effect of the substituent in the vinyloxy compound is stronger than a limiting value. Vinyloxy compounds with electron-donating character weaker than this value interact with TCNQ to form, exclusively, a charge-transfer complex which plays an important role in their alternating copolymerization. It is impossible to exclude definitely the possibility that cationic polymerization of the vinyl ethers studied here is caused by an unknown acidic contaminant in TCNQ (as was reported for tricyanoethenol in tetracyanoethylene[11]), even though TCNQ was purified as well as possible. However, the alternating copolymerizations are not affected by such an impurity even if it is contained in TCNQ. When maleic anhydride with much weaker electron-accepting character (EA = 0.11 eV)[12] is used in place of TCNQ (EA = 1.7 eV)[12], alkyl vinyl ethers do not homopolymerize at all but they still copolymerize alternatingly.[13] It is concluded, therefore, that balance between electron-donating and electron-accepting character of both monomers is a primary determining factor of the polymerization modes.

It is apparent from the results in the tables that alternating copolymerizations of TCNQ with CEVE and PhVE take place even in the absence of AIBN. It is also to be noted that in at least one instance (TA-2) AIBN markedly enhances the yield of polymer. These unusual effects cannot be discussed at this time in a meaningful way because the system is inhomogeneous except at very dilute concentrations of TCNQ. Further work to clarify these effects as well as the influence of solvent on the polymerization is currently in progress.

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Poly(2,3-epoxybutanes) and Poly(1,4-dichloro-2,3-epoxybutanes): Microstructure and Mechanism of Polymerization Studied by Carbon-13 Magnetic Resonance Spectroscopy[†]

Floyd F.-L. Ho* and E. J. Vandenberg

Research Center, Hercules Incorporated, Wilmington, Delaware 19899.

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ABSTRACT: Carbon-13 magnetic resonance (^{13}C NMR) spectra of meso and racemic 2,3-epoxybutanes and the related dimer and trimer fractions were obtained. These compounds were used as models to aid in assigning ^{13}C NMR signals from crystalline poly(2,3-epoxybutane)'s and poly(1,4-dichloro-2,3-epoxybutanes). Crystalline poly(*cis*-2,3-epoxybutane) and poly(*cis*-1,4-dichloro-2,3-epoxybutane) were found to have predominantly racemic triads (e.g., –RR–RR–RR–), while crystalline poly(*trans*-2,3-epoxybutane) and poly(*trans*-1,4-dichloro-2,3-epoxybutane) were found to have stereoblocks with –RS–RS–RS– (or –SR–SR–SR–) and –RS–RS–SR– (or –SR–SR–RS–) triad arrangements. The average sequence length of a block is approximately five units long (i.e., –RS–RS–RS–RS–RS–SR–SR–SR–SR–SR–). A mechanism of polymerization with exclusive inversion of configuration at the epoxide ring-opening carbon, first proposed by Vandenberg in 1961, was further confirmed by this work. Some degree of enantiomorphic selection in the polymerization of racemic *trans*-2,3-epoxybutane was also indicated.

In previous work on 2,3-epoxybutane polymerization, Vandenberg[1] demonstrated that polymerization of epoxides proceeds with clean inversion of configuration at the ring-opening carbon atom. This conclusion was based largely on the detailed analyses of dimer and trimer diols from cleavage studies on the polymer. This paper reports our recent investigation using carbon-13 magnetic resonance (^{13}C NMR) spectroscopy.

