ISSN 1070-4272, *Russian Journal of Applied Chemistry*, 2009, Vol. 82, No. 4, pp. 657−665. © Pleiades Publishing, Ltd., 2009.
Original Russian Text © V.T. Lebedev, D.N. Orlova, A.B. Mel'nikov, L.V. Vinogradova, 2009, published in Zhurnal Prikladnoi Khimii, 2009, Vol. 82, No. 4, pp. 661−668.

A Cold Neutron Scattering Study of the Association in D-Toluene of Sulfopolystyrene Ionomers with Varied Content of Ionogenic Groups

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Received December 3, 2008

Abstract—Intra- and intermolecular association in deuterotoluene of ionomers based on sulfopolystyrene with varied content of sulfonate groups (SO_3H) was studied by cold neutron scattering. The structural features of the primary associates were revealed, and their capability for mutual penetration and binding into supramolecular formations at contacts was evaluated.

DOI: 10.1134/S1070427209040223

Sulfonated polystyrenes (SPSs) are widely used as high-performance sorbents for separation of organic acids and oligosaccharides, for fabrication of membranes for analysis, purification, and demineralization of natural and potable waters, and for preparation of cation-exchange composite materials and polymeric electrolytes in fuel cells [1]. Owing to electrostatic interaction of ionogenic groups, strong physical bonds are formed between the macromolecules. These bonds are broken only on softening of the polymers. Ionomers (ionogenic group content <10 mol %) well combine the properties of thermoplastics, favorable for molding articles, with increased deformation resistance and rigidity [2–5]; they surpass hydrophobic polystyrene in physicomechanical properties.

Published papers on SPS-based ionomers deal with the behavior of SPS macromolecules in the bulk and in solutions [1, 2, 4, 6–12] and mainly concern ionomers with ionogenic groups in the salt form (SO_3Na). The related studies for the ionomers containing ionogenic groups in the acid form (SO_3H) are considerably fewer. As the physicochemical characteristics and practically important properties of SPSs depend not only on electrostatic dipole interactions of ionogenic groups but also on the presence of hydrogen bonds, the role of hydrogen bonding in self-organization of ionomers in low-polarity media requires additional studies.

Of growing importance for the development of nanotechnologies are processes of self-assembling of macromolecules. In complexly organized systems, such processes can lead to formation of highly ordered polymeric nanostructures exhibiting practically important functional properties. In solutions in low-polarity solvents of SPSs containing ionogenic groups in the acid form (SO_3H), enhancement of the self-organization of the macromolecules due to two factors, electrostatic interaction (formation of multiplets of ionogenic groups due to dipole–dipole attraction) and hydrogen bonding between SO_3H groups, should be expected. By varying the content of ionogenic groups, it is possible to control the self-organization in solutions and thus the subsequent formation of materials with a highly ordered morphology.

To gain deeper insight into conformational states of ionomers and into forms of intra- and intermolecular interactions, and also to reveal the role of hydrogen bonds, we examined in this study SPS ionomers containing 0.5 to 5.8 mol % ionogenic SO_3H groups by small-angle neutron scattering in deuterotoluene. We used the method of Fourier transform of scattering cross sections [13, 14], allowing direct determination of the spectrum of space molecular correlations, which can be presented as a result of three-dimensional scanning of objects on the scales from the chain segment length to the coil diameter and size of associates.

EXPERIMENTAL

Sulfonated polystyrenes containing 0.5, 2.6, 4.4, and 5.8 mol % sulfo (SO_3H) groups (samples SPS-1, SPS-2, SPS-3, and SPS-4, respectively) were prepared from monodisperse PS with $M_w = 115 \times 10^3$ and $M_w/M_n = 1.05$, synthesized by anionic polymerization (Exxon Research Center, USA).

Solutions of the PS precursor and ionomers in D-toluene (20°C) were prepared in the course of several days to attain the equilibrium. In neutron scattering experiments, the ionomer concentration was $c = 1$ g dl^{-1}.

The neutron scattering was measured with a Membrana-2 diffractometer (St. Petersburg Institute of Nuclear Physics, Russian Academy of Sciences) at transferred momentums $q = (4\pi/\lambda)\sin(\theta/2) = 0.03$–$1$ nm^{-1} (θ is the scattering angle, wavelength $\lambda = 0.3$ nm, spectrum width $\Delta\lambda/\lambda = 0.25$). To the range of momentums corresponded the area of space scales $\sim\pi/q$ from the length of the PS chain segment and larger (~1–100 nm), in which the molecular and supramolecular structure of solutions was manifested. The scattering in solution is isotropic in the plane of momentums, and therefore the intensity depends only on the modulus of the momentum. To determine the absolute scattering cross sections of solutions $\sigma(q) = d\sigma/d\Omega$ per unit solid angle Ω of the detector and 1 cm^3 of solution volume, the data were normalized to the intensities measured under the same conditions for an H_2O layer (1 mm thick, 20°C) serving as a reference with the known scattering cross section.

