$$Z = \mathbf{u}\prod_{i=1}^{N}\mathbf{W}_{A(j)}\mathbf{v} \qquad \text{(B-18)}$$

Average quantities can be calculated from eq B-18 according to eq 26.

The analogous Lifson–Roig model for the helix–coil transition in specific-sequence copolymers has been given above. Numerical results calculated by the Zimm–Bragg and Lifson–Roig copolymer models (not shown here) are essentially identical.[26] It is interesting to note that, for copolymer systems, a larger correlation matrix[27] is required for the Lifson–Roig model, the reverse situation being the case for homopolymers (3 × 3 *vs.* 4 × 4 for Lifson–Roig and Zimm–Bragg, respectively).

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(26) The values of σ and s used in sections III and IV were converted to v and w according to the conversion expressions given by eq B-6 and B-7.

(27) The increased matrix size is due to the existence in the Lifson–Roig model of additional triplets such as 151, 155, . . . , which do not occur explicitly in the Zimm–Bragg model.

Poly(ethyl α-chloroacrylates). Nuclear Magnetic Resonance Spectra and Tetrad Analysis

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ABSTRACT: Poly(ethyl α-chloroacrylates) of different tacticities have been investigated by nmr spectroscopy at 220 MHz. Tetrad assignments and relative intensities of the tetrads are reported. The results obtained indicate a stereoblock structure of the polymers.

In a previous paper the preparation of ethyl α-chloroacrylate polymers through anionic polymerization reactions was reported.[1] The steric structures of the polymers prepared were investigated with nuclear magnetic resonance spectroscopy. The use of spectra obtained at 60 MHz, as well as at 100 MHz, for the backbone methylene groups led to somewhat inaccurate estimates of the steric configurations of the polymers, owing to poor resolution and overlapping peaks in the spectra. Tacticity differences between polymers prepared under different conditions could be observed qualitatively. However, since it was found that the chemical shifts for the protons of the ethyl ester groups were sensitive to the stereochemistry of the adjacent pseudoasymmetric carbon atoms, quantitative triad analyses were performed by using the resonance signals from the methyl protons of the ethoxy groups. The relative triad intensities thus determined also contained errors because of overlapping peaks.

In the present paper nmr spectra at 220 MHz of the poly(ethyl α-chloroacrylates) are reported. With the increased shift differences realized with the 220-MHz instrument, as compared to 60- and 100-MHz instruments, more highly resolved spectra of the backbone methylene groups of the polymers could be obtained. Tetrad assignments in the spectra have been attempted, and quantitative estimates of the relative tetrad intensities on the basis of these assignments have been carried out.

Results and Discussion

Figure 1 shows nmr spectra at 220 MHz in the backbone methylene region of five samples of poly(ethyl α-chloroacrylate) of different tacticities, ranging from moderately isotactic to predominantly syndiotactic ones, according to the triad analysis reported previously.[1] At 220 MHz, the shift differences for the ethoxy groups of different triads are of approximately the same magnitude as the coupling constant within the ethoxy group. Accordingly, due to overlapping, the proton resonance signals from these groups cannot be used to estimate triad intensities, as was possible at 100 MHz. As shown by the figure, the backbone methylene region of the spectra is comparatively well resolved, although broadly overlapping peaks as well as some background signals complicate the interpretation of these spectra. The background signals can arise from the occurrence of structures having other than the regular head-to-tail arrangement of the ethyl α-chloroacrylate repeating units, because it was shown in the previous paper that a substantial amount of chlorine was lost in the polymerization reactions.[1] Furthermore, end effects might not be negligible since the molecular weights of the polymers in some cases were quite low.[1]

The spectra show a regular progression of the intensities of the different peaks with increasing syndiotacticity in the polymers. The most characteristic feature is the increase in intensity of the singlet at τ 7.09, which is assigned to the completely racemic tetrad, designated *rrr*. A doublet centered at τ 7.24 which decreases in intensity with increasing syndiotacticity is regarded as the upfield doublet of an AB spectrum and assigned to the isotactic *mmm* tetrad. The complete tetrad assignments are shown in Figures 2 and 3. The spectra were interpreted in terms of four AB spectra with geminal coupling constants of 15 Hz, arising from the heterosteric protons of *mmm*, *mmr*, *rmr*, and *mrr* tetrads, and two singlets from the homosteric protons of *rrr* and *mrm* tetrads.[2]

The chemical shifts and coupling constants, as well as the relative intensities of the tetrads, were determined by a curve-resolving technique which utilized computer simulation

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(1) B. Wesslén and R. W. Lenz, *Macromolecules*, **4**, 20 (1971).

