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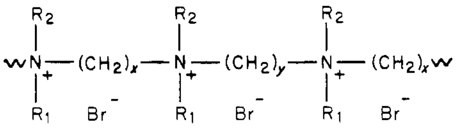
Communications to the Editor

A New Class of Cationic Polysoaps

We have prepared a novel class of macromolecules which contain the combined properties of polyelectrolytes and micellar electrolytes. These structures can be formed by the polymerization method of Rembaum[1,2] and have the general structure



$$\sim\overset{R_2}{\underset{R_1\ \ Br^-}{N^+}}-(CH_2)_x-\overset{R_2}{\underset{R_1\ \ Br^-}{N^+}}-(CH_2)_y-\overset{R_2}{\underset{R_1\ \ Br^-}{N^+}}-(CH_2)_x\sim$$

where *x* and *y* can have the same or different values, and R_1 and R_2 are alkyl groups of the same or of different lengths. Because these structures are ionene salts and because the R_1 and R_2 groups can be long chain alkyl groups, i.e., octyl or dodecyl, we refer to them as *ionene polysoaps* since they are analogous to the cationic polysoap structures first investigated by Strauss.[3-7] Ionene polysoaps differ from polysoaps inasmuch as the former structures contain the repeating charges and alkyl groups incorporated at definite distances in the backbone of the chain whereas the latter structures contain the repeating charges and alkyl groups pendant from the chain and statistically arranged. Using the appropriate diamine and dibromide comonomers, the values of *x* and *y* and R_1 and R_2 can be varied in the resulting ionene polysoaps.

Here we report the synthesis of the ionene polysoaps, poly[(methyldodecylimino)propylene bromide] (3-3R12), poly[(methyldodecylimino)pentylene bromide] (5-5R12), and poly[(methyloctadecylimino)pentylene bromide] (5-5R18), and their viscosity measurements in 0.0050 M KBr in 50/50 ethanol–water and in 0.0050 M KBr in absolute alcohol at 25 °C.

To prepare 3-3R12, the diamine comonomer was synthesized. One mole of dibromopropane was added dropwise to an ethanol solution containing 2 mol of *N*-methyldodecylamine and refluxed for 2 days. The diamine dihydrobromide, a white solid obtained after vacuum evaporation of the solvent, was treated with concentrated NaOH solution to pH 12. The free diamine was extracted with ether and the ether layer was dried over K_2CO_3. Equimolar amounts of the diamine and the dibromopropane dissolved in methanol–dimethylformamide solvents were mixed and allowed to react for 2 days at room temperature. The 3–3 ionene polysoap 3-3R12 was obtained as a white precipitate, which was washed with solvent and then acetone and vacuumed dried at 50 °C. Elemental analysis gave C, 57.26 (59.99); H, 10.90 (10.70); N, 4.56 (4.37); Br, 24.71 (24.94), with the theoretical values in parentheses. The nitrogen to bromine molar ratio was found to be unity.

To prepare 5-5R12 and 5-5R18, the diamine comonomer was synthesized first from the respective alkyl methylamine and glutaraldehyde. The amine was mixed with glutaraldehyde in a 2:1 ratio in 95% ethanol and then reduced with hydrogen over a Pd–charcoal catalyst. The resulting diamine was obtained by evaporating off the alcohol. It was purified by converting it to the hydrochloride followed by neutralization with 5% $NaHCO_3$ and extracting the diamine with ether. The ether solution was dried over K_2CO_3 and, after filtering, the ether was removed by vacuum evaporation. The 5–5 ionene polysoaps were obtained by reacting equimolar quantities of the diamines with dibromopentane under reflux at 28 °C. The lauryl diamine reaction was run in 25% methanol in dimethylformamide for 5 days, and the octadecyl diamine reaction was run in benzene for 5 days. In each case the ionene polysoap was obtained as a white precipitate. The precipitate was filtered off, washed with solvent and then acetone, and finally vacuum dried at 50 °C. Elemental analysis yielded the respective following percentages of carbon, hydrogen, nitrogen, and bromine with the theoretical values in parentheses: lauryl, 62.07 (58.73), 10.99 (10.83), 4.02 (4.20), 22.94 (25.30); and octadodecyl, 64.96 (64.15), 11.41 (11.45), 3.52 (3.07), 20.10 (18.15). The nitrogen to bromine molar ratios were unity.

