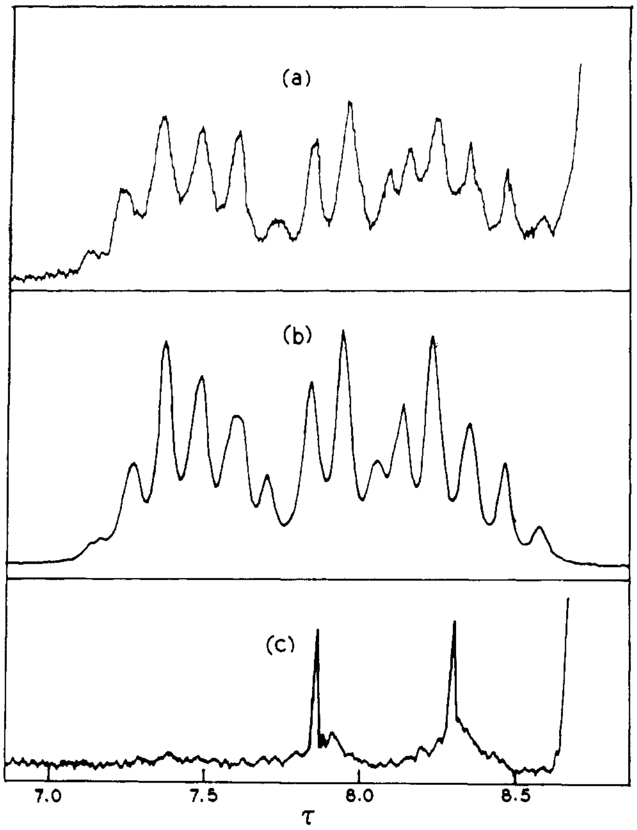


Fig. 1.—(a) Backbone proton spectrum of isotactic polyisopropyl acrylate; (b) calculated backbone proton spectrum of isotactic polyisopropyl acrylate; (c) backbone proton spectrum of polyisopropyl-α-*cis*-β-d_2 acrylate with deuterium irradiation.

spectrum of the nondeuterated polymer (Fig. 1a) was closely matched by a six-spin machine calculation (treating the polymer in effect as a cyclic dimer[6]) employing the following parameters: H_α τ 7.43; H_{β_1} τ 7.86; H_{β_2} τ 8.32; $J_{gem}(H_{\beta_1}-H_{\beta_2})$: -13.6 c.p.s.; $J_{vic}(H_\alpha-H_{\beta_1}, H_\alpha-H_{\beta_2})$ 6.50 c.p.s.; more distant couplings 0 c.p.s.; line width 2.5 c.p.s. The calculated spectrum is shown in Fig. 1b. (Methylene groups in syndiotactic sequences necessarily have equivalent protons and so give an entirely different spectrum[7]; it is believed that even a relatively small proportion of syndiotactic sequences, *i.e.*, more than *ca.* 5%, could have been detected.) In Fig. 1c, the spectrum of the β-deutero polymer is shown.[8] The peaks corresponding to *erythro* (τ 7.86) and *threo* (τ 8.32) methylene protons[9] appear to be nearly equal in intensity. (The resonance of residual α- and β-CH_2 protons makes exact measurement somewhat difficult.) Thus, in contrast to what is observed for polypropene, *the configuration of the polyacrylate chain is random with respect to the CHD groups and stereoregular with respect to the $CHCO_2R$ groups.*[10] This result seems to us to make it necessary to re-examine existing proposals for the mechanism of stereospecific anionic polymerization.[11] A possible interpretation is that "*cis*" and "*trans*" opening of the double bond are equally probable. Steric considerations, however, make it appear likely that the actual direction in space along which the active chain end and monomer approach each other is always *trans*; apparent "*cis*" addition must then result from a rotation of the newly formed chain end under the influence of the magnesium counter ion. These ideas, as well as the present experimental results, will be described in greater detail elsewhere. We are now extending these studies to other monomers and initiators.

In the accompanying communication by Yoshino, *et al.*,[12] it is shown that in the anionic polymerization of methyl acrylate with lithium aluminium hydride addition to the monomer double bond is stereospecific, in contrast to our findings; if our assignment of methylene peaks is correct, the addition must be *trans*, in contrast to the conclusions of Natta, *et al.*[3] The stereospecificity with regard to the ester groups, however, is not so high as with the Grignard initiator. Thus, different anionic initiators exert varying degrees of control at the CHR and CHD groups.

