ml of saturated aqueous $NaHCO_3$) and dried ($MgSO_4$). Concentration at reduced pressure followed by distillation yielded 4.0 g (33%) of 3-phenylcycloheptanone, bp 105° (0.5 mm). The semicarbazone melted at 219–220° (lit.[22] mp 220–221°).

3-Phenylcycloheptanol. A solution of 3-phenylcycloheptanone (3.50 g, 18.5 mmoles) in 45 ml of ether was added dropwise with stirring to a slurry of lithium aluminum hydride (500 mg, 13.2 mmoles) in 50 ml of ether at room temperature. Stirring was continued for 1 hr and the mixture was decomposed by dropwise addition of water. The ether layer was separated, washed (H_2O), dried ($MgSO_4$), and concentrated at reduced pressure yielding 3.50 g (99%) of 3-phenylcycloheptanol. Analysis by glpc (8 ft × 0.25 in., Carbowax, 240°) indicated a 50:50 mixture of *cis* and *trans* isomers with the following spectral properties: $\nu_{\max}^{CCl_4}$ 3600, 3400, 3080, 3055, 3025, 2930, 2855, 1500, 1490, 1450, 1025, 695 cm^{-1}; nmr (CCl_4), δ 7.09 (5 H, singlet), 3.84 (1 H, multiplet), 3.09–1.00 (11 H, multiplet); mass spectrum; *m/e* (relative intensity), 190 (12, molecular ion), 117 (43), 104 (100), 91 (69), 41 (46).

Anal. Calcd for $C_{13}H_{18}O$: C, 82.10; H, 9.47. Found: C, 81.85; H, 9.45.

Dehydration of 3-Phenylcycloheptanol. Phosphorus oxychloride (3.0 ml) was added dropwise with stirring to a solution of 3-phenylcycloheptanol (1.80 g, 9.5 mmoles) in 50 ml of pyridine at room temperature. The mixture was heated at 100° for 1 hr and, after cooling, was diluted with 200 ml of water and extracted with two 100-ml portions of ether. The ether extracts were washed (6 *N* HCl) and dried ($MgSO_4$). Concentration yielded 1.65 g of a mixture of olefins which was analyzed by glpc (8 ft × 0.25 in., 10% phenyldiethanolamine succinate, 140°). The mixture was separated into two components, in the ratio of 44 to 56%, having relative retention times of 1.00 and 1.10, respectively. No isomerization to 1-phenylcycloheptene was observed. The first component was identified as 3-phenylcycloheptene by comparison of its infrared spectrum and retention time to those of an authentic sample. The spectral properties of the second component established its structure as 4-phenylcycloheptene: $\nu_{\max}^{CCl_4}$ 3080, 3070, 3030, 2930, 2850, 1650, 1600, 1475, 1450, 1435, 685 cm^{-1}; nmr (CCl_4), δ 7.08 (5 H singlet), 5.87–5.62 (2 H, multiplet), 2.68–1.18 (9 H, multiplet); mass spectrum, *m/e* (relative intensity), 172 (56, molecular ion), 117 (92), 104 (100), 91 (81), 39 (56).

Anal. Calcd for $C_{13}H_{16}$: C, 90.70; H, 9.30. Found: C, 90.85; H, 9.26.

3-Phenyl-*cis*-bicyclo[5.1.0]octane (13). A slurry of Zn–Cu couple (1.04 g), 1.1 ml of methylene iodide, and a crystal of iodine in 25 ml of ether was heated under reflux for 1 hr. 4-Phenylcycloheptene (95.0 mg, 0.55 mmoles) was added in one portion. The mixture and stirred and refluxed for 60 hr. The inorganic material was filtered, and the ether solution was washed (saturated aqueous NH_4Cl and H_2O), dried ($MgSO_4$), and concentrated at reduced pressure yielding a residue of 176 mg, which was analyzed by glpc (8 ft × 0.25 in., LAC-728, 140°). There was one high-boiling component with retention time different from 4-phenylcycloheptene. This was identified as 3-phenyl-*cis*-bicyclo[5.1.0]octane (**13**) by comparison of spectral and chromatographic properties with those of an authentic sample.[14] There was no evidence for separation of epimers under any conditions tried. The stereochemistry of the product may therefore be either *endo* or *exo* or a mixture of both with a mass spectrum; *m/e* (relative intensity), 186 (73, molecular ion), 129 (31), 117 (48), 104 (100), 91 (67).

Aprotic Decomposition of 3-Phenylcyclooctanone Tosylhydrazone (9). The procedure was identical with that used in the aprotic decomposition of 2-phenylcyclooctanone tosylhydrazone (**1**). In a typical run, the decomposition of 700 mg (1.89 mmoles) of 3-phenylcyclooctanone tosylhydrazone (**9**) was promoted by 109 mg (2.02 mmoles) of sodium methoxide. This yielded a mixture of hydrocarbons (119 mg, 49%) which was analyzed by glpc (8 ft × 0.25 in., 20% LAC-728, 140°) to give the following compounds (the relative retention times are given in parentheses): 1-phenyl-*cis*-bicyclo[5.1.0]octane (**12**) (0.71), 3-phenyl-*cis*-bicyclo[3.3.0]-octane (**11**) (0.80), 3-phenyl-*cis*-bicyclo[5.1.0]octane (**13**) (0.96), 3-phenylcyclooctene (**3**) (1.00), 4-phenylcyclooctene (**10**) (1.05), unidentified (1.15). The composition of the mixture was determined by measuring peak areas with a planimeter and the reported percentages represent the average of three decompositions. Spectral data were obtained by recollecting from a 2 ft × 0.25 in., 20% SE-30 column at 180°.

