Influence of Polymer Association on the Interpretation of Nuclear Magnetic Resonance Measured Tacticity of Poly(vinyl chloride) in Solution

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ABSTRACT: Crystalline fractions of poly(vinyl chloride) (PVC) show limited solubility at the usual high-temperature solution conditions of nmr tacticity measurements. A number of PVC's made at low temperatures and a series of fractionated, low-molecular-weight PVC's made in *n*-butyraldehyde had solubilities of 0–90%, depending on the sample type and preparation. The solubilities were determined by comparing the PVC proton resonance area with that of an internal standard. These findings of incomplete solubility suggest a reexamination of published nmr determinations of tacticity in PVC. Particular attention must be paid to the fraction of the total polymer contributing to the nmr spectrum and to the conclusions about PVC structure drawn from partial results.

Over the past decade, a large number of papers have treated the proton nmr determination of tacticity of poly(vinyl chloride) (PVC) (see the bibliography in the 1969 paper of Heatley and Bovey[1]). Two major conclusions about the structure of PVC have been drawn from these nmr studies. (1) The amount of syndiotacticity decreases only slightly with decreasing polymerization temperature.[2-6] Conflicting suggestions[2,5] exist as to whether the small differences in tacticity are enough to account for the significantly large changes in T_g, T_m, brittleness, and other properties. (2) The PVC's polymerized in the presence of aldehydes (*e.g.*, *n*-butyraldehyde) are not significantly different in tacticity from conventional free-radical, emulsion, or suspension PVC's made at the same temperature.[2,3,4,7] Supposedly, they are highly crystalline only because they are linear and of low molecular weight.[7] We would suggest caution in the acceptance of these general conclusions. We have accumulated evidence of incomplete solubility, using internal standards in the nmr experiments, which shows that the nmr often does not "see" 10–40% or more of the total polymer. It should be pointed out that, in general, the amounts of syndiotacticity found in various PVC's are higher by infrared methods than by nmr (see ref 5 for a review of these findings).

The limited solubility of PVC even in the best known solvents has been recognized for well over two decades. In 1947, Doty and coworkers[8] demonstrated aggregation in PVC solutions by a combination of osmotic-pressure, light-scattering, and ultracentrifuge measurements. Oth,[9] Hengstenberg and Schun,[10] and more recently Crugnola and Danusso[11] very clearly demonstrated PVC aggregate formation under a variety of solvent–temperature conditions by ultracentrifugation. The latter workers showed that the percentage of polymer aggregated in solution increased markedly with decreasing polymerization temperature. Peterlin[12] and Hengstenberg[10] showed a strong dependence of aggregate formation on the mode of solution preparation.

Kratochvil[13] used light scattering to prove the existence of what he called microgel. By streaming birefrigence, Munk[14] observed aggregates with a negative optical anisotropy. This suggested a presence of crystal nuclei whose molecular chains were situated perpendicular to the long particle dimensions. Kratochvil and coworkers[15] have recently surveyed published anomalies in the solution properties of PVC and stated that most of the phenomena can be ascribed to the enhanced crystallizability of syndiotactic sequences in the molecules.

At least two published nmr papers directly or indirectly treat the solubility–structure problem. Pham[16] fractionated a PVC in cyclohexanone at 25° and showed that the insoluble portion had a higher concentration of syndiotactic diads and a longer average syndiotactic sequence length than the soluble fraction. He made his nmr measurements at 150° in *o*-dichlorobenzene, but he did not indicate how much of the polymers were "in solution" under those conditions. Bovey and coworkers[4] found that a greater line width was needed in the interpretation of nmr spectra from the −78° PVC than for polymers made at 0, 50, and 100°. Among the reasons for nmr line broadening,[17,18] we feel that two may be pertinent here. One reason may be the slow exchange between magnetically nonequivalent conformers in PVC. Also, the restricted motion of chains may cause an incomplete averaging of magnetic dipole–dipole interactions. Both of these would result from the presence of crystalline nuclei or ordered aggregates in solution.