Acknowledgment.—The authors acknowledge with pleasure their indebtedness to Dr. L. C. Synder and Mr. R. L. Kornegay for use of their machine program for n.m.r. spectral calculations. Financial support for the work at Syracuse by the National Science Foundation is gratefully acknowledged.

---

(6) W. C. Tincher, private communication.

(7) F. A. Bovey and G. V. D. Tiers, *J. Polymer Sci.*, **44**, 173 (1960) *Fortschr. Hochpolymer. Forsch.*, **3**, 139 (1963).

(8) This spectrum shows the appearance of the peaks when decoupled from deuterium by irradiation at 9.1 Mc. sec., using double resonance equipment manufactured by Nuclear Magnetic Resonance Specialties, Inc.; narrowing of the peaks upon decoupling is appreciable but much less than expected because the multiplet arising from H–D couplings is already partially collapsed. Evidently, deuterium nuclei on a polymer chain experience particularly effective quadrupole relaxation because of the relatively slow tumbling of the molecular framework.

(9) This assignment, although very probable, is not entirely certain; it is based on measurements reported for related small molecules. See L. M. Jackman, "Applications of Nuclear Magnetic Resonance in Organic Chemistry," Pergamon Press, London, 1959, pp. 121–125.

(10) The alternate possibility that the polymer may actually be *syndiotactic* with respect to the CHD groups should perhaps not be entirely dismissed, but is not considered here because it would be very difficult to construct a rational reaction mechanism to account for it.

(11) See C. Schuerch, *Ann. Rev. Phys. Chem.*, **13**, 195 (1962); C. E. H. Bawn and A. Ledwith, *Quart. Rev.* (London), **16**, 361 (1962).

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

COLLEGE OF FORESTRY
SYRACUSE UNIVERSITY
SYRACUSE, NEW YORK
BELL TELEPHONE LABORATORIES, INC.
MURRAY HILL, NEW JERSEY

C. SCHUERCH
W. FOWELLS
A. YAMADA
F. A. BOVEY
F. P. HOOD
E. W. ANDERSON

RECEIVED JULY 9, 1964

On the Propagation Steps of Free-Radical and Anionic Polymerization

Sir:

Many theories[1,2] have been proposed in regard to the propagation steps of free-radical and anionic polymerization. Although some of these theories conflict with others, they have not been proved or disproved because of lack of sufficient experimental bases. One of the most important and fundamental things required for considering the reaction mechanisms is whether or not monomer double bonds open in a definite mode of *cis* or *trans* in free-radical or anionic polymerization. For the purpose of confirming this point, methyl acry-

---

(1) Most of these theories are summarized by C. E. H. Bawn and A. Ledwith, *Quart. Rev.* (London), **16**, 361 (1962).

(2) C. E. H. Bawn, W. H. Janes, and A. M. North, *J. Polymer Sci.*, **C4**, 427 (1963).

late-α,β-d_2 with *cis/trans* molar ratio[3] γ different from unity was polymerized in toluene by using azobisisobutyronitrile and lithium aluminum hydride as initiators at 50 and −78°, respectively, and the n.m.r. spectra of the polymers obtained were measured by using a Varian HR-100 spectrometer.

The β-protons of a *meso*-methylene group in an isotactic sequence of polymethyl acrylate are chemically nonequivalent, while the β-protons of a racemic methylene group in a syndiotactic sequence are equivalent. Since protons on "backbone" carbon atoms of polymethyl acrylate-α,β-d_2 are separated from each other by four bonds, proton spin coupling is practically absent. Two methylene proton signals are, therefore, expected for isotactic sequences and one for syndiotactic sequences of a polymer prepared from a mixture of *cis*- and *trans*-methyl acrylate-α,β-d_2.

The n.m.r. spectra of the methyl acrylate-α,β-d_2 polymers prepared here are shown in Fig. 1. Since the signal at τ 7.39 of nondeuterated polymethyl acrylate shares one-third of the total intensity of the α- and β-proton signals of the polymer, the small signal of polymethyl acrylate-α,β-d_2 appearing at the same τ-value is ascribed to the α-protons due to methyl acrylate isomers with α-hydrogen atom contained in the monomer used. We found for nondeuterated polymethyl acrylate prepared by a radical process that the intensity of the triplet centered at τ 8.16 decreases with rise of temperature in polymerization from 50 up to 200°, while the signals near τ 7.8 and the signals near τ 8.4 increase their intensities. The signal at τ 8.16 in Fig. 1 of the deuterated polymers is, therefore, assigned to the racemic methylene protons, and the signals at τ 7.88 and 8.37 to the *meso*-methylene protons. The intensity ratio of these *meso*-methylene signals is nearly equal to unity for the free-radical polymer. This result shows that both *cis* and *trans* openings of monomer double bonds take place in free-radical polymerization.