(2) The notation describing the polymer configurations is that proposed by H. L. Frisch, C. L. Mallows, and F. A. Bovey, *J. Chem. Phys.*, **45**, 1565 (1966). This paper also describes the quantitative relationships between *n*-ads which must be upheld, regardless of stereosequence statistics.

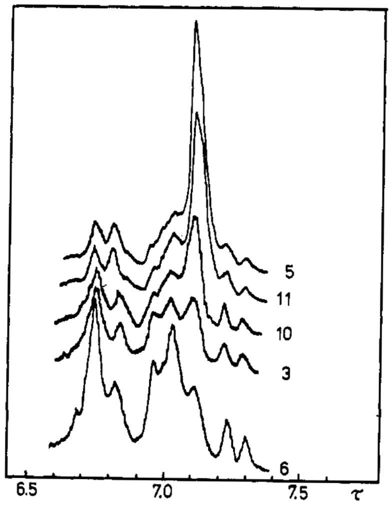

Figure 1. Nmr spectra at 220 MHz of poly(ethyl α-chloroacrylates). Backbone methylene region of the spectra shown.

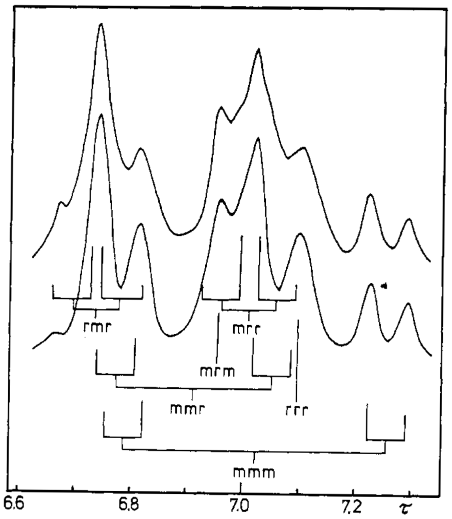

Figure 2. Tetrad assignments, experimental (upper line) and calculated (lower line) 220-MHz nmr spectra of polymer no. 6.

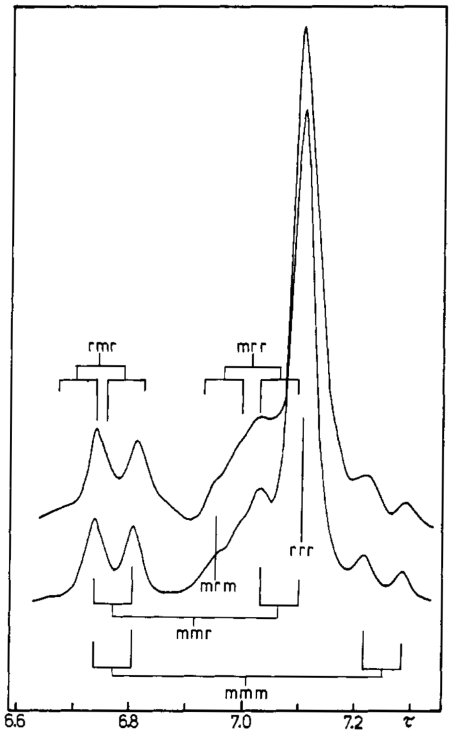

Figure 3. Tetrad assignments, experimental (upper line) and calculated (lower line) 220-MHz nmr spectra of polymer no. 5.

of the spectra. Experimental and simulated spectra were displayed simultaneously with a display unit controlled by the computer, and spectrum fitting was executed visually by changing the appropriate parameters in a dialogue with the computer. The set of shift parameters thus obtained (Table I) gave a good fit between experimental and simulated curves at different tacticities (Figures 2 and 3) and was constant within ±0.01 ppm between different polymers. Furthermore, the relative tetrad intensities determined were in fair agreement with the triad intensities reported previously (Table II), and the necessary quantitative relationships between the different tetrads were fulfilled,[2] *i.e.*

