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Wholly Water-Soluble Interpolymer Complexes Formed by Interaction of Strong Anionic and Cationic Polyelectrolytes

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ABSTRACT

The process of interpolymer complex formation was studied by viscometry and analytical ultracentrifugation in a system consisting of poly[acrylamide-co-(2-acrylamido-2-methyl-propylsulfonic acid)], ($\bar{M}_w = 2.5 \cdot 10^6$ g/mol), and poly(2-hydroxypropyl-1-dimethyl-ammonium chloride), ($\bar{M}_w = 3.6 \cdot 10^5$ g/mol). Investigations were conducted in two series in which the ratio, pointed out by Z, of the positive $=N^+=$ to negative $SO_3{}^-$ charged varied similarly in both, series in a range 0–330 mol%. Differences concerned the state of the anionic "host" polymer, designated generally as $Na_{[k]}$ COP X/Y, where: k denotes the degree of SO_3H groups neutralization; X the wt% of the AMPS and Y, that of the AAm comonomer in the repeating unit. In the first series the X/Y ratio varied at k = 0 (acidic form), in the second one k turned to be the variable keeping X/Y constant at the established optimal level 10/90. All complexes (symplexes) thus formed have proven to be wholly water-soluble even when obtained at the unit charge ratio Z = 1, which should be ascribed to the fact that beside wholly ionizable groups in both the counterparts additional nonionizable, but hydrophilic functions ($CONH_2$, CONH– and OH) were present. The highest increases in viscosity (η), exceeding that of the anionic "host" polymer by a factor up to 25, were observed at Z ~ 1. Beyond that point, the η vs. Z curves are decreasing and flattening off. On the grounds of established apparent sedimentation coefficients (s_c) an 8-fold relative increase in diameter (d_{rel}) for the symplex $Na_{[60]}$COP 10/90-1 (obtained at Z = 1) was estimated in relation to the "host" polymer. In the case

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of $Na_{[60]}$COP 10/90-12 where a12-fold excess of $=N^+=$ functions from the ionene prevailed, the respective value for d_{rel} was 4. Structures for the supramolecular particles were proposed which give rise to the high increases in viscosities.

Key Words: Interpolymer complexes; Symplexes; Water-solubility; Acrylamide/AMPS copolymers; Poly(2-hydroxypropyl-1-dimethylammonium chloride); Ionene; Viscosity increase; Viscosity dependence on composition; Viscosity dependence on neutralization; Schlieren pictures; Sedimentation constants.

INTRODUCTION

Among interpolymer complexes, those which are formed by compensation of oppositely signed charges, the so-called symplexes appear to be the most important. The process of their formation looks even simple considering the scheme shown in Fig. 1.

Realistically, however, it is sophisticated and due to the fact that mainly water-soluble species find applicability, intensive work has been reported during the past twenty years on how to avoid phase separations. Worth mentioning in that respect is an early report by Bungenberg de Jong and Dekker,[1] as well as later contributions provided by Kabanov and Zezin,[2] and by Dautzenberg *et al.*[3–6] who discerned many stages for the components aggregation. Also overviews have been published[7,8] from which was learned that distinct parameter limits always exist between which the one-phase system is preserved. Thus, the removal of this confinement still remains a challenging topic.

A deeper examination of papers dealing with the preparation of symplexes discloses the use of components very often having a high degree of amphiphilicity. In such cases the collapse of the particle structure is promoted by the mutual attraction of the hydrophobic fragments.

