2$ at low $[M]_0$ (0.02–0.05 M) led to the products with a high trimer content in benzene at 70 °C (Figure 3), and the amount of higher oligomers than hexamer was fairly small.

Addition of t-BuOH in the $BF_3 \cdot OEt_2$-catalyzed oligomerization also suppressed the higher oligomers to give the trimer as the main product (Figure 5). One disadvantage of the use of t-BuOH, however, is the competitive formation of *tert*-butoxy-capped oligomers along with the desired linear oligomers having unsaturated terminals. The two amines (n-$PrNH_2$ and pyridine) were ineffective for the selective oligomerization and only reduced the reaction rate.

It is of interest that metal halides seem good catalysts for the trimer (or tetramer) synthesis, while oxo acids effectively catalyze the selective dimerization.[4] Improvement of the selectivity for trimer (or tetramer) is now open to future investigations.

Determination of Transfer Constant. In all the systems examined in this work except for those with p-$CH_3C_6H_4SO_3H \cdot H_2O$, termination should be much slower than propagation and transfer, because limiting yields of polymer were not observed. Thus the growing chain will undergo either propagation reaction (eq 3) or transfer reaction (eq 4):



$$P_n^+ \xrightarrow{+\text{monomer}} P_{n+1}^+ \quad (k_p) \qquad (3)$$

$$P_n^+ \xrightarrow{-H^+} P_n \quad (k_{tr}) \qquad (4)$$

where P_n^+ and P_n are respectively the growing chain and the (dead) oligomer or polymer whose degree of polymerization is n; k_p and k_{tr} indicate the corresponding rate constants. The transfer reaction 4 may include β-proton elimination to give a terminal double bond and intramolecular cyclization leading to an indanic end structure. Monomer transfer was neglected here for simplicity.

If we assume the rate constants k_p and k_{tr} to be independent of n, as in Schulz's kinetic analysis on the chain polymerization,[8] the probability of obtaining oligomers with the degree of polymerization n is given by $\{k_p[M]/(k_p[M] + k_{tr})\}^n$. Therefore, the molar fraction N_n and the weight fraction W_n of n-mer in a given product are expressed as eq 5 and 6, respectively:

$$N_n = (\text{constant})\alpha^n \qquad (5)$$

$$W_n = nN_n = (\text{constant})n\alpha^n \qquad (6)$$

where

$$\alpha = \frac{k_p[M]}{k_p[M] + k_{tr}} = \frac{1}{1 + (k_{tr}/k_p)[M]} \qquad (7)$$

From eq 6, we obtain

$$\log (W_n/n) = n \log \alpha + \log (\text{constant}) \qquad (8)$$

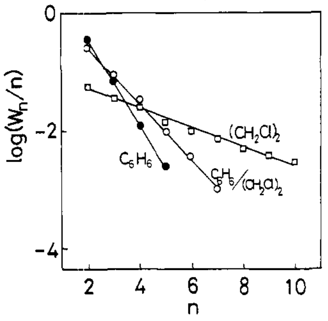


Figure 6. Plots of log (W_n/n) against n for the products formed by $AcClO_4$ in various solvents: $[M]_0 = 0.10$ M. Temperature: (●) 5 °C; (○, □) 0 °C.

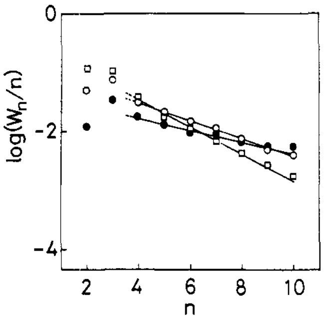


Figure 7. Plots of log (W_n/n) against n for the products formed by $BF_3{\cdot}OEt_2$ in C_6H_6: $[M]_0 = 0.10$ M. Temperature: (●) 50 °C; (○) 70 °C; (□) 80 °C.

Table IV
Effects of Solvent and Temperature on Transfer Constants for Styrene Oligomerization by the Oxo Acids ($[M]_0 = 0.10$ M)

		$(k_{tr}/k_p) \times 10^2$, L/mol		
catalyst	temp, °C	C_6H_6	$C_6H_6/(CH_2Cl)_2$ (1/1)	$(CH_2Cl)_2$
$AcClO_4$	0	22.9	11.1	2.4
	30		21.4	6.6
	50	59.4	41.8	11.2
	70	74.9		
CF_3SO_3H	70	22.0		
p-$CH_3C_6H_4SO_3H$	70	144		

If a linear relation between log (W_n/n) and n is obtained, it follows that α does not depend on n, and the independence of k_{tr}/k_p on n will be justified.

