

The mass spectra of compounds I–III (see Table II) showed very interesting fragmentation patterns.⁵ In all cases the most important fragmented ion was the ion IV, m/e 264. Most of the other ions were formed by further fragmentation of ion IV, as was confirmed by the presence of corresponding metastable ions. The loss of morpholidine from the molecular ions was observed in the spectra of II and III but not in the spectrum of I, suggesting that a bromine atom was lost more readily than both chlorine and hydrogen atoms. This agreed with the observed order of increasing relative molecular ion intensity: Ia < IIa < IIIa. The higher intensity of ion B, m/e 178, than that of ion A, m/e 179, and the relative low intensity of ion C, m/e 86, in the spectrum of III was a result of loss of morpholine from molecular ion IIIa directly.

The ease of formation of ion IV from halo enamines I and II can be rationalized insofar as ion IV is resonance stabilized. This suggested to us that under proper conditions I and II may undergo S_N1-type reactions.⁶

Although enamine III is quite stable and only reacts with water when acid is present, both I and II react with water rapidly in polar solvents. Benzoin, benzil, and morpholine hydrohalides were the major products. Addition of silver nitrate to solutions of I or II in different polar solvents resulted in the formation of silver halides immediately. Silver ion accelerated the solvolysis with water, giving similar product compositions to that of uncatalyzed reactions. These findings agree with a S_N1-type solvolysis which is also suggested by a primary kinetic study by nmr techniques. Detailed kinetic data are being collected.

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(5) For mass spectra of some aliphatic enamines, see: H. J. Jakobson, S. O. Lawesson, J. T. B. Marshall, G. Schroll, and D. H. Williams, *J. Chem. Soc.*, 940 (1966).

(6) For reported S_N1-type solvolyses of olefinic halides, see: (a) C. A. Grob and G. Cseh, *Helv. Chim. Acta*, 47, 194 (1964); (b) C. A. Grob, J. Csapilla, and G. Cseh, *ibid.*, 47, 1590 (1964).

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On the Formation of Isotactic α -Methine Configurations at the Growing Ends of Polyacrylate Anions

Sir:

It was reported previously¹ that the growing ends of polyacrylate anions react stereospecifically with H₂O, HCl, or CH₃COOH added to the Grignard-initiated polymerization solution. The present communication is concerned with determination of the position of addition preferred by the proton from H₂O, etc., on the terminal α carbon of the acrylate oligomer.

(1) T. Yoshino, H. Iwanaga, and K. Kuno, *J. Am. Chem. Soc.*, 89, 6773 (1967).

One of the two addition positions on the terminal α carbon which is to be occupied by the next monomer in an isotactic form is hereafter denoted by α_i , and the other position by α_s (see Figure 1). The steric relations of α_i and α_s to β_o and β_t of the terminal unit are shown in Figure 2 for three rotational isomers in which the terminal ester group (X) and the α carbon of the preceding unit (C_a) are in *trans*, *gauche*, and *gauche'* relations. Here β_o and β_t indicate the positions of a β proton oriented *gauche* and *trans*, respectively, to the vicinal two ester groups for the hypothetical planar zigzag skeletal conformation with the ester groups of the last two units on the same side of the plane (see Figure 1).

The probability that the terminal ester group is oriented *trans* to the α carbon of the preceding unit may be larger than that for orientation on either of the two *gauche* conformations. When this is applied to Ph(CHDCDX)₂H, the β_o proton of the last unit has higher or lower probabilities than the β_t proton to be *trans* to the terminal α proton, depending on whether the α proton is at α_i or α_s (see Figure 2). Since the *trans* coupling constant is known to be three to four times larger than the *gauche* coupling constant,² the signal separation in the β_o proton doublet is expected to be larger or smaller than the separation in the β_t doublet depending on whether the terminal α proton is at α_i or α_s .

The nmr spectra of Ph(CHDCDX)_nD prepared from isopropyl acrylate- α,β -*d*₂ with $\gamma = 6$ and $\gamma = 1/6$ are shown in Figures 1A, 1B, and 5 of a preceding paper.³ Here γ indicates the ratio of β -D *trans* to X to D *cis* in the monomer employed. The following relations were found³ between the intensity ratio $\kappa'(n)$ of the lower to the higher field β -proton signal⁴ of the last unit of Ph(CHDCDX)_nD and the intensity ratio $\kappa(n)$ of the lower to the higher field *meso*-methylene signal (assigned to β_o and β_t , respectively³) of the *n*th unit of a higher homolog with isotactic α -methine configurations formed in the same polymerization solution: $\kappa'(2) = \kappa(2)$; $[\kappa'(2) \text{ for } \gamma = 1/6] = 1/[\kappa(2) \text{ for } \gamma = 6] \approx 0.8$; for $n \geq 3$, $\kappa(n) \approx \gamma$ and $[\kappa'(n) \text{ for } \gamma = 6] \gg 1 \gg [\kappa'(n) \text{ for } \gamma = 1/6]$.⁴ From the relations between $\kappa'(n)$ and $\kappa(n)$ for $n \geq 2$, the lower and higher field β -proton signals of the last unit of Ph(CHDCDX)₂D are assigned to the β_o and β_t protons, respectively.

