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^{13}C-NMR-Spectroscopic Investigations on Precipitated Polyanion-Polycation-Complexes

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Summary

High resolution solid state ^{13}C-NMR spectra are reported for polyanion-polycation-complexes of poly(dimethyldiallyl)-ammonium chloride with some copolymers of acrylic acid and acrylamide, as well as for some component polyelectrolytes. The Coulombic interaction between the macro-ions definitely leads to changes in position and shape of the NMR signals, and an influence of anionic charge density on signal shape is observed. A stepwise transition from a disturbed ladder structure to a scrambled-egg structure with decreasing charge density of the anionic chain in the polysalt is concluded from the experiments.

Introduction

By interaction between polyanions and polycations polysalt precipitates ("symplexes") can be obtained (1). The supermolecular order of these solid symplexes still represents an open question. Two borderline structures have to be considered, i.e. an ordered ladder structure with well defined ionic bonds and a rather chaotic "scrambled-egg" structure with only a statistical charge compensation. The latter one had been proposed for the first time by MICHAELS (2) and is generally favored in the relevant publications. On the other hand, KABANOV (3) and we (4) found in some cases an indication of crystalline order as a result of WAXS investigations. As so far no solid state NMR work on these materials was found by us in the available literature, we tried to obtain further information on the supermolecular structure of symplexes by high resolution solid state ^{13}C-CP-MAS NMR spectroscopy, starting from the idea that small, well-resolved signals might indicate a rather high state of ordering of the macroions, while broad, poorly resolved signals should be more consistent with the scrambled-egg model. Some preliminary results with symplexes of different charge-density of the anionic component are summarized in this communication.

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Materials and Methods

Relevant data on the polymer samples employed are to be seen from Table 1. For symplex formation, a 1 % by weight aqueous solution of the anionic component was reacted under stirring with a 1 % by weight cationic polyelectrolyte solution. Dosage of the oppositely charged polyelectrolyte was performed continously by a peristaltic miniflow pump at a dosage rate between 5 and 10 ml/min. The addition of the cationic solution was stoped after flocculation of the symplex aggregates. The stoichiometric ratio of cationic to anionic groups at the flocculation point was in agreement with our recently published results (5). After standing for 12 h a phase separation was observed, the supernatant liquid was decanted and the symplex precipitate was dried at room temperature. The dry samples were desintegrated by cutting or milling, and then used for the ^{13}C-NMR-measurements.

The NMR-measurements were performed with a homebuilt ^{13}C-NMR pulse spectrometer, operating at 15.087 MHz. The proton decoupling field strength was 1.5 mT. Spectra were recorded with magic angle sample spinning at a rate of 2 kHz (6).

Table 1
Polyelectrolyte samples for symplex formation

Sample		Average distance between charge centers /nm/	$/\eta/$ in 0.1 n NaCl	Viscosimetric molecular weight in g/mol
A0	Na-polyacrylate	0.25	573.1 ± 9.6	$5.26.10^6$
A4	Copolymer of Na-acrylate and acrylamide	1.26	835.5 ± 5.6	$2.15.10^6$
A8	Copolymer of Na-acrylate and acrylamide	2.27	675.2 ± 4.5	$2.24.10^6$
A10	Copolymer of Na-acrylate and acrylamide	2.77	-	
PDMDAAC	Poly(dimethyl-diallyl)-ammonium-chlorid	0.38	62.47 ± 0.52	$4.0.10^4$

Results

The ^{13}C-NMR-spectra of the polyelectrolytes AO and PDMDAAC as well as of the symplexes AO/PDMDAAC, A4/PDMDAAC and A10/PDMDAAC are shown in Figure 1. With PDMDAAC, a fairly resolved group of signals is found in the region 20 to 90 ppm and is obviously to be assigned to the C-atoms of the different CH-, CH_2- and CH_3-groups of the repeating unit (Figure 2). With polyacrylic acid (sample AO) a group of well-resolved signals between 30 and 70 ppm is obtained, obviously originating from the CH-and the CH_2-groups of the backbone chain. The frequency range of this group of signals is rather small as compared to that of PDMDAAC. Furtheron, a well-resolved small signal is visible with AO at 187 ppm, originating from the C-atom of the carboxylic group. In contrast to the spectra of PDMDAAC and AO, no signal at all was found with the sample A8 in the frequency range of the -COOH-group, and only very weak, barely resolved signals were found in the CH-/CH_2-group region even after 10000 scans. The ^{13}C-NMR-spectra of the symplexes investigated so far, i.e. the combinations

AO/PDMDAAC - A4/PDMDAAC - A10/PDMDAAC

are generally characterized by rather well-resolved signals in the "carboxylic group range" as well as in the "CH/CH_2-group range", the carboxylic group signal being found at 180 ppm without significant differences in frequency between the three symplex samples. It should be stressed here that this signal is clearly visible even with the symplex combination A10/PDMDAAC, while with the anionic polyelectrolyte A8 alone of somewhat higher charge density no signal at all could be detected in this region.
In the order of the anionic components AO - A4 - A10 the signals in our symplex spectra become broader and poorer resolved. This holds especially true with the signal at 180 ppm, which is very small in the case of the A-O-symplex, but appears to be rather broad and asymmetric with the A10-symplex, while the signal shape of the A4-symplex takes a position between the other two.
A qualitative comparison of the signal intensities in the "carboxylic group" and the CH/CH_2-region of the three symplex spectra leads us to the conclusion, that the $-COO^-$- as well as the amide group are contributing to the signal at 180 ppm in the case of the A4- and the A10-symplex.

