TABLE II
RELATIVE TETRAD INTENSITIES FOR POLY(ETHYL α-CHLOROACRYLATES), AND OBSERVED AND CALCULATED TRIAD INTENSITIES

Polymer no.	Tetrads[a]						Traids: Calcd from tetrads[b]			Traids: Obsd[c]		
	mmm	*mmr*	*rmr*	*rrr*	*rrm*	*mrm*	*mm*	*mr*	*rr*	*mm*	*mr*	*rr*
6	0.19	0.18	0.18	0.08	0.24	0.13	0.28	0.52	0.20	0.36	0.39	0.25
3	0.16	0.14	0.18	0.17	0.22	0.13	0.23	0.49	0.28	0.33	0.32	0.35
10	0.15	0.14	0.12	0.33	0.18	0.08	0.22	0.36	0.42	0.19	0.38	0.43
11	0.13	0.14	0.04	0.50	0.14	0.04	0.20	0.23	0.57	0.15	0.35	0.50
5	0.12	0.11	0.04	0.59	0.11	0.03	0.17	0.18	0.65	0.07	0.22	0.71

[a] Relative error in tetrad intensities estimated to less than ±10%. [b] Triad values calculated according to ref 3: $(mm) = (mmm) + {}^1/_2(mmr), (rr) = (rrr) + {}^1/_2(rrm)$. [c] Determined from ethoxymethyl resonance at 100 MHz.[2]

TABLE III
SPECIFIC PERSISTENCE RATIOS FOR POLY(ETHYL α-CHLOROACRYLATES)[a]

Polymer no.	ρ	η_r	η_{rr}	η_{mr}	η_m	η_{mm}
6	0.95	0.95	0.87	1.00	0.96	1.21
3	1.02	1.02	1.17	0.86	1.00	1.45
10	1.33	1.17	1.31	0.83	1.38	1.70
11	1.89	1.23	1.29	0.89	1.40	2.03
5	2.14	1.19	1.23	0.83	1.59	2.61

[a] Reference 6.

this paper. The 220-MHz nmr spectra were recorded with a Varian HR 220 spectrometer at 100° in chlorobenzene solution, at concentrations of 10–15% (w/v). Chemical shifts are reported as τ values with tetramethylsilane as an internal standard.

Resolution of the nmr spectra into individual component peaks was performed with a Fortran IV curve-resolution program, developed at the Department of Polymer Technology, The Royal Institute of Technology, Stockholm, Sweden, and run on an IBM 360/75 computer equipped with an IBM 2250 graphic display unit. The experimental curve was digitized by reading its intensity at 2-Hz intervals, and shown together with the computed spectrum envelope on the screen of the display unit. Each component tetrad spectrum was characterized with an estimated mean chemical shift, the separation between centers of doublets in AB spectra, coupling constant, the line width at half-height, and a relative intensity parameter. The parameters were optimized by visual fitting of the computed curve to the experimental one in an on-line dialogue with the computer. The best fit was reached with a line shape obtained by a linear combination of Lorentzian and Gaussian functions, in the proportions 70:30 for the atactic and 90:10 for the syndiotactic polymers. Experimental and computed spectra were plotted with an on-line CalComp plotter.

Acknowledgments. Financial support for Bengt Wesslén was given by the Swedish Board of Technical Development, which is gratefully acknowledged. Thanks are due to Mr. James Larson for help with the preparation of the Fortran programs.

Nuclear Magnetic Resonance in Poly(vinyl acetate)

M. J. R. Hoch, F. A. Bovey, D. D. Davis, D. C. Douglass, D. R. Falcone, D. W. McCall,* and W. P. Slichter

Bell Telephone Laboratories, Incorporated, Murray Hill, New Jersey 07974.
Received July 19, 1971

ABSTRACT: Poly(vinyl acetate) (PVAc) has been studied by proton magnetic relaxation methods. The polymer exhibits a typical glass transition in that the nmr relaxation times behave in much the same way as observed for other substances. Pressure dependence results yield an activation volume of about 160 cm³/mol in the glass-transition region. Ester methyl reorientations, evident in dielectric studies, have almost no effect on the nmr parameters. Methyl group rotations dominate relaxation at low temperatures, and quantum mechanical tunneling is probably involved. The methyl rotational barriers are very small.