To study the behavior of ionomers in solutions, we used in this work the method of cold neutron scattering, which is the most adequate and efficient in analysis of self-organization of ionomers. In scattering on molecular ensembles, cold neutrons with the energy lower than the energy of thermal motion of atoms interact mainly with nuclei, without perturbing the structure of separate molecules, their state in the space, and supramolecular structure of the system.

Optimization of experimental conditions. The choice of samples of SPS ionomers with different content of SO_3H groups was governed by the necessity of widely varying the mean length of nonpolar PS fragments between ionogenic groups randomly distributed in the chain: from long segments (~200 units) to short fragments (~17 units) comparable in length with the Kuhn segment A ~2 nm (~8 units) [15]. In going from the minimal (0.5 mol %) to the maximal (5.8 mol %) degree of sulfonation of SPS, an increase in the potential of the dipole interaction of ionogenic groups adjacent in the chain can reach two orders of magnitude, which should cardinally change the behavior of ionomers in solution.

To optimize conditions of studying ionomers in solutions by neutron scattering, we initially considered the characteristics of the PS precursor, determined by dynamic light scattering (20°C, toluene) [16]. From the forward diffusion coefficient of PS $D_{PS} = 3.3 \times 10^{-7}$ cm^2 s^{-1}, we determined the hydrodynamic Stokes diameter of the coil in the approximation of a spherical particle, $d_H = 25$ nm, which corresponded to the unperturbed chain size $h_\theta = BM_w^{1/2} = 24$ nm (constant $B = 0.070 \pm 0.002$ nm^{-1}) [15]. This means that θ conditions were observed in the solution. According to the Debye criterion [17], from the intrinsic viscosity of PS $[\eta] = 0.52$ dl g^{-1} (measured in Ostwald capillary viscometer [11]) we estimated the polymer concentration $c^* = 1/[\eta] = 1.9$ g dl^{-1} that is boundary between dilute and semidilute (in which coils start to overlap) solutions.

The above data suggest that introduction of polar SO_3H groups into nonpolar PS chains should lead to distortion of θ conditions and favor association of ionomer chains. In our experiments we used polymer solutions of the concentration $c = 1$ g dl^{-1}, which is two times lower than the threshold concentration c^*. Under these concentration conditions, the mean distance between the peripheral regions of the coils approached their radius of gyration $R_G \approx h_\theta/6^{1/2} \sim 10$ nm, with appreciable probability of chain interaction by fluctuation contacts.

Analysis of neutron scattering in SPS solutions in the momentum space. Figure 1 shows the dependences of the neutron scattering cross section σ on the momentum q for solutions of PS precursor and for all the samples of SPS ionomers in D-toluene. As seen from these data, an increase in the content of ionic SO_3H groups from 0.5 to 2.6 mol % leads to a noticeable increase in the cross section σ at momentums $q \le 0.5$ nm^{-1}, which suggests the

Table 1. Characteristics of PS, SPS ionomers, and parameters of data approximation by functions (2) and (4)

Sample	σ_0, cm^{-1}	R_C[a]	R_C[b]	$a_G \times 10^{-5}$	$a_1 \times 10^{-5}$	$a_2 \times 10^{-5}$	Δ_1	Δ_2
		nm		cm^{-1} nm^{-3}			nm	
PS	0.63 ± 0.03	5.1 ± 0.2	3.5 ± 0.3	77 ± 13	1.33 ± 0.37	0.24 ± 0.04	6.1 ± 0.5	13.8 ± 0.8
SPS-1	0.69 ± 0.04	4.8 ± 0.3	3.6 ± 0.5	87 ± 20	1.27 ± 0.65	0.54 ± 0.06	5.2 ± 0.7	16.0 ± 0.7
SPS -2	2.56 ± 0.12	8.4 ± 0.3	8.8 ± 0.2	33 ± 1	0.97 ± 0.07	0.46 ± 0.08	9.3 ± 1.2	6.5 ± 0.4
SPS -3	2.37 ± 0.14	8.3 ± 0.4	8.3 ± 0.3	35 ± 2	0.09 ± 0.09	0.30 ± 0.18	10.4 ± 10.0	8.1 ± 0.9
SPS -4	2.16 ± 0.11	8.0 ± 0.3	7.0 ± 0.3	45 ± 4	0.50 ± 0.16	0.28 ± 0.03	4.1 ± 0.7	10.0 ± 0.7

[a] Obtained by data approximation by function (2).

