

¹³C-NMR Determination of the Tacticity of Polyepichlorohydrin*

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Synopsis

The microstructure of polyepichlorohydrin was directly studied by high-field ¹³C-NMR. Spectral features were found that correspond to different tacticities. By using curve deconvolution techniques, the different tacticities were assigned and quantified.

INTRODUCTION

Polyepichlorohydrin (PECH) is used as an elastomer in a variety of applications.¹ Like all elastomers, the end-use properties of PECH depend partly on the tacticity of the polymer. A determination of its tacticity by reducing the polymer to poly(propylene oxide) with LiAlH₄ was previously reported by Steller using ¹³C-NMR at 22 MHz.² The same approach was repeated by Dworak,³ who obtained similar results.

In this work, we have undertaken a direct study of PECH using high field NMR (90 MHz for ¹³C). With resolution enhancement and curve deconvolution techniques, the amounts of isotactic, heterotactic, and syndiotactic triads can be directly determined. The method is fast and obviates the need for LiAlH₄ reduction.

EXPERIMENTAL

The polymers were all experimental samples made via Vandenberg's process.⁴ These were dissolved as 20–30% solutions in d₆-dimethylsulfoxide and run on a Nicolet NT360WB spectrometer at 135°C. The instrumental conditions were: spectrometer frequency, 90.56 MHz; sweep width, 5400 Hz; memory size, 32K, zero-filled to 64K before processing; 1-pulse experiment, 70° pulse; repetition rate, 3s; negative linebroadening (EM = -0.5 Hz) to enhance resolution. Curve deconvolution was carried out on the Nicolet 1280 computer by the NMCCAP subprogram.

RESULTS AND DISCUSSION

In the ¹³C-NMR spectrum of polyepichlorohydrin three resonances are found, corresponding to backbone methine (78 ppm), backbone methylene (69 ppm), and branch methylene (43 ppm). These resonances should be sensitive to the configuration (tacticity) of the side chains, giving rise to tacticity splittings. In the case of PECH, however, due to the intervening oxygen between adjacent monomer units, this effect is considerably diminished. In the spectrum of Steller,² for example, the backbone methine and the branch

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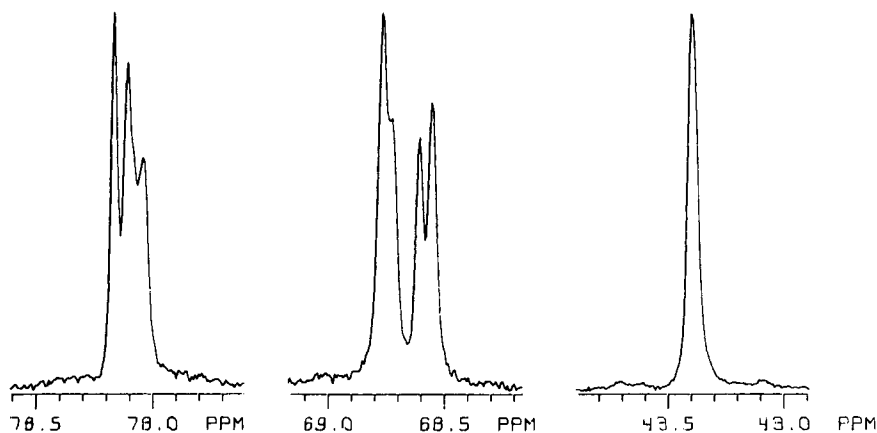
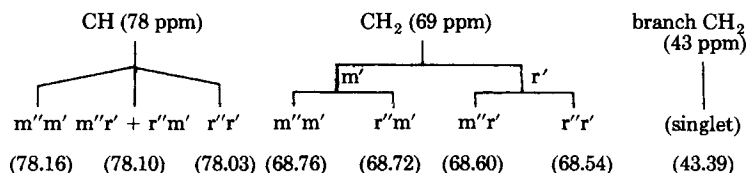


Fig. 1. Expanded plots of ^{13}C -NMR spectrum of atactic polyepichlorohydrin.

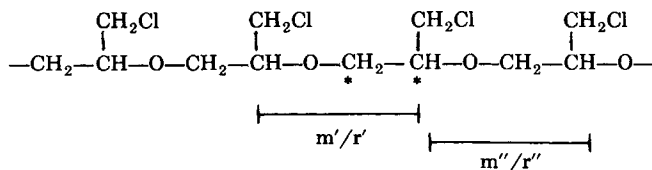
methylene were both singlets; only the backbone methylene showed up as a doublet corresponding to isotactic and syndiotactic dyads. The spectrum of Dworak³ gave no splitting because of poor spectral resolution and lower magnetic field strength (20 MHz).