Nuclear magnetic resonance (nmr) relaxation times T_2, T_1, and $T_{1\rho}$ have been measured for poly(vinyl acetate) (PVAc) over a wide range of temperature and a moderate range of pressure. In this paper we report the results and offer some interpretations in terms of molecular motions. Three kinds of molecular activity are known to occur in PVAc. The glass transition is well established and our results are in satisfactory agreement with other measurements, *i.e.*, dielectric and dynamic mechanical studies. Ester group reorientation has virtually no effect on the nmr parameters. We were somewhat surprised by this lack of sensitivity, but the result does not conflict with our ideas of side-group motions. Methyl group reorientation is particularly interesting owing to its persistence to very low temperatures. It is suggested that quantum mechanical tunneling is involved, but we do not have a detailed model capable of explaining all of the data.

Experimental Section

Measurement techniques have been described previously.[1,2]

(1) D. W. McCall, D. C. Douglass, and D. R. Falcone, *J. Phys. Chem.*, 71, 998 (1967).
(2) G. P. Jones, D. C. Douglass, and D. W. McCall, *Rev. Sci. Instrum.*, 36, 1460 (1965).

The low-temperature measurements were carried out with a Janis Super Vari-Temp liquid helium dewar. The polymer studied was kindly provided by D. H. Mullins of the Union Carbide Corp. The material is a homopolymer, and high-resolution nmr results indicate that it is a random, atactic structure. The clear pellets were dried and measured directly. In connection with low-temperature relaxation studies, the polymer was converted to poly(vinyl alcohol) (PVA) and then reacetylated with CD_3COCl to give $(CH_2CHOCOCD_3)_n$ (PVAc-d_3). When reacetylation was carried out with CH_3COCl, the resulting polymer gave nmr relaxation times identical with those of the starting material. This shows that the reacetylation does not alter the structure of the polymer appreciably. Note that only the proton signal has been studied in this work. This means that only the nuclei attached to the main chain were observed in PVAc-d_3. However, nuclear magnetic relaxation of these protons could be caused by rotations of the $-CD_3$ group in the low-temperature range, *via* nuclear dipolar coupling with the protons.

Results and Discussion

The nmr data have been analyzed according to previously published procedures.[1] Briefly, T_2 is taken from free induction decays, $T_2 \sim t_{1/2}/\ln 2$, where $t_{1/2}$ is the time required for the induction to decay to half its initially observed value. One must keep in mind that there is an instrumental recovery period of about 6 μsec before the nuclear signal is detected. Further, the decay tails are not exponential. $\nu_c \sim 1/\pi(T_2)_{LT}$ in the neighborhood of a T_2 transition. (ν_c is the correlation frequency characteristic of the molecular motion and $(T_2)_{LT}$ is the "plateau" value of T_2 on the low-temperature side of the transition.) A 180–90° pulse sequence is used to measure T_1. $\nu_c \sim \sqrt{2}\nu_0$ at the temperature of a T_1 minimum. ν_0 is the resonance frequency. $\nu_c \sim \gamma H_1/\pi$ at the temperature of a $T_{1\rho}$ minimum. When $\nu_c \ll 1/T_2$ and no interfering relaxations occur, $\nu_c \sim {}^1/_2\pi T_{1\rho}$.

(A) The Glass Transition. Glass-transition phenomena have been studied in a wide variety of systems including most important polymers. It is an empirical observation that nmr relaxation behavior in the glass-transition region is much the same for all substances, independent of their molecular nature.[3] Ionic compounds, low molecular weight organics, hydrogen-bonded materials, and high polymers present similar nmr relaxation time curves. The PVAc results shown in Figure 1 look very much like nmr data found in other glass-forming substances. The absolute values of T_1 and $T_{1\rho}$ at their respective minima are consistent with theoretical expectations.

$$(T_{1\rho})_{min} \cong 4\gamma H_1(T_2)_{LT}^2 = 10^{-4} \text{ sec}$$

compared with 4×10^{-4} sec observed and

$$(T_1)_{min} \cong \left(\gamma H_0/\sqrt{2}\right)(T_2)_{LT}^2 = 1.3 \times 10^{-2} \text{ sec}$$

compared with 5×10^{-2} sec observed. These comparisons, within a factor of 4 in each case, are about as close as can be expected. $(T_2)_{LT}$ is the value of T_2 in the glassy region.