It seemed therefore, reasonable to employ exclusively components distinguished by the possibly highest hydrophilicity. Therefore, the system applied in the present work was set up by a "host" component provided by the copolymer, COP, of acrylamide, AAm, with 2-acryl-amido-2-methyl-propanesulfonic acid, AMPS, and an ionene as the "guest" component. The latter was supplied by "Aldrich" being a polyelectrolyte prepared via a

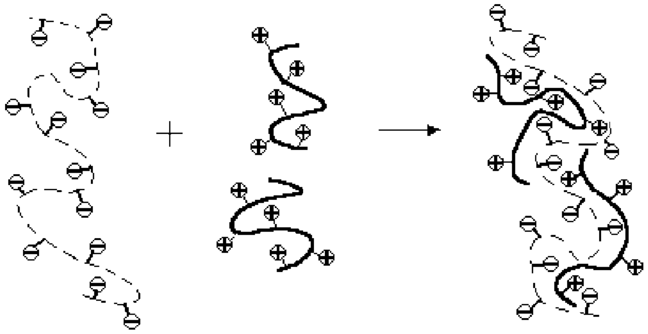

Figure 1. Schematic illustration of the symplex formation.

step growth polyreaction involving epichlorohydrin, ECh, dimethylamine, DMA, and a small amount of ethylenediamine, EDA. The anionic copolymer was laboratory made by a random radical polymerization in water from 10 wt% AMPS and 90 wt% AAm. Therefore, it was designated as COP 10/90, which ratio was found to be optimal in preliminary investigations. Respective structures and relevant data concerning the "host" and the "guest" components are presented in Fig. 2.

It should be observed that the AMPS/AAm copolymer carries three hydrophilic groups: $CONH_2$, CONH– and SO_3H, whereas the ionene contains a hydroxyl group in each unit in addition to the ammonium quat. All symplexes considered in this work were prepared by combining a stock solution (0.6 wt%) of the COP 10/90 with a stock solution (0.35 wt%) of the ionene. The mixing was carried out at room temperature and after aging the systems were submitted for investigation. The symplexes differed by two crucial parameters: the ratio of the positive to negative charges designated by "Z", and the degree "k", expressed in %, to which the SO_3H groups present in the COP 10/90 copolymer were neutralized by NaOH prior to combining both the components. The individual species were designated by sample codes derived from the general formula $Na_{[k]}$COP 10/90-Z in which the symbols "k" and "Z" were substituted by the appropriate numerical values. The measurements focused mainly on changes in rheological properties caused by altering the "k" and "Z" parameters. Investigations carried out by means of analytical ultracentrifugation were aimed at the explanation of features concerning the symplex formation.

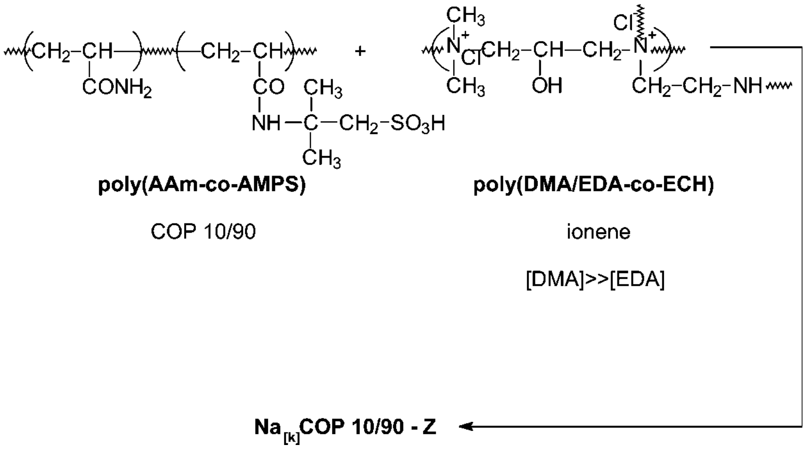

Figure 2. Particular scheme for the symplex formation, where: COP 10/90 represents the sample code for the anionic "host" copolymers prepared from 10wt% 2-acrylamido-2-methyl-propanesulfonic acid, AMPS, and 90 wt% acrylamide, AAm; $Na_{[k]}$COP 10/90-Z represents the general sample code for the symplexes: [k] means the degree (in %) of neutralization of the SO_3H groups by NaOH; Z indicates the ratio of the N^+ functions vs. SO_3^- groups; poly(DMA/EDA-co-ECH) represents the ionene used as the cationic "guest" counterpart prepared from dimethylamine, DMA, ethylenediamine, EDA, and epichlorohydrin, ECH; $\bar{M}_w$—weight average molecular mass; $D = \bar{M}_w/\bar{M}_n$ coefficient of polydispersity.