^{13}C NMR has been shown to be a powerful tool for studies of the microstructure of polymer.[2,3] In the case of polyethers, ^{13}C NMR studies have been reported on poly(ethylene oxide),[4,5] poly(propylene oxide),[6-8] and ethylene oxide–propylene oxide copolymers,[5] among

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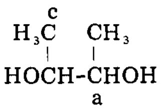
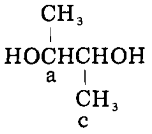
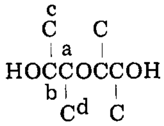
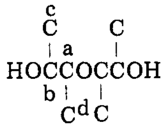
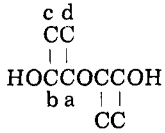
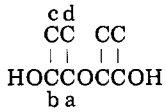
Table I
^{13}C NMR Chemical Shifts of Butylene Glycols and Dibutylene Glycols

glycols	C atom config	formula	methine, ppm a	methine, ppm b	methyl, ppm c	methyl, ppm d
monomer						
meso 2,3-butanediol	RS	 $\mathrm{HOCH{-}CHOH}$	71.38		17.37	
racemic 2,3-butanediol	RR SS	 $\mathrm{HOCHCHOH}$	72.77		19.49	
dimer fractions						
fraction I, racemic diisotactic	RR-RR SS-SS	 $\mathrm{HOCCOCCOH}$	77.00	70.74	19.23	15.77
fraction II, meso 2 disyndiotactic	RR-SS	 $\mathrm{HOCCOCCOH}$	82.53	72.38	19.62	18.41
fraction III, meso 1 disyndiotactic	RS-SR SR-RS	 $\mathrm{HOCCOCCOH}$	76.96	70.35	18.32	14.35
fraction IV, meso diisotactic	RS-RS	 $\mathrm{HOCCOCCOH}$	78.56	70.09	17.28	16.38

others.[9] As expected, there is only one ^{13}C NMR signal from poly(ethylene oxide), while there are several signals from poly(propylene oxide). In the latter, there is a true asymmetric carbon in each monomer unit, so that one can obtain polymer chains with different sequences of asymmetric centers. To date, no study concerning the ^{13}C NMR of the poly(2,3-epoxybutane)'s has been reported. In these polymers, there are two asymmetric carbons in each monomer unit and the stereochemistry could be more complex. In this paper ^{13}C NMR data on crystalline poly(2,3-epoxybutanes) prepared from the *cis*- and *trans*-2,3-epoxybutanes, together with a few pertinent model compounds, are discussed. ^{13}C NMR data from crystalline poly(1,4-dichloro-2,3-epoxybutanes), a new class of polyethers containing 50% Cl,[10] are also included. Analyses of spectra from the amorphous homopolymers and copolymers are underway and will be reported separately.

Experimental Section

Chemicals. Commerical meso 2,3-butanediol (Celanese Corp.) and racemic 2,3-butanediol (K&K Laboratories) were purified by fractionating at 50 mm in a 85-plate column at an 85:1 reflux ratio. The purity was confirmed by gas chromatography. Syntheses of dimer and trimer diols listed in Tables I and II were previously described.[1] The preparation of the polymers was also reported[1] earlier. Polymer samples examined in Table III are highly crystalline materials, which had been repeatly recrystallized from hot *n*-heptane. The synthesis and some properties of poly(1,4-dichloro-2,3-epoxybutanes) have been reported earlier.[10]

^{13}C NMR Measurements. Except for crystalline poly(*cis*-2,3-epoxybutane), all measurements were made in C_6D_6 solution at about a 20% concentration at an ambient probe temperature of about 30 °C. For crystalline poly(*cis*-2,3-epoxybutane), measurements were made in *o*-dichlorobenzene at 127 °C. A Bruker HFX-90 spectrometer operating at 22.6 MHz was used in this study. This instrument was equipped with a Nicolet BNC-20 computer for Fourier transform operation. A pulse width of 10 μs, equivalent to a spin tipping angle of about 50°, was employed. The pulse repetition rate was 1 s and the spectral widths were 4000 Hz. Tetramethylsilane (Me_4Si) was used as the internal standard for the room temperature spectra and *o*-dichlorobenzene employed as a secondary internal reference at 127 °C.

