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Notes

NMR Spectra of Polyelectrolytes in Poor Solvents Are Consistent with the Pearl Necklace Model of the Chain Molecules

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A theory formulated by Kantor and Kandar[1] and elaborated by Rubinstein and his collaborators[2] predicted that the molecular chains of polyelectrolytes assume in poor solvent media a "pearl necklace structure" in which parts of the chain collapsed to compact beads are connected by flexible chain segments. This prediction was confirmed by Geissler and his collaborators,[3] who studied poly(methacryloylethyltrimethylammonium methyl sulfate) (PEMS) with a molecular weight of 26 × 10^6 in a water/methanol mixture close to the polymer precipitation point. Dynamic light scattering and SANS data were interpreted as indicating that $^2/_3$ of each chain molecule contained in three compact globules with a radius of 28.3 nm were connected by flexible chain segments. Here we show that the difference in the NMR spectra of three polyelectrolytes in water and in a water/methanol mixture close to the polymer precipation point is consistent with the "pearl necklace structure".

Some years ago, Spěváček and Schneider[4] showed that when isotactic and syndiotactic poly(methyl methacrylate) (PMMA) form a stereocomplex in solution, the association of chain segments leads to a drastic reduction of their mobility so that their high-resolution ^{1}H spectrum is no longer observable. A similar behavior in solutions containing only isotactic PMMA, only syndiotactic PMMA, or poly(vinyl chloride) could also be used to study their molecular association.[5a] More recently, Spěváček and his collaborators used the reduction in the NMR spectral intensity to demonstrate a thermal phase tramsition with the formation of globular structures in a D_2O solution of poly(vinyl methyl ether)[5b] and in a gel of poly(*N*,*N*-diethylpropionamide).[5c] In a similar manner, Durand, Hourdet, and Lafumo[6] studied the behavior of poly(acrylic acid) carrying grafts of poly(*N*-isopropylacrylamide) and found that the NMR spectrum of the side chains gradually disappeared as the temperature was raised, reflecting their association to compact structures. The proposal of the pearl-necklace structure would then lead us to expect that with a polyelectrolyte in a poor solvent only the flexible chain segments connecting the compact globules would contribute to the NMR spectrum.

Table 1 lists for the sodium salts of poly(styrenesulfonic acid) (PSS), poly(acrylic acid) (PAA), poly(methacrylic acid) (PMA) and for polyacrylamide (PAAm) the molecular weight *M*, the concentration *c*, the volume fraction of methanol in a water/methanol mixture which leads to the precipitation of the polymer, $(v_m)_p$, the volume fraction of methanol in the mixture in which the NMR spectrum was recorded $(v_m)_{NMR}$, and the ratio *R* of the NMR spectral intensity in the water/methanol mixture to that in water. It is seen that the spectral intensity decreases sharply in the poor solvent for the polyelectrolytes but remains essentially unchanged for the uncharged polyacrylamide. It should be stressed that the portion of the polyelectrolyte spectrum still observed in the poor solvent exhibits a similar resolution as in water. These observations indicate that while part of the polyelectrolyte chains have collapsed to compact globules, the segments of the chain connecting these globules retain the flexibility characteristic of their behavior in a good solvent medium.

Table 1. Reduction of the NMR Spectral Intensity of Polyelectrolyte Solutions Close to Their Precipitation Point

	PSS	PAA	PMA	PAAm
M	70000	50000	730000	340000
c (g/mL)	0.0064	0.0095	0.0024	0.0066
$(v_m)_p$	0.69	0.31	0.47	0.28
$(v_m)_{NMR}$	0.65	0.30	0.46	0.28
R	0.73	0.68	0.68[a]; 0.61[b]	1.05

[a] Methyl protons. [b] Methylene protons.

The *R* values of 0.73 for PSS and 0.68 for PAA suggest that 27% and 32%, respectively, of the mass of these polyelectrolytes collapsed to compact globules which did not contribute to the NMR spectrum. The PMA results exhibited a special feature: Whereas the *R* value was identical, within experimental error, for the aromatic and aliphatic protons in PSS and for the methine and methylene protons in PAA, the PMA *R* values were 0.68 for the methyl and 0.61 for the methylene protons, suggesting that the methyl groups retain some freedom of rotational motion in the globules.

In comparing our results with those of Geissler and his collaborators,[3] the following points may be made: (a) Our estimate of the fraction of the polyions in which motions are so restricted that the NMR spectrum is no longer observed is much smaller than their estimate of the fraction of the polyion in the compact globules. This difference may be due to our use of polymers of much lower chain length where a low molecular weight fraction might not have exhibited globule formation. (b) Our approach did not allow us to estimate the size of the globules. (c) On the other hand, the fact that the spectral resolution of the residual NMR spectrum in the poor solvent is the same as in water allowed us to conclude that the segments of the polyion connecting the globules in the poor solvent have the same characteristics as the polyion chains in a good solvent medium. This is not clearly apparent from the study using SANS and dynamic viscosity.

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Finally, two points should be made. (a) Whereas for uncharged polymers the coil−globule transition occurs in a single stage and is accompanied by phase separation,[7] the data of Geissler and his collaborators as well as those in the present study show that the collapse of polyelectrolyte chains occurs in two distinct stages: first to a pearl necklace structure and only later to a globule and polymer precipitation. (b) In water, solvation is favored by the attachment of ionic substituents to the hydrophobic backbone of a polymer such as polystyrene. It was polyelectrolytes of this type which were the subject of the theoretical studies of Rubinstein and his collaborators.[2,8] However, although the un-ionized PAA and PMA are soluble in both water and methanol, they precipitate from methanol solution at a critical degree of ionization.[9,10] This has been interpreted as due to the "condensation" of the counterions on the polyion in a medium of relatively low dielectric constant and the mutual attraction between the ion-pair dipoles.[10] By contrast, the precipitation of the PSS salt from aqueous solution on addition of methanol should be due both to the ion-pair interaction and the insolubility of the polystyrene backbone in both water and methanol. It is then significant that the pearl necklace structure forms in water/methanol solution in both these cases.

Experimental Section

PSS and PAA were obtained from Polysciences, and the molecular weight of these polymers as quoted by the supplier was accepted. PAAm and PMA were obtained by free radical polymerization in water solution. Since PMA tends to cross-link when vacuum-dried at elevated temperature, it was purified by dialysis and freeze-dried. The molecular weights of PMA and PAAm were estimated from their intrinsic viscosity, using the Mark−Houwink parameters of Wiederhorn and Brown[11] for PMA and of Scholtan[12] for PAAm. Polyacrylamide was dissolved in deuterium oxide or a deuterium oxide/methanol-*d* mixture. The polymeric acids were first neutralized with aqueous NaOH, before dilution with D_2O or a D_2O/methanol-*d* mixture. ^1H NMR spectra were recorded on a Bruker DPX-300. The chemical shifts in water were centered for the number of hydrogens at: PSS (δ 1.5, 3H; δ 6.8−7.7, 4H); PAA (δ 1.5, 2H; δ 2.1, 1H); PMA (δ 0.9, 3H; δ 1.6, 2H); PAAm (δ 1.6, 2H; δ 2.2, 1H). The integration of the polyelectrolyte spectra was normalized by comparison with a dimethyl sulfoxide standard.

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