EXPERIMENTAL

Materials

Acrylamide (Aldrich, AAm), reagent grade, was recrystallized from chloroform, dried in vacuum and checked for purity by its melting point.

Ionene, a terpolymer (Aldrich), reagent grade, prepared by the supplier from epichlorohydrin, dimethylamine and ethylenediamine, mol. mass $\bar{M}_w = 3.6 \cdot 10^5$ g/mol, delivered as a 50 wt% aqueous solution, was used without further treatment.

2-Acrylamido-2-methyl-propanesulfonic acid (Fluka, AMPS), reagent grade, recrystallized from methanol.

Water was deionized and redistilled. Reagents for analyses were analytical grade.

Procedures

Polymerization of the AMPS/AAm copolymer, designated as $Na_{[0]}$COP10/90, was carried out in water as the solvent without using an initiator. AAm (27 g) and AMPS (3 g) were introduced into a thermostated 1 L vessel, equipped with a reflux condenser, stirrer, thermometer, an inert-gas inlet, and dissolved in 470 g water. Argon was bubbled continuously the entire time of the polymerization, which lasted for 6 h and was performed at 60°C. The monomer conversion was found to be 99.2%.

The Preparation of Symplexes

The preparation of the symplexes was accomplished at room temperature by combining stock solutions of the components. Five anionic stock solutions were made ready which differed by the degree of SO_3H groups neutralization over k = 0; 20; 40; 60, and 80%, respectively. In the first step, the polymerization product was adjusted to contain 6 wt% of the $Na_{[0]}$COP10/90 polymer. From this solution, aliquots of 50 g were taken, which in four cases were neutralized by the use of 0.1 M NaOH to the predetermined k values. Thereafter, the volumes of the five solutions were brought up exactly to 500 cm^3, thus fixing the polymer content in relation to $Na_{[0]}$COP10/90 at 0.6 g/dL.

The stock solution of the cationic component was prepared in the same manner by dissolving 3.5 g of the ionene contained in the 50 wt% solution (determined by freeze drying) to 500 cm^3, by which means this stock solution was fixed at 0.35 g/dL.

After aging for 24 h, adequate volumes were taken from the particular stock solutions and combined to fit the predetermined Z, and these values reflect the ratio of positive to negative charges. After 24 h, the resulting systems were submitted for investigation.

Measurements

Dynamic viscosities η of the symplexes were determined with a low-shear viscometer type HAAKE Rotovisco RV-20 connected on a computer. Volumes of 9 cm^3 were taken for the measurements which were performed according to a formulated program providing steady speeding up the rotor to 30 rps within the first 120 s, maintaining this velocity for a further 30 s, and thereafter slowing it down steadily to the starting point again during 120 s. The values for η were processed and computed by the HAAKE ROT 3.03. program based on adjusting the flow curve to that of Bingham.[9] For each sample, measurements were carried out twice.

Determination of the apparent sedimentation coefficients s_c were accomplished by the use of a reconstructed analytical ultracentrifige MOM 3180. The pattern uptake was changed principally by replacing the film cassette through a video camera of a CCD type, coupled on a computer over a video card FG 2000. Every few minutes, the Schlieren pattern was registered and transferred on-line into the computer program. The rotor velocity was fixed at 50000 rpm. The measurements were always confined to one concentration (0.59 g/dL), at 22°C.

Number- and weight-average molecular weights, from which the coefficients of polydispersity D for the components resulted, were determined using a KNAUER GPC-chromatograph conected to a computer equipped with refractometric and viscometric detectors (viscotec type). Two columns 300 × 7.5 mm each, Polymer Laboratories, packed with aquagel-OH were used. The mobile phase consisted of 0.1 M $NaNO_3$ solution in water, adjusted to pH = 7. Temperature 30°C, flow velocity of the eluate 0.5 cm^3/min. For calibration standards of pullane (Polyscience) were used.

