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Topochemical Effects in Polymerization of Vinylsulfonate Attached to an Ionene Matrix

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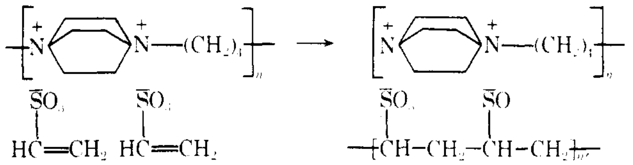
ABSTRACT: Proton and ^{13}C NMR spectra of sodium poly(vinylsulfonate) separated from ionene matrix (PVS-1) are compared with the spectra of sodium poly(vinylsulfonate) prepared in aqueous solution (PVS-2). X-Ray diffraction patterns of polyelectrolyte complexes between ionene and PVS-1 and PVS-2, respectively, are shown. Influence of the ionene matrix on the tacticity of PVS-1 is discussed.

We have recently reported the results of our study of the kinetics of free-radical polymerization of styrenesulfonic acid on ionene matrices[2] and the formation of highly ordered polyelectrolyte complexes which result from such polymerization in the case of vinylsulfonic acid and the poly(diazabicyclo[2.2.2]octyl-1-butane) or ionene.[3] We have also described the separation of the poly(vinylsulfonic acid) from its matrix.[2b,4] We would like to report here the results of preliminary NMR investigations of the tacticity of a "reference" and of a matrix-prepared poly(vinylsulfonic acid).



The reference poly(vinylsulfonic acid) (PVS-2) was prepared by free-radical polymerization in concentrated aqueous solution at 55°. The conversion was 35% and the M_n = 30,000. The poly(vinylsulfonic acid) prepared on the matrix (PVS-1) was obtained by complexing the acidic monomer with a stoichiometric amount of ionene hydroxide (mol wt = 4000). The polymerization was carried out in aqueous solution at 70° with a free-radical initiator. The detailed procedure for polymerization and separation of polymer and matrix has been reported elsewhere.[2b,4] The matrix polymer used here was as obtained after one separation step. Elementary analysis indicated the presence of some 2–3% unseparated ionene matrix, possibly fragments permanently attached to the poly(vinylsulfonate) through covalent bonding. The proton magnetic resonance spectra were obtained at room temperature in D_2O with a HR-300 MHz spectrometer, using sodium trimethylsilylpropanoate-d_5 as internal standard. The ^{13}C spectra were run using a JEOLCO NMR spectrometer and 50% (by weight) solutions of sodium poly(vinylsulfonate) in D_2O with tetramethylsilane as standard at room temperature. Each spectrum is an accumulation of 7,000 scans obtained at 25.14 MHz at room temperature. Figure 1a gives the proton magnetic resonance spectrum of PVS-2; the methine protons appear in the 3.5–4.0 ppm region and the methylene in the 1.5–2.6 ppm area. Figure 1b gives the PMR spectrum of the matrix-polymerized and separated poly(vinylsulfonate), PVS-1. Here a group of peaks appear between 1.6 and 2.6 ppm and another between 2.9 and 3.8 ppm. Determination of the ratio of the methine to methyne peak areas for PVS-1 indicates some contamination by unseparated matrix. Assuming that 16 of the 20 ionene protons will contribute to the methine peak area of PVS-1, the spectra indicate that approximately three monomeric ionene fragments remain, per 100 monomeric vinylsulfonate units. Neglecting the contribution of ionene contamination to the methylene area (approximately 6% of the total) and assuming that the ionene contribution in the methine area is in the 2.8–3.2 ppm range (shaded region), one can see a drastic difference between the spectra of the two polymers.

Figures 2a and 2b give the ^{13}C spectra of PVS-2 and PVS-1, respectively. The methine area of the reference polymer shows two approximately equal peaks at 55.769 and 54.941 ppm. The methylene area is more complicated. For the matrix-separated polymer the relative peak intensities in the methine and methylene areas increase with in-

