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with the osmometry and viscosity data.

An important consequence of the present report is that specific site binding of inorganic anions to polyanions may occur and has to be taken into account in discussions of anion-dependent properties of acidic polysaccharides.

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Studies on Comblike Polymers. 6. Tacticity of Poly(octadecylethylene) by ^{13}C NMR and Differential Scanning Calorimetry

Comblike polymers have been intensively studied in recent years owing to their interesting structure and properties.[1] These polymers are known to crystallize through side-chain packing and, for most of them, the crystallization takes place independent of stereoregularity. Recent studies,[2,3] carried out in our laboratory have indicated that the stereoregularity of long-side-chain polyolefins and polyethers can be correlated with their thermal properties. Indeed, the crude products of the stereospecific polymerizations have been shown to be composed of two immiscible crystalline phases which can be separated by appropriate solvent fractionation.[4] In agreement with a previous suggestion made by Aubrey and Barnatt[5] for poly(hexadecylethylene), we supposed that the higher melting polymer was isotactic and that the lower melting one was atactic. We thought, therefore, that a simple calorimetric method could be used for a rough determination of the degree of tacticity of these polymers. To prove this, a direct measure of the stereoregularity of the polymers investigated was necessary. However, no such measure has been described so far for any of the comblike polymers studied, including the intensively investigated[5–9] long-side-chain polyolefins. We thought that useful information could be obtained by ^{13}C NMR. In this Communication we report the preliminary results of this study. A comparison of the ^{13}C NMR data with DSC data is also made.

Poly(octadecylethylene) was prepared by stereospecific polymerization with α-TiCl$_3$–Al(i-C$_4$H$_9$)$_3$ (1/3.3 mole ratio) as already described.[2] The crude product of the polymerization (sample C, Table II) was extracted in a Kumagawa apparatus with boiling ether, giving a soluble fraction (sample E) and a residue (sample B). Sample A was obtained as described previously[4] by double crystallization from heptane solution. Sample D was a blend of samples A and E (32/68 w/w).

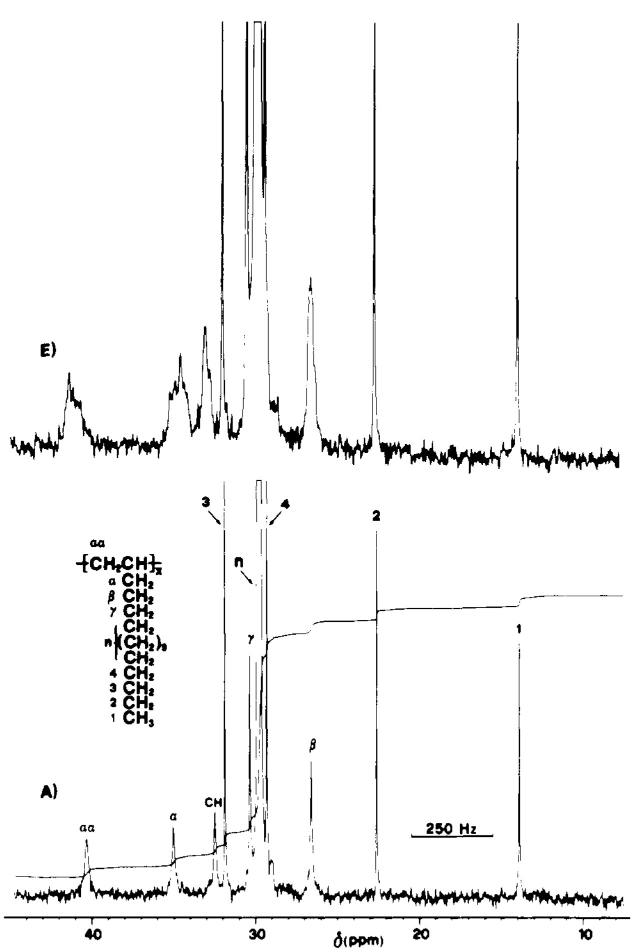

Figure 1. 50.28-MHz ^{13}C NMR spectra of poly(octadecylethylene) samples A and E in CDCl$_3$ (cf. Table II for sample identification).