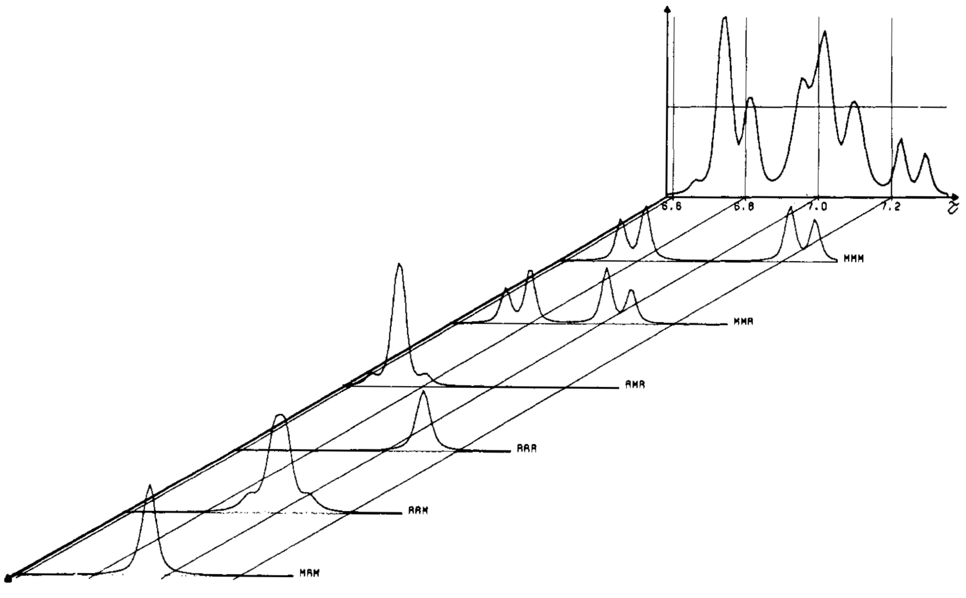

Figure 4. Tetrad spectra comprising the calculated spectrum in Figure 2.

$$(mmr) + 2(rmr) = (rrm) + 2(mrm)$$

Other tetrad assignments were considered, but these had to be rejected because the conditions mentioned above could not be upheld.

The spectral lines were found to be rather wide in all the spectra, approximately 7 Hz at half-height for *m*-centered tetrads and 10 Hz for *r*-centered tetrads; owing to an irregular line shape, a good fit for the broad singlet at τ 7.09, assigned *rrr* tetrad, was difficult to attain. Furthermore, for the same reasons, the calculated spectra deviated from the experimental ones in the region τ 6.8–6.9. The total difference between calculated and experimental curves, measured as the goodness of fit, was 15–18%.[3] The broadening of the peaks, as well as other irregularities in the spectra, is presumably due to influences from longer configurational sequences, *i.e.*, hexads,[4] and from irregular structures and end groups.

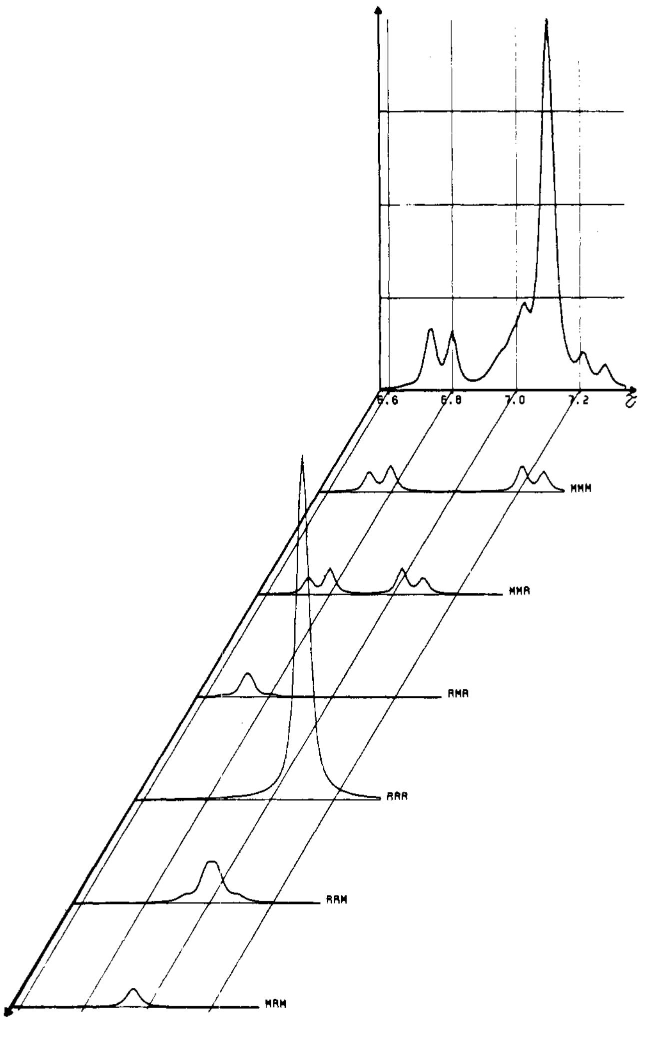

Figure 5. Tetrad spectra comprising the calculated spectrum in Figure 3.