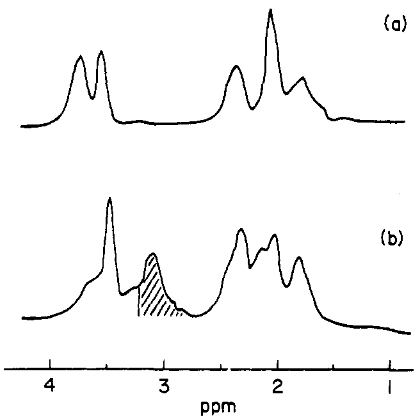


Figure 1. PMR spectra: (a) reference sodium poly(vinylsulfonate) (PVS-2); (b) matrix polymerized sodium poly(vinylsulfonate) (PVS-1).

creasing field strength. Figure 2b shows several smaller peaks, in addition to those present in the methine and methylene areas. The main impurity in the 48-ppm region is assigned to the six carbons of the dicycloocto ring of the ionene matrix. The small peaks in the 52-ppm region are assigned to the 1–4 methylene carbons of the ionene. The 2–3 methylene carbons of the ionene are assigned to the 25–26 ppm area, which also contains the methyl and half of the methylene carbons of the end groups (cyanovaleric acid used as initiator, 1 per 30–35 monomer units). The intensities of peaks attributed to the unseparated ionene contamination are in agreement with the values predicted on the basis of approximately 3 monomeric ionene fragments per 100 monomeric vinylsulfonate units. The NMR spectra, therefore, can be used as a very sensitive method for checking on the completeness of separation from the matrix since the ionene and poly(vinylsulfonate) absorptions do not overlap.

Assuming that, in the proton spectrum of the reference polymer, the peak at 3.75 ppm corresponds to the syndiotactic triads *rr* and the peak at 3.55 to the heterotactic triads *rm* and that the isotactic content is small enough to be buried in the base line, we obtain $rr = 0.65$ and $2mr = 0.35$. An alternate assignment would be to assume that the peak at 3.75 ppm corresponds to $2mr + rr = 0.65$. This would mean that the peak at 3.55 ppm corresponds to $mm = 0.35$. The latter interpretation, however, appears unlikely since it would imply an unacceptably high isotactic content for free-radical polymerization of acidic monomers. Indeed, it has been reported by several authors that ionization of the asymetric group of the monomer consistently favors syndiotactic addition.[6–8] It is therefore to be expected that the polymerization of vinylsulfonic acid in water solution (fully ionized side groups) would lead to a high content of syndiotactic triads in the polymer.

For the matrix-prepared polymer, assuming that the isotactic triad appears at approximately 3.3 ppm, we can estimate the following: $rr = 0.23$, $2mr = 0.64$, and $mm = 0.13$. Thus, the proton spectra would seem to indicate a strong increase in heterotacticity and isotacticity, at the expense of the syndiotactic triads in the matrix-prepared polymer. The ^{13}C spectra qualitatively bear out this conclusion, again assuming that the lowest-field peak corresponds to the syndiotactic contribution. This assignment of tacticity was obtained by analogy with data published for poly(acrylic acid) by Schaefer[5] who showed that the isotactic contribution appears upfield from the syndiotactic and heterotactic peaks, respectively.

Although our assignments must be considered as tentative in the absence of a more detailed NMR analysis, it is clear that the stereoconfiguration of the poly(vinylsulfonate) is largely influenced by the complexation with the ionene. The influence of linear[9] and two-dimensional[10] solid matrices on the tacticity of polymers obtained by free-radical polymerization of monomer inclusion compounds has been reported, but we believe the present results to be the first reported instance of influence on tacticity by a linear polymeric counterion.