^{13}C NMR spectra were run on a Bruker WP 200 apparatus operating at 50.28 MHz. The spectral conditions were as follows: pulse width 60°, relaxation delay 2 s, acquisition time 1 s. Since the T_1 values of the backbone carbons as well as those of the C$_\alpha$ and C$_\beta$ carbons are less than 300 ms, the relevant resonances, which are sensitive to tacticity, were fully relaxed under these conditions. Different solvents and temperatures were tested: the best results were obtained with CDCl$_3$ solutions (5–10% w/v) at 323 K. Ppm, originally recorded from CHCl$_3$, were converted to the Me$_4$Si scale.

The DSC traces were obtained as described previously.[10]

The ^{13}C NMR spectra of samples A and E (cf. Table II for sample identification) are shown in Figure 1. The spectrum of sample A consists of well-defined, sharp signals and this fact has been considered as indicative of a regular enchainment of the monomer units, as expected for substituted vinyl polymers of high stereoregularity. The carbon assignments, in terms of a single repeating unit, have been made according to Lindeman and Adams.[11] The observed and calculated values of the chemical shifts are collected in Table I.

The spectrum of sample E (Figure 1) shows a more complex pattern. The resonances of the C$_{\alpha\alpha}$ and C$_\alpha$ methylene carbons appear as multiplets. Their fine structure may be reasonably attributed to tacticity effects and points to a low degree of stereoregularity of the sample. Sensitivity to stereosequences is also exhibited, to a lesser

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Table I
Observed and Calculated ^{13}C Chemical Shifts for Poly(octadecylethylene) Sample A

	chem shift/ppm (from Me_4Si)	
signal[a]	obsd	calcd[10]
CH	32.6	32.91
$\alpha\alpha$	40.4	40.26
α	35.1	34.97
β	26.5	27.52
γ	30.4	30.21
n	30.0	30.00
4	29.3	29.71
3	31.9	32.40
2	22.7	22.65
1	13.9	13.86

[a] Cf. Figure 1.

Table II
Tacticity of Poly(octadecylethylene) Samples by ^{13}C NMR and DSC

	^{13}C NMR		DSC	
sample[a]	% atactic	% isotactic	% atactic	% isotactic
A	5	95	0	100
B	33	67	30	70
C	50	50	47	53
D	63	37	67	33
E	100	0	100	0

[a] Sample identification: sample A, polymer crystallized twice from heptane solution (2% w/v); sample B, residue of the extraction with boiling ether; sample C, crude product of the stereospecific polymerization; sample D, blend of samples A and E (32/68 w/w); sample E, polymer soluble in boiling ether.

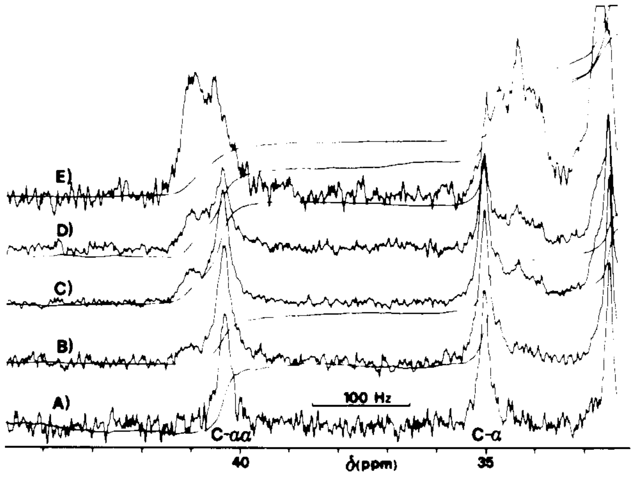

Figure 2. ^{13}C NMR spectra (expanded region of the $C_{\alpha\alpha}$ and C_α resonances) of poly(octadecylethylene) samples (cf. Table II for sample identification).