Acknowledgment. This project was completed under the supervision of Professor Frederick D. Greene, whose many valuable suggestions are greatly appreciated.

Effect of Preceding Mer Units on Stereospecific Polymerization Found in Oligomers of Isopropyl Acrylate

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Abstract: A series of oligomers was prepared by adding heavy water to a solution of isopropyl acrylate-α,β-d_2, which was polymerizing by an anionic mechanism under conditions which give, without hydrolysis, a highly diisotactic polymer through *trans* opening of the double bond. Nmr analysis of the products showed that the oligomers comprised a homologous series, all mer units of which had isotactic α-methine configurations. The first and second units of each oligomer, however, had β-methylene carbons of nearly random configuration and all units added later had isotactic β configurations corresponding to *trans* opening of the double bond like the high polymers produced in this system. Apparently regular isotactic placement of the terminal α-methine carbon of a growing anion does not require the prior occurrence of an isotactic placement and is independent of the mode of incorporation of the β carbon of the terminal unit into the growing chain. Mer units other than the last two of a growing anion are not required to direct the mode of approach of another monomer into a transition state.

The effect of preceding mer units on the placement of the terminal unit of a growing chain can be derived from the intensities of the nmr signals characteristic of dyads, triads, tetrads, etc., of mer units of the polymer obtained. It has been found[1] from the intensities of the dyad and triad signals that anionic polymerizations of methyl methacrylate usually cannot be explained by a *single Bernoullian* process. In any non-Bernoullian as, for example, multistate[2] polymerization, the intensities of the signals of tetrads and higher

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[1] F. A. Bovey and G. V. D. Tiers, *J. Polymer Sci.*, **44**, 173 (1960).

[2] B. D. Coleman and T. G. Fox, *J. Chem. Phys.*, 38, 1065 (1963).

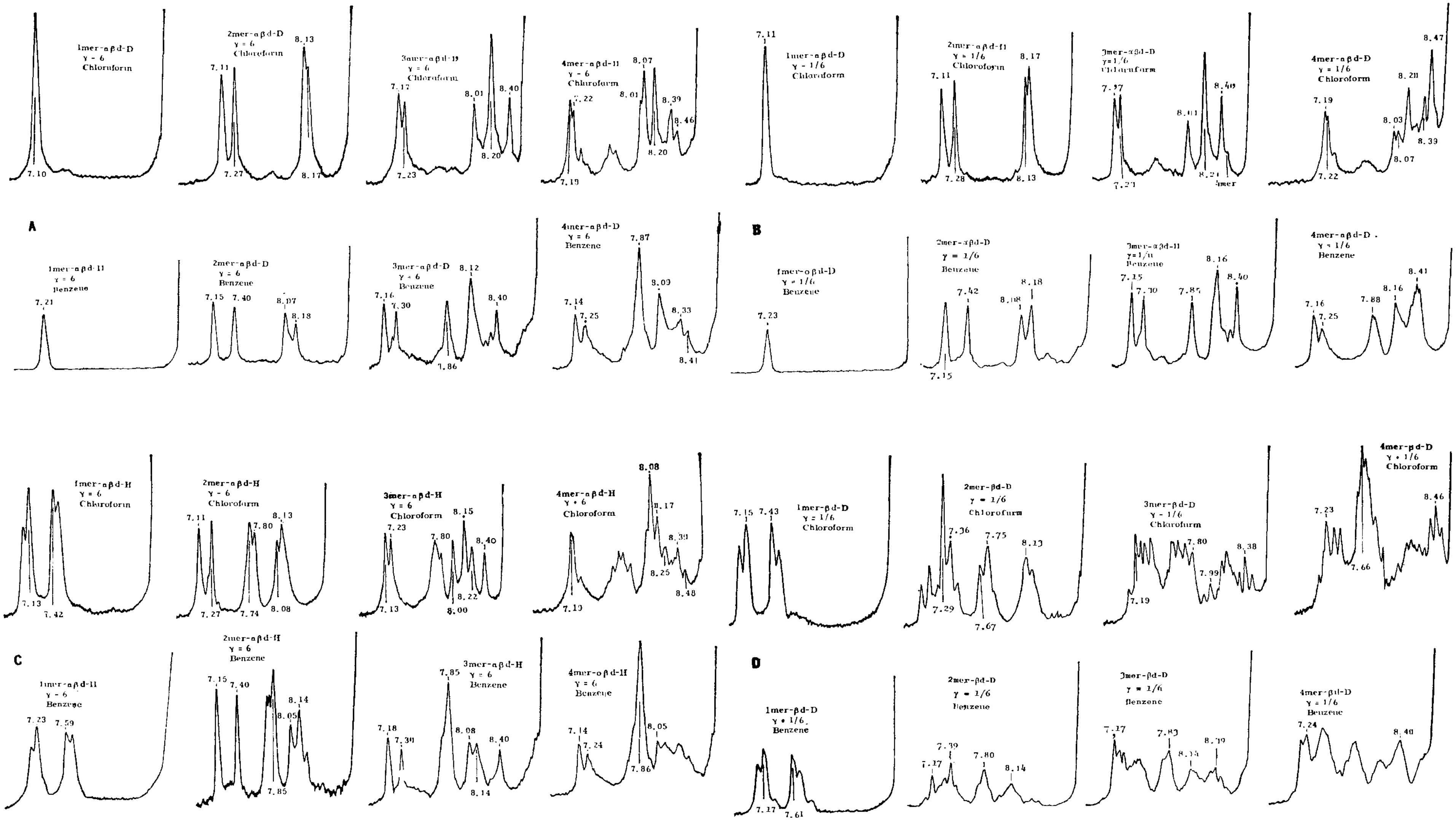

Figure 1. Backbone proton spectra of 1mers, 2mers, 3mers, and 4mers of deuterated isopropyl acrylates. The numerical values shown in the spectra are the τ values of the signals.

ads are required for finding the effect of the preceding units. However, intensity measurement of these signals is not an easy task because of small signal separations. For a polymer of high tacticity, the measurement is hardly possible because some of these signals are extremely weak.