Discussion and Conclusions

The results presented here indicate rather clearly that symplex formation between an anionic and a cationic polyelectrolyte does not lead to a mere superposition of the ^{13}C-NMR-spectra of the components, but to a definite change in the frequency position and the shape of the signals. This holds especially true for the signal at 187 ppm assigned by us to the $-COO^-$- and the $C(O)NH_2$-group. This is on line with other investigations (7) of sodium acrylate-acrylamide copolymers in aqueous solution by ^{13}C-NMR-spectroscopy with signals observed between 185 and 180 ppm. By symplex formation this signal is shifted from 187 to 180 ppm in the solid state ^{13}C-NMR-spectra and simultaneously becomes generally smaller and better resolved by this interaction. While with a copolymer of acrylamide and acrylic acid of low charge density no signal at 187 ppm was detectable, this signal became clearly visible after symplex formation of a similar polyanion of even somewhat lower charge density with PDMDAAC. For an interpretation these findings we assume that the transfer of magnetization from protons to the C-atoms, i.e. the occurrence of cross polarization is favored by the neighbourship of sequences of the PDMDAAC-chain to the COO^{-} - resp. $C{\lesssim}^{O}_{NH_2}$-groups. This effect obviously overcompensates a counteracting one, i.e. a possible line-broadening by the presence of N-quadrupol nuclei in the environment of

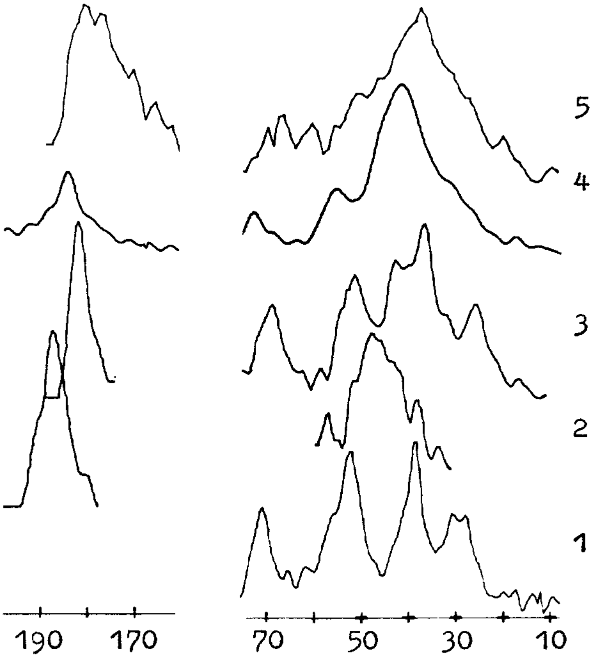

Figure 1:
^{13}C-NMR spectra
1 - PDMDAAC
2 - AO
3 - AO/PDMDAAC
4 - A4/PDMDAAC
5 - A10/PDMDAAC

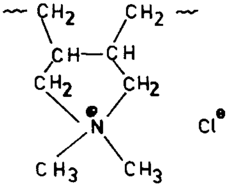

Figure 2: Repeating unit of PDMDAAC

the carboxylic resp. carboxamide C-atoms.
Besides these general effects of symplex formation on the ^{13}C-NMR-spectra of the component polyelectrolytes, a special influence of charge density on the symplex spectra compared here is observed. With decreasing charge density of the anionic component, signal resolution becomes poorer and a signal broadening is observed. The pronounced asymmetry of the 180 ppm signal in the case of the combination A10/PDMDAAC might be caused by a rather broad distribution of conformational states of the anionic chains, although a distribution of different states of tacticity may play some part, too. As here also the signals in the CH/CH$_2$-region are significantly broadened as compared to the symplex A0/PDMDAAC, and as the anionic chain obviously contributes to a minor extend only to this group of signals, a rather wide distribution of structural states may also be concluded for the cationic chains in that symplex.
Our ^{13}C-NMR spectroscopic results available up to now on symplexes indicate that at least some short-range supermolecular order exists here, which affects the solid state NMR spectrum without leading in any case to crystalline peaks in the WAXS pattern. With decreasing charge density of one symplex component, in our case the anionic one, this state of supermolecular order obviously decreases and finally approaches the borderline case of a chaotic "scrambled-egg" structure. This continuous transition from a "disturbed ladder structure" to a "scrambled-egg structure" with decreasing charge density, i.e. increasing distance between charge centres along the anionic chain, seems to be reasonable from a sterical point of view, as the probability of a good "steric fit" in the Coulombic interaction between anionic and cationic groups along a larger sequence of the polyelectrolyte chains is diminished by an increasing difference in component charge density. These consideration on the influence of charge density on the supermolecular ordering of symplexes of course require further experimental evidence before being definitely proven, but they are in agreement also with the macroscopic properties of our symplex samples, i.e. a high degree of brittleness in the case of A0, and a more leather - or rubber-like behavior in the case of A10 as the anionic component.

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