[b] Obtained by data approximation by function (4).

presence in solution of enlarged scattering objects. This correlates with the concept of the association of ionomer chains on the scales $1/q \geq 2$ nm, exceeding the length of the PS chain segment.

The dependences of the neutron scattering cross section multiplied by the momentum squared ($q^2\sigma$) on the momentum q (Kratky representation) are shown in Fig. 2. As can be seen, in the case of the PS precursor and SPS with a low content of ionogenic groups (0.5 mol %), the function $q^2\sigma$ is ascending at $q \leq 0.5$ nm^{-1}. At higher values of q, the curves flatten out. For ionomer samples with a higher content of SO_3H groups, saturation is observed at momentums $q \geq 0.3$ nm^{-1}, but the qualitative pattern is preserved. Just this behavior of scattering cross sections is typical of Gaussian polymeric coils for which the form factor squared $F^2(q)$ is described, to a first approximation, by the Zimm function

$$F^2(q) = [1 + (qR_C)^2]^{-1}, \tag{1}$$

where R_C is the correlation radius of a coil, proportional to its radius of gyration: $R_G = R_C \times 3^{1/2}$.

Thus, it follows from Kratky representation of the data (Fig. 2) that ionomer macromolecules in the associated state are in the Gaussian coil conformation.

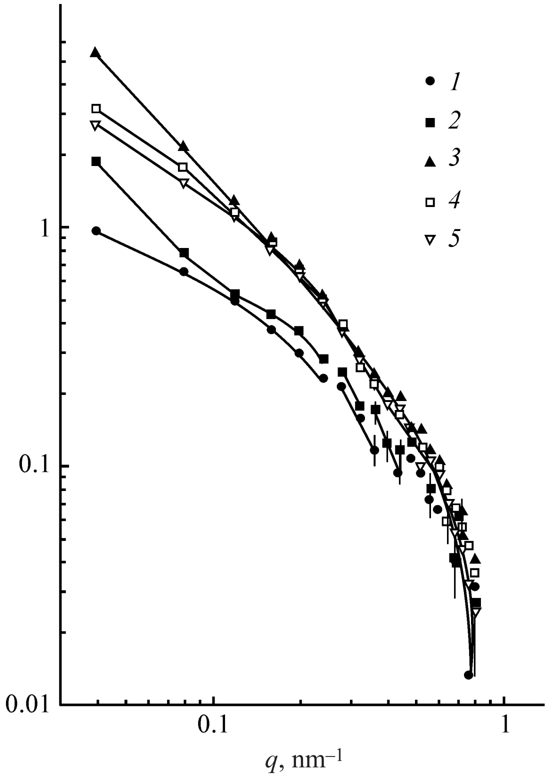


Fig. 1. Scattering cross section σ as a function of momentum q in D-toluene (20°C). (*1*) PS precursor and (*2–5*) SPS ionomers containing 0.5, 2.6, 4.4, and 5.8 mol % sulfonate groups, respectively; the same for Figs. 3, 5, and 6. The lines denote spline functions.

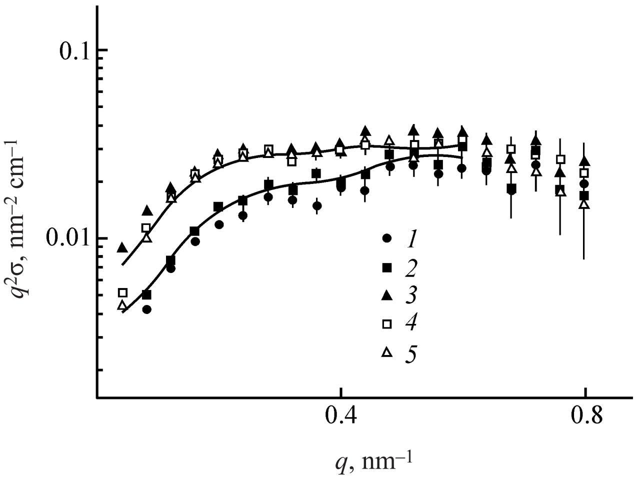


Fig. 2. Neutron scattering cross section multiplied by momentum squared $q^2\sigma$ as a function of momentum q. (*1*) PS precursor and (*2–5*) ionomers (Kratky representation). The upper and lower curves are smoothing functions related to SPS-1 and SPS-4 samples, respectively.