The oligomerizations with all the oxo acids and $AcClO_4$ gave linear plots of log (W_n/n) against n. Figure 6 shows typical examples of these plots for the oligomerization with $AcClO_4$ in various solvents. Slopes of the straight lines gave α values, from which transfer constants (k_{tr}/k_p) were calculated on the basis of eq 7. Table IV summarizes the values obtained for various oxo acids. In the calculation, [M] in eq 7 was taken as the mean of the initial and final monomer concentrations in each run, because eq 8 was applied mostly to the products obtained at high conversions. In the oligomerization with the oxo acids in benzene, k_{tr} was similar in magnitude to k_p. The k_{tr}/k_p values for $AcClO_4$ (Table IV) increased with increasing temperature and with lowering solvent polarity as expected from Figure 1.

In clear contrast, plots of eq 8 for metal halides showed linearity only for $n \geq 4$ or 5, as shown in Figures 7 and 8. Straight lines were obtained for $n \geq 4$ with the reactions by $BF_3{\cdot}OEt_2$ in benzene (Figure 7), whereas for $n \geq 5$ with those by $SnCl_4$ and $EtAlCl_2$ in benzene and by $BF_3{\cdot}OEt_2$ in $(CH_2Cl)_2$ (Figure 8). These facts indicate that, in the metal halide catalyzed oligomerizations, the transfer constant depends on the chain length of the propagating carbocation (see below).

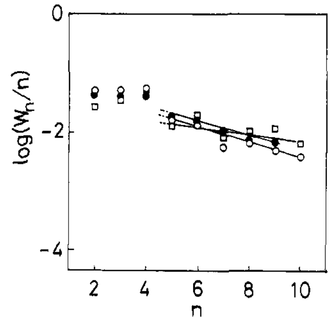


Figure 8. Plots of log (W_n/n) against n for the products formed by metal halides at 70 °C, $[M]_0 = 0.10$ M: (●) $SnCl_4$ in C_6H_6; (○) $EtAlCl_2$ in C_6H_6; (□) $BF_3{\cdot}OEt_2$ in $(CH_2Cl)_2$.

Table V
Transfer Constants for the Styrene Oligomerization by Metal Halides ($[M]_0 = 0.10$ M)

catalyst	solvent	temp, °C	$(k_{tr}/k_p) \times 10^2$,[a] L/mol
$BF_3{\cdot}OEt_2$	C_6H_6	50	6.3
	C_6H_6	70	8.3
	C_6H_6	80	8.9
	$(CH_2Cl)_2$	80	8.1
$SnCl_4$	C_6H_6	70	11
$EtAlCl_2$	C_6H_6	70	6.9

[a] Determined from α values for $n \geqslant 4$ or 5.

Table V lists the k_{tr}/k_p values determined from the linear portions of the plots. They are all smaller than those for the oxo acids under the same conditions, which indicates that the latter catalysts are more suitable for production of lower molecular weight oligomers (see Figures 1–3 and Table I). Table V also shows that the difference in k_{tr}/k_p within the metal halides is much smaller than that between the oxo acids and the metal halides.

We thus found that k_{tr}/k_p values for the oxo acids do not depend on n but those for the metal halides do. As the interaction between a growing carbocation and a counteranion derived from an oxo acid is strong (see the previous section), the nature of the propagating species (k_{tr}/k_p value) should be determined mostly by this interaction at the chain end and should be independent of its chain length. On the other hand, when a counteranion derived from a metal halide, bulkier and lacking nucleophilic oxygen atoms, is involved, the growing end may relatively be free from such an interaction, and hence the nature of the propagating species will correlate closely with its carbocationic moiety itself. Its chain length (n), therefore, may well have some effects on the transfer constant as observed. The dependence of k_{tr}/k_p values on n (Figures 7 and 8) suggests that the nature of a dimeric or trimeric growing carbocation differs from that of the carbocations with larger chain lengths. In particular, the unexpectedly small dimer (and trimer) contents imply that these short growing chains are much less liable to undergo transfer than longer ones. The reason for these differences remains unexplained and should be discussed in future investigations.