The dependence of T_1 on temperature under hydrostatic pressures of 1 and 680 atm is shown in Figure 2. The curve is shifted by about 27°/1000 atm, which is close to $\Delta T/\Delta p$ frequently found[4] for glass transitions. In terms of activation volume

$$\Delta V^{\ddagger} \equiv -RT(\partial \ln \nu_c/\partial p)_T = \Delta H^{\ddagger}\Delta T/T\Delta p \sim 160 \text{ cm}^3/\text{mol}$$

The corresponding activation energy is about 50 kcal/mol. These large values are consistent with the extensive molecular freedom present above the glass-transition temperature. The

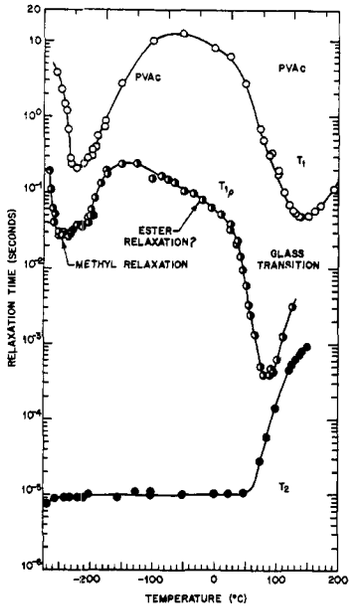

Figure 1. Proton nmr relaxation times T_1, $T_{1\rho}$, and T_2 for PVAc.

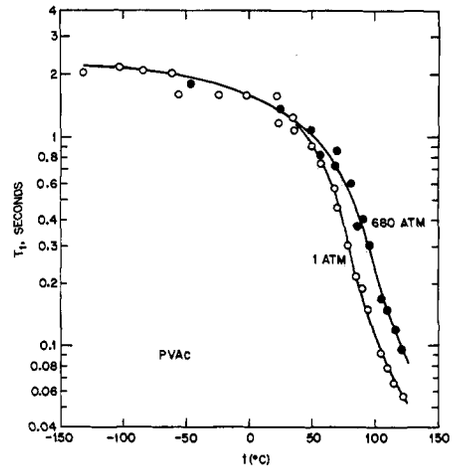

Figure 2. The effect of hydrostatic pressure on the temperature dependence of T_1 in PVAc.

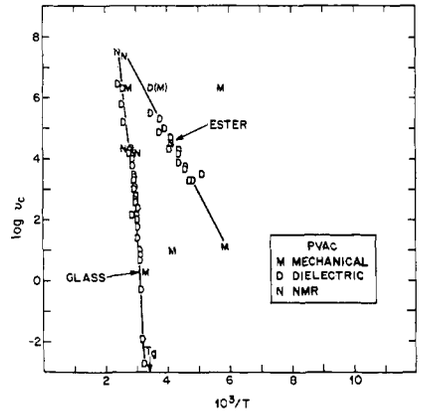

Figure 3. An Arrhenius plot for PVAc. Dielectric results are indicated by D, dynamic mechanical results by M, and nmr results by N. The two relaxation loci indicate the glass transition and ester reorientation.

(3) D. W. McCall, *Accounts Chem. Res.*, 4, 233 (1971).

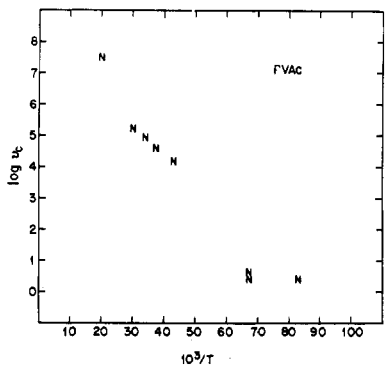

Figure 4. Arrhenius plot for PVAc in the low-temperature region. Note that these correlation frequencies, ν_c, have been deduced from nmr data assuming a random jump model. If tunneling is important, these results are subject to alteration.

average molecular entity whose barrier-limited motion is rate determining is large, a reasonable result.

Figure 3 is an Arrhenius plot showing dielectric, dynamic mechanical, and nmr results.[4-12] The dielectric and nmr results are in close agreement, while the dynamic mechanical results lie to the right of the dielectric locus. Although the mechanical points appear fairly close to the dielectric locus, there is a substantial frequency discrepancy owing to the steep slope. This probably results from the well-known ambiguity in analyzing mechanical data. Tan δ was used for the points plotted.

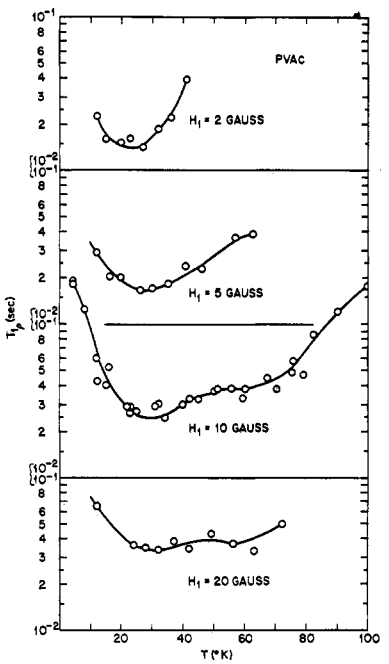

Figure 5. The effect of rotating frame field strength on the temperature dependence of $T_{1\rho}$.