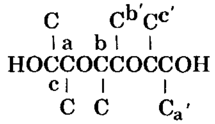
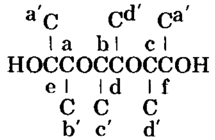
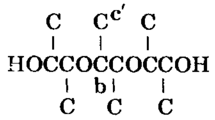
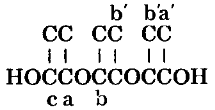
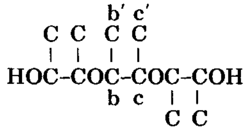
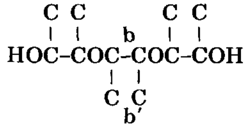
For the spin–lattice relaxation (T_1) measurements on a poly(*trans*-2,3-epoxybutane) sample, a standard $180°-\tau-90°$ pulse sequence was used. The recovery time, τ, was varied from 0.25 to 2.50 s with 15 s (i.e., $>>5T_1$) allowed between each pulse. A "stacked" plot representation with T_1 data is given in Figure 1.

Discussion of Results

The ^{13}C NMR chemical shifts are sensitive to the type and to the steric arrangement of substituents. This point may be readily illustrated by inspection of the data for the meso and racemic butanediols shown in Table I. The methyl and methine carbons in the two isomers have quite different chemical shifts.

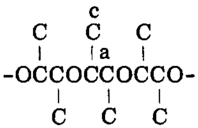
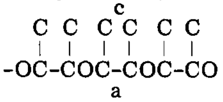
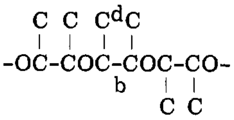
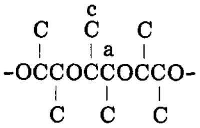
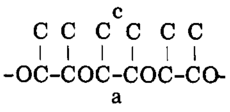
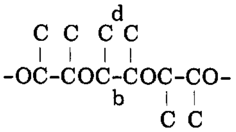
Signal assignments for the dimer fractions are generally quite straightforward and are supported by literature data[11,12] on dialkyl ethers (R–O–R) and their parent alcohols (R–OH). Thus, by replacing a hydrogen in the hydroxyl group of a parent alcohol with an alkyl group, it was shown that the α carbons are deshielded by 4.5–10.7 ppm, the β carbons shielded by 2.3–2.8 ppm, while the effect on the γ and δ carbons is relatively small, being less than 0.5 ppm. Steric effects play an important role also in determining the carbon shifts in our dimer fractions. For example, replacing a hydrogen in the racemic diol (e.g., the RR isomer) by a like enantiomorph (e.g., the RR–RR fraction) shifts the methine signals at the α and β position by +4.23 and −2.03 ppm, respectively. On the other hand, replacement by an opposite enantiomorph (e.g., the RR–SS fraction) shifts these carbons by +9.67 and −0.39 ppm. A

Table II
^{13}C NMR Chemical Shifts of Tributylene Glycols

glycols	formula	methine a	methine b	methine c	methine d	methine e	methine f	methyl a′	methyl b′	methyl c′	methyl d′	methyl e′	methyl f′
fraction I RR-SS-RR SS-RR-SS	 $\mathrm{HOCCOCCOCCOH}$	82.14	81.84 (82.14)[a]	73.37				19.01	18.75 (18.54)[a]	17.07			
fraction II RR-SS-SS SS-RR-RR	 $\mathrm{HOCCOCCOCCOH}$	82.14	80.29 (80.50)[a]	78.51	76.92 (76.61)[a]	72.81	71.00	18.92 (2)[b]	18.28	17.54 (18.15)[a]	15.60 (2)[b] (15.90)[a]		
fraction III RR-RR-RR SS-SS-SS	 $\mathrm{HOCCOCCOCCOH}$		(74.97)[a]							(15.51)[a]			
fraction IV RS-RS-RS SR-SR-SR	 $\mathrm{HOCCOCCOCCOH}$	79.42	78.17 (77.27)[a]	69.79				17.37	16.16 (2)[b] (16.29)[a]				
fraction V RS-RS-SR SR-SR-RS	 $\mathrm{HOC{-}COC{-}COC{-}COH}$		(77.53)[a]	(75.67)[a]					(17.33)[a]	(14.26)[a]			
fraction VI RS-RS-SR SR-SR-RS	 $\mathrm{HOC{-}COC{-}COC{-}COH}$		(75.93)[a]						(15.30)[a]				

[a] Calculated from data in Table I with calculation procedure explained in the text. [b] Signal intensity twice as large.