We have devised a method which enables us to find the effect of the preceding units on placement of the terminal unit and on monomer orientation in a highly isotactic polymerization. We shall suppose that the anionic polymerization of an α,*trans*-β-d_2 or α,*cis*-β-d_2 vinyl monomer CHD=CDX initiated with phenylmagnesium bromide, for example, proceeds according to eq 1 and gives a highly diisotactic polymer Ph-

$$\mathrm{Ph(CHDCDX)}_{n-1}^- + \mathrm{CHD{=}CDX} \longrightarrow \mathrm{Ph(CHDCDX)}_n^- \quad (1)$$

$\mathrm{(CHDCDX)}_n\mathrm{H}$. The characteristic of the present method is to find from the polymer obtained (a) whether the initial few monomer units with random placement of CDX and/or CHD group are followed by units with highly stereoregular placement or whether stereoregularity increases gradually in the initial several units and (b) where the sudden transition from random to regular placements occurs if such a transition exists.

It is, however, difficult to determine precisely the structures of the initial several units of long polymer chains, and structural determination of the remaining parts of the polymer chains is not necessary in the present method. We have, therefore, applied the present method to oligomers prepared by hydrolysis of living oligomers which would have grown to higher oligomers and/or polymers under the same conditions without hydrolysis. These oligomers were found to have the structures represented by $\mathrm{Ph(CHDCDX)}_n\mathrm{D}$ when polymerization of α,β-d_2 monomer was interrupted by addition of heavy water, as expected from the reaction expressed by eq 1.

A reaction mixture prepared at −80° from phenylmagnesium bromide (ether solution), magnesium dibromide, isopropyl acrylate-α,β-d_2 with $\gamma = 6$ or $^1/_6$,[3] and toluene (the molar ratio = 1:1:3:30) was selected for a variety of reasons. (i) Side-reaction products, which hinder determination of the molecular structures of oligomers, are scarcely formed at −80° in this reaction mixture even at the high initiator–monomer ratio employed to increase the oligomer yield.[4] (ii) The separations between the signals of the *erythro*- and *threo-meso* and racemic methylene protons of an acrylate polymer are fairly large[5–7] and such large signal separations are expected also for acrylate oligomers. (iii) The nmr signal of the phenyl group incorporated in an oligomer is distant from the other signals of the oligomer. (iv) The methylene proton signal of the mer unit adjacent to the phenyl group of an oligomer is expected to appear at a lower field than the other methylene signals and assignment of the signals is facilitated in this situation. (v) The use of magnesium dibromide results in formation of an isotactic polymer almost exclusively through *trans* opening of the monomer double bond, while, without the dibromide, diisotactic processes with *cis* and *trans* openings were found to occur at −80°.[8] Magnesium dibromide was employed to make easier the present study by simplifying the polymerization process. (vi) The use of the α,β-d_2 monomer simplifies the oligomer spectra by removing signal splittings due to proton spin coupling and γ different from unity is required to find whether or not the placement of the monomer about to be polymerized is regular.

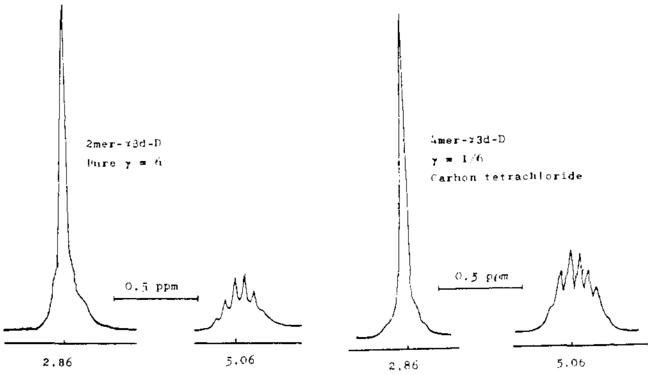

Figure 2. Phenyl and ester methine signals of two examples of oligomers.

In the present paper oligomers mentioned above are expressed by *n*mer-$\alpha\beta d$-D ($\gamma = 6$) or *n*mer-$\alpha\beta d$-D ($\gamma = {}^1/_6$) for the purposes of simplicity and distinction between 1mer and monomer. In the symbols of oligomers, $\alpha\beta d$ and ($\gamma = 6$) mean that α,β-d_2 monomer with $\gamma = 6$ was employed and D means that heavy water was used to interrupt polymerization.

Assignment of Nmr Signals

Oligomers were fractionated by vacuum distillation from an oligomer mixture which was derived from the polymerization solution of isopropyl acrylate-α,β-d_2 with $\gamma = 6$ previously mentioned. The nmr spectra (100 Mc) of the distilled fractions were measured at room temperature on pure liquid (except the viscous 4mer) and on 20% solutions in chloroform, benzene, and carbon tetrachloride for reasons given later. The backbone proton spectra measured on benzene and chloroform solutions are shown in Figure 1.