At a higher magnetic field (90 MHz), the situation improves considerably (Fig. 1). The spectral resolution can be further enhanced by employing a slightly negative line-broadening factor. This produces more pronounced fine structures for the backbone carbon resonances. In Figure 1, the backbone methylene resonance is seen to contain four lines, whereas the methine is split into either three or four lines depending on the sample. The branch methylene, however, is a broad singlet, thereby not usable for tacticity determination.

The assignment of the fine structural features to the proper tactic sequences was accomplished by comparing samples with varying tacticities. The interpretational scheme is shown below:



The numbers in parentheses give the ^{13}C chemical shifts. It is of interest that both methine and methylene backbone carbons are sensitive up to triads. Furthermore, because of the intervening oxygen that spaces out the monomer units, $m' \neq m''$ and $r' \neq r''$.



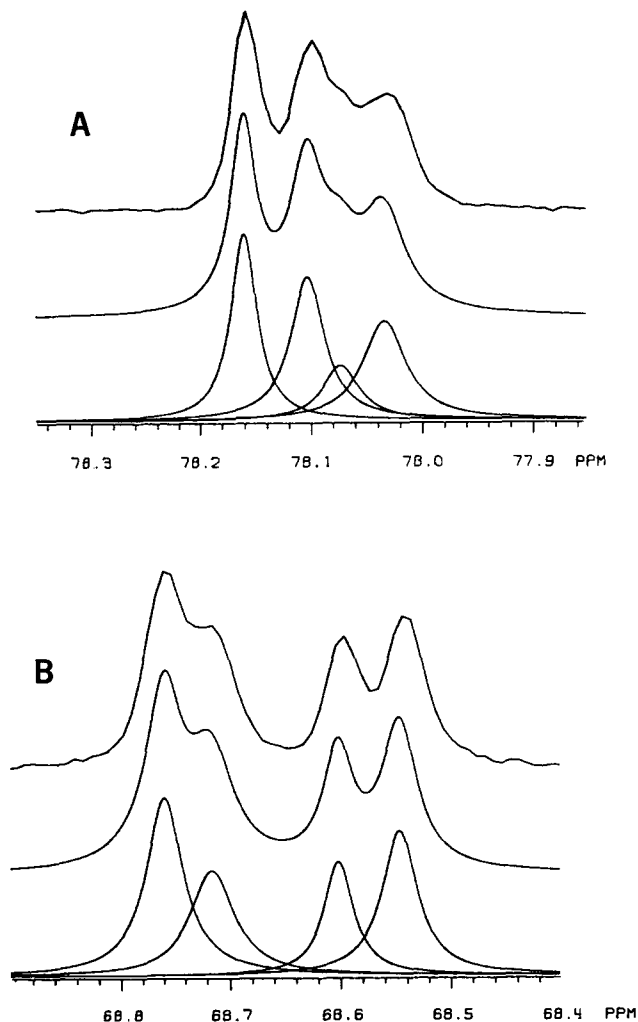


Fig. 2. Curve deconvolution of (a) the methine carbon resonance and (b) the methylene resonance. In each plot, the upper curve is the observed spectrum, the middle curve is the fitted spectrum, and the lower curve gives the component peaks.

In order to determine the tacticity with better precision, we used the curve deconvolution technique. A result of curve deconvolution is shown in Figure 2(a) (methine) and 2(b) (methylene). The methylene region contains four lines which can be readily deconvoluted to give fairly precise results. The methine region is more crowded because the triads $m''r'$, $r'm'$, and $r'r'$ are closer together. The precision in the methine region is therefore lower.

The results for four samples of poly(epichlorohydrin) are summarized in Table I. The observed tacticities can be fitted to first-order Markovian statistics. In all cases, $P_{mr} + P_{rm} < 1$. It should be noted that in none of the samples studied were any inverted sequences (head-to-head and tail-to-tail) found. The absence of inverted sequences was also shown earlier by Steller² and Dworak³ in their LiAlH_4 studies.

TABLE I
Triad Distribution of PECH as Determined by ^{13}C -NMR

Sample	Methylene ^a				Methine ^b			1st Order Markov	
	mm	mr	rm	rr	mm	mr + rm	rr	P_{mr}	P_{rm}
1	25	29	18	29	26	31	34	0.485	0.448
2	34	20	20	27	31	46	24	0.370	0.426
3	44	14	21	22	40	36	24	0.285	0.443
4	84	3	9	4	84	6	9	0.067	0.600

^aError range = 0-4%.

^bError range = 2-10%; the error is smallest for mm and largest for rr.

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