The use of the T_g of an alternating copolymer as T_{gAB} in random copolymers is a useful concept and we have used it in several other polymer systems. The value used in this work of 122° for T_{gAB} or the T_g of an αMS-AN dyad worked very well in predicting the T_g's of random copolymers. This value, along with other data, was also used to predict the T_g's of many αMS terpolymers. This work will be published in the near future.

Acknowledgments. The author acknowledges the technical assistance of Mr. J. E. Simborski and the cooperation of Dr. B. L. Joesten of Union Carbide in obtaining the DSC data presented in this work.

Sequence Distributions in Ethylene–Vinyl Acetate Copolymers. I. ^{13}C Nuclear Magnetic Resonance Studies

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ABSTRACT: The sequence distribution of ethylene–vinyl acetate copolymers has been studied using ^{13}C nmr spectroscopy. Signal attributions were obtained both by following the rules of Grant and Paul as well as by comparison of spectra of samples of varying composition. Quantitative analysis at low vinyl acetate content are reported. Zeroth-order Markoffian distribution of the monomer units in the copolymer chain was verified. In addition, a ^{13}C spectrum of solid polymer was obtained.

A large number of papers have been published on the applications of nmr to the study of structural problems of homo- and copolymers.[1] One of the most important applications from the theoretical as well as from the technological point of view is the determination of the amount of the relative sequences in copolymers. However, due to the overlapping and consequent distortion of several resonances, no unambiguous determination is possible in some cases. This is the case for ethylene–vinyl acetate copolymers.

The high-resolution proton magnetic resonance (pmr) spectra of these copolymers, ranging from final composition mole fraction M_E = 0 to 0.7, have been previously reported.[2] By comparison of the experimental and calculated spectra, a zeroth-order Markoffian monomer distribution in the chain was deduced.[2] The same conclusions have been reached by different authors.[3-5] However, because of the overlapping of the resonance peaks due to different monomer distributions these conclusions cannot be considered unequivocal. Moreover, no results have been reported at lower vinyl acetate content because of the increasing difficulties in observing the different resonance peaks, since the strong ethylene $-CH_2-$ signal covers all the other weak peaks.

Because ^{13}C magnetic resonance (cmr) has several advantages over pmr (spin-spin coupling easily removed by heteronuclear decoupling resonance lines widely spaced, less broadening by dipolar interactions due to the smaller nuclear magnetic moment of the ^{13}C nucleus), we have examined the ^{13}C spectra of ethylene–vinyl acetate copolymers, with the aim of improving previously reported information and obtaining data relative to the copolymers with lower vinyl acetate content. Furthermore we tried also to obtain ^{13}C spectra on solid polymers.

Experimental Section

Materials. Ethylene–vinyl acetate copolymers were obtained by radical copolymerization[6] and the products were used without further purification. Solution viscosities indicated that molecular weights of all copolymers were high. The purity of the compounds as well as their composition were determined by elemental analysis and by both ^{13}C and ^{1}H nmr spectra. The results obtained with the two different methods agreed within ±1%.

All the solvents were spectroscopic grade Merck products and were used without further purification.

All nmr spectra have been run on a Varian XL-100 high-resolution Fourier transform nmr spectrometer operating at 25.2 and 100 MHz for ^{13}C and ^{1}H, respectively. The spectrometer was equipped with a Varian 620 i computer system. The Fourier transform spectra were obtained under the following conditions: acquisition time 0.8 sec; spectral width 5000 Hz; pulse width 60 μsec; data were stored in 8K channels; the pulse interval was 0.8 sec; approximately 3000–5000 transients were collected for each spectrum.

The sample was contained in a 12-mm tube. Chemical shifts were measured from Me_4Si internal reference and are reported in parts per million from $^{13}CS_2$, assumed to be at −194.2 ppm from Me_4Si.

Results and Discussion

In Figures 1–4 are reported ^{13}C spectra of ethylene–vinyl acetate copolymers having different monomer ratios, in solution as well as in the solid state. The different resonances are easily assigned: CH_3 at 173 ppm, CH_2 between 173 and 155 ppm, and CH between 128 and 120 ppm. The carbonyl resonances (not shown in the figures) are between 22 and 25 ppm. In general the variation of the relative monomer ratio (with the exception of very weak signals, which are probably spurious) affects only the intensities of the peaks, not their multiplicity.