If we are allowed to consider that the CHD group of a monomer molecule forms a bond with the CDX ($X = COOCH_3$) group at the growing end of a polymer chain, the above result shows that the placement of the terminal CDX group is not decided to be isotactic or syndiotactic with respect to the CDX group of the penultimate unit until after the next monomer unit has been added. This isotactic or syndiotactic placement is independent of whether the hydrogen atom of the terminal unit is oriented *trans* or *gauche* to the carboxyl group of the preceding unit for the hypothetical planar zigzag skeletal conformation. The ratio $\alpha/(1 - \alpha)$ between the probabilities of these two configurations of a CHD group with respect to the CDX group of the preceding unit is, therefore, the same for both *meso*- and racemic methylene groups. The intensity ratio κ of the lower to the higher field signal of *meso*-methylene protons is, therefore, expressed by $[\alpha\gamma + (1 - \alpha)]/[(1 - \alpha)\gamma + \alpha]$, and α is evaluated to be 0.5 for $\kappa = 1$.

The descriptions given above indicate that the ratio of the isotactic to the syndiotactic placements of CDX groups is determined mainly by the potential energy due to interaction between the penultimate unit and the terminal unit which is in interaction with a monomer molecule, while the ratio $\alpha/(1 - \alpha)$ is determined mainly by the potential energy due to interaction between the terminal unit and an approaching monomer molecule.

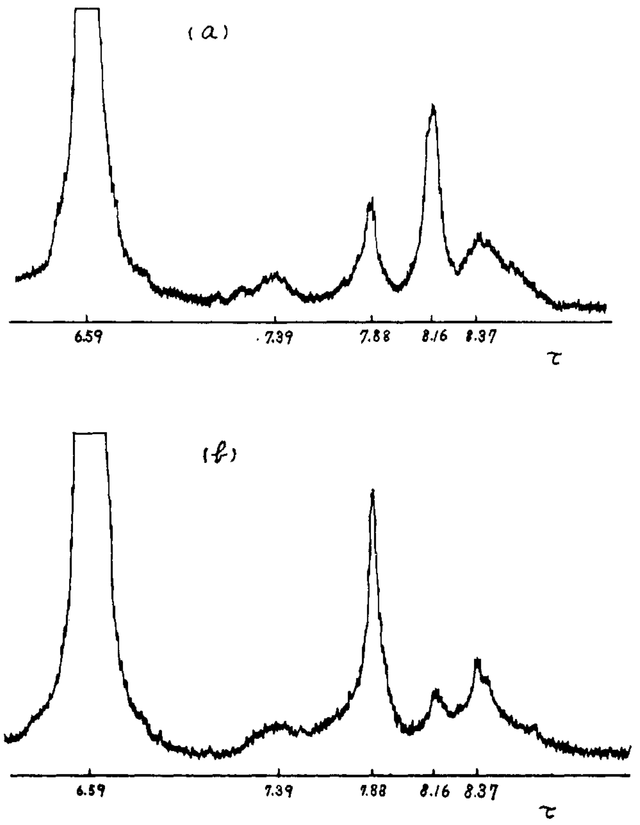


Fig. 1.—N.m.r. spectra of methyl acrylate-α,β-d_2 polymers prepared with (a) azobisisobutyronitrile in toluene at 50° and (b) lithium aluminum hydride in toluene at −78°. The spectra are measured on 10% solutions of the polymers in benzene.

The methyl acrylate-α,β-d_2 polymer prepared here by anionic polymerization has high isotacticity as seen in Fig. 1, in spite of the lack of the α-alkyl group which has been supposed[4] to play an important role in stereospecific polymerization. The intensity ratio of the *meso*-methylene signals of this polymer is 3:1 as seen from Fig. 1, and is equal to the *cis/trans* molar ratio in the monomer employed for the anionic polymerization. These results show that monomer double bonds open in a definite mode of either *cis* or *trans* and that monomer molecules are attacked on the same side by a growing polymer anion. Then we see that a monomer molecule which adds to the growing end of a polymer chain must be in a definite orientation (or orientations leading to the same isotactic configuration) with respect to the terminal unit before the monomer molecule forms a bond with the polymer end.