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Polymerization under a Pressure of 6 GPa

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ABSTRACT: Pressures of 6 GPa (ref 52) generated in a tetrahedral anvil pressure apparatus were used for polymerization of addition monomers. With this technique, polymers of moderate and high molecular weight were obtained from selected α-olefins, internal olefins, dienes, and trioxane. The polymers were characterized by their elemental analysis and IR and ^{1}H NMR spectra and have the structure of addition polymers without rearrangements. Success of the polymerization depended on the proper containment of the monomers, which were usually low-boiling liquids; the reaction vessels, specially designed for these pressure experiments, were sealed platinum ampules. The polymerization of a number of monomers which had not been polymerized before has been achieved. It depended on the favorable dependence of the rate of propagation over the rate of termination or transfer. The polymerization reaction mechanism appears to be a thermally initiated radical process with the possible exception of trioxane.

High pressure has been used to carry out reactions not possible at atmospheric pressure and to accelerate the rate of other reactions.[1,2] Rates of reaction in the condensed phase are accelerated under high pressure and many chemical equilibria depend very much on pressure.[3] The effect of pressure on kinetics varies, but rate constants in favorable cases can increase by several orders of magnitude. This acceleration is usually attributed to effects on the volume of the transition state and in rare cases inverse effects have been found.

Several pressure ranges have been studied for pressure reactions which are determined by the availability of pressure vessels and devices to produce the corresponding pressures and for the specific reactions which are desired to be performed. The lower pressure range is the range below 100 MPa; a second pressure range is between 100 MPa and 1 GPa and a number of chemical processes, especially gas phase reactions, are carried out in the pressure range up to 400 MPa. A third range consists of pressures of more than 2 GPa.

In the fifties pressure apparatus was developed based on Bridgman's "principle of massive support" and solid pressure transmitters and possessing useful working volume. This made synthesis research practical at pressures of more than 5 GPa and temperatures up to 1500 °C. A most convenient device for this work is the tetrahedral anvil apparatus, developed by Hall[4–6] and modifield at the National Bureau of Standards. The early studies were limited to solids because no container was known which could contain liquids in the tetrahedral anvil apparatus. Recent development[8–12] of a device to contain liquids with boiling points as low as −10 °C has allowed study of the polymerization of liquids under these heroic conditions. A preliminary account was published some time ago.[8]

Most studies of polymerization under pressure have been made in the pressure range up to 1.2 GPa. It has been found that the ceiling temperature of polymerization was greatly affected by increases in pressure; for example, it was shown that the ceiling temperature of α-methylstyrene was increased from 61 °C at 0.1 MPa to 170 °C at 650 MPa. It is therefore not surprising that a number of polymers with ceiling temperatures much below room temperature, for example, polymers of aliphatic aldehydes, have been first prepared under pressures of about 1 GPa.[13]

Perhaps the most important commercial polymer prepared under pressure is polyethylene where pressures up to 400 MPa are used. This polymer has a branched structure as prepared under these conditions; however, if the pressure is increased to 1 GPa an essentially linear polymer of polyethylene is obtained.[14–18] Other compounds which cannot be polymerized under normal conditions are perfluorinated α-olefins notably hexafluoropropylene.[19] Other perfluoro-α-olefins with long side chains polymerize only under pressures of up to 2 GPa.[20] 1,1-Disubstituted ethylenes, such as α-methylstyrene,[21] polymerize even to higher molecular weight under high pressure.

Attempts made to polymerize *trans*-stilbene at 90 °C and 500 MPa were unsuccessful.[22] However, it is known that stilbene, 2-butene, and cyclopentene copolymerize readily with ethylene even at normal pressures but require coordination catalysts.[23] 1,2-Disubstituted ethylenes have not been homopolymerized to high molecular weight polymers even under elevated pressures.[24,25] Some functionally substituted 1,2-disubstituted olefins, containing a carboxylate group, have however been polymerized and it has been found that they polymerize under higher pressure[22,26,27] to higher molecular weight.

Tri- and tetrasubstituted ethylenes have also been subjected to high pressures in attempts to obtain polymers. A very small yield of dimer was obtained from α,β-dimethylstyrene at 500 MPa and 120 °C. Trimethylethylene

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