The degree of conversion for the polymerization product was calculated from the double-bond content which was determined by means of the potassium bromate/bromide titration method.[10]

The Cl^--ion content in the ionene was estimated using the Mohr titration method.[11] For two symplexes (cf. Table 1) increases in particle volumes related to the volume of the "host" copolymer were estimated via relative diameter ratios $d_{rel} = d_Z/d_{Z=0}$ calculated from respective ratios of the Stoke's relationship $w_{sed} = d^2(\rho_s - \rho)\omega^2 r/18\eta$ in which the sedimentation velocity w_{sed} was provided by the apparent sedimentation constant $s_{c(Z)}$. By neglecting small differences in the density parameters $(\rho_s - \rho)$ for both the polymers taken into account, ratios of the Stoke's equation abbreviate to:

$$d_{rel} = \frac{d_Z}{d_{Z=0}} = \left(\frac{s_{c(Z)}\eta_Z}{s_{c(Z=0)}\eta_{Z=0}}\right)^{\frac{1}{2}}.$$

Table 1. Ratios of positive to negative charges Z, apparent sedimentation constants $s_{c(Z)}$, and relative diameters d_{rel} of symplexes $Na_{[60]}$COP 10/90-Z vs. the diameter of the "host" copolymer $Na_{[60]}$COP 10/90.

Z	$s_{c,Z}$ [Sv]	η_z [mPa s]	d_{rel}
0	3.98	5.85	—
1(a)[a]	9.00	180.0	8.34
1(b)[a]	7.99	180.0	7.86
12	7.01	53.34	4.01

[a] Values relating to peak "a" and peak "b" displayed on the Schlieren pattern in Fig. 6 for the poly-paucimolecular system.

RESULTS AND DISCUSSION

The aim of the present investigations was to broaden the scope for water-solubility of symplex particles formed by combining oppositely charged polyelectrolytes. This goal seemed to be attainable via employing components with a high density of functional groups from which one in each component was always ionizable in the whole range of pH's, and the other ones were nonionizable at all, but were hydrophilic. The above requirement was fulfilled by such hydrophilic functions as $-\overset{|}{\underset{|}{N}}{}^{\pm}-$, $SO_3{}^-$, $CONH_2$, $CONH-$, and OH present either in the AMPS/AAm copolymer, or in the respective ionene, which both provided the components (Fig. 2) in the five series of symplex preparations.

The concept appeared to be correct. As a result of mixing the non- or partly neutralized copolymers designated accordingly as $Na_{[0]}$COP10/90, $Na_{[20]}$COP10/90, $Na_{[40]}$COP10/90, $Na_{[60]}$COP10/90 and $Na_{[80]}$COP10/90 with the ionene in amounts fitting the predetermined Z ratios of opposite charges, water-soluble symplexes always originated and no phase separation occured. Without exception, all the samples prepared in 5 series which differed by the degree of neutralization (k) exhibited considerable increases in dynamic viscosity, the highest in the vicinity of $Z \sim 1$, i.e., the zero charge point (Fig. 3).

From Fig. 3, it is evident that two parameters determine the viscosity: first of all, it is the charge ratio Z and the degree of the SO_3H groups neutralization, indicated by "k" in the respective sample code.

Solubility is a key factor for many application features of symplexes and that is the reason why it still remains to be a subject of investigations. Transparency not always provides the proof for homogenity. A translucent phase, for example, set up by combining oppositely charged polyelectrolytes at polymer concentrations exceeding 5% by weight[12] exhibits a confined solubility at dilution. For practical reasons, however, it is more important to dispose of wholly soluble symplexes at moderate, or even low, concentrations. Therefore, the main focus in the literature was directed on one phase systems formed at rather low concentrations of supramolecular moieties.

