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Communications to the Editor

A Novel Type of Ionomer Based on a Nonstoichiometric Polyelectrolyte–Surfactant Complex

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Ionomers are usually defined as nonpolar polymers with a hydrocarbon backbone carrying up to 10 mol % salt groups. Normally, ionomers are obtained either by a copolymerization reaction of appropriate monomers or by chemical modification of a polymer via covalent bonding of polar groups to a nonpolar polymer.[1] Such reactions result in copolymer formation with a microstructure predetermined by synthesis. Therefore, the microstructure cannot be altered without the disruption of covalent bonds. The location of the salt groups in an ionomer chain can influence substantially the aggregation of the salt groups and the structure and properties of an ionomer in nonpolar solvents and in the bulk.

In this paper we propose the synthesis of a novel type ionomer based on a nonstoichiometric complex (NPC) between a polyelectrolyte (PE) and an oppositely charged surfactant (SA). Such an NPC may be considered as an amphiphilic compound consisting of polar and relatively nonpolar structural segments. Most of the PE chain units form coulombic bonds with SA molecules, thus providing a relatively nonpolar structural segment of the NPC. Excessive PE chain units (up to 10–16 mol %) carrying ordinary low-mass counterions can play the role of salt groups of the ionomer with a pronounced tendency to aggregate in nonpolar media. One can anticipate that the location of salt groups in such ionomers will not be strictly fixed because of the possibility of mutual migration of SA and other low-mass ions, i.e., due to ion-exchange reactions in nonpolar media.

The synthesis of NPC with a slight excess of (up to 10–16 mol %) PE chain units is difficult. Interaction between PE and oppositely charged SA molecules can lead to the formation of polymer–colloidal complexes in a water solution.[2–8] The formation of either water-soluble or nonsoluble (PE–SA) complexes takes place at different [SA]/[PE] concentration ratios.[2,5] In the latter case stoichiometric complexes (SPC) with equimolar contents of PE chain units and SA molecules are formed. Since the composition of water-soluble complexes depends on [SA]/[PE], one could suggest the synthesis of NPC of the above type by mixing water solutions of PE and SA taken at the proper concentration ratio. However, there is a disproportionation in a water solution of PE and SA mixtures which occurs at [SA]/[PE] > 0.2 (molar concentration ratio).[5] An increase of the SA concentration above [SA]/[PE] > 0.2 leads to phase separation in the SA–PE mixture with the formation of SPC in the precipitate, while the {PE–SA} complex with [SA]/[PE] = 0.2 composition remains in solution. A further increase of [SA] in the mixture ([SA]/[PE] > 0.2) is accompanied by an increase of the mass of SPC at the expense of NPC of the same composition.[5] The disproportionation in PE–SA mixtures, which is due to hydrophobic interactions,[9] precludes the synthesis of NPC in a water solution with a composition above 0.2.

In order to eliminate disproportionation in the PE–SA mixture, we have tried to synthesize NPC in nonaqueous organic solvents. Our recent data have shown[10] that in such relatively polar organic solvents as DMSO or aliphatic alcohols, where both PE and SA are soluble, one still cannot obtain NPC because of their dissociation into individual components.

However, one can synthesize NPC using relatively nonpolar organic solvents. We have found recently[11] that SPC obtained from oppositely charged PE and SA of various chemical nature in a water solution are dissolved in such relatively nonpolar organic solvents as, for example, chloroform and benzene. The dissociation into the individual components is prevented, since at least one of the components of SPC, i.e., PE, is not soluble in the nonpolar solvent.[11]

We used poly(*N*-ethyl-4-vinylpyridinium bromide) (PEVP), synthesized from poly(4-vinylpyridine) (Scientific Polymer Products),[12] and sodium dodecyl sulfate (SDS), purchased from Sigma, as PE and SA components of the SPC, respectively. The degree of quaternization of PEVP ($\overline{DP}$ = 500) was greater than 95% based on IR and UV spectroscopy.[11,12] The SPC was obtained by mixing PEVP and SDS aqueous solutions, isolating the resulting precipitate, washing it 2–3 times with twice-distilled deionized water, and drying in a vacuum desiccator over P_2O_5 for 5 days.[5,11] The synthesis of NPC was carried out in the mixed organic solvent with 99.5 vol % chloroform and 0.5 vol % methanol. The initial PEVP and SDS are not soluble in this mixed solvent, while SPC{PEVP–SDS} is soluble in the same solvent. We used an exchange reaction between SPC and PE to obtain NPC of a certain composition. The exchange reaction was carried out by mixing the PEVP solution in methanol and the SPC{PEVP–SDS} solution in chloroform in the volume proportion mentioned above.