The spectra of the backbone protons of Ph(CHDCDX)₂H prepared from isopropyl acrylate- α,β -*d*₂ with $\gamma = 6$ using H₂O to terminate the polymerization are shown in Figures 3a and 3b. The signal groups near τ 7.8 and 8.2 were previously³ assigned to the α and β protons of the second unit, respectively. Four peaks are found in the β signal group. The peaks with a separation of 8.7 cps are assigned to the β_o proton and the peaks with a separation of 7.2 cps to the β_t proton, because only these combinations are compatible with the separation between the two large peaks of the α proton and with the chemical shift of the β_o and β_t signals of

(2) For example, T. Yoshino, Y. Kikuchi, and J. Komiyama, *J. Phys. Chem.*, 70, 1059 (1966).

(3) T. Yoshino, J. Komiyama, and H. Iwanaga, *J. Am. Chem. Soc.*, 89, 6925 (1967).

(4) For $n \geq 3$, only one methylene signal was found for the last unit. The τ value of the signal in benzene solution decreases with increase of γ of the monomer employed, showing that the signal is composed of β_o and β_t signals with a small separation and $[\kappa'(n) \text{ for } \gamma = 6] \gg 1 \gg [\kappa'(n) \text{ for } \gamma = 1/6]$.

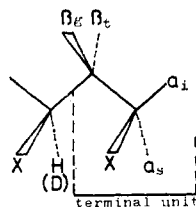


Figure 1. Graphic explanation of the positions denoted by α_i , α_s , β_g , and β_t of the terminal unit.

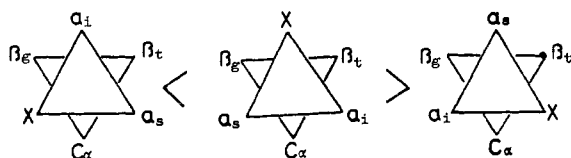


Figure 2. Steric relations of α_i and α_s to β_g and β_t of the terminal unit for three rotational isomers. The inequality signs are concerned with the populations of the isomers.

the second unit of $\text{Ph}(\text{CHDCDX})_2\text{D}$.³ The observation that the separation in the β_g doublet is larger than that in the β_t doublet shows that most of the hydrogen atoms from H_2O , etc., are at α_i . This result was confirmed by the following observation on $\text{Ph}(\text{CHDCHX})_2\text{D}$ in which the ratio of the α_i to the α_s protons is reversed.

The backbone proton spectra of $\text{Ph}(\text{CHDCHX})_2\text{D}$ prepared from isopropyl acrylate- β - d_1 with $\gamma = 1/6$ and $\gamma = \infty$ using D_2O to terminate polymerization and the β -proton spectra of the second units of the oligomers decoupled from the α protons of the first units are shown in Figures 3c-f. Three peaks are found in each of the decoupled spectra. The central peak is regarded as composed of the higher field component of the β_g doublet and the lower field component of the β_t doublet, and the lower and the higher field peaks are regarded as the other components of the β_g and β_t doublets, respectively. Only these assignments are compatible with the requirement that the lower field component is stronger than the other in either of the β -proton doublets, with the chemical shift of the β_g and β_t signals of the second unit of $\text{Ph}(\text{CHDCDX})_2\text{D}$, and with the previous observation³ that the intensity ratio of the β_g to the β_t signal was found to be smaller in the oligomer prepared from the α,β - d_2 monomer with $\gamma = 1/6$ than in the oligomer prepared from the α,β - d_2 monomer with $\gamma = 6$. The present observation that the separation in the β_g doublet is smaller than that in the β_t doublet shows that the deuterium atoms from D_2O are mostly at α_i .

The preference of α_i of the proton from H_2O , etc., shows that formation of a regular isotactic configuration at the growing end is scarcely contributed from the molecular structure and orientation of the monomer about to be polymerized.

According to the present result, either of the following two mechanisms (a and b) or a mechanism intermediate between them is considered to be reasonable for the propagation and termination of isotactic polymerization in the present polymerization system. (a) A stereospecific configuration⁵ is formed at the end of a growing anion prior to interaction with the next monomer, and

(5) For example, the counterion is at α_i .

