

## $^{13}\text{C}\text{—}\{^1\text{H}\}$ Nuclear Magnetic Resonance Spectroscopy of Poly(vinyl chloride) and its Model Compounds

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The  $^{13}\text{C}\text{—}\{^1\text{H}\}$  high-resolution NMR is of great interest in the study of higher order stereochemical placement of vinyl polymers<sup>1–4</sup>, because carbon is the most essential atom constituting the skeletal bonds of the polymer chain.

Recently Schaefer<sup>5</sup> showed the Fourier Transforms of the noise-decoupled, natural abundance  $^{13}\text{C}\text{—}\{^1\text{H}\}$  NMR of free induction decays of poly(vinyl chloride) (PVC), but the configurational assignments were not shown clearly.

We measured  $^{13}\text{C}\text{—}\{^1\text{H}\}$  NMR spectra of PVC and its dimer model compounds, *i.e.*, *meso*- and *racemic*-2,4-dichloropentanes. PVC was supplied by Prof. Benoit for the IUPAC Study Programm on Molecular Characterization of Commercial Polymers, and PVC-B was a commercial polymer with relatively high syndiotacticity produced by the Châtillon S.p.A. (Italy).

$^{13}\text{C}\text{—}\{^1\text{H}\}$  spectra were observed by external locked field sweep in absorption mode at 25.14 MHz, using a JNM PS-100 spectrometer. Chemical shifts were represented in terms of parts per million using enriched  $^{13}\text{CH}_3\text{OH}$  as an external reference. The measurements of NMR were made using the neat liquid for the model compounds and the 20-%(w/v) solution of dimethylsulfoxide for PVC. The *o*-dichlorobenzene was also used as the solvent for PVC but no significant difference was observed. The NMR samples of PVC were first heated at about 150°C for several minutes to form a uniform solution and then settled at 70°C. At this temperature the solution formed a slightly loose gel and a change in color was not observed during a NMR measurement. Details of NMR measurement

are described in ref 3.

$^{13}\text{C}\text{—}\{^1\text{H}\}$  spectrum of the mixture of dimer model compounds, wherein the molar ratio of *meso*-isomer to *racemic*-isomer was approximately 1 : 3, is shown in Figure 1. The assignments of peaks are on the basis of their multiplet structures of weakly proton decoupled  $^{13}\text{C}$  spectrum. All carbons of *racemic*-isomer appeared in a lower field compared to *meso*-isomer.

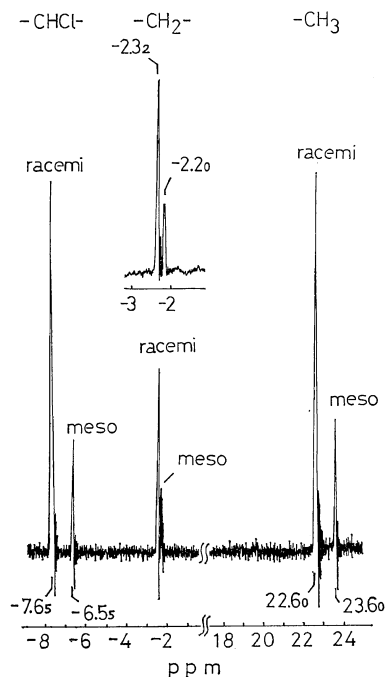
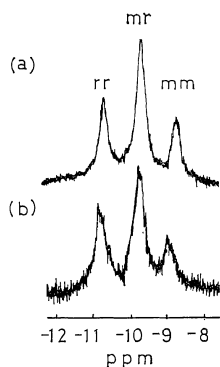


Figure 1.  $^{13}\text{C}\text{—}\{^1\text{H}\}$  spectrum of 1 : 3 mixture of *meso*- and *racemic*-2,4-dichloropentane observed at 25.14 MHz, at room temperature.

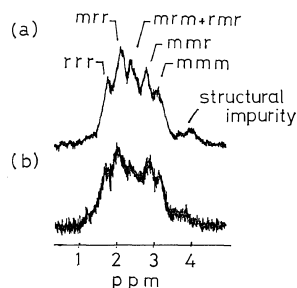
<sup>13</sup>C—<sup>1</sup>H) resonance of methine carbon of PVC is split into three components, attributable to triads as shown in Figure 2. Comparing the spectrum of model compounds, these three lines could be tentatively assigned to syndio- (*rr*), hetero- (*mr*), and isotactic (*mm*) triads, from



**Figure 2.** <sup>13</sup>C—<sup>1</sup>H) spectra of methine carbon of PVC observed at 25.14 MHz, in 20-% (w/v) solution in dimethylsulfoxide at 70°C: (a) PVC-A; (b) PVC-B. The spectra are the accumulation of 256 scans. Each scan swept 27 ppm/250 sec.