Methyl acrylate-α,β-d_2 was prepared by addition of heavy hydrogen to methyl propiolate at 20° using the Lindlar catalyst.[5] The methyl propiolate was obtained by oxidation of propargyl alcohol[6] and succeeding esterification. The n.m.r. signals of the methyl acrylate-α,β-d_2 shown in Fig. 2 were assigned by using the chemical shifts and the proton coupling constants of the ethylenic protons of nondeuterated methyl acrylate.[7] The *cis/trans* molar ratio was obtained from

---

(3) The isomer with deuterium atoms in the *cis* configuration is here called *cis*.

(4) See, for example, ref. 1, p. 384.

(5) H. Lindlar, *Helv. Chim. Acta*, **35**, 446 (1952).

(6) V. Wolf, *Chem. Ber.*, **86**, 735 (1953).

(7) W. Bruegel, Th. Ankel, and F. Krueckeberg, *Z. Elektrochem.*, **64**, 1121 (1960); S. Castellano and J. S. Waugh, *J. Chem. Phys.*, **34**, 295 (1961).

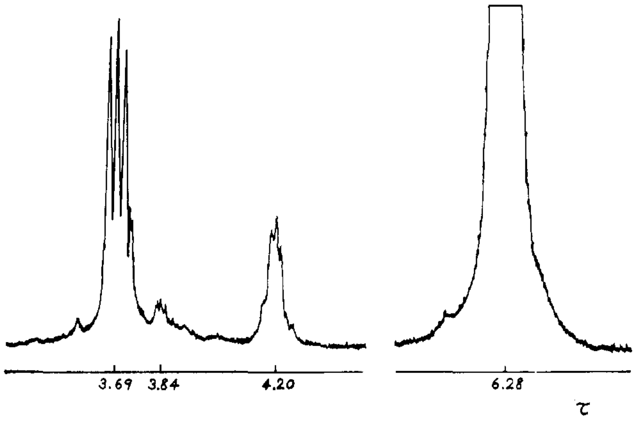


Fig. 2.—N.m.r. spectrum of methyl acrylate-α,β-d_2 monomer used in the present experiment. Signals are assigned as follows: τ 6.28 signal to the ester methyl group; τ 3.69 and 4.20 triplets to the β-protons of the *cis*- and *trans*-α,β-d_2 isomers, respectively; signals near τ 3.84 to the α-protons of the -d_1 and the -d_2 isomers; small signals at τ 3.56 and 3.73 to the β-protons of the *trans*-β-*d* isomer.

the intensity ratio of the β-proton signals at τ 3.69 and 4.20 to be 3:1. After every run of polymerization the unreacted monomer was recovered by distillation from the polymerization medium. The *cis*/*trans* molar ratio in the recovered monomer was found to be just the same as the ratio in the initial monomer. The ratio of α-protons to β-protons was found to be approximately the same for the initial and the recovered monomer and the polymer, showing that deuterium exchange scarcely took place in the course of polymerization.

BASIC RESEARCH LABORATORIES
TOYO RAYON COMPANY
KAMAKURA, KANAGAWA, JAPAN

TSUNEO YOSHINO
JIRO KOMIYAMA
MASAYASU SHINOMIYA

RECEIVED AUGUST 3, 1964

Ion Pairs in Acetolysis of *p*-Chlorobenzhydryl Acetate[1]

Sir:

Acetolysis of *p*-chlorobenzhydryl chloride (RCl) involves carbonium chloride ion pairs which lose configuration and return to racemic starting material much more rapidly than they dissociate, solvolyze, or exchange their chloride counterion with added radiolabeled common ion salt.[2a,b] The rate of ionization is substantially higher than that of solvolysis or exchange. Analogously, substantial gaps are observed between ionization and exchange or solvolysis rates for RCl[2c] and the corresponding *p*-nitrobenzoate[2d] (ROPNB) in 80% acetone.

It is instructive to consider the case of a substrate molecule whose negative counterion in the R^+X^- ion pair is the lyate ion of the solvent being employed. Such a situation is especially favorable for the leaving anion to merge into the solvent structure and be replaced by a new solvent molecule or anion.