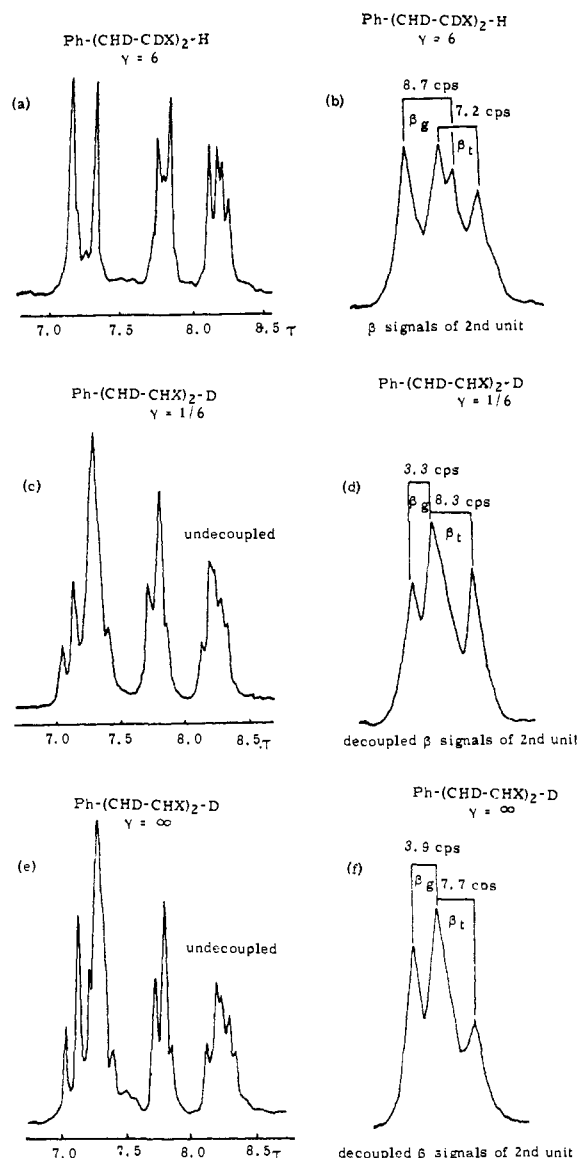


Figure 3. Backbone proton spectra of $\text{Ph}(\text{CHDCDX})_2\text{H}$ and $\text{Ph}(\text{CHDCHX})_2\text{D}$. The decoupling frequency is 77 cps.

the stereospecificity is preserved⁶ at the incorporation of the next monomer or H from H_2O , etc. (b) Without relationship to the configuration⁷ of the end of the growing anion or in spite of the absence of stereospecific configuration of the terminal unit,⁸ the next monomer or H from H_2O , etc., is introduced to give a stereospecific configuration to the terminal α carbon.⁹ Examples of a and b are given in the references.⁵⁻⁹ The formation of the stereospecific configurations mentioned in a and b is mainly a contribution from the monomer unit immediately preceding the terminal unit, because the regular isotactic placement of the terminal α carbon does not require the prior occurrence of an isotactic α -methine configuration and is independent of the mode of incorporation of the β methylene of the terminal unit.³

(6) For example, the next monomer or H replaces the counterion at α_i .

(7) For example, the counterion is at α_i and α_s with equal or unequal probabilities.

(8) For example, the counterion is not near the terminal α carbon.

(9) For example, the next monomer or H attacks the reaction end on the side opposite X' of the planar zigzag $-\text{CH}_2-\text{CHX}'-\text{CH}_2-\text{CH}-\text{X}$.

Isopropyl acrylate- α,β - d_2 with $\gamma = 6$ and isopropyl acrylate- β - d_1 with $\gamma = 1/6$ were prepared as described previously.³ Isopropyl acrylate-*trans*- β - d_1 was prepared by reduction of isopropyl propiolate- β - d_1 in H_2O according to the method of Botti and Furman.¹⁰ Preparation and purification of the oligomers were performed by the method described previously.^{1,3} The nmr spectra were measured on pure liquids by a Varian HR-100 spectrometer at room temperature.

(10) R. S. Botti and N. H. Furman, *Anal. Chem.*, **27**, 1182 (1955).

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Rapid Rearrangements in the *t*-Amyl Cation and the Relative Sign of the Coupling Constants

Sir:

Rearrangements of carbonium ions have long been postulated to explain numerous reactions in organic chemistry. Recently, it has been possible to observe these reactions directly through nmr spectroscopy of several stable carbonium ions.^{1,2} We report here a study of the temperature-dependent nmr spectrum of *t*-amyl cation which yields information about the rearrangement mechanism and also the relative signs of the two coupling constants visible in the spectrum.