Experimental Section

To put these findings on a quantitative basis, it was necessary to determine how much of the total PVC was contributing to the

(1) F. Heatley and F. A. Bovey, *Macromolecules*, **2**, 241 (1969).
(2) F. A. Bovey and G. V. D. Tiers, *Chem. Ind. (London)*, **81**, 1826 (1962).
(3) F. A. Bovey, F. R. Hood, E. W. Anderson, and R. L. Kornegay, *J. Phys. Chem.*, **71**, 312 (1967).
(4) W. C. Tincher, *Makromol. Chem.*, **85**, 20 (1965).
(5) G. Pezzin, *Plast. Polym., Conf. Suppl.*, **No. 3**, 295 (1969).
(6) G. Talamini and G. Vidotto, *Makromol. Chem.*, **100**, 48 (1967).
(7) O. C. Bockman, *J. Polym. Sci., Part A*, **3**, 3399 (1965); *Brit. Plast.*, **38** (6), 364 (1965).
(8) P. Doty, H. Wagner, and S. Singer, *J. Phys. Colloid Chem.*, **51**, 1, 32 (1947).
(9) A. Oth, 27th International Congress on Chemical Industry, Brussels, 1954.
(10) J. Hengstenberg and E. Schun, *Makromol. Chem.*, **74**, 55 (1964).
(11) A. Crugnola and F. Danusso, *Polym. Lett.*, **6**, 535 (1968).
(12) A. Peterlin, Simposio Internationale di Chemica Macromolecolare, Milan, 1954, p 553.
(13) P. Kratochvil, *Collect. Czech. Chem. Commun.*, **30**, 1119 (1965).
(14) P. Munk, *ibid.*, **32**, 787 (1967).
(15) P. Kratochvil, M. Bohdanecky, K. Solc, M. Kolinsky, M. Ryska, and D. Lim, *J. Polym. Sci., Part C*, **No. 23**, 9 (1968).
(16) Q. T. Pham, *Polym. Lett.*, **7**, 103 (1969).
(17) A. L. Segre, *Macromolecules*, **1**, 93 (1968).
(18) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, N. Y., 1959.

TABLE I
DESCRIPTION OF PVC SAMPLES FOR SOLUBILITY STUDY

Sample no.	Comments on sample preparation: Polymerization conditions	Sample work-up
1	0°, γ initiated	Whole polymer
2	−80°, γ initiated	Whole polymer
3	−80°, tributylborane catalyst	Whole polymer
4	40°, isopropyl peroxidicarbonate catalyst, 1 mol of *n*-butyraldehyde/mole of VCl	Original polymer dissolved in boiling *o*-dichlorobenzene and cooled, solution ultracentrifuged 1 hr at 30,000 rpm, polymer from supernatant solution precipitated in methanol; thus no. 4 is a soluble fraction of the whole polymer
5	Same as no. 4	Whole polymer
6	Same as no. 4	Sediment from ultracentrifugation in no. 4, washed in methanol; thus no. 6 is a crystalline fraction of the whole polymer
7	Same as no. 4	Repeat of no. 6 but final nmr solution contained 2% (w/v) PVC
8	Same as no. 4	Original polymer dissolved in boiling cyclohexanone, cooled, ultricentrifuged 1 hr at 30,000 rpm, sediment dissolved in boiling THF, cooled, ultracentrifuged, THF dissolution and ultracentrifugation repeated two more times, final sediment washed with methanol, vacuum dried
9	Geon[a] 102 EP, 50° commercial free-radical PVC	Whole polymer

[a] The B. F. Goodrich Chemical Co.

nmr absorbance peaks. Toward this end, we used either recrystallized Carbowax, a low-molecular-weight $(CH_2CH_2O)_x$ polymer, or tetralin (1,2,3,4-tetrahydronaphthalene) as internal standards to calculate the concentration of PVC in the *o*-dichlorobenzene solutions. These standards were chosen because of their extremely high boiling points and because their nmr resonance peaks were sufficiently removed from the PVC methyne proton resonance peaks to facilitate easy area measurements. The procedure was to add accurately weighed amounts of the PVC and Carbowax or tetralin to the *o*-dichlorobenzene and compare the measured resonance areas with the known concentrations. Each vinyl chloride monomer unit in PVC contributes one proton to the spectrum in the region 4.00–4.83 ppm relative to hexamethyldisiloxane. Carbowax (CH_2CH_2O) units contribute four protons at 3.52 ppm and the four tetralin 1,4 protons absorb at 2.48–2.80 ppm.