Table 2. Degree of association of ionomers and reduced concentration of units at various content of sulfo groups in the chain

Sample	Content of SO_3H groups, mol %	Degree of association n_E	Reduced concentration of units ρ/ρ_{PS}
PS	–	1	1
SPS-1	0.5	1.1 ± 0.1	1.4 ± 0.3
SPS-2	2.6	4.1 ± 0.3	1.9 ± 0.3
SPS-3	4.4	3.8 ± 0.3	1.7 ± 0.3
SPS-4	5.8	3.4 ± 0.2	1.6 ± 0.2

To determine the parameters of the associates, we plotted the dependences of the reciprocal cross sections σ^{-1} on the momentum squared q^2 (Fig. 3). In the interval $0.01 \le q^2 \le 0.5$ nm^{-2}, these dependences are linear, whence follows that the data are described by the Zimm law:

$$\sigma(q) = \sigma_0 F(q), \qquad (2)$$

where $\sigma_0 = (\Delta K)^2 N_p V_P^2$ is the scattering cross section in the limit $q \to 0$, proportional to the squared factor of contrast $(\Delta K)^2$ in scattering between the polymer and solution; N_p is the numerical concentration of chains each of which has the dry volume V_P.

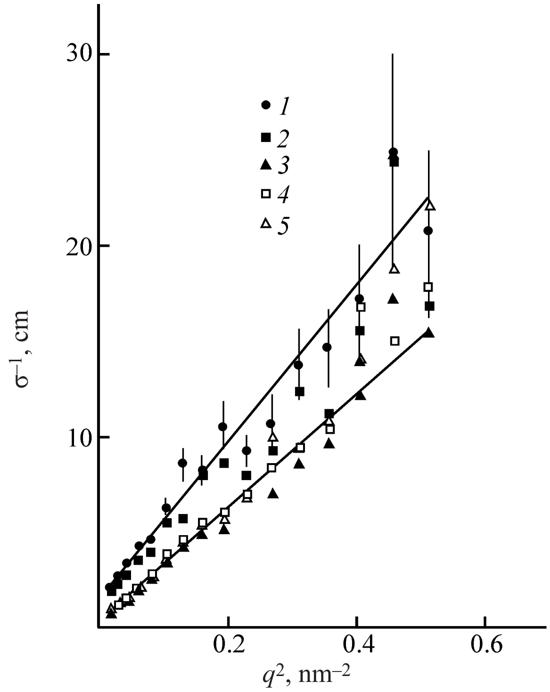


Fig. 3. Reciprocal scattering cross section σ^{-1} as a function of momentum squared q^2. The upper and lower lines refer to approximating functions (2) for the PS precursor and SPS-4 ionomer.

The approximation parameters σ_0 and R_C for the PS precursor and ionomers are given in Table 1.

As seen from data description by the Zimm function, ionomer molecules form a primary associate which scatters as a common chain structure. Therefore, the quantity $\sigma_0 = (\Delta K)^2 N_p V^2_P = (\Delta K)^2 \varphi V_P$ is proportional to the volume fraction of the polymer φ in solution and dry volume V_P or weight of such particle (associate). Thus, variation of the scattering cross section σ_0 with variation of the content of ionic groups in chains at a given solution concentration characterizes changes in the degree of association of macromolecules in solution. The ratio $\sigma_0/\sigma_{0PS} = n_E$ serves as an estimate for the number of chains in the associate (degree of association) (Fig. 4, Table 2).

Estimation of the mean number of macromolecules in associates of SPS ionomer containing 2.6 mol % sulfonate groups gives for the maximal degree of association the value $n_E \sim 4$. With an increase in the content of ionogenic groups (4.4–5.8 mol %), n_E decreases. At the maximal content of ionogenic groups (5.8 mol %), n_E is about 3 (Fig. 4, curve *1*). With an increase in the associate weight, its size increases also, as indicated by the behavior of the squared correlation radius of associate normalized to the related quantity for PS, $(R_C/R_{CPS})^2$, in relation to the content of ionogenic groups in the ionomer chain (Fig. 4, curve *2*). The observed increase in the associate size is considerably less pronounced than in the case of Gaussian coils of the same weight, for which holds