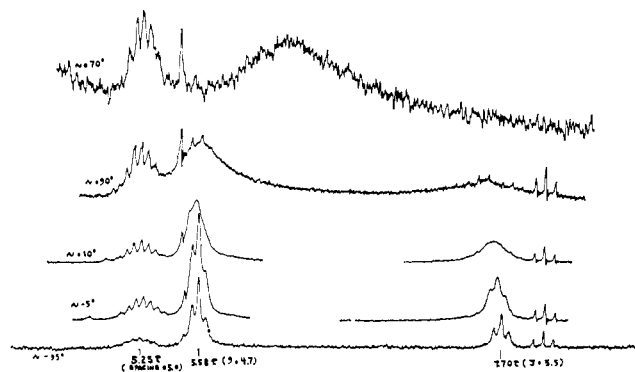


Figure 1.

We prepared *t*-amyl cation by allowing 2-chloro-2-methylbutane to react with excess antimony pentafluoride in sulfuric acid in a vacuum line at -90° with stirring. Below -40° its nmr spectrum, taken in a coaxial cell to provide a standard peak, was very similar to that previously reported,^{3,4} with impurity peaks at the position of *t*-butyl cation and at high field (Figure 1). Up to 140° the spectrum showed only continuation of the changes visible in Figure 1, the methylene multiplet remaining unchanged at higher temperatures. Upon recooling the sample, the original spectrum was reobtained. The spectral changes dem-

(1) M. Saunders, G. Olah, and P. Schleyer, *J. Am. Chem. Soc.*, **86**, 5680 (1964).

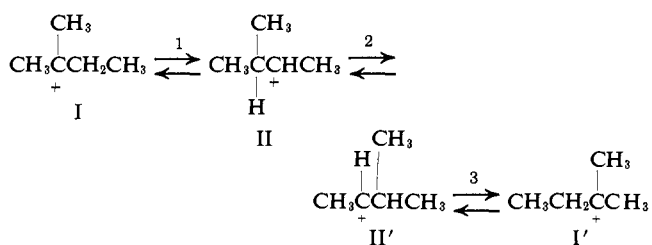
(2) M. Saunders in "Magnetic Resonance in Biological Systems," A. Ehrenberg, Ed., Pergamon Press, Ltd., Oxford, 1967, pp 85-99.

(3) G. A. Olah, E. B. Baker, J. C. Evans, W. S. Tolgyesi, J. S. McIntyre, and I. J. Bastein, *J. Am. Chem. Soc.*, **86**, 1360 (1964).

(4) G. A. Olah and J. Lukas, *ibid.*, **89**, 4739 (1967).

onstrate interchange of the two types of methyl without mixing in the CH_2 hydrogens.

We have accounted for the temperature dependence of the nmr spectrum as shown.



All other simple rearrangements of *t*-amyl cation give primary carbonium ions and are therefore considered less likely. Furthermore, mechanisms involving primary ions could easily completely mix all types of hydrogen. Step 2 is analogous to the 1-2 rearrangement in pentamethylethyl cation. Nmr line-shape and spin-echo methods have so far yielded only a lower limit for this rate, of $\sim 5000 \text{ sec}^{-1}$ at -180° .⁴ Nevertheless, we feel that step 2 is rate determining, since hydride shifts are generally more rapid than analogous methide shifts.

Both unimolecular and bimolecular processes have been proposed in the rearrangement of 2-chloro-2-methylbutane^{5,6} induced by aluminum chloride. However, dimer formation followed by rearrangement and cleavage can be ruled out in our case, since interchange of either methyl or methylene hydrogens between molecules would be expected. The unchanged fine structure in the methylene multiplet at high temperature is inconsistent with rapid intermolecular exchange of hydrogen.

A careful consideration of the origin of the various lines of this multiplet leads to the conclusion that, were the two separate coupling constants of this methylene to the adjacent methyl and to the downfield methyl opposite in sign, interchange of methyls would collapse this fine structure. Since this does not occur, we conclude that the signs of these coupling constants (through three and four bonds) are identical. This method of using a fast reaction to determine relative signs of coupling constants has not been previously reported.

Theoretical curves for the spectrum as a function of rate were calculated using the general many-site computer program previously described.^{1,2,7} The small temperature dependence observed here of the chemical shift below -30° was extrapolated to give the shifts which were used. The observed nmr spectrum of the upfield triplet at -20.0° was recorded digitally on magnetic tape. Convolution with this curve in the computer introduced both the natural line shape in the absence of exchange and the triplet structure, and made it possible to determine accurate rate constants using the low-temperature spectra. The use of the usual Lorentzian line shapes led to points off the Arrhenius line. At different temperatures either the peak intensity ratios, the widths of the coalesced multiplets, or the frequency of maximum intensity of the broad single line of the experimental spectra was compared with similar features

(5) G. J. Karabatsos and F. M. Vane, *ibid.*, **85**, 729 (1963).

(6) G. J. Karabatsos, F. M. Vane, and S. Meyerson, *ibid.*, **85**, 733 (1963).

(7) M. Saunders, *Tetrahedron Letters*, 1699 (1963).