The reaction consists of an exchange of dodecyl sulfate and bromide anions between SPC and PEVP, respectively. The occurrence of this reaction was confirmed by the formation of a transparent solution after the SPC and PEVP solutions were mixed. The same experiment in the absence of SPC leads to the formation of a highly dispersed precipitate, since PEVP is not soluble in the mixed solvent. The final NPC was isolated by vacuum evaporation of the mixed solvent. The isolated NPC was further dried under vacuum at T = 40 °C for about 1 day to completely eliminate trace amounts of solvents. The samples of NPC with 5, 10, and 16 mol % excess PEVP groups were

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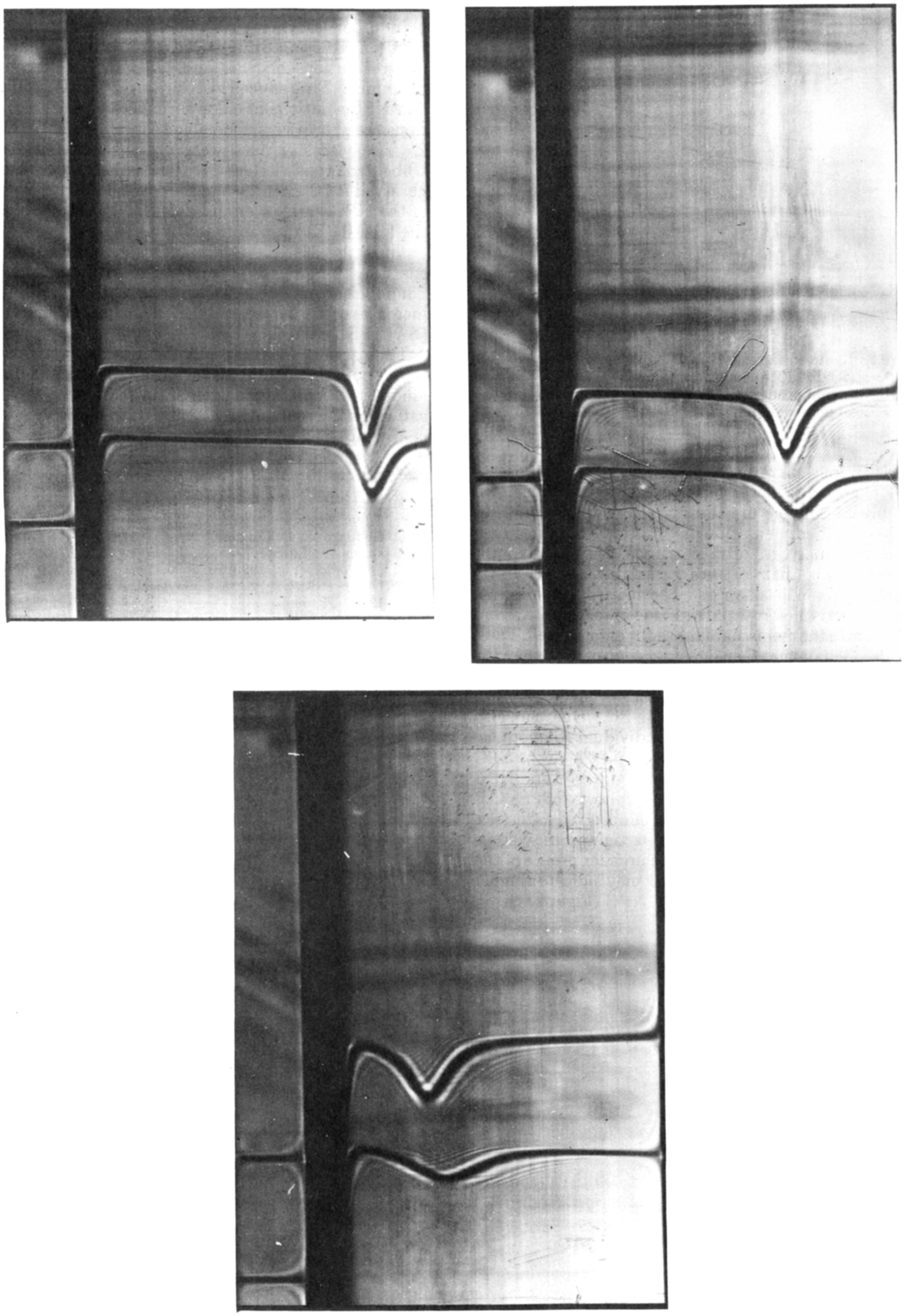

Figure 1. Schlieren patterns of a SPC solution (upper curve) and a NPC solution (lower curve) in chloroform. Pictures were taken after (a) 32, (b) 56, and (c) 120 min. The right side of the pictures corresponds to the bottom of a sedimentation cell and the left side to the meniscus. [SDS]/[PEVP] (in mol/monomeric unit) are 1.0 (upper curve) and 0.9 (lower curve). [PEVP] = 0.7 g/dL.

obtained. The composition of the NPC was confirmed by elemental analysis.