Because of different correlation times, the relative intensities of the resonances of the backbone ^{13}C nuclei and of those attributed to side chains (carbonyl and acetyl methyl) may not be reliable for quantitative analysis in the experimental conditions we chose. No effort was made to choose a different sequence of pulses because actually we did not need these data, inasmuch as we chose to carry out the analysis on spectral peaks whose relative intensities can be used without any correction at all. Relative in-

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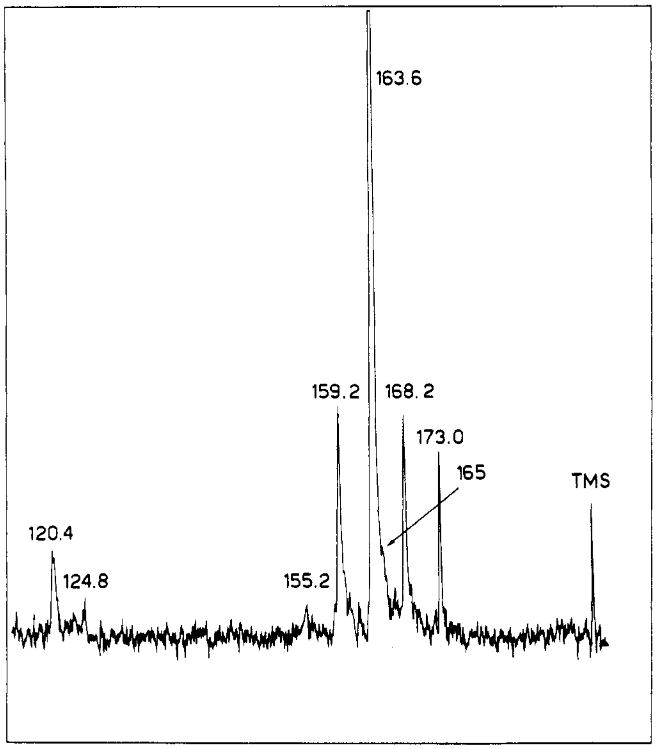

Figure 1. ^{13}C nmr spectrum of ethylene–vinyl acetate copolymer 0.18 *M* fraction of vinyl acetate in benzene solution at 25.2 MHz. The chemical shift values are in parts per million from $^{13}CS_2$.

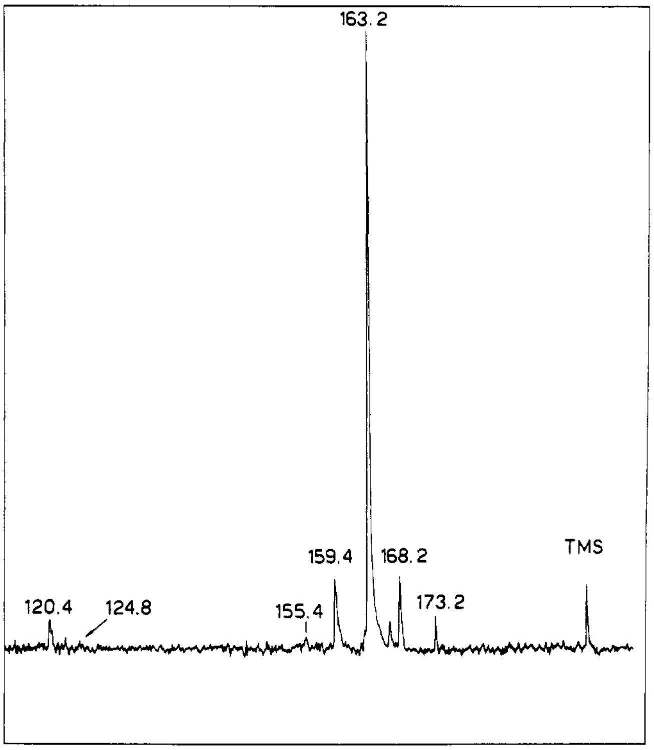

Figure 3. ^{13}C nmr spectrum of ethylene–vinyl acetate copolymer 0.09 *M* fraction of vinyl acetate in benzene solution at 25.2 MHz. The chemical shift values are in parts per million from $^{13}CS_2$.