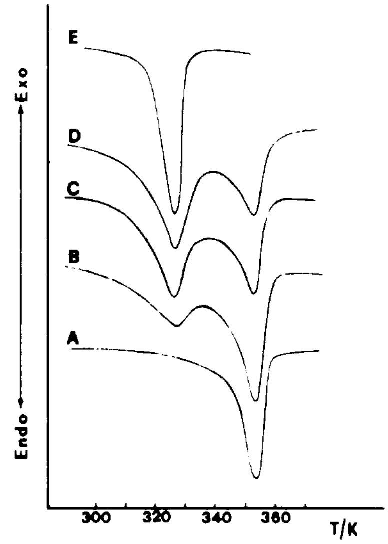

Figure 3. Rerun heating DSC traces of poly(octadecylethylene) samples (cf. Table II for sample identification).

extent, by the CH and C_β carbons.

For a qualitative assignment of the resonances in terms of stereoisomerism a comparison with the ^{13}C NMR spectra of isotactic and atactic polypropylene[12] seemed useful. This comparison was considered valid since the chain conformational statistics for polypropylene and poly(octadecylethylene) are likely to be similar. The spectra of Figures 1 and 2 indicate that the resonances of the $C_{\alpha\alpha}$ and C_α carbons of sample A show upfield and downfield shifts, respectively, as compared with the corresponding multiplets of sample E. The same trend is displayed by the resonances of the methylene and methyl carbons of isotactic polypropylene.[12] Therefore, it seems reasonable to conclude that sample A consists of isotactic poly(octadecylethylene).

The assignment to specific stereosequences of the minor signals of the multiplets of the $C_{\alpha\alpha}$, C_α, and CH carbons of sample E could not be made owing to partial overlapping. Nevertheless, the conclusion that sample E is predominantly atactic can safely be drawn from the relevant spectra shown in Figures 1 and 2. It is clearly seen, in fact, that the C_α band is made up of three components with intensity ratios roughly equal to 1:2:1 reasonably ascribable to mm, mr, and rr triads, as can be expected for an atactic polymer.

The presence in such spectra of some sharp peaks characteristic of isotactic sequences suggests that sample E is not "ideally atactic". This is not surprising since long isotactic sequences may be present in this sample either as blocks in atactic macromolecules or as isotactic macromolecules, of probably lower molecular weight, passed in solution during the ether extraction.

Despite the above limitations, a comparative analysis of the ^{13}C NMR spectra of the samples of poly(octadecylethylene) allows the evaluation of their relative content of isotactic and atactic polymer. Figure 2 shows the expanded region of the resonances of the $C_{\alpha\alpha}$ and C_α carbons for all poly(octadecylethylene) samples investigated. A quantitative approach to a measure of the degree of tacticity of these samples was made by assuming that sample E is 100% atactic and that the Overhauser enhancement of the $C_{\alpha\alpha}$ and C_α carbons is not dependent on the tacticity. This latter assumption seems justified since stereoregularity has never been found to have an effect on NOE, though influencing the ^{13}C spin-lattice relaxation time.[13] The choice of appropriate cuts on the spectra allows a satisfactory, internally consistent analysis. The results are collected in Table II.

In Figure 3 the DSC rerun heating traces of the poly(octadecylethylene) samples are reported. It is apparent that both samples A and E, i.e., the highly isotactic and the highly atactic polymers, display single melting transitions at 353 and 327 K, respectively. The samples of intermediate stereochemical composition show both melting phenomena. This demonstrates that our previous assumption that the two transitions must be ascribed to the immiscible phases formed by isotactic and atactic poly(octadecylethylene)[2] is correct.

Since the heat effects associated with the fusion of the two crystalline phases have been shown[10] to be comparable, an estimation of the degree of tacticity can be obtained from a measure of the DSC peak areas. The results of such an approach are compared in Table II with the data obtained through ^{13}C NMR. The agreement between NMR and DSC data can be considered very satisfactory.

To our knowledge, poly(octadecylethylene) is the first reported example of a polymer whose degree of tacticity has been measured so easily with a simple and rapid calorimetric technique. The DSC traces reported in previous literature[2,5,8,9] indicate that most allegedly isotactic long-side-chain polyolefins investigated so far contained significant amounts (20–30%) of atactic material.

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