TABLE I

CHEMICAL SHIFTS AND COUPLING CONSTANTS FOR BACKBONE METHYLENE PROTONS OF POLY(ETHYL α-CHLOROACRYLATES)

Tetrad	Chemical shift,[a] τ, ppm	Coupling constant, Hz	Peak width at half-height, Hz
mmm	6.78	15	7.0
	7.24		
mmr	6.78	15	7.0
	7.05		
rmr	6.71	15	7.0
	6.76		
rrr	7.10		10.0
mrr	6.97	15	10.0
	7.05		
mrm	6.95		10.0

[a] ±0.01 ppm.

The spectra show some similarities with the 220-MHz nmr spectra of poly(vinyl chloride) reported by Heatley and Bovey,[5] and also to some extent with spectra of poly(methyl methacrylates).[4] However, the present tetrad assignments differ from those reported for these polymers. The chemical shifts for the geminally heterosteric protons in *m*-centered tetrads of the poly(ethyl α-chloroacrylates) were found to be very sensitive to changes in the second nearest pseudoasymmetric center (Figures 2 and 3, Table I), as also found for poly(vinyl chloride).[5] The *rmr* tetrad shows the least heterosteric character, and the shift difference between the geminal protons increases on substituting *m* for *r* in this tetrad. The mean chemical shift for the protons in the *m*-centered tetrads decreases regularly in the same order (*rmr* > *rmm* > *mmm*), *i.e.*, the protons become increasingly shielded, and this is in contrast to what has been reported for poly(vinyl chloride)[5] and poly(methyl methacrylate).[4] For the *r*-centered tetrads the shift progression is the same as for the other polymers, the mean chemical shift increasing in the order *rrr* < *rrm* < *mrm*. The anomalous shift progression in the *m* tetrads may be due to an anisotropy effect caused by the difference in conformation of the pendant ethoxycarbonyl groups between syndiotactic and isotactic placements in the ethyl α-chloroacrylate polymers, previously demonstrated by ir analysis of these polymers.[1]

The observed stereosequence distribution (Table II) deviates from simple Bernoullian statistics in all cases, even for the sample (11) prepared by free-radical polymerization. This is shown by the fact that the specific persistence ratios ρ, η_r, η_{rr}, and η_{mm}, are greater than one (Table III).[6] It should be noted that similar conclusions can be drawn from values for relative triad intensities reported by Matsuzaki and coworkers[7] for methyl α-chloroacrylate polymers prepared with anionic as well as free-radical initiation. The conditions for a first-order Markov distribution of the stereosequences are not fulfilled, since $\eta_{mr} \neq \eta_{rr}$.[6] The high values of the specific persistence ratios indicate, however, a stereoblock structure for the polymers.

Experimental Section

For the preparation of the polymers used in this investigation, see ref 2. The numbering of the polymers is the same as used in

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(3) The goodness of fit, R, was calculated from

$$R = \left\{\sum_{i=1}^{n}(f_{\mathrm{oi}} - f_{\mathrm{ci}})^2 \Big/ \sum_{i=1}^{n} f_{\mathrm{oi}}^2\right\}^{1/2}$$

where f_{oi} and f_{ci} are the observed and calculated sum curve intensities, respectively: J. R. Dombroski, A. Sarko, and C. Schuerch, *Macromolecules*, **4**, 93 (1971).

(4) R. C. Ferguson, *ibid.*, **2**, 237 (1969).

(5) F. Heatley and F. A. Bovey, *ibid.*, **2**, 241 (1969).

(6) A specific persistence ratio is the ratio between the actual length of a tactic sequence and the length calculated assuming Bernoullian statistics for the sequence distribution, *i.e.*, $\rho \equiv 2(m)(r)/(mr)$; $\eta_{mr} \equiv (mrr)/(r)(mr)$, etc. See J. C. Woodbrey in "The Stereochemistry of Macromolecules," Vol. 3, A. D. Ketley, Ed., Marcel Dekker, New York, N. Y., 1968, p 61 ff, and references therein.

(7) K. Matsuzaki, T. Uryu, and K. Ito, *Makromol. Chem.*, **126**, 292 (1969).

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]			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.

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Nuclear Magnetic Resonance in Poly(vinyl acetate)

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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]

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(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).