**Table I.** The triad microtacticity of PVC obtained from the <sup>13</sup>C—<sup>1</sup>H) spectra reproduced in Figure 2

	Triad tacticity			$\frac{4(mm)(rr)}{(mr)^2}$
	( <i>mm</i> )	( <i>mr</i> )	( <i>rr</i> )	
PVC-A	0.22	0.49	0.29	1.06
PVC-B	0.18	0.49	0.33	0.99



**Figure 3.** <sup>12</sup>C—<sup>1</sup>H) spectra of methylene carbon of PVC observed at 25.14 MHz, in 20-%(w/v) solution in dimethylsulfoxide at 70°C: (a) PVC-A; (b) PVC-B. The spectra are the accumulation of 256 scans. Each scan swept 27 ppm/250 sec.

**Table II.** The tetrad microtacticity of PVC

	PVC-A		PVC-B	
	Obsd <sup>a</sup>	Calcd <sup>b</sup>	Obsd <sup>a</sup>	Calcd <sup>b</sup>
<i>rrr</i>	0.16	0.15	0.18	0.19
<i>mrr</i>	0.26	0.27	0.27	0.28
<i>mmm</i>	0.24	0.25	0.23	0.24
<i>rmr</i>				
<i>mmr</i>	0.21	0.23	0.19	0.21
<i>mmm</i>	0.13	0.10	0.13	0.08

<sup>a</sup> Obtained from the <sup>13</sup>C—<sup>1</sup>H) spectra reproduced in Figure 3.

<sup>b</sup> Calculated using the statistical parameter  $P_m = 0.47$  for PVB-A and  $P_m = 0.43$  for PVC-B.

left to right in order of increasing field. The triad tacticities of the polymers determined from these spectrum were tabulated in Table I. The relative intensities of syndiotactic triad of these polymers were slightly higher than those of isotactic triad and these results are consistent with the general trend of PVC prepared from free radical polymerization.<sup>6,7</sup>

The following relation

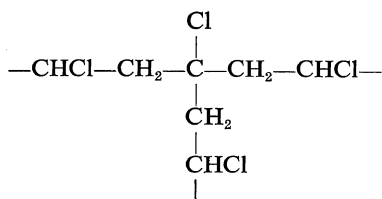
$$4(mm)(rr)/(mr)^2 = 1$$

was held satisfactorily as listed in the last column of Table I. Thus the stereospecific polymerization mechanisms of these polymers can reasonably be assumed to be the Bernoulli trial process.<sup>8</sup> <sup>13</sup>C—<sup>1</sup>H) spectrum of methylene carbon of PVC is split into five components, attributable to tetrads as shown in Figure 3. The assignments of these lines were made comparing the spectrum of model compounds and the intensities calculated from the Bernoulli statistics.<sup>4</sup>

The tetrad tacticity of these polymers was tabulated in Table II. The agreements between the experimental and calculated values were fairly good.

The appearance of a small peak at the highest field of methylene resonance designated as an structural impurity in Figure 3 must be assigned to the methylene carbons in some heterogeneous structures.

The intensities of these small peaks were about 5~6% of total intensities of methylene resonance. The most probable structure is the branching.



The methylene groups adjacent to the branch point should be slightly different from other methylene groups in the polymer. Thus each branch point will influence the resonances of at least three methylene carbons. If this were true, the number of branch points per 100 monomer units was approximately 1.5~2.

These results basically agree with previously reported values.<sup>9</sup> The resonance of the quaternary carbon at the branch point cannot as yet be distinguished from the noise. It is necessary to carry out accumulation more than 256 times in order to identify the quaternary carbon resonance, because of the lack of signal enhancement due to the nuclear Overhauser effect.

It is noted that the methine carbon resonances are as sharp as methylene carbon, so the line

broadening brought about by the quadrupole effects of the chlorine atom is considered to be small.

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