In order to preserve solubility two routes have been worked up and reported in the literature.[8] Following the first one, Kabanov and Zezin[2] proposed to react high molecular weight "host" polyions with much shorter "guest" counterions at molecular mass ratios ranging between 3:1 and 10:1. According to the authors this route is confined to nonstoichiometrical systems, otherwise precipitation occurs. Contrary to Kabanov, Dautzenberg *et al.*[3–6] prepared symplexes by combining oppositely charged polyelectrolytes with comparable chain lengths. The restriction was on working at low polymer concentrations ranging between 10^{-3} and 10^{-1} g/dL, also in a nonstoichiometrical system.

The fact that in the present work the preparation of soluble symplexes was not bound to nonstoichiometrical conditions renders a new feature in that field of research. Nevertheless, the question arises over what time the solubility of such systems could be preserved?

For that purpose, measurements have been carried out correlating values of η with times of storing the samples.

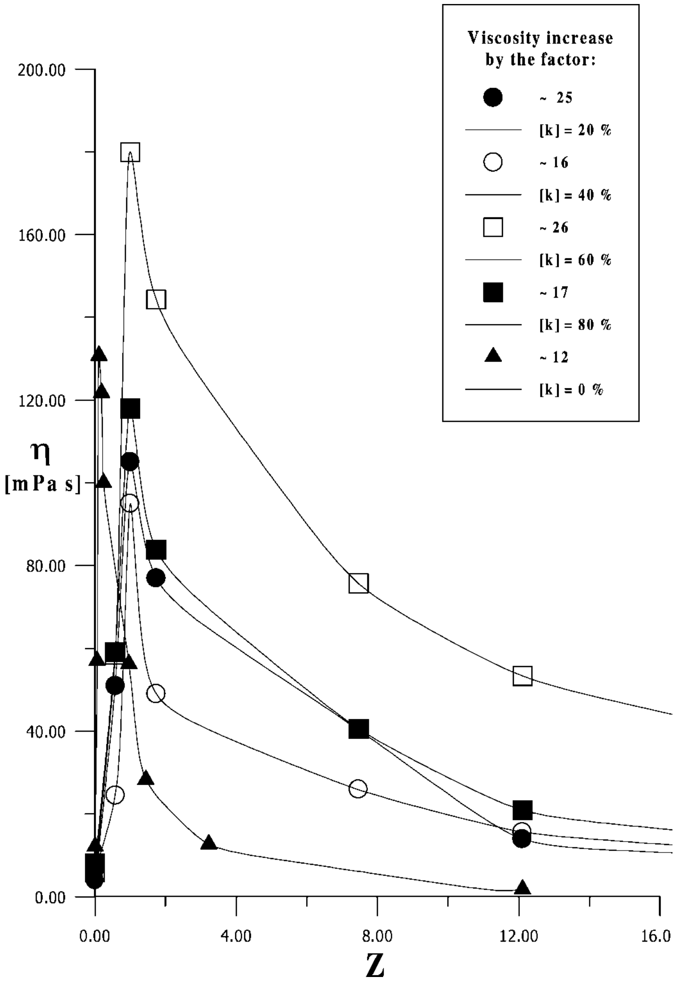

Figure 3. Dynamic viscosity, η, vs. Z relationships for series of the $Na_{[k]}$COP 10/90-Z symplexes, where [k] denotes (in %) the degree of neutralization of the SO_3H groups by NaOH and Z represents the ratio of the N^+ vs. SO_3^- functions.

In order to get an insight into the state of the aggregated particles which are forming the colloidal system some selected samples were submitted to sedimentation measurements in the centrifugal field of an analytical ultracentrifuge. Apparent sedimentation coefficients s_c ($c = 0.59\,g/dL$) were calculated from the sedimentation velocity and extrapolated to the rotation time $\tau = 0$. In Fig. 5 the diagram "a" displays the s_c vs. τ relationship for the "host" copolymer $Na_{[60]}$COP10/90-0, whereas the diagram "b" shows what happened after combining this "host" copolymer with the ionene to form the symplex $Na_{[60]}$COP10/90-1 which corresponds to the zero charge point.