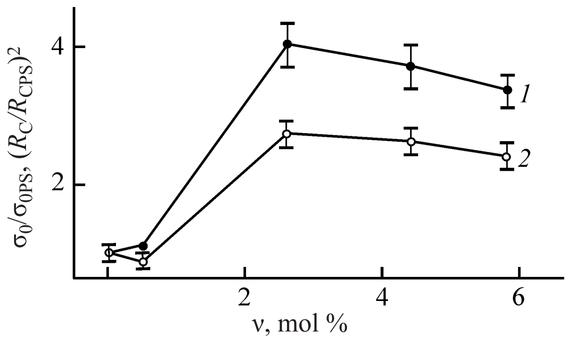


Fig. 4. (*1*) Normalized scattering cross section σ_0/σ_{0PS} and (*2*) correlation radius squared $(R_C/R_{CPS})^2$ as functions of the degree of sulfonation of the ionomers ν.

$$\sigma_0/\sigma_{0PS} = n_E = (R_C/R_{CPS})^2.$$

The experimental curves for the normalized values of the cross section σ_0/σ_{0PS} (Fig. 4, curve *1*) and correlation radius squared $(R_C/R_{CPS})^2$ (Fig. 4, curve *2*) do not coincide. Curve *2* lies below curve *1*. This fact indicates that the associates are more compact and therefore denser than PS coils of the same weight.

Table 2 presents the estimates obtained from the experimental data for the degree of association n_E of all the ionomers and for the ratio of the mean concentration of polymer units in the associates ρ to that in PS coils of the same molecular weight, ρ_{PS}, calculated by the formula

$$\rho/\rho_{PS} = n_E^{\,3/2}/(R_C/R_{CPS})^3.$$

As can be seen, at the ionogenic group content of 0.5–2.6 mol %, owing to electrostatic interactions of sulfo groups and hydrogen bonds, ionomers SPS-1 and SPS-2 form associates in which the concentration of units is 1.4–1.9 times higher than that in the Gaussian coil. At the degree of sulfonation exceeding 2.6 mol % (SPS-3, SPS-4), further densification of the associates does not occur. The mean concentration of units ρ/ρ_{PS} within the associate volume even somewhat decreases.

Fourier analysis of neutron scattering data. To obtain the most adequate information on the structure of ionomers and their associates on the molecular and supramolecular levels, we analyzed the data by the method of Fourier transform of momentum dependences of the cross sections $\sigma(q)$ into space correlation functions $\gamma(R)$ [13, 14]:

$$\sigma(q) = (\Delta K)^2 N_p V_P^2 \sigma_0 F(q)^2 F(q), \quad (3)$$

$$\gamma(R) = (\Delta K V_1)^2 \langle \Delta n(0)\, \Delta n(R) \rangle$$
$$= (1/2\pi)^3 \int \sigma(q)[\sin(qR)/(qR)]\, 4\pi R^2 dR. \quad (4)$$

Formula (3) relates the scattering cross section $\sigma(q)$ for a system of N_p chains to its structural factor $S(q)$, form factor $F(q)$, dry volume of separate chain V_P, and factor ΔK of scattering contrast between the polymer and solvent. Correlation function (4) is proportional to the chain unit volume squared, $(V_1)^2$, and characterizes the system structure on the scale $R \sim 1/q$ of the order of reciprocal momentums. It is the averaged product of deviations $\Delta n(0)$ and $\Delta n(R)$ of the numerical concentrations of chain units (relative to the mean concentration) in various points of the sample at a distance R. In the case of isotropic systems, the function $\gamma(R)$ multiplied by R^2 is used; it describes the distribution of chain units in a spherical layer at a distance R from a certain chain unit $(R^2\gamma(R))$.

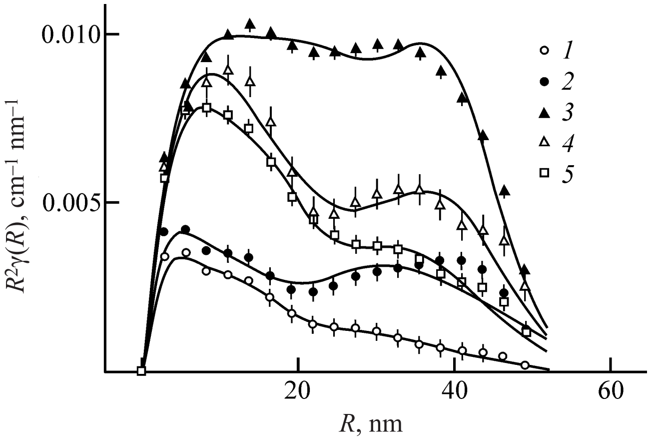


Fig. 5. Correlation function $R^2\gamma(R)$ as a function of radius R. Lines refer to approximating functions (4).