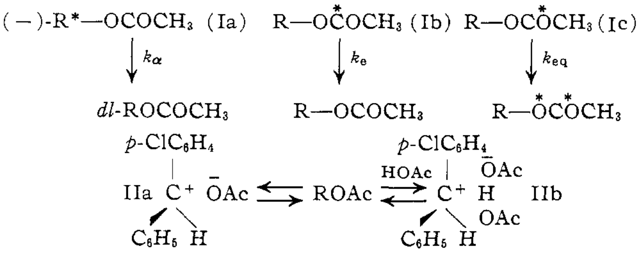
It is interesting to measure the extent to which the R^+ carbonium ion species under such circumstances can still discriminate between the original X^- partner and the rest of the solvent. In this connection, we have examined the behavior of optically active ROAc (Ia), ^{14}C-carboxylate-labeled ROAc (Ib), and ^{18}O-carbonyl-labeled ROAc (Ic) in ordinary glacial acetic acid with and without added LiOAc. For comparison, the behavior of Ia–c was examined under $HClO_4$ catalyzed conditions where the conjugate acid of ROAc undergoes heterolysis and a R^+O^-Ac ion pair is not involved. Summarized in Table I are the first-order polarimetric (k_α), exchange (k_e), and ^{18}O-equilibration (k_{eq}) rate constants at 75.0°.

TABLE I

RACEMIZATION, EXCHANGE, AND ^{18}O-EQUILIBRATION OF *p*-CHLOROBENZHYDRYL ACETATE IN ACETIC ACID AT 75.0°

[LiOAc], $10^2 M$	$10^6 k$, (sec.$^{-1}$) k_α	k_e	k_{eq}
0	1.30 ± 0.08[a]	1.00 ± 0.02[b]	0.284 ± 0.027
0[c]	(1.04)	(0.99)	(0.39)
1.00	1.04 ± 0.05	0.99 ± 0.02	
1.20		0.995 ± 0.05	0.400 ± 0.008
3.60		1.05 ± 0.035	0.378 ± 0.006
5.00	1.12 ± 0.06		
9.80		1.11 ± 0.03	0.404 ± 0.011
12.5	1.18 ± 0.05		
$HClO_4$[d]	31.5	32.6	

[a] First 30% reaction; some upward drift. [b] 1.25 from rate of ^{18}O-loss starting with Ic. [c] k^0 values extrapolated to zero salt concentration from data with added LiOAc. [d] 1.79×10^{-4} *M* $HClO_4$ at 50.0°; first 30% reaction; slight downward drift.



With added 1.79×10^{-4} *M* $HClO_4$ at 50°, k_α and k_e for Ia and Ib, respectively, are equal[3] within experimental error. Furthermore, starting with Ic, no ^{18}O-scrambling could be detected in the residual unexchanged ROAc under these conditions. Evidently, the original acetic acid molecule produced in the heterolysis of the ROAc conjugate acid is lost from the solvation shell of the carbonium ion before the latter collapses to covalent material.

With 0.01 *M* and higher concentrations of LiOAc in the acetic acid solvent, k_α and k_e are again equal within experimental error and also quite insensitive to salt concentration. However, under these conditions ^{18}O-equilibration in the ester is a definite competing phenomenon. Without added LiOAc, there appears to be some indication that k_α is slightly larger than k_e and therefore also slightly larger than the k_α^0 value extrapolated to zero salt concentration from the data with added LiOAc. Correspondingly, k_{eq} appears slightly low. The discrepancies are small, however, and may well be due to generation of acid catalyst from the Ia and Ic samples which were not distilled and as highly purified as Ib. Consistently, k_e estimated from ^{18}O-loss starting with Ic also tended to be slightly high.

It is quite evident that the carbonium ion from ionization of ROAc in acetic acid solvent shows only a

---

[1] Research sponsored by the National Science Foundation.

[2] (a) S. Winstein, J. S. Gall, M. Hojo, and S. Smith, *J. Am. Chem. Soc.*, **82**, 1010 (1960); (b) A. F. Diaz, A. Ledwith, and M. Hojo, unpublished work; (c) S. Winstein, M. Hojo, and S. Smith, *Tetrahedron Letters*, **No. 22**, 12 (1960); (d) H. L. Goering and J. F. Levy, *J. Am. Chem. Soc.*, **86**, 120 (1964).

[3] A similar equality of k_α and k_e has been reported by Pocker for acetolysis of *p*-methylbenzhydryl acetate: Y. Pocker, *Proc. Chem. Soc.*, 226 (1959); Y. Pocker in "Progress in Reaction Kinetics," Pergamon Press, Vol. 1, 1961, pp. 227–228; Y. Pocker, private communication.