The mean of the n values of oligomers, $\bar{n}$, in each of the distilled fractions was found to be approximately equal to 1, 2, 3, or 4, from the intensity ratio of the phenyl signal to the ester methine, ester methyl, or backbone methylene signals (Figure 2). The $\bar{n}$ value was confirmed by measuring the intensity ratio of the methylene signals of the first mer unit (τ 7.15∼7.45 in benzene and 7.1∼7.3 in chloroform) to those of the other units (Figure 1) and also by examining the intensity distribution in the ester methyl signals since the ester methyl groups of the first mer unit (of all oligomers except 1mer) appear as two doublets with components of equal intensity, being made nonequivalent by the adjacent phenyl group (Figure 3).

The amount of $(n-1)$mer and $(n+1)$mer contained in the fraction with $\bar{n} \approx n$ was estimated from the intensities of the signals characteristic of the respective

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[3] Here γ means the molar ratio of the isomer with D *trans* to the ester group to the other isomer with *cis* D.

[4] In the reaction mixture was found a small amount of side-reaction product which is distilled out earlier than the oligomer with one monomer unit, *i.e.*, isopropyl hydrocinnamate.

[5] T. Yoshino, J. Komiyama, and M. Shinomiya, *J. Am. Chem. Soc.*, **86**, 4482 (1964).

[6] T. Yoshino and J. Komiyama, *ibid.*, **88**, 176 (1966).

[7] C. Schuerch, W. Fowells, A. Yamada, F. A. Bovey, F. P. Hood, and E. W. Anderson, *ibid.*, **86**, 4481 (1964).

[8] T. Yoshino and K. Kuno, *ibid.*, **87**, 4404 (1965).

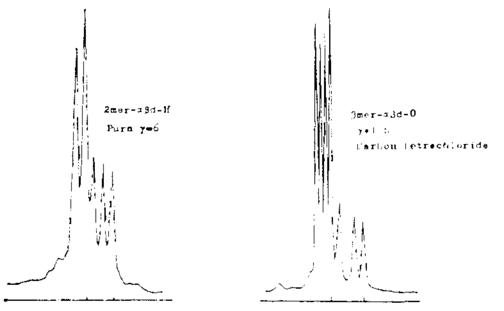

Figure 3. Ester methyl signals of two examples of oligomers.

oligomers. The higher field one of the two methylene signals of the first unit of *n*mer in benzene can be used for the estimation, because it appears at different τ values depending on *n*, while the other signal is almost independent of *n* as seen in Figure 1. (This is not true of the 1mer in which the methylene signals are singlet. Different relationships between *n* and chemical shift appear in chloroform.) The amount of $(n + 1)$mer in the distilled fraction with $\bar{n} \approx n$ can be estimated more accurately from the intensities of the methylene signals of the *n*th unit of $(n + 1)$mer than from those of the first unit. According to these methods, the distilled fractions with $\bar{n} \approx 1$ and 2 were found, respectively, to be almost free from 2mer-$\alpha\beta d$-D and 1mer- and 3mer-$\alpha\beta d$-D and the fractions with $\bar{n} \approx 3$ and 4 were found to contain about 10% of 4mer-$\alpha\beta d$-D and 3mer-$\alpha\beta d$-D, respectively.

For the purpose of assigning the backbone proton signals of *n*mer-$\alpha\beta d$-D ($\gamma = 6$), oligomers represented by *n*mer-$\alpha\beta d$-D ($\gamma = {}^1/_6$), *n*mer-βd-D ($\gamma = {}^1/_6$), and *n*mer-$\alpha\beta d$-H ($\gamma = 6$) were also prepared by the same method as stated above except that α,β-d_2 monomer with $\gamma = {}^1/_6$ or β-d_1 monomer with $\gamma = {}^1/_6$ or hydrolysis by light water was employed The spectra of these oligomers were measured under the conditions described above and the backbone proton spectra of chloroform and benzene solutions are shown in Figure 1.

The 1mers were identified as isopropyl hydrocinnamate by the coincidence of their signal positions with those of the same compound prepared from hydrocinnamoyl chloride and isopropyl alcohol. The other oligomers also have spectra consistent with the structures represented by $Ph(CHDCDX)_nD$,[9] $Ph(CHDCDX)_nH$, or $Ph(CHDCHX)_nD$ (Figure 1). Here X means $COOCH(CH_3)_2$. The τ values measured in chloroform solutions are used in the descriptions hereafter except when mentioned otherwise, because some of the methine and methylene signals measured in a benzene solution appear in the same region from τ 7.8 to 7.9.

The signals near 7.2 of 2mers, 3mers, and 4mers, which are near the methylene signals of 1mers and far apart from the other backbone proton signals of 2mer-, 3mer-, and 4-mer-$\alpha\beta d$-D, are assigned to the methylene protons of the first units, because their low τ values are considered to be due to the neighboring phenyl groups. The signals near τ 8.2 of 2mers, 3mers, and 4mers are assigned to the methylene protons of the last units because the proton spin coupling found in *n*mer-$\alpha\beta d$-H is absent in *n*mer-$\alpha\beta d$-D.

The remaining signals at τ 8.01 and 8.40 of 3mer-$\alpha\beta d$-D are assigned to the methylene protons of the second unit because of lack of the proton spin coupling found in 3mer-βd-D. The observed two signals nearly equally share most of the intensity expected for a single proton.

Two *meso* and one (or two with a small separation) racemic methylene signals are conceivable for the second mer unit of 3mer-$\alpha\beta d$-D and the *meso* signals are not expected to overlap each other because large separations of about 0.5 ppm were found in the spectra of methyl *meso*-α,α'-dimethylglutarate[10] and isotactic polyacrylates.[5-7] At least one of the observed two signals must be, therefore, ascribed to the *meso* protons.