Analysis of the behavior of the function $R^2\gamma(R)$ on the scale R = 0–50 nm offers detailed information on the internal structure of macromolecules and supramolecular formations (Fig. 5). In the molecular correlation spectrum of the PS precursor, a broad peak with the maximum at $R^* \sim 5$ nm dominates. This value is close to the correlation radius R_C (Table 1), which is the parameter of the correlation function of the PS Gaussian coil:

$$R^2\gamma(R) \sim (R/R_C) \exp(-R/R_C). \quad (5)$$

Function (5) is the Fourier image of function (1) and has a maximum at the radius $R = R_C$.

In the $R^2\gamma(R)$ spectrum of the PS precursor (Fig. 5), the structural levels are clearly separated, which well illustrates the advantages of going to the real space. Along with the above-considered correlation peak (within the PS chain), chain interactions with mutual penetration on the scale $R \sim 10$–50 nm are manifested in the spectrum. These distances are comparable with, or exceed the radius of gyration $R_G = 3^{1/2}R_C$ (~9 nm) and the coil diameter $d_G = 18^{1/2}R_C$ (~20 nm) (root-mean-square distance between chain termini) (Table 1).

As shown above, ionomer chains tend to form primary associates in which the chains are not observed separately (Fig. 3, Table 1). This conclusion is confirmed by the character of the correlation spectra (Fig. 5).

With an increase in the content of ionogenic groups in ionomer chains from 0.5 to 2.6 mol %, the correlation

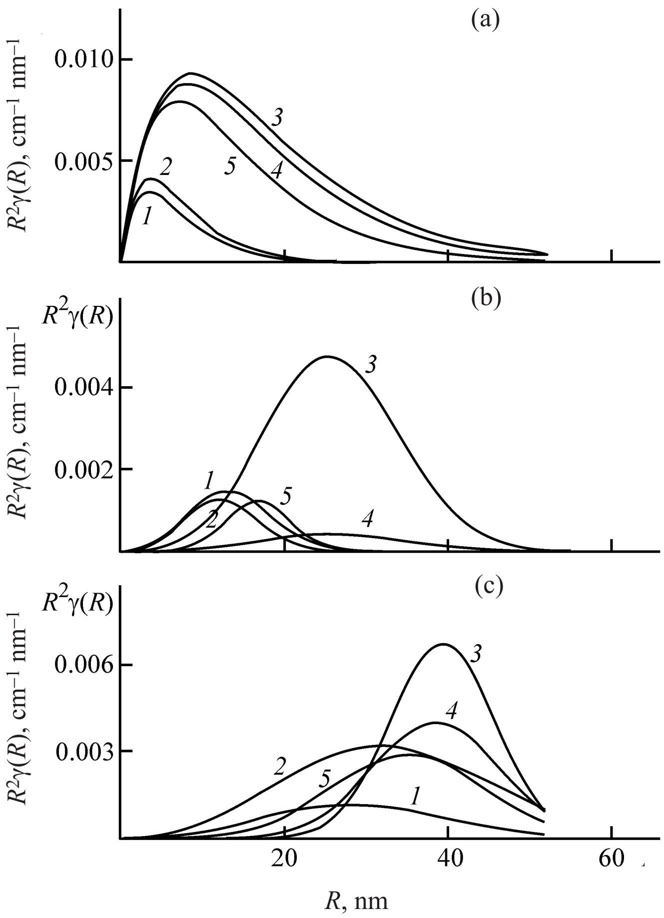


Fig. 6. Partial correlation functions $R^2\gamma(R)$ describing (a) correlation of units within primary associates and intermolecular interactions in the case of (b) penetration and (c) contact of associates [which corresponds to the first, second, and third terms of function (4)], as functions of the radius R.

peak at R ~0–20 nm increases, and its maximum shifts to R^* ~10 nm. At the degrees of sulfonation exceeding 2.6 mol %, the trends become opposite (Fig. 5), which is due to changes in the contributions of intra- and intermolecular association to self-organization of the ionomer in solution.

To understand these processes, it was necessary to quantitatively describe molecular correlations using the model function

$$R^2\gamma(R) = \alpha_G RR_C \exp(-R/R_C) + \alpha_1 R^2 \exp[(-R - L_1)^2/2\,\delta_1^2] + \alpha_2 R^2 \exp[(-R - L_2)^2/2\,\delta_2^2]. \quad (6)$$

The first term describes intramolecular correlations of units. The coefficient α_G is proportional to numerical concentration of chains in solution. The second term takes into account possible mutual penetration of chains (engagements, entanglements, and dipole interactions and hydrogen bonds of ionogenic groups from different chains), when a shift of the center of mass of the two chains relative to each other can vary from zero to the chain diameter, being equal, on the average, to 1/2 of the chain diameter (this quantity is denoted as L_1). The third term corresponds to chain contacts without penetration, when their centers of masses are at a distance of chain diameter (parameter L_2). The quantities δ_1 and δ_2 characterize the variances of L_1 and L_2. The coefficients α_1 and α_2 are proportional to the probabilities of interactions of such types.