By extrapolating the particular s_c vs. τ relationships to $\tau = 0$, the apparent sedimentation coefficients $s_{c(Z)}$ were found and listed in Table 1, which coefficients, together with respective values of viscosities η, gave means for the assessment of relative increases in diameters (d_{rel}) of certain symplex particles vs. the particle of the "host" copolymer (Table 1).

The viscosity curves shown in Fig. 3 are similar in shape which is characterized by a steep ascent up to the maximum value of η followed by a more or less falling off. Comparing the particular series, there are differences by which the levels of the maximum values do exceed those values of the respective anionic "host" polymers. The highest increase in viscosity is observed for the series designated by a 60% neutralization of the SO_3H groups.

In the formation of the symplex particles various interaction forces are taking part. Beside the attracting or repulsing Coulombic forces, and the hydrophobic interactions, associations via hydrogen bonds should be considered involving all the feasible functional groups and water as solvent. The latter type of interaction may explain why the said particles do not precipitate at the zero charge point. In any case, however, the structure formation is certainly complex.

It is assumed that regardless of whether the anionic "host" polymer or the ionene is in excess, the corns of the particles are always alike consisting of oppositely signed and mutually compensated chain parts as was shown by Schlenhoff and Dubas.[13] Differences are inherent in the outer layers.

CONCLUSION

In all instances, mixing of anionic AMPS/AAm host–copolymers with poly(2-hydroxypropyl-1-dimethylammonium chloride) functioning as guest–polymer provided water-soluble symplexes.

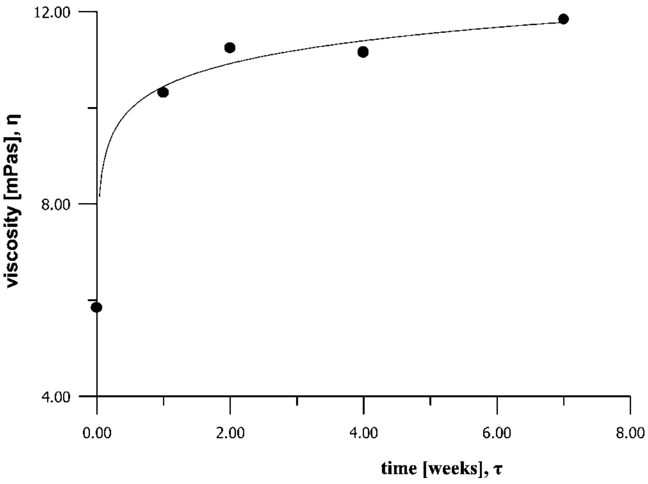

Figure 4. Changes in the dynamic viscosity η for the symplex $Na_{[60]}$ COP 10/90-1 as a result of the time of storing τ.