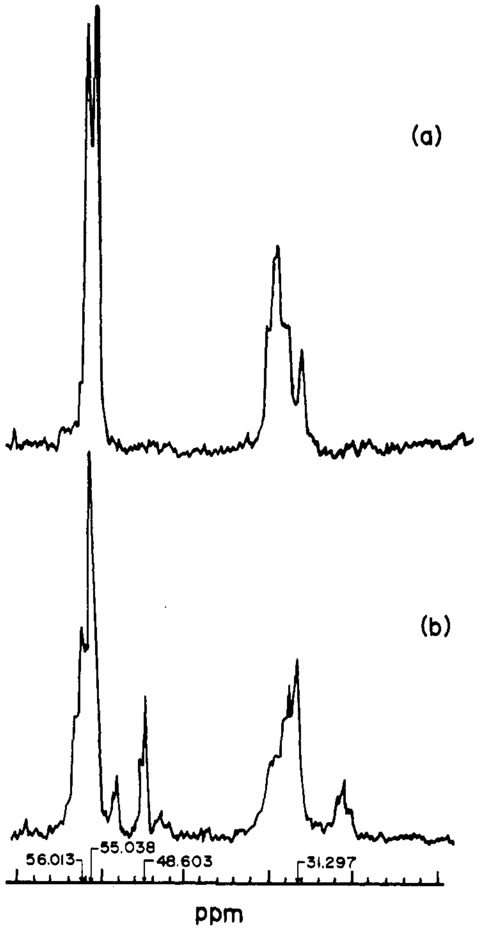


Figure 2. ^{13}C NMR spectra: (a) reference sodium poly(vinylsulfonate) (PVS-2); (b) matrix polymerized sodium poly(vinylsulfonate) (PVS-1).

The following observation supports the conclusions about the differences in stereoconfiguration between PVS-1 and PVS-2; when the separated polymer PVS-1 is mixed with the matrix it gives an insoluble complex which after drying shows a powder X-ray pattern with four distinctive bands: two sharp at 5.6 and 9.8 Å and two broad at 4.4 and 5 Å. A reference sodium poly(vinylsulfonate) of approximately the same molecular weight ($M_n = 5000$) gives only two broad bands at 5.6 and 9.8 Å and a halo at about 7 Å. The two X-ray patterns are shown in Figure 3. Thus, it is apparent that the matrix prepared poly(vinylsulfonate) gives a more organized complex upon recombination with the matrix. This points toward a specific interaction pattern of the matrix synthesized polymer and the matrix, possibly due to a more favorable stereoconfiguration.

During polymerization in solution syndiotactic placements are favored by electrostatic repulsion between SO_3^- side groups. During matrix polymerization, however, the monomer molecules are attached to the ionene as counterions and the similar orientation of side groups in neighboring monomers, all pointing toward the macromolecular matrix, will favor isotactic placements. One must expect

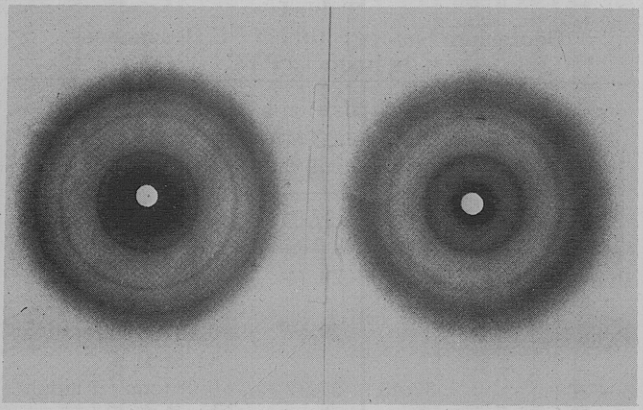


Figure 3. Powder X-ray patterns of precipitated polyelectrolyte complexes between ionene bromide and sodium poly(vinylsulfonate): (a) PVS-1; (b) PVS-2.

isotactic sequences in the poly(vinylsulfonate) to be very short (2–3 monomer units). Otherwise the polymer would acquire a helicoidal conformation forcing the SO_3^- side groups away from the linear matrix, which they must neutralize. Thus, a high number of "crossovers" into syndiotactic additions must occur and this would result, as observed, in a net increase in the number of heterotactic and isotactic triads in the poly(vinylsulfonate) prepared on the ionene matrix.

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Identification of Branches in Poly(vinyl chloride) by Reduction with $LiAlD_4$

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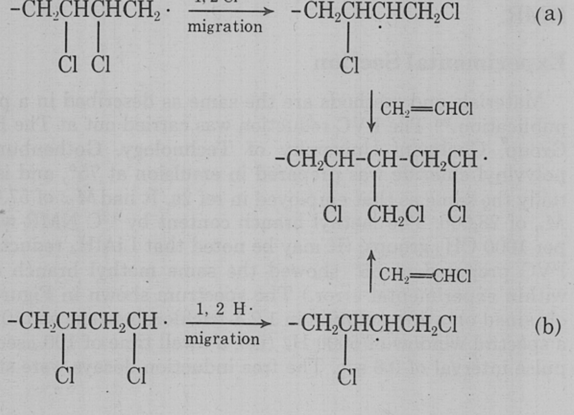
ABSTRACT: Reduction of poly(vinyl chloride) with lithium aluminum deuteride replaces each chlorine atom with a deuterium. The characteristic splittings and isotope shifts observable in the carbon-13 spectrum of the reduced product permit us to demonstrate conclusively that the branch structure in poly(vinyl chloride) is . . . $-CH_2C(Cl)H-C(CH_2Cl)H-CH_2-C(Cl)H-$. . . . This structure was previously proposed by us from the observation of the lithium aluminum hydride reduction product, but this did not provide a complete proof of structure.

