The Microstructure of Poly(ethyl cyanoacrylate)

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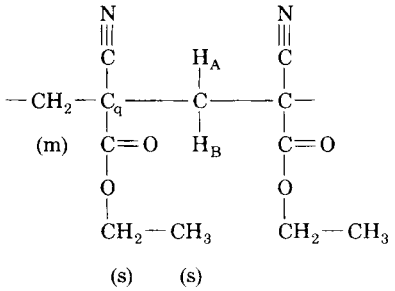
Alkyl cyanoacrylates are polymerized both by bases[1-5] and by free radicals,[5-7] the former reaction, conveniently rapid for many uses, being stimulated by alkyl lithium, amines, pyridine, phosphines, alcohols, and water, but being prevented by acids such as acetic acid, methylsulphonic acid, and SO_2. Until now there has been no report of a study of the microstructure of the linear polymer chain, which may be tactic for each residue contains a chiral carbon:



Scheme 1. Two ethylcyanoacrylate residues in meso diad.

We have used the proton and carbon-13 NMR methods[8] for studying the microstructure of these polymers. The most similar type of polymer recently to be studied by these methods is the poly(alkyl alpha-chloroacrylate)s.[9]

Polymerizations of ethylcyanoacrylate were performed by adding one gramme of monomer, stabilized with less than 100 ppm of methylsulphonic acid, to a solution of an organic nitrogen base (0.02 g) in a suitable solvent (10 mls). After a reaction period of five min, the polymer was precipitated by pouring the solution into methanol that had been acidified with hydrochloric acid, was collected on a scintered glass disk and dried in a vacuum oven. We summarize the reaction conditions in Table I. The data for the proton and C-13 NMR spectra that we show were recorded on a Bruker WH 400 spectrometer, and converted into spectra with the software in the normal manner. Details of the spectrometer settings and data manipulation are recorded in the captions to the figures.

In this letter we show parts of the spectra from polymers A5 and A2 that were prepared with the bases cinchonidine and sparteine in the solvents tetrahydrofuran and acetone respectively. We first assigned the chemical shifts of the protons and of the carbons in spectra that we obtained at 90 and 250 MHz, by using the pattern of shifts within a particular spectrum and by a comparison with the spectra of shifts that

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TABLE I
Reaction conditions for preparation of the polymer samples

Sample	Base	Solvent	Yield g	M_w†	P_i*
A5	Cinchonidine	tetrahydrofuran	0.92	229,000	0.54
A2	Sparteine	acetone	0.90	153,000	0.68

†M_w from styrene-calibrated GPC column, with THF as solvent.
*Calculated with the Bernoullian probability relationships of reference 8.

we have obtained of other alkyl cyanoacrylate polymer. We have entered the shifts in Table II. The chains consisted, as far as could be determined, of head to tail sequences of the one residue. The signals from the main chain methylene and quaternary carbons apparently overlap near 44 ppm, the former having a larger dispersion of shifts. The fine structure of this region and of most of the other carbons will be discussed in another place; here we confine ourselves to the fine structure of the side chain methylene carbon (Fig. 1) and the fine structure of the proton spectrum of the main chain methylene protons (Fig. 2), which have been recorded at high field. It can be seen that these parts of the spectra are sensitive to the method of preparation: in each figure, parts (a) and (b) clearly differ in the relative intensities within a pattern of the individual components. For the two preparations, either, and most simply the difference of solvent, or the difference of chiral base is responsible for the difference in the polymer microstructure that the spectroscopy has detected.

The 100 MHz spectra of the side chain methylene carbons from both poly(ethylcyanoacrylate)s, as seen in Figure 1 parts (a) and (b), have three well-resolved peaks. Some of these show shoulders or other features that became peaks upon resolution enhancement (parts c and d) by modifying the FID prior to the Fourier transform, in the manner that is indicated in the caption to the figure. As is appropriate and most simple for a carbon that is attached to one main chain chiral atom and is located midway between two others (7), we regard the three peak pattern as deriving from stereochemical triads, the approximate 1:2:1 ratio of polymer A5 indicating approximate atacticity and the very different pattern of polymer A2 indicating a bias towards tacticity of some kind, for the down-field peak is much reduced in intensity, and the upfield peak is of slightly greater magnitude than the central heteroatactic peak. The classical NMR approach to tacticity assignment is based upon the proton spectrum of the main chain methylene groups, to which we now turn (Fig. 2).

If the methylene group proton signal showed diad sensitivity,[8] we would expect a single peak from the racemic or syndiotactic dyad and an AB or AX quartet from the meso or isotactic dyads (with a coupling constant of about −14 Hz,[11] a spacing which is indicated by a bar on the figure). Since there are more than 5 peaks or shoulders, the

TABLE II
Chemical shifts of protons and carbons δ*

	$-\overset{\vert}{C}=O$	$-C\equiv N$	CH_2 (m)	C_q	CH_2 (s)	CH_3 (s)
^1H			2.6–2.8†		4.26	1.32
^{13}C	166.2	115.7	44	44	64.4†	13.7

*Shifts were measured in ppm relative to TMS at 120°C for protons in dimethyl sulfoxide-d_6 and 26°C for carbons in acetone-d_6. The atoms are labeled in Scheme 1.
†The fine structure of these nuclei is shown in the figures and is discussed in this paper.