The intensity ratio of two *meso* signals in 3mer-$\alpha\beta d$-D ($\gamma = 6$) is expected to be the reciprocal of that of 3mer-$\alpha\beta d$-D ($\gamma = {}^1/_6$) and the ratios can be equal to unity, as realized in the present case. The observed signals are, therefore, assigned to the *meso* protons and neither of them is regarded to be contributed appreciably from the racemic protons. The present assignment is also supported by the fact that these signals measured on a methyl formate or benzene solution (at τ 8.05 and 8.39 in methyl formate and 7.85 and 8.40 in benzene) appear nearly at the same positions as the methylene signals of methyl *meso*-α,α'-dimethylglutarate in methyl formate (τ 8.0 and 8.6)[10] and isotactic polyacrylates in benzene (methyl ester, 7.9 and 8.4; isopropyl ester, 7.8 and 8.2).[5,6]

The signals at τ 8.02, 8.07, 8.39, and 8.46 of 4mer-$\alpha\beta d$-D are assigned to the methylene protons of the second and third units because of lack of the proton spin coupling found in 4mer-βd-D. These signals may be assigned to the *meso* protons because their τ values are nearly equal to those of the *meso* proton signals of 3mer-$\alpha\beta d$-D and because the intensity ratio of the signals at τ 8.07 and 8.46 of 4mer-$\alpha\beta d$-D ($\gamma = 6$) is reversed in the spectrum of 4mer-$\alpha\beta d$-D ($\gamma = {}^1/_6$). The reciprocal intensity ratios show that the signals at τ 8.07 and 8.46 are both given by one of the second and third units and the signals at 8.02 and 8.39 with nearly equal intensities are given by the other unit. The lower and the higher field signals of the *meso*-methylene protons of 3mer- and 4mer-$\alpha\beta d$-D may be assigned to the protons on the same and the opposite side of the planar zigzag from X (*gauche* and *trans* to X; in *erythro* and *threo* positions), respectively, by analogy to the assignment established in methyl *meso*-α,α'-dimethylglutarate.[10]

The two groups of signals near τ 7.3 and in the region 7.6∼7.8 of each of 2mer-, 3mer-, and 4mer-βd-D are assigned to the α protons, because they are much smaller in the spectrum of *n*mer-$\alpha\beta d$-D. The higher field signal group is contributed from the terminal α proton in the region near τ 7.8 where the α-proton signals of *n*mer-$\alpha\beta d$-H appear. The lower field one of 2mer-βd-D is, therefore, ascribed to the α proton of the first unit. The lower field one of each of 3mer- and 4mer-βd-D, which appears near that of 2mer-βd-D, is then found to be contributed from the α proton of the first unit. Since the intensity ratio of the higher to the

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(9) Small α-proton signals and partial splitting of methylene signals by coupling with α protons are found in the spectra of 4mer-$\alpha\beta d$-D, showing that H–D exchange occurred at high distillation temperature.

(10) T. Yoshino, M. Shinomiya, and J. Komiyama, *J. Am. Chem. Soc.*, **87**, 387 (1965).

lower field α-proton signal group increases with n and is about 3:1 in 4mer-βd-D, the higher field signal group with the center at τ 7.7 is contributed in the region 7.6～7.7 from the second and third units.

According to the assignment of the α-proton signals given above, it was expected that the *threo-meso* proton of the third unit of 4mer-βd-D would be decoupled from the vicinal α protons by irradiating the region near τ 7.65 (the *erythro* proton signal is too close to the region to be decoupled), while the *threo-meso* proton of the second unit would be decoupled from only one of the vicinal α protons by irradiating the region near τ 7.3 or the region near 7.65. This difference between the *threo-meso* protons of the second and third units was used to assign the *meso*-methylene peaks of the second and third units of 4mer-$\alpha\beta d$-D.

A strong decoupled signal was found at τ 8.46 in the spectrum of 4mer-βd-D ($\gamma = {}^1/_6$) measured with irradiation at 80-cps lower field (Figure 4), but no other strong decoupled signal was found in the spectra measured by changing the difference of measuring and irradiating frequencies. The signal at 8.46 and its partner at 8.07 of 4mer-$\alpha\beta d$-D are, therefore, assigned to the *meso* protons of the third unit and the other pair at 8.39 and 8.02 to the *meso* protons of the second unit.

Placements of CHD and CDX Groups in Oligomers and Information from the Placements

The methylene signals of the first unit of each of 2mer-, 3mer-, and 4mer-$\alpha\beta d$-D seem to be equal in their intensities and the equality is confirmed from the intensity ratio of these signals independent of γ of the monomer employed. The equal intensity means that the nonequivalent methylene protons of the first unit are equal in their numbers. We can, therefore, conclude that *cis* and *trans* opening of the monomer double bond occurs with equal probability at the first unit.

The *meso*-methylene signals of the second unit of each of 3mer- and 4mer-$\alpha\beta d$-D nearly equally share most of the intensity expected for a single proton.[11] This observation shows that two different orientations of monomer occur with nearly equal probabilities when the second unit is added and that predominantly isotactic placement of the second ester group occurs irrespective of the mode of incorporation of the β carbon of the second mer unit. The former is also confirmed from the fact that nearly equal intensities were found for the two methylene signals of the second unit of 2mer-$\alpha\beta d$-D,[11] which are separated from each other in the spectra measured in benzene solution and on pure liquid (Figure 5).