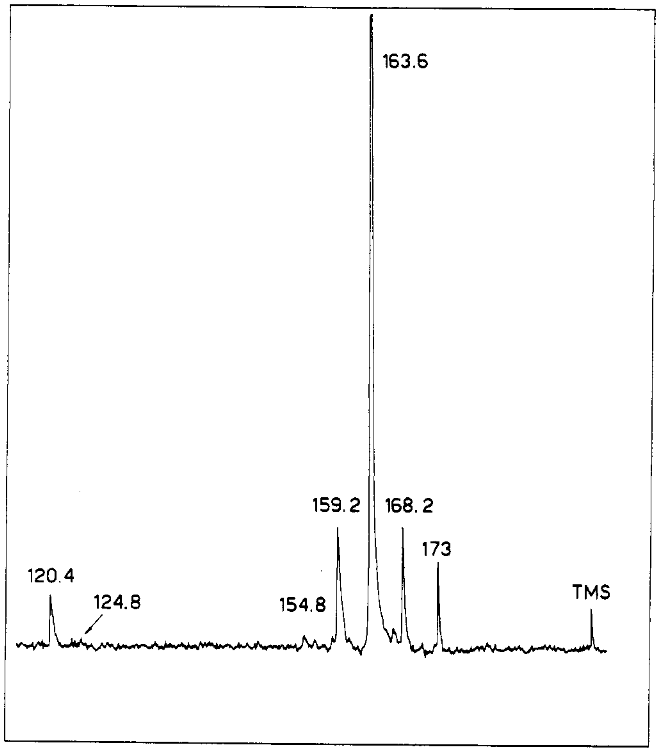

Figure 2. ^{13}C nmr spectrum of ethylene–vinyl acetate copolymer 0.13 *M* fraction of vinyl acetate in benzene solution at 25.2 MHz. The chemical shift values are in parts per million from $^{13}CS_2$.

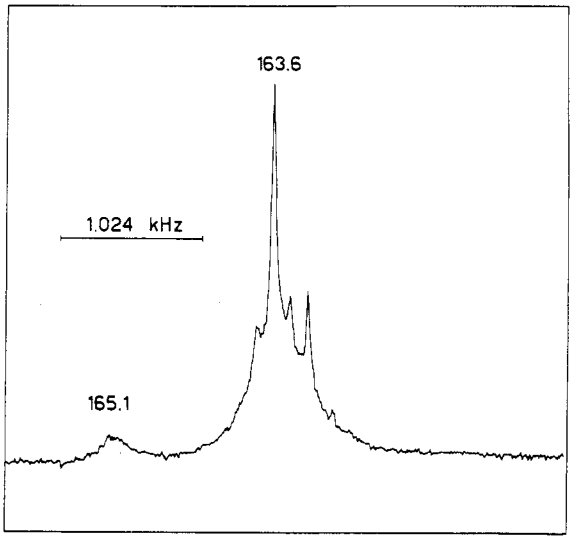

Figure 4. ^{13}C nmr spectrum of ethylene–vinyl acetate copolymer 0.18 *M* fraction of vinyl acetate in solid state. The chemical shifts are in parts per million from $^{13}CS_2$.

tensities can be taken into account for quantitative analysis by considering chemically equivalent ^{13}C nuclei, *i.e.*, various signals belonging to different CH_2 signals of ethylene and vinyl acetate can be compared without making any appreciable error. Moreover, from the ^{13}C spectrum of the vinyl acetate polymer (Figure 5) we can observe that the intensities of the backbone carbon resonances are nearly the same, so that no large error is introduced in comparing the intensities of methine and methylene ^{13}C nuclei.

We tried to make an assignment of the CH_2 and CH residues, without taking into account their stereoisomerism, both by following the rules of Grant and Paul[7] as well as by comparison of spectra of samples of varying composition. The additive contribution of the acetyl group was deduced from literature data.[8] If A = vinyl acetate and B = ethylene, the possible sequences and calculated ^{13}C chemical shifts values are as reported in Table I. In