It was shown that the NPC's obtained in this way are soluble in chloroform. Schlieren sedimentation patterns

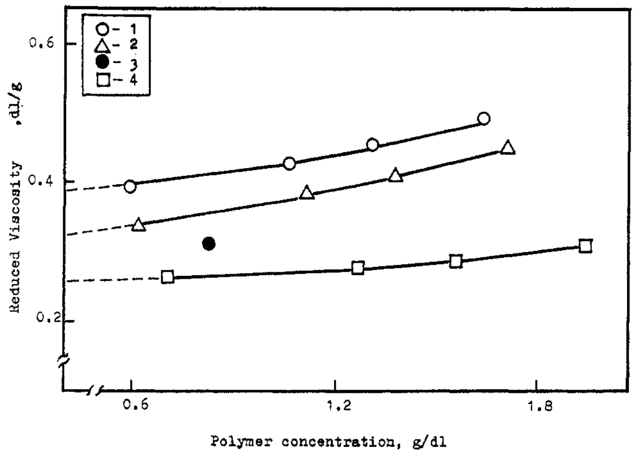

Figure 2. Reduced viscosity versus polymer concentration for SPC (1) and NPC (2–4) solutions of variable compositions in chloroform. Compositions, expressed as the [SDS]/[PEVP] molar ratio of monomeric units, are 1.0 (1), 0.95 (2), 0.90 (3), and 0.84 (4).

of SPC (upper curve) and NPC with 10 mol % excess PEVP chain units (lower curve) in chloroform are shown in Figure 1. The pictures were taken over the course of 32–120 min. Sedimentation pictures were obtained on a Beckman-E analytical ultracentrifuge, ω = 48 000 rpm.[13] One can stress that in both cases the sedimentation patterns represent peaks oriented downward. The position of both peaks is moving from right to left in time, i.e., from the bottom to the meniscus of the sedimentation cell. Thus, one can conclude that there is a migration of both the SPC and the NPC complexes.[14] The observed migration may be due to the higher density of chloroform compared to the density of the SPC and the NPC. One can also conclude that SPC and NPC are individual compounds. This is evidenced by the symmetrical profile of the SPC and NPC peaks. From comparison of the SPC and NPC peaks at different periods of time, it follows that SPC is migrating at a slightly higher rate. The observed difference in rate may be related to the smaller partial specific volume of the NPC compared to SPC. The broader profile of the NPC peak compared to the SPC peak may indicate a higher diffusion coefficient in the case of NPC (Figure 1).

In order to clarify the conformational differences between NPC and SPC, we have studied the behavior of dilute solutions of SPC and NPC by the viscometry technique. The reduced viscosities, η_{red}, of SPC solutions and NPC solutions in chloroform with various compositions are shown versus polymer concentration in Figure 2. The viscosity data were obtained on a standard Ubbelohde type viscometer. The highest value of $[\eta]$ is observed for the SPC, while the corresponding $[\eta]$ values of the NPC's are lower and decrease upon a decrease of the [SA]/[PE] ratio in the NPC.

Thus the viscosity data indicate a more compact conformation of NPC compared to SPC particles in a nonpolar solvent. The extent of the NPC coil contraction increases with a decrease of the NPC composition, i.e., the [SA]/[PE] ratio.

The viscosity and ultracentrifugation data demonstrate some similarities in the behavior of NPC and traditional ionomers in nonpolar solvents. In both cases an aggregation of salt groups may occur in a nonpolar solvent which is accompanied by coil contraction in a dilute solution.

References and Notes

(1) Fitzgerald, J. J.; Weiss, R. A. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1988**, *C28* (1), 99.
(2) Goddard, E. D. *Colloids Surf.* **1986**, *19*, 301.
(3) Dubin, P. L.; Stephens, S. T.; Leong, M. G.; Chew, C. H. *Macromolecules* **1990**, *23*, 2500.
(4) Dubin, P. L.; Gan, L. M.; Chew, C. H. *J. Colloid Interface Sci.* **1989**, *128*, 566.
(5) Ibragimova, Z. Kh.; Kasaikin, V. A.; Zezin, A. B.; Kabanov, V. A. *Vysokomol. Soedin.* **1986**, *A28*, 1640 (translated in *Polym. Sci. USSR* **1986**, *28*, 1826).
(6) Zezin, A. B.; Fel'dshtein, M. M. *Molek. Biol.* **1974**, *8*, 142.
(7) Musabakov, K. B.; Abilov, Zh. K.; Samsonov, G. V. *Kolloidn. Zh.* **1978**, *4*, 694.
(8) Thalberg, K.; Lindman, B.; Bergfield, K. *Langmuir* **1991**, *7*, 2893.
(9) Efremov, V. A.; Khokhlov, A. R.; Shikina, Yu. V. *Polym. Sci. USSR* **1992**, *34*, 484.
(10) Unpublished data.
(11) Bakeev, K. N.; Yang, M. S.; Zezin, A. B.; Kabanov, V. A. *Dokl. Acad. Nauk SSSR* **1993**, *332*, 451.
(12) Fuoss, R. M.; Strauss, V. P. *J. Polym. Sci.* **1948**, *3*, 246.
(13) Bakeev, K. N.; Chugunov, S. A.; Teraoka, I.; MacKnight, W. J.; Zezin, A. B.; Kabanov, V. A. *Macromolecules*, in press.
(14) Williams, J. W. *Ultracentrifugation of Macromolecules*; Academic Press: New York, 1972.