The *meso*-methylene signals of the third unit of 4mer-$\alpha\beta d$-D share most of the intensity expected for a single proton. The intensity ratio of the *erythro-* to the *threo-meso* proton is approximately equal to γ of the monomer employed, in contrast to the ratio nearly equal to unity found for the second unit of each of 3mer- and 4mer-$\alpha\beta d$-D. These observations show that the placement of the third ester group is mostly isotactic and that one of the two monomer orientations, which results in *trans* opening of the double bond in isotactic placement of the third ester group, occurs predominantly when the third unit is added. The latter agrees with the observation that the methylene signal of the third unit of 3mer-$\alpha\beta d$-D in benzene appears at different τ values depending on whether the monomer with $\gamma = 6$ or the other monomer with $\gamma = {}^1/_6$ is employed.

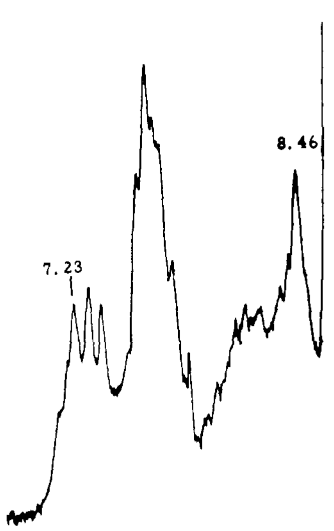

Figure 4. Backbone proton spectrum of 4mer-βd-D ($\gamma = {}^1/_6$) in chloroform measured with irradiation at 80 cps lower fields.

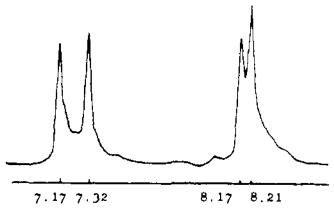

Figure 5. Backbone proton spectrum of 2mer-$\alpha\beta d$-D ($\gamma = {}^1/_6$) without solvent.

The observation that the β configuration is stereoregular in the third unit but random in the first and second mer units means that the stereoregular incorporation of monomer only begins after two monomers are incorporated into the growing anion, but does not require more than two preceding mer units.

An oligomer mixture with $\bar{n} \approx 4.5$～5 can be distilled out, but it is difficult to estimate the amounts of respective oligomers with different n in the distillate. As seen in Figure 6, the spectrum of the distillate is almost the same as that of 4mer except that the *erythro-* or *threo-meso* methylene signal is much stronger depending upon whether γ of the monomer employed is equal to 6 or ${}^1/_6$. We can, therefore, consider that the methylene signals of the first, second, third, and last units of the oligomers in the distillate are nearly equal to those of 4mer, respectively, in their τ values and intensities, and that the signals of the fourth unit of 5mer are nearly equal to the signals of the third unit in their intensities and τ values. Then the placements of the CHD and CDX groups of the fourth unit of 5mer-$\alpha\beta d$-D are regarded to be the same as those found for the third unit of 4mer-$\alpha\beta d$-D. The stereoregular placement of the CHD group of the fourth unit of 5mer-$\alpha\beta d$-D agrees with the observation that the methylene

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(11) Although the two methylene signals of the second units of each of 2mer- and 3mer-α-βd-D are nearly equal in intensity, the intensity ratio of the lower to the higher field signal is slightly larger in the oligomer derived from the monomer with $\gamma = 6$ than in the oligomer derived from the other monomer with $\gamma = {}^1/_6$. This tendency shows that one of the modes of monomer orientation, which predominates in the addition of the third mer unit, is slightly preferred to the other mode in the addition of the second mer unit where the penultimate unit is absent.

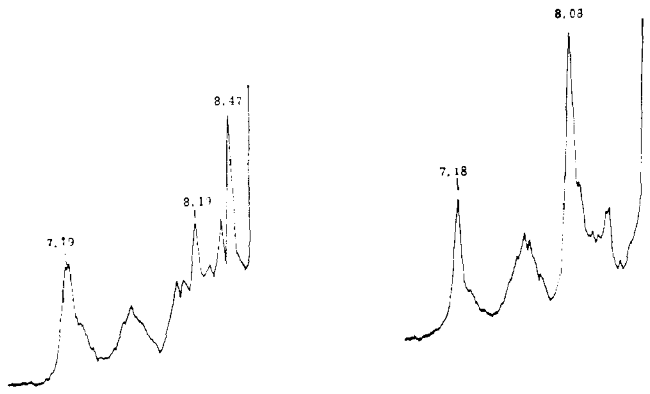


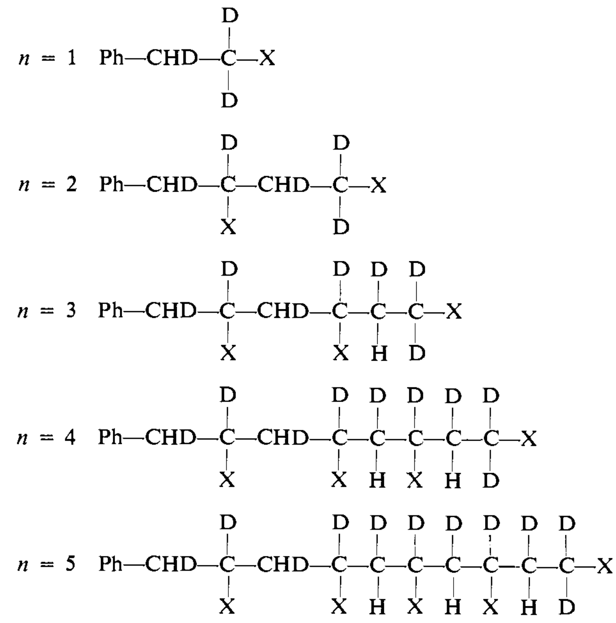
Figure 6. Backbone proton spectra of chloroform solutions of $\bar{n}$mer-$\alpha\beta d$-D ($\gamma = {}^1/_6$) with $\bar{n} \approx 4.5$ (left) and $\bar{n}$mer-$\alpha\beta d$-H ($\gamma = 6$) with $\bar{n} \approx 5$ (right).

signal near τ 8.1 of the fourth unit of 4mer-$\alpha\beta d$-D in benzene appears at different τ values depending on whether the monomer with $\gamma = 6$ or the other monomer with $\gamma = {}^1/_6$ is employed.