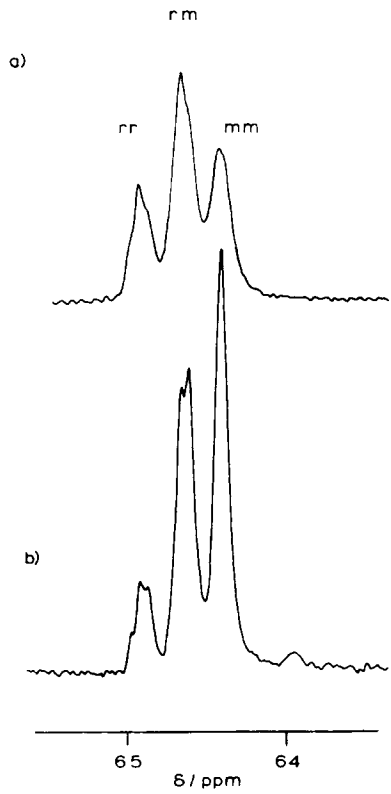

Fig. 1. Carbon-13 NMR spectrum of the side chain methylene groups of poly(ethyl cyanoacrylate) at 100 MHz. Sample A5 was used for parts (a) and (c), and sample A2 was used for parts (b) and (d). The samples (about 200 mg) were dissolved in acetone-d6 at 299°K: PW 12 μs, AQ 0.66 ms, NS 2048. For parts (a) and (b) the FID was multiplied by an exponential function with an LB of −3.0 Hz, and a Gaussian Broadening factor of GB = 0.2 was used: for parts (c) and (d), LB was −5.0 Hz and GB was 0.35, to enhance the resolution further.[10]

system displays at least partial tetrad sensitivity. This we now attempt to analyze for the purpose of identifying the type of tacticity that predominates.

We have labeled the peaks at 2.75 and 2.70 ppm a and b respectively, and have distinguished them because they are apparently single line features: their width at half height is 9 or 10 Hz, they are separated by 20 Hz from each other and by at least 18 Hz from the nearest other feature. They are not readily interpreted in terms of parts of one or more AB systems (except in the sense that $\Delta\nu_{AB}$ is vanishingly small), and so probably derive from r-centred diads. The smaller peak, a, may be from the rrr sequence, and the larger peak, b, may be from rrm, mrr sequences, whose probability will be larger than the rrr sequence, if, as seems appropriate, the chains are mainly isotactic. The features to the left and right of the pattern are clearly composed of a number of multiplet lines, as is appropriate for a meso dyad assignment. It is the small values of the relative areas of the a and b peaks within the patterns which indicate that both polymers may be predominantly isotactic. The labels rr, rm/mr, and mm have thus been attached to the ^{13}C spectrum of Figure 1(a) and (b), the smaller, low field, signal being judged to be from the rr triad and the larger upfield signal from the mm triad. From the relative areas of these, by assuming Bernoullian statistics,[8] values

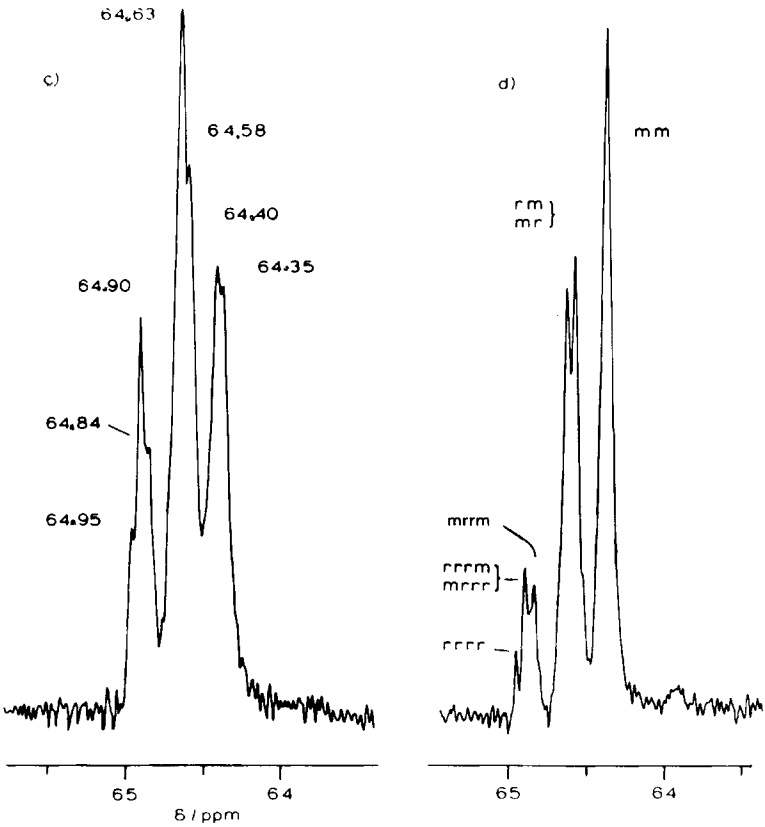

Fig. 1. (*Continued from the previous page.*)