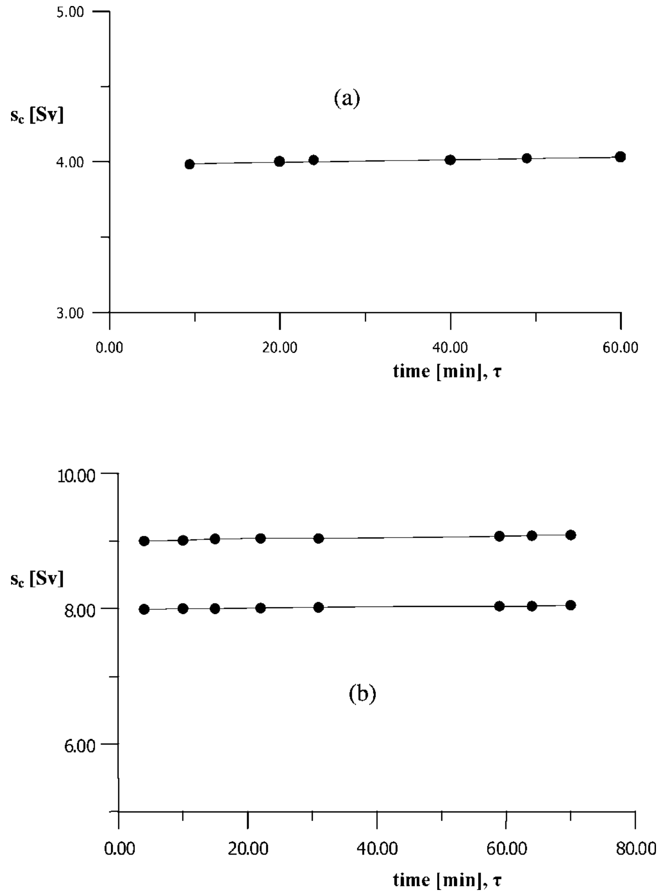

Figure 5. Apparent sedimentation coefficients, s_c, measured at the concentration $c = 0.59\,g/dL$, as a function of time, τ, of rotation ($n = 50\,000$ rpm) for the symplex $Na_{[60]}$ COP 10/90-0 (a), and $Na_{[60]}$ COP 10/90-1 (b), respectively.

Beside degrees of neutralization of SO_3H groups present in the copolymers which differed by amounts of AAm vs. AMPS units, the mole ratio Z of opposite $=N^+=$ vs. $SO_3{}^-$ charges appeared to be the main factor affecting changes in viscosity of the systems, never causing a phase separation. Carrying out the measurements at a constant moderate polymer concentrations ($c = 0.95\,g/dL$), the increase in η was the highest in the case of the $Na_{[60]}$COP10/90-1 sample and the symplex viscosity exceeded that of the anionic "host" copolymer by the factor 25. The curves shown in Fig. 3, corresponding to the particular series, display similar shapes with the maximal points about $Z \sim 1$. The only exception appeared in the $Na_{[0]}$COP10/90-Z series where the highest viscosity appeared at a somewhat lower Z-value.

Measurements correlating values of η with time of storing the samples are exemplarily shown in Fig. 4 by a curve referring to the optimal $Na_{[60]}$COP10/90-1 symplex. Determinations of η were continued over 7 weeks. They revealed a certain

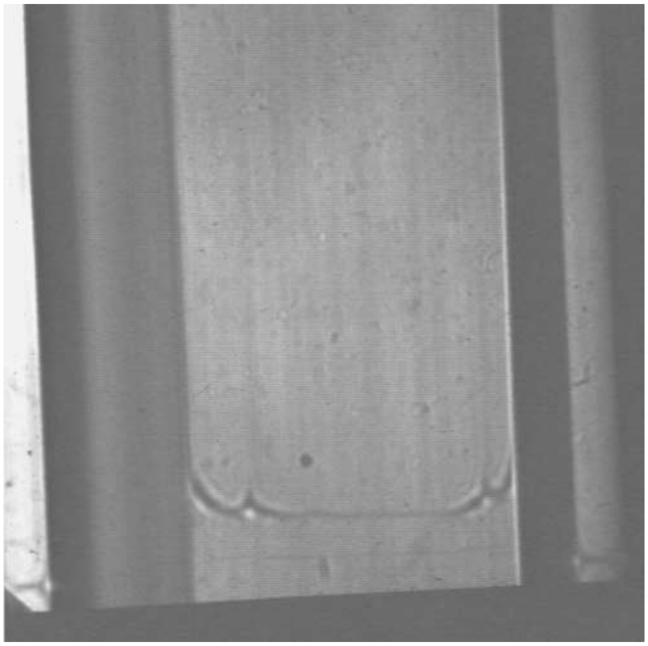

Figure 6. Schlieren pattern displayed by the symplex $Na_{[60]}$ COP 10/90-1.

increase in viscosity during the first 20 days followed by a stretching out of the curve. This increase may be attributed to conformational changes and disentanglements occurring during structure formation.[8] Keeping the samples over months at room temperature no sedimentation was observed and the samples remained dilutable with water. However, a salting out occurred at NaCl concentrations exceeding 0.6 g/dL.