(4) J. M. O'Reilly, *J. Polym. Sci.*, **57**, 429 (1962).
(5) See *Nat. Bur. Stand. (U. S.), Spec. Publ.*, **No. 301**, 475 (1968).
(6) T. Kawai, M. Sasaki, A. Hirai, T. Hashi, and A. Odajima, *J. Phys. Soc. Jap.*, **15**, 1700 (1970).
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(9) D. J. Mead and R. M. Fuoss, *J. Amer. Chem. Soc.*, **63**, 2832 (1941).
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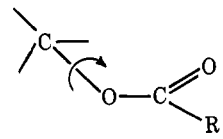
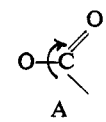
(11) K. Schmeider and K. Wolf, *ibid.*, **134**, 149 (1953).
(12) O. Broens and F. H. Muller, *ibid.*, **140**, 121 (1955).

(B) Side-Chain Rotations. The Arrhenius plot (Figure 3) indicates a relaxation locus, defined mainly by dielectric data, that has been associated with rotation of the ester side group



(Rotation about the bond shown in A is probably restricted by



A

a much higher barrier and preference for the trans conformation shown.[13]) The nmr data provide little evidence for this motion. T_2 might be expected to change near $-20°$ and a $T_{1\rho}$ minimum would be expected in the same region. In fact, however, the behavior of the relaxation time is similar to that of natural rubber near its T_g (see Figure 9 of ref 3 and references therein). This is understandable in view of the fact that the methyl groups are already in rapid rotation (see below); rotation about the ester bond can contribute little further to the methyl intragroup interactions or to the methyl–backbone interactions.

The nmr data of Figure 1 show that methyl group reorientations are active down to very low temperatures. An Arrhenius plot based only on the nmr results in the 20–50-K range is shown in Figure 4. The slope corresponds to a very small activation energy, not exceeding 1.0 kcal/mol. The rotational barrier in gaseous acetaldehyde has been reported as 1.15 kcal/mol.[14] The temperature dependence of T_ρ at various rf field strengths, H_1, is shown in Figure 5. The low temperatures and small depths (an order of magnitude shallower than expected for classical random jumps) of the T_1 and $T_{1\rho}$ minima, the absence of any observable change in T_2 in this temperature range, and the low activation energy are all consistent with quantum mechanical tunneling.[15] Motions of this type have been established in some low molecular weight organic compounds.[16]

Tunneling frequencies for $-CD_3$ groups are known to be substantially lower than for CH_3 groups. Therefore, the backbone proton relaxation was examined for PVAc-d_3. The data, shown in Figure 6, show the expected reduction in

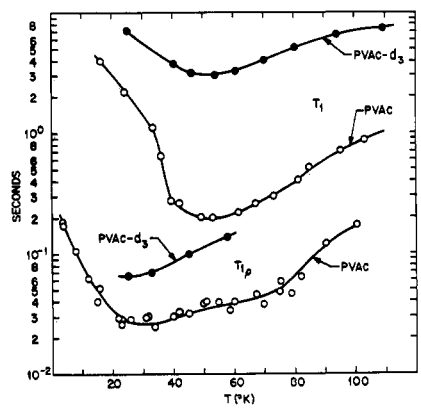


Figure 6. Comparison of the temperature dependences of T_1 and $T_{1\rho}$ for PVAc and PVAc-d_3 (*i.e.*, PVAc with deuterated methyl groups).

(13) T. Miyazawa and K. S. Pitzer, *J. Chem. Phys.*, **30**, 1076 (1959).
(14) R. W. Kilb, C. C. Lin, and E. B. Wilson, Jr., *ibid.*, **26**, 1695 (1957).
(15) For a general discussion of tunneling phenomena, we suggest V. Narayanamurti and R. O. Pohl, *Rev. Mod. Phys.*, **42**, 201 (1970).
(16) G. P. Jones, R. G. Eades, K. W. Terry, and J. P. Llewellyn, *Proc. Phys. Soc., London*, **1**, 415 (1968).

relaxation strength, *i.e.*, the T_1 and $T_{1\rho}$ minima are shallower. Owing to incomplete deacetylation of the original PVAc, about 10% CH_3 groups remain. We ascribe the remanent relaxation, Figure 6, to these CH_3 groups. This result is consistent with the tunneling mechanism but less conclusive than we had hoped.