The above results obtained for the configurations of 1mer-, 2mer-, 3mer-, 4mer-, and 5mer-$\alpha\beta d$-D are summarized in Figure 7. As seen in the figure, the placements of the CHD and CDX groups in the *m*th unit of *n*mer-$\alpha\beta d$-D are independent of *n*. The independencies show that a living oligomer which gives the *n*mer in hydrolysis is formed through addition of a monomer to a smaller living oligomer which gives the $(n - 1)$-mer in hydrolysis; that is, living oligomers with different numbers of mer units are formed through the same route of polymerization.

It was found by the following experiments that the living oligomers which give 1mer, 2mer, 3mer, and 4mer in hydrolysis grow up to higher oligomers or polymers in the continued polymerization. After reaction of 15 min in a polymerization solution of isopropyl acrylate-α,β-d_2 with $\gamma = 6$ previously mentioned, a large amount of nondeuterated monomer was added to the solution and then heavy water was added after 20 hr of polymerization. The amount of oligomers with $n \leq 4$ separated from this polymerization solution was almost equal to the amount of oligomers with $n \leq 4$ separated from a polymerization solution hydrolyzed immediately after the initial 15 min. However, the amount of α,β-d_2 mer units in the former oligomer mixture was found to be half the amount in the latter, from the intensity ratios of the ester methine to the backbone proton signals measured on these oligomer mixtures.

It is difficult to imagine that stereospecific placement which takes place at the incorporation of the *m*th monomer requires more conditions and/or more preceding units than those required for stereospecific placement which takes place at the incorporation of the $(m - 1)$th or an earlier monomer into the growing chain with a reaction end of the same species. Therefore, the following may be concluded for stereospecific placements which take place in the formation of the oligomers shown in Figure 7 and their higher homologs. The regular isotactic placement of the terminal methine group of a growing chain does not require the prior occurrence of an isotactic placement and is independent of the mode of incorporation of the β carbon of the terminal unit. The stereospecific mode of approach of a monomer to the growing anion and the stereospecific incorporation of its β carbon into the growing chain are not contributed from mer units other than the last two in the growing anion. The last two mer units are considered to be required for stereospecific incorporation of the β carbon of the fourth or a later monomer by analogy to the observed fact that the first and second mer units of a two-unit oligomer anion contribute to stereospecific incorporation of the β carbon of the third monomer.



$$n = 1\quad \mathrm{Ph{-}CHD{-}}\underset{D}{\overset{D}{C}}\mathrm{{-}X}$$

$$n = 2\quad \mathrm{Ph{-}CHD{-}}\underset{X}{\overset{D}{C}}\mathrm{{-}CHD{-}}\underset{D}{\overset{D}{C}}\mathrm{{-}X}$$

$$n = 3\quad \mathrm{Ph{-}CHD{-}}\underset{X}{\overset{D}{C}}\mathrm{{-}CHD{-}}\underset{X}{\overset{D}{C}}{-}\underset{H}{\overset{D}{C}}{-}\underset{D}{\overset{D}{C}}\mathrm{{-}X}$$

$$n = 4\quad \mathrm{Ph{-}CHD{-}}\underset{X}{\overset{D}{C}}\mathrm{{-}CHD{-}}\underset{X}{\overset{D}{C}}{-}\underset{H}{\overset{D}{C}}{-}\underset{X}{\overset{D}{C}}{-}\underset{H}{\overset{D}{C}}{-}\underset{D}{\overset{D}{C}}\mathrm{{-}X}$$

$$n = 5\quad \mathrm{Ph{-}CHD{-}}\underset{X}{\overset{D}{C}}\mathrm{{-}CHD{-}}\underset{X}{\overset{D}{C}}{-}\underset{H}{\overset{D}{C}}{-}\underset{X}{\overset{D}{C}}{-}\underset{H}{\overset{D}{C}}{-}\underset{X}{\overset{D}{C}}{-}\underset{H}{\overset{D}{C}}{-}\underset{D}{\overset{D}{C}}\mathrm{{-}X}$$

Figure 7. Configurations of Ph(CHDCDX)$_n$D from α-*trans*-β-d_2 monomer. CHD in the figure means a random placement. The configuration of the fifth unit of 5mer in the figure is supposed to be as shown but has not been established.

These conclusions are believed to be applicable to formation of a polymer having the same stereoregularity as the third units of the oligomers.

Experimental Section

A polymerization solution was prepared in an apparatus composed of two flasks A and B combined to form a single neck stopped with a silicone rubber plug. An ether solution of magnesium dibromide was introduced by means of a syringe into A of the apparatus filled with argon. After the ether was removed *in vacuo*, the apparatus was filled with argon again. Toluene was introduced into A and B (13 ml in each) and then 3 ml of monomer and an ether solution of phenylmagnesium bromide was added to the solvents in A and B, respectively. The molar ratio of phenylmagnesium bromide, magnesium dibromide, monomer, toluene, and ether (from the Grignard solution) was 1:1:3:30:4.