From sedimentation measurements displaying s_c vs. τ relationships for the host–copolymer $Na_{[60]}$COP10/90-0 (Fig. 5a), and for the symplex $Na_{[60]}$COP10/90-1 formed by combining the above copolymer with the ionene (Fig. 5b), it should noticed that the respective Schlieren pattern for the above symplex shows not one but two peaks moving toward the bottom with different velocities (Fig. 6).

It is a clear evidence that the said system is pauci-polymolecular in the vicinity of the zero charge point what may be due to the influence of shear forces on huge particles during the sedimentation. The secondary particles thus formed differ significantly in sizes.

If, however, there is an excess of the ionene as is the case with the symplex $Na_{[60]}$COP10/90-12, the system appears to be uni-polymolecular (Fig. 7). It is the consequence of smaller primary particles present in the system capable of resisting the shear forces.

If the mutual charge compensation corresponds to $0 < Z \leq 1$, the outer shell is dominated by the copolymer with its long segments carrying $CONH_2$, CONH−, and the noncompensated SO_3^- groups. The latter vanish when the borderline $Z = 1$ is reached. The long segments protrude into the bulk aggregating with neighboring particles via hydrogen bonds formed by the amide groups. As a result, large supramolecular moieties originate giving rise to a high level of viscosity.

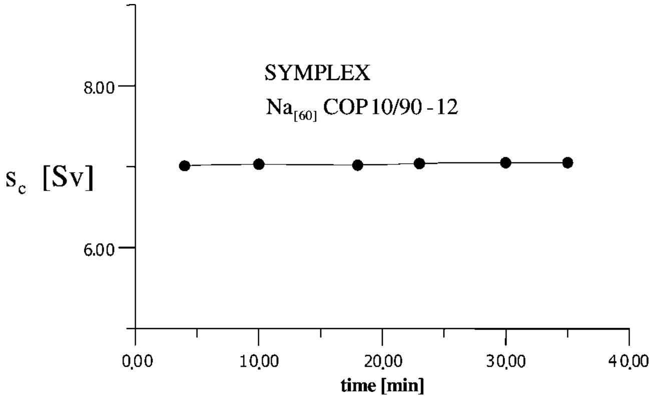

Figure 7. Relationships between apparent sedimentation coefficients, s_c, (c = 0.59 g/dL) and time, τ, of rotation (n = 50 000 rpm).

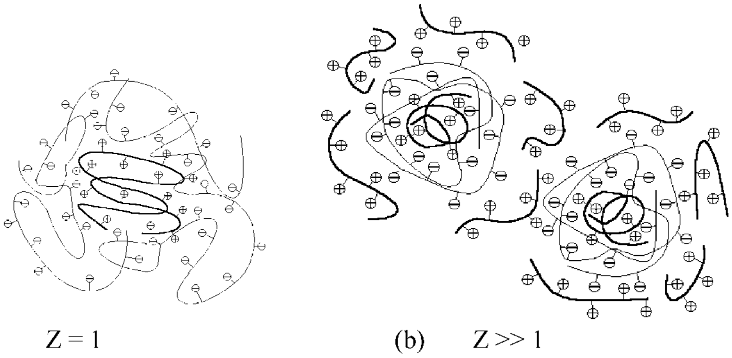

Figure 8. Schematic presentation of the mechanism of symplex formations in cases: (a) at the stoichiometrical ratio Z = 1; (b) at $Z \gg 1$.

If, however, the ionene is in excess (at $Z > 1$) the "host" copolymer becomes confined in the corn and now the outer layer is formed by much shorter segments carrying OH groups beside the abundant $=N^+=$ functions. Thus, a hydration of the particles is provided indeed, but a bridging association by hydrogen bonds involving amide groups is substantially restricted. As a consequenc, the symplex aggregates remain smaller, displaying lower viscosities. The differences in the symplex structures are visualized by the schemes shown in Fig. 8.

According to Sch. "a" secondary aggregates are being formed, contrary to Sch. "b" where the primary particles sustain, stabilized by the surface charge.

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