In a previous paper we have shown that the polyethylene obtained from poly(vinyl chloride) by reduction with lithium aluminum hydride has approximately 3 methyl branches per 1000 CH_2 groups. Two alternative mechanisms were suggested by which such branches could arise: (a) a 1,2 Cl migration in the growing chain radical resulting from an occasional head-to-head monomer addition, as suggested by Rigo et al.; (b) rearrangement of the normal growing chain radical by a 1,2 hydrogen shift. Both mechanisms give the same branch structure:



$$-\mathrm{CH_2}\underset{\mathrm{Cl}}{\mathrm{CH}}\underset{\mathrm{Cl}}{\mathrm{CH}}\mathrm{CH_2}\cdot \xrightarrow[\text{migration}]{1,2\,\mathrm{Cl}\cdot} -\mathrm{CH_2}\underset{\mathrm{Cl}}{\mathrm{CH}}\underset{\cdot}{\mathrm{C}}\mathrm{HCH_2Cl} \qquad \text{(a)}$$

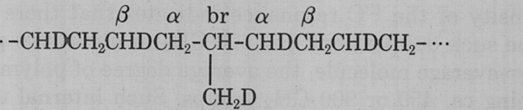
$$\downarrow \mathrm{CH_2{=}CHCl}$$

$$-\mathrm{CH_2}\underset{\mathrm{Cl}}{\mathrm{CH}}-\underset{\mathrm{CH_2Cl}}{\mathrm{CH}}-\mathrm{CH_2}\underset{\mathrm{Cl}}{\mathrm{CH}}\cdot$$

$$\uparrow \mathrm{CH_2{=}CHCl}$$

$$-\mathrm{CH_2}\underset{\mathrm{Cl}}{\mathrm{CH}}\mathrm{CH_2}\underset{\mathrm{Cl}}{\mathrm{CH}}\cdot \xrightarrow[\text{migration}]{1,2\ \mathrm{H}\cdot} -\mathrm{CH_2}\underset{\mathrm{Cl}}{\mathrm{CH}}\underset{\cdot}{\mathrm{C}}\mathrm{HCH_2Cl} \qquad \text{(b)}$$

$LiAlD_4$ Reduction. Reduction with lithium aluminum hydride confirms that one or the other of these mechanisms (or both) are operating, but does not rigorously demonstrate the structure of the branch unit, since all chlorines are replaced by hydrogen and information as to their position in PVC is lost. This information can be retained by reduction with lithium aluminum deuteride, $LiAlD_4$, which replaces each chlorine atom with a deuterium. If the branch structure proposed above is correct, the reduced product should have the structure



$$\cdots-\overset{\beta}{\mathrm{CHD}}\mathrm{CH_2}\overset{\alpha}{\mathrm{CHD}}\mathrm{CH_2}-\underset{\mathrm{CH_2D}}{\overset{\mathrm{br}}{\mathrm{CH}}}-\overset{\alpha}{\mathrm{CHD}}\mathrm{CH_2}\overset{\beta}{\mathrm{CHD}}\mathrm{CH_2}-\cdots$$

The spectra shown in Figure 1 are entirely in accordance with this prediction. The lower spectrum, marked "1×", shows only the main resonances for CH_2 and CHD carbons. The latter is a triplet from $^{13}C-^{2}H$ scalar coupling of 19.0 Hz, corresponding to a $^{13}C-^{1}H$ coupling of 123.8 Hz, a normal value for a paraffinic chain. Direct bonding of deuterium to ^{13}C shifts the resonance upfield, as can be clearly seen. The main CH_2 resonance is itself also shifted upfield from the normal polyethylene position (see Table I and discussion below). The lines of the CHD triplet are somewhat