Table III
^{13}C NMR Chemical Shifts Data of Crystalline Poly(2,3-epoxybutanes) and Poly(1,4-dichloro-2,3-epoxybutanes)

polymers	configuration	structure	methine		methyl	
			a	b	c	d
(1) poly(*cis*-2,3-epoxybutane)	-RR-RR-RR- -SS-SS-SS-	 -OCCOCCOCCO-	76.22 (74.97)^a		15.04 (15.51)^a	
(2) poly(*trans*-2,3-epoxybutane)						
meso diisotactic	-RS-RS-RS -SR-SR-SR-	 -OC-COC-COC-CO	78.27 (78.17)^a		17.50 (16.16)^a	
structural defect	-RS-RS-SR- -SR-SR-RS-	 -OC-COC-COC-CO-		77.40 (76.60)^b		16.74 (15.80)^b
(3) poly(*cis*-1,4-dichloro-2,3-epoxybutane	-RR-RR-RR- -SS-SS-SS-	 -OCCOCCOCCO-	79.34 (76.18)^c		43.69 (15.04)^c	
(4) poly(*trans*-1,4-dichloro-2,3-epoxybutane) meso diisotactic	-RS-RS-RS- -SR-SR-SR-	 -OC-COC-COC-CO-	80.13 (78.34)^c		44.21 (17.50)^c	
structural defect	-RS-RS-SR- -SR-SR-RS-	 -OC-COC-COC-CO-		77.86; 76.58 (77.52)^c		44.21 (16.72)^c

[a] Chemical shift of the central unit of model trimer fractions with terminal hydroxyls listed in Table II. [b] Average of the chemical shifts of the two-carbon signals in the central unit of the model trimer fraction RS-RS-SR in Table II. [c] Reduced with LiAlH$_4$.

similar situation occurs in the case of the meso diol (RS) and the derived dimer fractions (RS–RS and RS–SR) as shown in Table I.

The replacement shifts in a particular combination of dimer units, calculated from the observed shifts in Table I, are particularly useful in helping to assign signals in the trimer fractions (Table II). These values are also useful in estimating chemical shifts of the trimer fractions which are not presently available. As an example, in trimer fraction IV, which has an RS–RS–RS arrangement (Table II), the chemical shift for the carbons in the central unit can be calculated beginning with the data of the meso diisotactic (RS–RS) dimer given in Table I. This is accomplished using replacement shifts derived from the RS diol and the RS–RS dimer (i.e., the differences in chemical shifts of the corresponding carbons between the RS diol and the RS–RS dimer listed in Table I). As can be seen from Table II, the calculated value for methine and methyl carbons in the central unit in this fraction is 77.27 and 16.29 ppm, respectively, in close agreement with observed values of 78.17 and 16.16 ppm. Good agreement between calculated and observed shifts was also seen for fractions I and II in Table II. In most cases, the agreement is better than 0.5 ppm. This close agreement for the available trimer fractions enables one to place some confidence on the similarly derived values for a few trimer fractions which were not available for ^{13}C NMR examination. These values are also listed in Table II and are valuable in assigning triad arrangements in the polymers.