It should be noted that, for PS, function (6) described the correlations within the chains and between them. For the ionomers, the main structural elements (actually, "effective chains") are primary associates, because separate macromolecules are not observed in the scattering pattern. Primary associates of ionomers can mutually penetrate or contact at a distance of the diameter $d_E = 3 \times 2^{1/2}R_C$, related to the correlation radius of the associate R_C (Table 1). For the ionomers, the parameters $L_1 = d_E/2$ and $L_2 = d_E$ of function (6) are set by the diameter of the primary associate d_E, and the quantities δ_1 and δ_2 take into

Table 3. Areas under curves of partial correlation functions and parameters characterizing association of ionomers

Sample	S_G	S_1	S_2	n_{EF}	P_P	P_T	n_T
	cm^{-1}						
PS	0.033 ± 0.008	0.018 ± 0.006	0.032 ± 0.008	1	0.56 ± 0.23	0.99 ± 0.34	2.6 ± 0.5
SPS-1	0.040 ± 0.014	0.014 ± 0.008	0.094 ± 0.018	1.2 ± 0.4	0.35 ± 0.23	2.34 ± 0.91	4.6 ± 1.3
SPS-2	0.218 ± 0.012	0.098 ± 0.019	0.106 ± 0.020	6.7 ± 0.4	0.45 ± 0.09	0.48 ± 0.10	13.0 ± 3.3
SPS-3	0.198 ± 0.018	0.010 ± 0.009	0.075 ± 0.046	6.1 ± 0.5	0.05 ± 0.05	0.38 ± 0.23	8.7 ± 2.6
SPS-4	0.150 ± 0.019	0.012 ± 0.005	0.065 ± 0.011	4.6 ± 0.6	0.08 ± 0.03	0.43 ± 0.09	7.0 ± 1.8

account the variance of distances at which the primary associates interact. Data for all the samples (Fig. 5) were approximated by function (6) with the parameters R_C, α_G, $\alpha_{1,2}$, and $\delta_{1,2}$ (Table 1). The components of function (6) are plotted in Fig. 6.

Specific features of ionomer association in D-toluene. As shown above, preliminary conclusion on formation of primary associates follows from analysis of data in the momentum space [formulas (1) and (2)]. More correct and complete concept of the formation and behavior of associates was obtained by Fourier treatment of the results.

As seen from the data presented in Fig. 6a and Table 3, the correlation radius of the associates R_C increases from approximately 4 for nonsulfonated PS to 9 nm for SPS-2 (2.6 mol % sulfo groups). At a higher content of ionogenic groups, the size of the associates somewhat decreases (Table 3), which is qualitatively consistent with the results of data treatment by the Zimm model (Table 1). At the same time, the results of Fourier analysis are more accurate quantitatively, as they were obtained with separation of contributions from various types of interactions of units.

The strongest correlation peaks with maxima at R ~25 and ~40 nm are indicative of mutual penetration and contact of the primary associates, which is manifested to the greatest extent at an ionogenic group content of 2.6 mol % (SPS-2, Fig. 6b). For SPS-3 and SPS-4 containing 4.4 and 5.8 mol % sulfo groups, respectively, the trend is opposite: The correlation peaks decrease in the amplitude and shift toward smaller radii (Figs. 6b, 6c). This trend is due to weakening of the interactions between the associates, involving a decrease in their mass and size, owing to the prevalence of local association, i.e., of mutual binding of polar groups adjacent in the chain, the distance between which becomes as short as two Kuhn segments. When the polar groups in the chain are separated by long PS fragments (in SPS-1 chain, the distance between the adjacent polar groups includes about 40 PS segments) and the amount of ionic groups within the coil volume is small, the probabilities of binding of polar groups adjacent in the chain and remote from each other are comparable with the probability of interchain association at mutual penetration of ionomer coils in solution.

To understand in more detail the primary association and higher levels of organization, we calculated the areas S_G, S_1, and S_2 under the curves in Figs. 6a–6c (Table 3). The area of the major peak S_G for the ionomers, normalized to the related quantity (S_{GPS}) for the PS precursor, gives the mean number of chains in the primary associate, $n_{EF} = S_G/S_{GPS}$ (Table 2). The quantities n_{EF} characterizing the degree of aggregation found by Fourier analysis of the data are fairly accurate and can be considered as final relative to the above-obtained quantities n_E (Table 1) serving as estimates.