(C) Other Relaxations. In some specimens of PVAc, a T_1 minimum is observed in the neighborhood of $-60°$, and $T_{1\rho}$ is affected near $-130°$. High-resolution nmr spectra reveal the presence of an impurity in these specimens. It is likely that the impurity is copolymerized and contains a methoxy group. A dynamic mechanical loss maximum reported[10] near $-100°$ at 2×10^6 Hz may also be due to this impurity.

Acknowledgments. We are indebted to Mr. G. H. Williams for aid in obtaining the polymer specimens. Mr. J. J. Ryan assisted in connection with deuteration of the PVAc.

Conformational Structure and Vibrational Spectra of Poly(methyl methacrylate) and of Its Models

B. Schneider,* J. Štokr, S. Dirlikov,† and M. Mihailov†

Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, Prague, Czechoslovakia. *Received January 26, 1971*

ABSTRACT: By analysis of vibrational spectra of the dimethyl ester of 2,2,4,4-tetramethylglutaric acid, the stable conformers of this most simple model of poly(methyl methacrylate) have been determined. Vibrational spectra and conformational structure of crystalline and amorphous poly(methyl methacrylate) and of the stereo complex are discussed on the basis of known conformational structures of model compounds.

The conformational structure of crystalline poly(methyl methacrylate) (PMMA) was investigated theoretically[1,2] and by X-ray diffraction.[2-4] By the latter method, helical structure with 5_1 and 5_2 helices was observed in crystalline isotactic PMMA. For syndiotactic PMMA, a complete X-ray analysis has not been performed so far. Only in the stereo complex (iso:syndio = 1:2) a structure of the syndiotactic sequences has been proposed by Liquori,[5] based on X-ray analysis. This structure was criticized by Gotlib[1] on the basis of a theoretical analysis of conformer energies.

In all these studies, the conformation of amorphous PMMA has not been considered, and even the conformation of syndiotactic dyads in the crystalline polymer has not been determined unequivocally. In this paper, we have attempted to determine the conformational structure of PMMA from infrared spectra of the polymer, based on a study of its simplest model—the dimethyl ester of 2,2,4,4-tetramethylglutaric acid (DMTG). In addition to DMTG, we also analyzed some of its deuterio derivatives [the dimethyl ester of 2,2,4,4-tetramethylglutaric-*3*-d_1 acid (DMTG–CHD) and the dimethyl-d_1 ester of 2,2,4,4-tetramethylglutaric acid (DMTG–$COOCH_2D$)] and the methyl ester of 2,2,4,4-tetramethylvaleric acid. From the knowledge of the stable conformers of DMTG and their infrared spectra, we have attempted to elucidate the conformational structure of dyads in PMMA.

Experimental Section

Synthesis of Models. Methyl 2,2,4,4-tetramethylvalerate was prepared by esterification of 2,2,4,4-tetramethylvaleric acid by diazomethane. The acid was prepared by carbonization of 1,3,3-trimethylpentylmagnesium chloride[6] with solid CO_2. The trimethylpentyl chloride was obtained by addition of HCl to diisobutylene.[7]

Dimethyl 2,2,4,4-tetramethylglutarate[8] was prepared from diethyl 3-hydroxy-2,2,4,4-tetramethylglutarate, obtained by the Reformatski reaction of ethyl 2-bromoisobutyrate with ethyl formate. After hydrolysis, the free acid was reduced with HI to tetramethylglutaric acid which was esterified by diazomethane.

Di(methyl-d_1) 2,2,4,4-tetramethylglutarate[8] was prepared by addition of diazomethane to tetramethylglutaric-d_2 acid; this was obtained from tetramethylglutaric acid by isotopic exchange with excess D_2O.

Dimethyl 2,2,4,4-tetramethylglutarate-*3*-d_1[8] was obtained by an analogous method as dimethyl 2,2,4,4-tetramethylglutarate; the ethyl formate-*1*-*d* was obtained from formic acid d_2 (Merck AG) and ethanol-d_1 (Isocommerz).

The chemical purity of all these compounds was controlled by physical constants, elementary analysis, and infrared spectra, and was better than 99.9%. The isotopic purity of the deuterated compounds was determined by nmr spectra: DMTG–$COOCH_2D$, 65%; DMTG–CHD, 100%.

Polymers. The tacticity of the PMMA samples was determined by nmr spectra:[9] syndiotactic PMMA (85% S, 15% H, 0% I), isotactic PMMA (0% S, 2% H, 98% I). The stereo complex (iso:syndio = 1:2) was prepared from a solution of PMMA in acetonitrile.[5]

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† Institute of Organic Chemistry, Bulgarian Academy of Sciences, Sofia, Bulgaria.

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