All spectra were obtained on a Varian A-60 nmr spectrometer equipped with a Varian variable-temperature controller and probe. Time averaging was done with a Varian C-1024 computer of average transients. The solutions were held at 125° in an oven for 0.5–4 hr before they were placed in the Varian A-60 variable-temperature probe. The total time at 140 or 170° in the spectrometer ranged from 0.5–1.5 hr. The solutions of PVC polymerized in the presence of *n*-butyraldehyde darkened considerably at these elevated temperatures. The high-molecular-weight, low-temperature polymerized PVC solutions darkened only slightly. Study of the 5.5–5.8-ppm proton resonance region showed no measurable −CH=CH− present even in the darkest solutions.

Results and Discussion

Table I lists the conditions under which the PVC's were polymerized and prepared or fractionated for the nmr analysis. As shown in Table II, samples 1–7, polymerized and fractionated under a variety of conditions, showed solubilities ranging from about 65 to 90%. Sample 8 consisted primarily of single crystals of PVC, as described in a recent publication of Smith and Wilkes.[19] The material was essentially insoluble in *o*-dichlorobenzene at 170°, as evidenced by the complete absence of a PVC nmr signal even after collection of 49 scans on the time-averaging computer. We will soon publish X-ray and infrared evidence that the crystalline fractions of PVC are indeed highly syndiotactic. Sample 9, a commercial free-radical-polymerized PVC made at 50°, was 89–96% soluble. The expected deviation in these measurements is of the order of ±5% absolute. We observed that sample 7, a 2% solution, had a greater apparent solubility than sample 6, a 10% solution (see Table II). It is not known at this point if the solubility will approach 100% at very low concentrations. In any case, it becomes quite difficult to obtain informative spectra at concentrations lower than this. Also, it is well known that there are solvents for PVC better than *o*-dichlorobenzene (*e.g.*, nitrobenzene, cyclohexanone). However, the purpose of this work was to examine the validity of published nmr results on PVC solutions, most of which had chlorobenzene or *o*-dichlorobenzene as the solvent.

TABLE II
SOLUBILITY OF PVC'S IN *o*-DICHLOROBENZENE

Sample no.	Concn (w/v), %	Temp, °C	Internal std	Scans with time-averaging computer	% solubility
1	10	140	Tetralin	16	84, 80, 89
2	10	140	Tetralin	16	70, 71
3	10	170	Carbowax	38	81
4	10	170	Carbowax	16	84
5	10	170	Carbowax	16	74
6	10	170	Carbowax	42, 17, 25	63.5, 65, 65.5
7	2	170	Carbowax	49	89.5
8	2	170	Carbowax	49	0
9	10	140	Tetralin	16, 16, 17	89, 89, 96

Of the samples listed in Tables I and II, all those whose solubilities were 80% or greater were perfectly clear solutions at 140–170°. Thus, the aggregates (insoluble portions) were of a size too small to scatter light. Samples with a solubility between 65 and 80% were faintly cloudy. Thus aggregation was visually apparent. Sample 9, with 0% solubility, was obviously a suspension of large PVC particles (crystal aggregates) and was not a solution at all.

Since these insoluble fractions were not contributing to the nmr spectra, assessment of the tacticity of the whole polymer was not possible by this technique. Although the nmr method lends itself very nicely to quantitative measurements and although the interpretation and chemical shift assignments of the various tactic structures are well characterized, we must be concerned that the information obtained is not complete.

Based on these findings, we feel that the general conclusions on the effect of polymerization temperature and such complexing agents as aldehydes on the structure of PVC need to be reexamined. A quantitative spectroscopic method which measures the structure of the whole polymer is a necessary part of any investigation of this type.

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(19) R. W. Smith and C. E. Wilkes, *Polym. Lett.*, 5, 433 (1967).