The parameters $P_P = S_1/S_G$ and $P_T = S_2/S_G$, found from the ratios of areas under the curves (Fig. 6), characterize the mean numbers of other similar particles bound to a primary associate owing to mutual penetration or contact (Table 3).

Summation of the probabilities of all interactions of a chain with surrounding chains (primary and higher levels of association) gives the mean number of chains n_t in the total associate (Table 3):

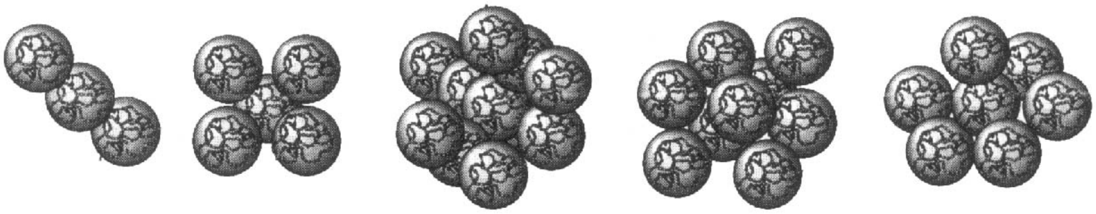
$$n_t = (S_G + S_1 + S_2)/S_{GPS}.$$

Table 3 shows that PS chains and primary associates of ionomers at a moderate degree of sulfonation (≤2.6 mol %) exhibit comparable capability for mutual penetration: its probability is P_P ~0.4–0.6. At a higher content of ionogenic groups, this probability decreases by an order of magnitude. Primary associates containing 4.4 and 5.8 mol % ionic groups in the macromolecule are virtually incapable of mutual penetration. Simultaneously they lose the capability for binding at contacts, characterized by the parameter P_T. This parameter reaches a maximum, P_T ~2.3, for SPS-1 (0.5 mol % ionogenic groups), after which it decreases to P_T ~0.4 at ionogenic group content of 2.6–5.8 mol %.

Taking into account primary association and the considered secondary binding processes, the mean total number of chains with which a macromolecule is associated increases from n_t ~3 for PS precursor to n_t ~13 for SPS-2 ionomer containing 2.6 mol % sulfo groups. Further increase in the ionogenic group content causes a decrease in the total degree of association. At the maximal degree of sulfonation (5.8 mol %), n_t decreases by a factor of almost 2 (Table 3).

The dynamics of variation of the primary associate mass with an increase in the degree of sulfonation can be described by the evolving model of a cluster of spherical particles. Initially the cluster (associate) consists of a

Scheme.



PS SPS-1 SPS-2 SPS-3 SPS-4

central particle (branching node) with 2–3 particles attached to it. As the associate grows in size, reaching the state of total association (n_t ~13), the central particle becomes connected to 12 particles, which corresponds to the model of the closest packing of spheres (12 particles in the first coordination sphere), as in hexagonal or face-centered lattice. With an increase in the degree of sulfonation, the packing becomes less dense: n_t decreases to 9 (for SPS-3) and 7 (for SPS-4), which corresponds to 8 and 6 particles in the first coordination sphere, as in body-centered and simple cubic lattices (see Scheme).

CONCLUSIONS

(1) Structural transformations of ionomers with variable content of ionogenic groups (SO_3H) in deuterotoluene are multilevel and involve both primary association of chains and supramolecular-scale processes expressed in mutual penetration and contact of associates in solutions.

(2) The observed phenomena are due to competition between formation of multiplets of ionogenic groups belonging to the same macromolecule and to different chains or associates.

(3) At a low content of ionogenic groups (up to 2.6 mol %), ionomer macrmolecules owing to electrostatic interactions and stabilizing effect of hydrogen bonds form primary associates of 5–7 chains, demonstrating pronounced capability for contacts and mutual penetration. Primary associates of ionomers with a high content of sulfo groups (4.4 and 5.8 mol %) lose these properties because of prevalence of internal local association through mutual binding of polar groups adjacent in the chain.

(4) Association of the ionomers containing in the chains 1 mol % ionogenic groups and more is described by models of particle packing in crystal lattices, demonstrating unusual character of ionomer self-organization in solutions.

ACKNOWLEDGMENTS

The study was supported by the Russian Foundation for Basic Research (project no. 07-03-00074a).

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