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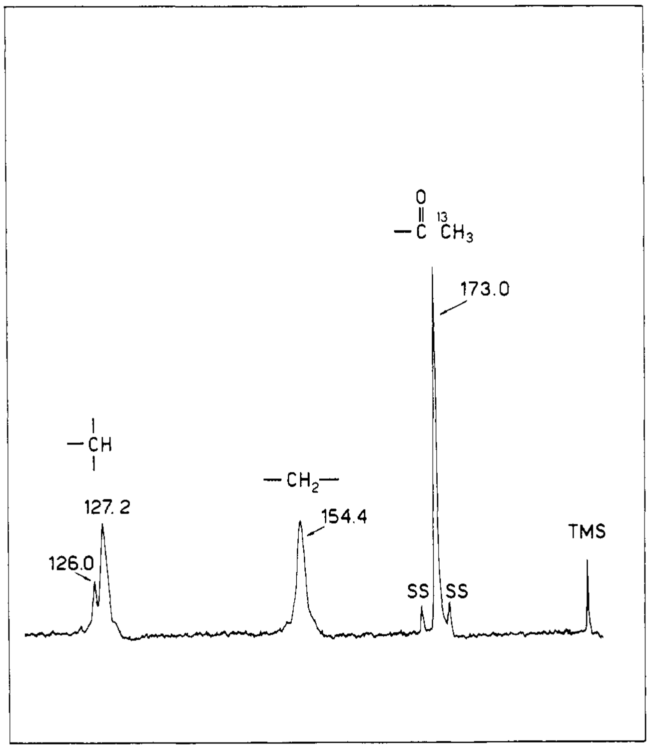

Figure 5. ^{13}C nmr spectrum of poly(vinyl acetate) in benzene solution at 25.2 MHz. The chemical shift values are in parts per million from ^{13}CS$_2$.

Table I
^{13}C Shifts According to Grant and Paul (in ppm from CS$_2$)

Triad Sequences	CH	CH$_2$	Pentad Sequences	CH	CH$_2$
A*A*A	128.0	156.3	AA*A*AA	128.2	156.7
			AA*A*AB	128.0	156.0
			BA*A*AB	127.8	155.9
B*A*A	124.1	156.0	AB*A*AA	124.3	156.7
			BB*A*AA	124.1	155.9
			AB*A*AB	124.1	156.0
			BB*A*AB	123.9	155.2
A*A*B	123.9	160.4	AA*A*BA	124.1	160.8
			AA*A*BB	123.9	160.1
			BA*A*BA	123.9	160.1
			BA*A*BB	123.7	159.9
B*A*B	120.2	160.2	BB*A*BB	120.0	159.7
			AB*A*BB	120.2	159.9
			AB*A*BA	120.4	160.6
	CH$_2$(1)	CH$_2$(2)		CH$_2$(1)	CH$_2$(2)
A*B*A	172.1	160.4	BA*B*AB	172.1	160.4
			AA*B*AB	172.3	160.5
			AA*B*AA	172.5	161.2
B*B*A	168.4	159.8	BB*B*AB	168.2	159.7
			AB*B*AB	168.4	159.8
			BB*B*AA	168.4	159.8
			AB*B*AA	168.6	159.9
A*B*B	168.2	165.0	BA*B*BB	168.2	165.0
			AA*B*BB	168.4	165.1
			BA*B*BA	168.4	165.1
			AA*B*BA	168.6	165.8
B*B*B	164.3	164.3	BB*B*BB	164.3	164.3
			AB*B*BB	164.5	164.4
			AB*B*BA	164.7	165.1

Table II

	(δ_{ppm} ^{13}CS)
$\mathrm{-CH(OCOCH_3)CH_2CH(OCOCH_3)}\mathit{CH}_2\mathrm{CH(OCOCH_3)CH_2\text{-}CH_2\text{-}CH_2CH(OCOCH_3)}\mathit{CH}_2\mathrm{\text{-}CH(OCOCH_3)CH_2\text{-}}$	155.2
$\mathrm{-CH(OCOCH_3)CH_2CH(OCOCH_3)}\mathit{CH}_2\mathrm{CH_2CH_2\text{-}}$	159.2
$\mathrm{-CH_2CH_2CH(OCOCH_3)}\mathit{CH}_2\mathrm{CH_2CH_2\text{-}}$	
$\mathrm{-CH(OCOCH_3)CH_2CH_2}\mathit{CH}_2\mathrm{CH(OCOCH_3)CH_2\text{-}}$	
$\mathrm{-CH_2CH_2CH_2}\mathit{CH}_2\mathrm{CH(OCOCH_3)CH_2\text{-}}$	
$\mathrm{-CH_2CH_2}\mathit{CH}_2\mathit{CH}_2\mathrm{CH_2CH_2\text{-}}$	163.6
$\mathrm{-CH(OCOCH_3)CH_2CH_2}\mathit{CH}_2\mathrm{CH_2CH_2\text{-}}$	165.0
$\mathrm{-CH(OCOCH_3)CH_2}\mathit{CH}_2\mathrm{CH_2CH_2CH_2\text{-}}$	168.2
$\mathrm{-CH_2CH_2}\mathit{CH}_2\mathrm{CH_2CH(OCOCH_3)CH_2\text{-}}$	
$\mathrm{-CH(OCOCH_3)CH_2}\mathit{CH}_2\mathrm{CH_2CH(OCOCH_3)CH_2\text{-}}$	172.2
Acetyl	173.0