It should be noted, however, that the triad arrangement in the polymer chain is different from that in the trimer fractions. The latter are hydroxyl terminated. Therefore, carbons in the central unit of hydroxy terminated trimers are in a slightly different structural environment than the corresponding carbons in the triad unit of a large polymer molecule. Hence, the agreement between the chemical shift observed in the polymer and that derived from the trimer fraction might not be as good as one would prefer. For example, in the spectrum of crystalline poly(*cis*-2,3-epoxybutane), which was known[1] to have predominantly racemic diisotactic (RR–RR or SS–SS) carbon sequences, there is a single dominant signal at 76.22 ppm for the methine carbons and another one at 15.04 ppm for the methyl carbons. The corresponding values for the central unit in an RR–RR–RR (or SS–SS–SS) trimer fraction were estimated to be 74.97 and 15.51 ppm (Table II). The agreement in the case of the methyl carbon shift is excellent while the difference in the methine carbon shift in the two sets of data is relatively large (1.25 ppm). Differences in the solvents used and the temperature employed in the measurements of the polymeric and model systems may also contribute to this discrepancy. It is nevertheless interesting to note that a racemic polymer with predominantly regular –RR–RR–RR– triads was observed from a meso (RS) oxide. This finding therefore confirms Vandenberg's earlier proposal[1] that the polymerization proceeds with inversion of configuration at the ring-opening carbon.

In contrast to the exceedingly simple spectrums from poly(*cis*-2,3-epoxybutane), the spectrum (Figure 1) of poly(*trans*-2,3-epoxybutane) shows *two* signals in the methine carbon region and *two* signals in the methyl carbon region. The chemical shifts of these signals are listed in Table III. The intensitity ratio of the two methine signals of the poly(*trans*-2,3-epoxybutane) at the lower field is 1.4, as is the ratio of the two methyl signals at higher field. Spin–lattice relaxation times (T_1) for the two methine carbon signals were found to be 0.26 and 0.28 s

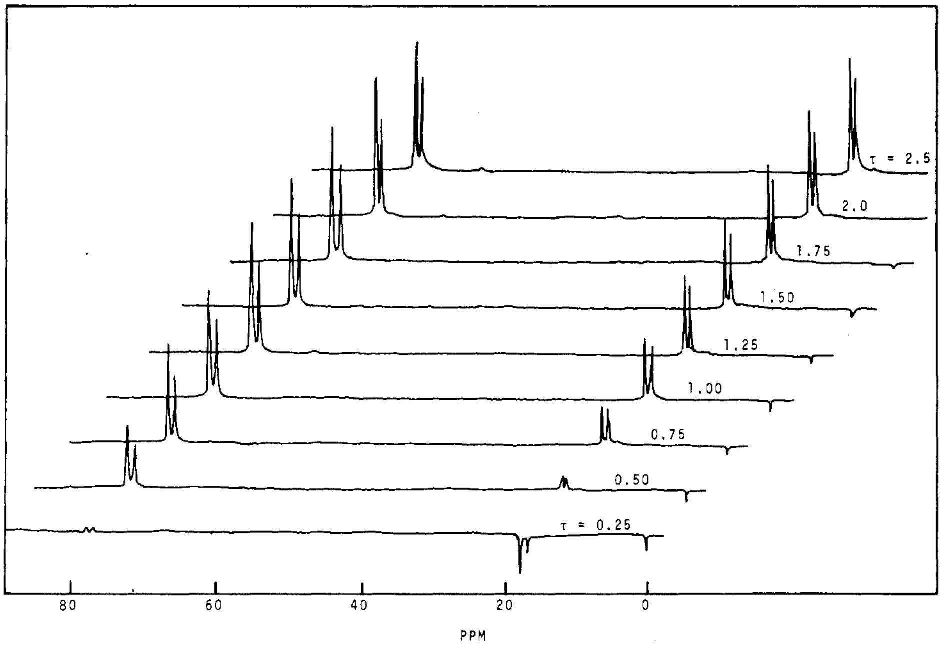


Figure 1. A "stacked" plot of carbon-13 magnetic resonance spectra of a solution of a crystalline poly(trans-2,3-epoxybutane) (τ = recovery time in seconds between pulses in a 180°–τ–90° sequence).

and for the two methyl carbons 0.37 and 0.38 s. The relatively slower rate of relaxation found for the methyl carbons is in accord with some segmental motion of the methyl groups. This T_1 experiment was undertaken to insure that the intensity ratio measured was not affected by partial spin saturation.