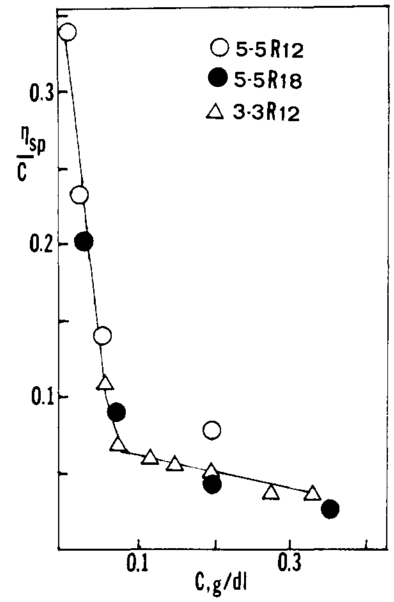


Figure 1. Reduced viscosities in 0.0050 M KBr absolute ethanol.

The NMR spectra obtained of the pure diamines and their respective polysoaps, 11% in D_2O, were very similar, exhibiting a strong absorption at δ 1.4 due to the methylene groups and weaker absorption in the δ 2.0 region. Infrared spectra exhibited absorption only in the C–H stretching region from 2500–3000 cm^{-1} and at 1420 cm^{-1} due to the C–N stretch.

The viscosity measurements were performed at 25 °C in 0.0050 M KBr solution, using an absolute ethanol and a 50% ethanol–water mixture as solvents. A Canon-Ubbelhode dilution type viscometer was used.

The long chain alkyl groups pendant from each quaternized nitrogen in the ionene polysoaps render them of limited solubility in water and so viscosity measurements were performed using 0.0050 M KBr in 50/50 water–alcohol mixtures and in absolute alcohol. Figure 1 shows the viscosity results for the 5-5R12, 5-5R18, and 3-3R12 in absolute alcohol solutions of 0.0050 M KBr. Two features of Figure 1 are of immediate note. The curve is fairly independent of polysoap concentration at the higher concentrations and increases sharply with dilution approaching the ordinate asympotically, and all of the ionene polysoaps fall on the same curve within experimental error. The shape of the curve is reminiscent of the viscosity behavior of linear, flexible polyelectrolytes in salt-free or

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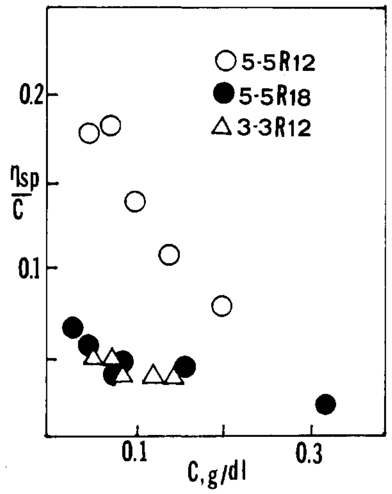

Figure 2. Reduced viscosities in a 0.0050 M KBr 50/50 water–ethanol mixture.

in extremely dilute salt solutions. On dilution in such solvents, the charges in the ionic atmosphere about the polyion distribute themselves at large distances from the chain causing decreased shielding of the backbone charges with concomitant elongation. It is interesting that 3-3R12 and 5-5R12 show this polyelectrolyte effect to the same extent, indicating that while the linear charge density is important, another effect is dominant. The reduced viscosities at a definite concentration can be used to compare the effective hydrodynamic volumes of the polymer molecules if the contour degrees of polymerization of the polymers are similar. Linear 3–3 and 4–4 ionene bromides are reported[8] to have molecular weights over a small range when they are prepared by the method used to prepare the ionene polysoaps. In our laboratory, $[\eta]$ in aqueous 0.40 M KBr for samples of linear 3–3 and 4–4 ionene bromides were found to be 0.13 and 0.12 dL/g, respectively. There is no reason to expect that the main backbone of the ionene polysoaps would have lengths differing greatly from those of their linear analogues. Then the relative effective hydrodynamic volumes of the ionene polysoaps presented here could be compared at the same concentration even if this approximation is somewhat crude. The results in Figure 1 indicate that each of the ionene polysoaps has the same degree of compactness in ethanol solution regardless of whether the alkyl side chain is a dodecyl or an octadecyl group. This indicates that the apolar interactions of these alkyl branches are not only dominant over the electrostatic effect of the linear charge density of the chain, but are independent of the length of the alkyl branches and independent of the charge density of the chain. It would be of interest to investigate ionene polysoaps with smaller alkyl branches.