every spectrum in benzene we can observe, between 173 and 155 ppm, five different peaks respectively at 155.2, 159.2, 163.6, 168.3, and 173 ppm (plus a shoulder at ~165 ppm). Using the calculated peak positions in Table I, assignments of the different resonances have been made as shown in Table II. Since the vinyl acetate content was less than 20 mol% in all our samples, the absence of an appreciable content of ABA is not surprising. This result is confirmed by the small value of the intensity of the AAA + BAA signal (155.2 ppm). The methine part of the spectrum confirms these assignments, as evidenced by the lack of any peak at 128 ppm (AAA triad) and by the very small the peak at 124 ppm (AAB + BAA triad).

With the assumption that an ABB unit and a BBA unit have the same probability,[9] we can make a quantitative analysis of the spectrum without using the intensity of the shoulder at ~65 ppm, the intensity determination of which is at present inaccurate. This assumption is correct if the distribution of the monomers is a zeroth-order Markoffian, as it seems to be from previous studies.[2] The results obtained are reported in Table III. It is worthwhile to observe that the ratio of the AAB and BAB triads is also verified in the CH region of the spectra. Moreover, it is possible to make a quite accurate analysis of the vinyl acetate content merely on the basis of the ^{13}C spectrum, even at low vinyl acetate content.

Examination of the CH part of the spectrum reveals that the 120.3-ppm peak is actually not a singlet; we explain this multiplicity as due to partially resolved pentads.

In addition, upon decreasing the vinyl acetate content, a small peak at 166.9 ppm appears. Two effects may eventually explain its presence: folding[10] of the polymer and/or cross-linking. In any event, we do not at present attempt any explanation of small peaks whose presence is not directly attributable to any sequence of the copolymer.

It is necessary to point out that the zeroth-order Markoffian distribution presently assumed is implicit when we assume an equal content of ABB and BBA; to check its validity we are presently beginning the study of polymers at higher vinyl acetate content as well as the study of solvent effects on the ^{13}C spectrum in order to see if it is possible to obtain the pentad distribution. We observe that the resonance at 155.2 ppm, attributed to the BBA triads, has its maximum centered exactly where we expect to find the BBAAB sequence according to Grant's calculation. This unit, the vinyl acetate–ethylene ratio being low,

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(9) It is worthwhile to observe that these units present different chemical shifts (see Table I).

(10) T. K. Wu, *Macromolecules*, 3, 610 (1970).

should be the most probable of the pentads deriving from BAA triads. Similar observations can be made for every peak in the spectrum; again, the observed frequences correspond to the calculated pentad sequences with higher ethylene content. Owing to the low number of transients presently used we think that an analysis at even lower vinyl acetate content is possible; experiments on polymers containing a very small amount of each monomer are in progress.

Another interesting result is given by the spectrum of the copolymer with 0.18-mol fraction vinyl acetate obtained using a solid sample (Figure 4). Fine structure is present similar to that obtained with the same sample in benzene solution. The carbonyl signal (not shown in Figure 4) appears to be shifted in respect to the corresponding signal in solution, respectively at 11.2 and 24.8 ppm, showing the shielding effect of the aromatic solvent. Other chemical shifts appear unaffected. Further experiments on solid samples are in progress. Although this result must be considered in greater detail, the possibility of obtaining data for such a polymer in the solid state is evident.

Aknowledgment. This work was sponsored by the Consiglio Nazionale delle Ricerche. The authors thank Dr. F. Wehrly of Varian for running the spectra.

Structure Analysis of Poly(propylene-*β*-*d* oxide) by Proton Nuclear Magnetic Resonance Spectroscopy

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ABSTRACT: *cis*- and *trans*-propylene-*β*-*d* oxide were prepared and nmr spectra of their polymers were analyzed. The polymerization of propylene-*β*-*d* oxide proceeded through exclusive inversion or retention of configuration at the carbon atom attacked by propagating species. Conformation of these polymers in solution was discussed, based on the coupling constants between main-chain protons of polymers obtained from both monomers.