It is most interesting that this sample possesses two methine carbon signals and two methyl carbon signals, indicating the presence of some structural defects, probably in the form of stereoblocks. The major set of signals can be identified with the -RS-RS-RS- triad (see Table III). This polymer was known[1] from cleavage studies to have primarily this arrangement. Furthermore, comparison of ^{13}C chemical shift results with the corresponding simple trimer fraction chemical shifts is most favorable (Table III). This evidence of a meso polymer with a -RS-RS-RS- triad arrangement made from a racemic oxide (RR or SS) further confirms the mechanism of polymerization involving inversion of configuration at the ring-opening carbon atom.

The minor pair of signals shown in Figure 1 is tentatively identified with an -RS-RS-SR- (or an -SR-SR-RS-) triad. It was noted that the two methine carbons of the central unit in the simple, hydroxyl-terminated RS-RS-SR trimer fraction (fraction V in Table II) have slightly different chemical shifts. This is attributable to the lack of molecular symmetry in this trimer. The average of these two chemical shifts was used to compare that observed from the polymer (Table III). As mentioned earlier, the simple trimer fractions having terminal hydroxyl groups are only an approximate model for the triads in the polymer chain, so that these comparisons are made with caution.

The assignment of the minor pair of signals in the spectrum (Figure 1) to the -RS-RS-SR- (or -SR-SR-RS-) triad can be justified from two considerations. First, this assignment leads to the measurement of the molar ratio of [-RS-RS-RS-]/[-RS-RS-SR-] = 1.4, which is in very good agreement with a ratio of trimer fractions IV and V from the same polymer as reported earlier.[13] Second, the alternate assignment to an -RS-SR-RS- triad is not consistent with the observation that only *two* triad signals were observed in the polymer ^{13}C NMR spectrum, because this assignment of an -RS-SR-RS- triad in a polymer with a predominant -RS-RS-RS- arrangement would necessarily lead to a third triad -RS-RS-SR- with a ratio of -RS-RS-SR- to -RS-SR-RS- being strictly 2 to 1. In such a case, a total of *three* triad signals would have to be present.

Thus, the observation that the triad -RS-SR-RS- is not present in observable amounts indicates that the polymerization does not proceed with very much, if any, *single* alteration of enantiomorphs. Furthermore, an observed triad ratio [-RS-RS-RS-]/[-RS-RS-SR-] of 1.4 suggests that the polymerization proceeds with some degree of enantiomorphic selection. This result can be explained best by a block polymer with an average sequence length of five units in each block, i.e., -RS-RS-RS-RS-RS-SR-SR-SR-SR-SR-. Therefore, the degree of enantiomorphic selectivity is estimated to be about 80%. That is, on the average, only one out of every five encounters (or 20%) in the polymerization of the racemic 2,3-epoxybutane resulted in enantiomorphic alternation. This observation also accounts for the low probability of the -RS-SR-RS- triad, a product from a double alternation.

The enantiomorphic alternation in the polymerization of *trans*-2,3-epoxybutane would become impossible if one uses an optically pure monomer, rather than using a racemic mixture. This is verified from a ^{13}C NMR spectrum taken from a polymer made from an optically active SS isomer.[1] There is only one methyl signal and one methine signal in the spectrum, corresponding in chemical shift to the major set of signals in Figure 1. Therefore, this polymer has exclusively -RS-RS-RS- sequences. This result is consistent with our earlier finding[1] that this polymer is optically inactive and is much less soluble in benzene than the polymer made from the racemic monomers. The difference in solubility was attributed to the structural defects present in the latter polymer.

The difference in stereoregularity observed in this study from the trans and cis polymer probably arises from the difference of catalysts used in the polymerization.[1c] The cis polymer was made from a coordination catalyst Et_3Al–0.5·H_2O–0.5·acetylacetone and possesses very high crystallinity. As was mentioned in the Experimental

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–.

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

T. Higashimura,* M. Hiza, and H. Hasegawa

Department of Polymer Chemistry, Kyoto University, Kyoto 606, Japan.

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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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