Figure 2 shows the reduced viscosity results of 3-3R12, 5-5R12, and 5-5R18 in 0.0050 M KBr, using a 50/50 ethanol–water mixture. Here the 5-5R18 and the 3-3R12 appear to have the same degree of compactness over the concentration range employed. It is interesting that *linear* 3–3, 4–4, and 6–6 ionene bromides prepared in our laboratory had reduced viscosities at 0.3 g/dL in 0.005 M KBr in 50/50 ethanol–water mixtures of 0.29, 0.38, and 1.31, respectively, indicating a more extended structure than the ionene polysoaps compared in Figure 2. Upon comparison with the reduced viscosity values for these polysoaps in Figure 1, it is noted that above 0.1 g/dL the reduced viscosities are essentially the same as those in absolute ethanol and in 50% ethanol, while below this polysoap concentration the rise in the curve with dilution is steeper in pure ethanol. Similar findings have been reported for poly(2-vinyl-*N*-*n*-dodecylpyridinium bromide) in water and in 92.80% ethanol,[3] where the greater rise in the reduced viscosity curves was found with the lower dielectric solvent. In Figure 2 it is apparent that the 5-5R18 is more compact than the 5-5R12 polysoap, probably due to greater apolar interactions. Analogously, it was reported that the greatest reduced viscosity decrease occurred in increasing the percent of polysoap character of poly(4-vinyl-*N*-ethylpyridinium bromide).[6]

Interesting and potentially useful ionene polysoap structures can be synthesized without great difficulty. They may provide useful models for cell membranes.

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References and Notes

(1) H. Noguchi and A. Rembaum, *Macromolecules*, **5**, 253, 261 (1972).
(2) H. Noguchi and A. Rembaum, *J. Polym. Sci., Polym. Lett. Ed.*, **7**, 383 (1969).
(3) U. P. Strauss and E. G. Jackson, *J. Polym. Sci.*, **6**, 649 (1951).
(4) E. G. Jackson and U. P. Strauss, *J. Polym. Sci.*, **7**, 473 (1951).
(5) U. P. Strauss, S. J. Assony, E. G. Jackson, and L. H. Layton, *J. Polym. Sci.*, **9**, 509 (1952).
(6) U. P. Strauss and N. L. Gershfeld, *J. Phys. Chem.*, **58**, 747 (1954).
(7) U. P. Strauss, N. L. Gershfeld, and E. H. Cook, *J. Phys. Chem.*, **60**, 577 (1956).
(8) D. Casson and A. Rembaum, *Macromolecules*, **5**, 75 (1972).

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On the Poly(β-DL-aspartic acid)

The determination of the ratio of α and ω linkages in aspartyl, glutamyl, and lysyl residues in polypeptides or poly(amino acids) is an important problem. However, until recently no general method for the determination of α- and ω-amino acid residues in poly(amino acids) has been reported. In the previous study from this laboratory, the determination of α- and ω-amino acid residues of aspartic acid,[1] glutamic acid,[2] and lysine[3] in poly(amino acids) by potentiometric titration has been reported. In a series of studies of the α- and ω-linkage determination, it is necessary to characterize authentic poly(β-DL-aspartic acid) (β-PAA) in order to test the applicability of the analytical method. The β-PAA was prepared by two different methods.[4,5] However, the structure of both β-PAAs prepared was a mixture of α- and β-aspartyl residues. The fact is an unexpected result, and we would like to report the analytical results in this communication.

One preparation of β-PAA was carried out by using the six-membered *N*-carboxyanhydride (NCA).[4] In this preparation, α-methyl DL-aspartate was converted to its corresponding NCA, and the NCA was polymerized in dioxane, using triethylamine as an initiator. The resulting poly(α-methyl β-DL-aspartate) was hydrolyzed partially with KOH–methanol at room temperature to obtain poly(β-DL-aspartic acid) [β-PAA(OH)]. The other poly(β-DL-aspartic acid) [β-PAA(H)] was synthesized by the active ester method.[5] The β-PAA(H) was prepared by polycondensation of α-benzyl β-pentachlorophenyl DL-

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