Numerous studies have been carried out on the ring-opening reaction of epoxides, and *β*-opening reaction is generally accepted to occur preferentially for propylene oxide.[1] In the polymerization reaction of propylene oxide by PrONa catalyst, *β* opening was assumed to be the main reaction based on the experimental result that the end group of polymer is secondary alcohol.[2] If *β* opening is accompanied by *α* opening, the resulting polymer chain should contain head-to-head and tail-to-tail linkages in addition to head-to-tail linkages. Actual existence of head-to-head and tail-to-tail linkages in poly(propylene oxide) was first discovered by Price and Spector[3] in the structure of dimers obtained by ozonolysis of the polymer, and later supported by our nmr analysis of poly(propylene-*α*-*d* oxide).[4]

Since propylene-*β*-*d* oxide has two asymmetric carbon atoms, four isomers, racemic cis and racemic trans, should exist. If the polymerization proceeds exclusively by *β* opening and either by retention or by inversion of configuration at the attacked carbon atom, *i.e.*, *β* carbon, a polymer composed of monomeric units having exclusively an erythro or threo configuration is expected to be formed. Nmr analysis of the polymer obtained from *cis*- and *trans*-propylene-*β*-*d* oxide was investigated, therefore, to obtain information on the type of ring opening and supporting evidence concerning the nmr analysis of poly(propylene-*α*-*d* oxide).

Experimental Section

Preparation of *cis*- and *trans*-Propylene-*β*-*d* Oxide. These compounds were prepared, in overall yield of about 50%, from *cis*- and *trans*-propylene, respectively, which were prepared by a known procedure from 1,2-dibromopropane. Separation of *cis* and *trans* isomers was carried out by preparative glpc of 1-bromopropylene. A series of reactions leading to cis- and trans-propylene-*β*-*d* oxide proceeded stereospecifically.

(1) 1,2-Dibromopropane. 1,2-Dibromopropane was prepared by bromination of propene in carbon tetrachloride. The product was distilled under reduced pressure, bp 70–72° (75 mm).

(2) *cis*- and *trans*-1-Bromopropene.[5] *cis*- and *trans*-1-Bromopropene were prepared by dehydrobromination of 1,2-dibromopropane (606 g, 3.0 mol) with sodium phenoxide (3 mol) in isoamyl alcohol (1.2 l.) at 80° with stirring. The fraction boiling at 52–63° (272 g) consisted of 2-bromo-1-propene, *cis*- and *trans*-1-bromo-1-propene in about equimolar ratio. The above mixture was fractionally distilled with a spining band rectifying column of 40 theoretical plates. The fraction boiling at 48–49°, 2-bromopropene, was removed. The residual *cis*- and *trans*-1-bromo-1-propene could not be fractionated by distillation.

Separation of these materials[6] was carried out by preparative glpc technique (Varian Aerograph 700). The glpc column (20 ft) was packed with 25% dipropylene glycol dibenzoate on 30–60 mesh fire brick. The separated products were stored at −78° to prevent isomerization. The purity of each product was over 98% by glpc; ir spectra were the same as that reported by Harwell and Hatch.[7]

(3) *cis*- and *trans*-Propene-1-*d*.[8] A dispersion of lithium (2.3 g, 0.23 mol) in dry ether (50 mol) was placed in a three-necked flask equipped with a thermometer, a dropping funnel, and a reflux condenser. The top of the reflux condenser was equipped with a gas outlet tube connected to a trap cooled to −78°. The ether solution (50 ml) of 1-bromo-1-propene (14.3 g), dried over calcium chloride, was introduced through a dropping funnel into diethyl ether containing the lithium dispersion cooled to −10° with stirring by a magnetic stirrer. After addition of the ether solution of 1-bromo-1-propene, the solution was maintained at −10° for 4 hr. Half the volume of ether (50 ml) was removed under reduced pressure, and the dropping funnel was exchanged to one containing D_2O (6 ml). D_2O was added to the residual solution at −10° over 0.5 hr. Propene-*1*-*d* produced was caught with a trap cooled at −78°, through a reflux condenser cooled by ice–water and an outlet tube. Then, in order to remove propene-*1*-*d* dissolved in the resulting ether solution, the hydrolyzed solution was maintained at 40° for 1 hr. The products were not characterized in this step.

(4) *threo*- and *erythro*-1-Chloropropane-2-ol-1-*d*. Preparation

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