After the contents attained −80°, the initiator solution in B was poured into A and the mixture was transferred between A and B several times. After reaction of 2, 2.5, or 3 min, heavy water was added at −80° and the mixture was kept at −80° for 20 hr. The three reaction mixtures with different polymerization periods were collected and washed with three 50-ml portions of 10% hydrochloric acid. The toluene layer and the ether extract from the aqueous layer were combined and the combined solution was washed with three 30-ml portions of a saturated sodium chloride solution and dried. The volume of the solution was reduced to 30 ml by partial evaporation of the solvents *in vacuo* and then polymer was removed by precipitation in petroleum ether (bp 30 ~ 70°). The solvents were removed from the solution *in vacuo* and then the residue (about 5 ml from 9 ml of monomer) was fractionated by vacuum distillation at 0.07~0.08 mm in nitrogen atmosphere. Oligomers with $n = 1$, 2, and 3 were distilled out at about 70, 115, and 155°, respectively, and 4mer and an oligomer mixture with $\bar{n} \approx 5$ were distilled out at bath temperatures of 260 ~ 280 and 290~300°, respectively. The value of $\bar{n}$ of the distillation residue was about 10.

Owens, *et al.*, reported that extensive decomposition was found in the pot in distilling the reaction product formed at 0~4° in an equimolar mixture of isopropyl acrylate and phenylmagnesium bromide in ether.[12] Under the conditions we adopted for preparation of samples and distillation, chemical change in distillation was not found in the distillate except the H–D exchange described previously and formation of isopropyl alcohol described below. In the distillation at bath temperatures above 250°, isopropyl alcohol was found in the distillate trapped at $-80°$ but was absent in the distillate trapped at room temperature. No other decomposition products were found in the spectrum of the distillate. The amount of isopropyl alcohol found in the distillate was about 3% of the amount of isopropyl groups found in the oligomer mixture before the distillation.

Phenylmagnesium bromide was prepared in ether without using any initiator. The Br/Mg ratio was found to be 1.00 ± 0.01 by Mohr's method for bromine and acid titration for basic magnesium. The phenyl/magnesium ratio was found to be 0.95 by measuring the amount of iodobenzene formed by adding an ether solution of iodine on a vapor phase chromatograph.[13] Magnesium dibromide was prepared from dibromoethylene and magnesium metal in ether. α,β-d_2 monomer with $\gamma = 6$ was prepared by adding heavy hydrogen to isopropyl propiolate using the Lindlar catalyst[14,15] as described previously.[8] α,cis-β-d_2 monomer was prepared by reducing isopropyl propiolate in heavy water by a method analogous to that of Botti and Furman.[16] The γ value of the monomer was adjusted to $^1/_6$ by adding a small amount of the monomer with $\gamma = 6$. β-d_1 monomer with $\gamma = {}^1/_6$ was obtained by hydrogenation of isopropyl propiolate-β-d_1 using the Lindlar catalyst.[14,15] The deuterated propiolate (99% D) was prepared from isopropyl propiolate by repetitions of H–D exchange with heavy water added with a trace of sodium metal (refluxed for 3 hr in each time), followed by neutralization with a deuterated aqueous solution of sulfuric acid.

Nmr spectra were measured by a Varian HR-100 spectrometer.

Acknowledgment. The authors gratefully acknowledge the suggestions of Professor Conrad Schuerch, State University College of Forestry at Syracuse, regarding English usage.

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Isotope Effects on the Basicity of 2-Nitrophenoxide, 2,4-Dinitrophenoxide, Hydroxide, and Imidazole in Protium Oxide–Deuterium Oxide Mixtures[1,2]

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Abstract: The ion product of D_2O was found to be $1.38 \times 10^{-15}\ M^2$ at 25° using precisely calibrated glass electrode measurements. The ion products of D_2O-H_2O mixtures have also been precisely measured. The value of the constant $K_n{}'$ for the equilibrium $DO^- + (^1/_2)H_2O \rightleftharpoons HO^- + (^1/_2)D_2O$ was calculated by nonlinear least squares to be 2.120 ± 0.190 at 25° from our data on the dissociation of 2-nitrophenol; data on other acids from the literature, used in similar calculations, gave similar values for $K_n{}'$. Precise data on imidazole in D_2O-H_2O mixtures has also been determined. Corrections for measurements of pL (L = H and/or D) in D_2O-H_2O mixtures (using a glass electrode and pH meter) are given.

Constant K for equilibrium 1 is determined by the autoprotolysis constants of pure isotopic light and

$$2H_2O + D_3O^+ + DO^- \overset{K}{\rightleftarrows} 2D_2O + H_3O^+ + HO^- \qquad (1)$$

heavy water: $K = K_{H_2O}/K_{D_2O}$; or by the constants of the exchange equilibria (2 and 3)

$$2D_3O^+ + 3H_2O \overset{L}{\rightleftarrows} 2H_3O^+ + 3D_2O \qquad (2)$$

$$2DO^- + H_2O \overset{(K_n')^2}{\rightleftarrows} 2HO^- + D_2O \qquad (3)$$

since $K = L^{0.5}K_n{}'$.

K_{D_2O} has been determined by several authors[3-8] and K calculated; the values range from 5.17[4] to 7.4.[8]

L can be deduced from the exchange constant of the reaction

$$2D_3O^+ + 3H_2O + 2Cl^-(D_2O) \overset{L'}{\rightleftarrows} 2H_3O^+ + 3D_2O + 2Cl^-(H_2O) \qquad (4)$$

taking into account the different activities of chloride ion in H_2O and in D_2O

$$L' = L\frac{(\gamma_{Cl^-})^2{}_{H_2O}}{(\gamma_{Cl^-})^2{}_{D_2O}}$$

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(1) Supported by the U. S. Atomic Energy Commission, Contract AT (30-1)-3041, and by the National Science Foundation, Grant GP-2937.

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