of a single probability parameter, for isotactic placement, P_i, have been obtained. Thus

$$P_{rr} = (1 - P_i)^2, \quad \text{and so on}^8$$

We now re-examine the spectra to see how well the fine structure is consistent with this interpretation. It may be seen, from the entries in Table III that the triad probabilities, obtained for the triad features of the side chain methylene group's C-13 spectra of Figure 1, are predicted well by this model for both polymers: there is no strong indication of the need of a Markov model, with a second parameter, being required. The tetrad assignments that we have made of the main chain methylene protons are in good agreement, and the three rr-centred pentads of the side chain methylene are quite well reproduced.

These two polymers show a slight and a moderate bias towards isotacticity. While it is possible that a chiral anion, derived from the chiral base and associated by coulombic effects with the propagating anion,[2-4] might promote the formation of an isotactic, rather than a syndiotactic polymer, it may be that the simplest explanation of the bias towards isotacticity is appropriate: that it is controlled by the process of adding the monomer to the unassociated but solvated anionic propagating end of the polymer. From the present experiments it is not possible to deduce which mechanistic factor is responsible for the bias towards isotacticity, but other work is planned.

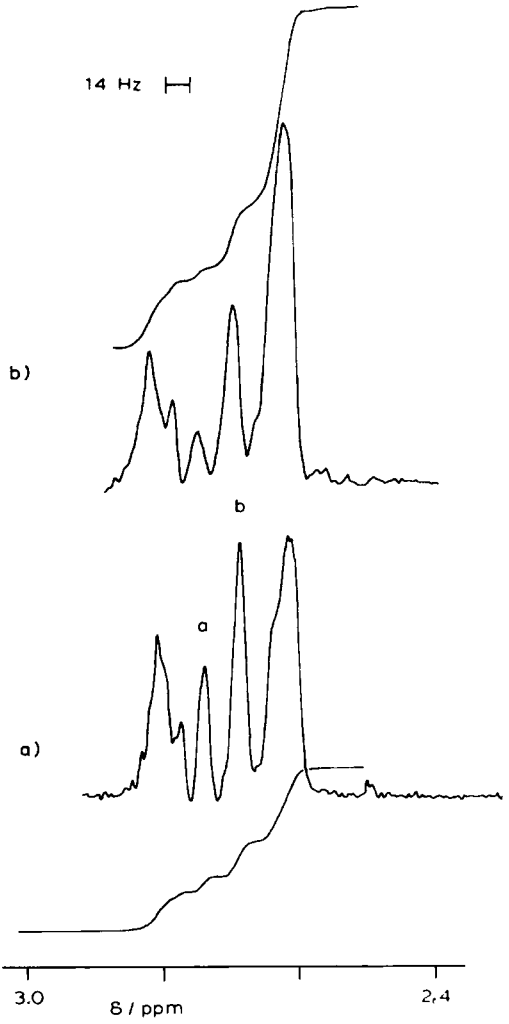

Fig. 2. Proton NMR spectra of the main chain methylene groups of poly(ethyl cyanoacrylate) at 400 MHz. The samples were dissolved in dimethyl sulfoxide-d_6 at 393°K. To increase the resolution, a LB factor of −7.0 Hz and a Gaussian factor of 0.06 were used in weighting function prior to the Fourier transform.[10] (a) Sample A5, (b) sample A2.

TABLE III
Observed and predicted* intensities of the assigned fine structure features of polymers A2 and A5

Intensity	Nucleus group	A2, $P_i = 0.67_5$		A5, $P_i = 0.54_3$	
		Found	Calculated	Found	Calculated
P_{rr}	^{13}C	0.12	0.11	0.22	0.21
P_{rm}	CH_2 (s)	0.43	0.44	0.49	0.50
P_{mm}		0.45	0.46	0.30	0.29
P_{rrr}	^1H	0.04	0.03	0.09	0.10
$P_{rrm} = P_{mrr}$	CH_2 (m)	0.17	0.14	0.22	0.23
P_{rrrr}	^{13}C	0.02	0.01	0.03	0.04
P_{mrrr}	CH_2 (s)	0.05	0.05	0.12	0.10
P_{mrrm}		0.05	0.05	0.07	0.06

*Calculated with the Bernoullian probability relationships of reference 8.

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