Macromolecules **1994,** *27,* 1751-1758

Aggregation and Critical Micellization Behavior of Carboxylate-Terminated Monochelic[1] Polystyrene

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Received September 17, 1993; Revised Manuscript Received December 17, 1993[●]

ABSTRACT: A series of carboxylate-terminated monochelic polystyrenes were synthesized by anionic polymerization of styrene initiated with *sec*-butyllithium, followed by reaction with CO_2, acidification, and neutralization with different bases, i.e., alkali-metal hydroxide and tetraalkylammonium hydroxide. These functionalized polymers were studied by viscometry and light scattering. They were found to form aggregates or reverse micelles in solvents of low dielectric constant, i.e., cyclohexane, carbon tetrachloride, toluene, chloroform, etc. Well-defined aggregation numbers and critical micelle concentrations (cmc's) were determined by curve fitting of light-scattering data. The aggregation numbers vary between 3 and 17 and cmc's between $<10^{-6}$ and 10^{-4} M, depending on the polystyrene chain length, the size of the counterion, and the dielectric constant of the solvent. Compared to linear polystyrene, the Θ temperature of these aggregates is reduced in cyclohexane, and the second virial coefficient is depressed in the other solvents.

Introduction

Ionomers have been the subject of considerable interest for more than 2 decades. The introduction of a small amount of ionic groups into a polymer chain changes or improves many of the physical properties of the resulting materials.[2-7] Moreover, it can enhance the miscibility of two incompatible polymers via ionic interactions.[8-12] The reason for the unusual behavior of ionomers lies in the fact that ionic groups aggregate in media of low dielectric constant. While the detailed picture of the morphology of the ionic aggregates is not yet available, a recent model[13] has been proposed which suggests that the aggregates form multiplets of several ion pairs; it is the presence of these ion pairs and their effect on the surrounding material which give rise to the unusual behavior.

Three major types of ionomers can be distinguished, i.e., random ionomers, telechelic ionomers, and block ionomers. The random ionomers are usually polymers containing a small amount of ionic groups randomly distributed along the chain. In the telechelic ionomers, the linear polymer chains contain only two ionic groups, one at each chain end. The block copolymers with long nonionic blocks and short ionic blocks constitute the block ionomers. These will be discussed more extensively below. If the composition is inverted, one can speak of block polyelectrolytes.

The random ionomers have been studied much more extensively than the other two families. They are complex systems because of the random distribution of the ionic groups, which makes more difficult the correlation between the molecular structure, the morphology, and the physical properties. In addition, the formation of a physically cross-linked network in these ionomers discourages the characterization in solution by conventional methods such as nuclear magnetic resonance (NMR), size exclusion chromatography (SEC), light scattering (LS), etc., which can provide information on chemical structure, molecular weight, molecular weight distribution, and chain conformations.

In the telechelic ionomers, the ionic groups are fixed at the ends of the polymer chains of low polydispersity, which can be easily obtained by anionic polymerization. The specific ion placement as well as the low polydispersity facilitates the investigation in terms of structure–property relationships. One feature of these materials is that the ionic groups aggregate into ionic domains, which effectively cross-link the polymer chains. The resulting networks can be swollen in some solvents. The swelling by toluene of α,ω-dicarboxylpolybutadiene neutralized by magnesium methoxide and titanium isopropoxide has been investigated by SAXS.[14] It was found that the swelling does not disrupt the ionic aggregates down to approximately 10 wt % polymer and that the phase separation remains very sharp while the chain network is distorted by the swelling pressure. When the swelling is allowed to proceed further, it leads to the complete disruption of the network with formation of a viscous solution (sol–gel transition) or phase separation (demixing transition). Extensive studies on these phenomena have been performed, which dealt with the influence of different factors, such as the nature of polymers, the polymer molecular weight and polydispersity, the counterions, the solvent, and the temperature.[15] However, the study of such gels remains difficult compared to that of normal polymer solutions, and the aggregation number of the ionic domains cannot be easily determined.

Recently, block ionomers have been prepared by anionic block copolymerization of, for example, styrene and vinylpyridine and subsequent quaternization of the pyridine group[16] or of styrene and *tert*-butyl methacrylate and subsequent saponification of the *tert*-butyl group.[17] The block lengths can be controlled, and the molecular weight distributions are usually narrow. These ionomers have been found to form regular ionic domains in the solid state[18,19] and reverse micelles in solution[20-22] as well as two-dimensional micelles[23-26] or foams[27] on water surfaces. SEC,[20,22] viscometry,[20,21] LS,[21] small-angle X-ray scattering (SAXS),[28-30] and NMR[30,31] were carried out on the reverse micelles in solution. The studies show that the reverse micelles are spherical, are relatively monodisperse in size, and are very stable. The aggregation numbers vary mostly between ca. 20 and ca. 100, and the mobility of the chain segments near the ionic core is very restricted.[31] Because these aggregates are micellar, they are easily soluble in the solvent which is good for the corona. Because of their solubility, a wide range of studies can be performed for these materials, which are being pursued in this and other laboratories.

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[●] Abstract published in *Advance ACS Abstracts,* February 15, 1994.

0024-9297/94/2227-1751$04.50/0

One complication that arises with these block ionomer micelles, which can be compared to the reverse micelles of low molecular mass amphiphiles, is the fact that they are comprised of chains which, while they have a relatively narrow molecular weight distribution, are still much more polydisperse than low molecular weight amphiphiles. For example, a block ionomer containing an average of five ionic repeating units with a Gaussian distribution and a polydispersity index of 1.1 will contain 1% blocks of one unit, 4% of two, 11% of three, 21% of four, 25% of five, 21% of six, 11% of seven, 4% of eight, and 1% of nine. Consequently, this ionomer forms "mixed" micelles in solution, and the most important parameters, such as the aggregation number, the radius of core, etc., will depend not only on the average chain lengths but also on the polydispersity index of the chains.[28] Very recently, it has been shown[32] that polydispersity can have a major effect on the critical micelle concentration in block copolymers.

While the polydispersity index of the nonionic blocks can be determined by SEC, its experimental determination for the ionic block is presently impossible. This is due to the fact that during the anionic block copolymerization, either only the first block or the complete copolymer can be withdrawn for SEC analysis; the block which is subsequently converted to the ionic block is usually the second block, and because it is short and cannot be separated from the long block, its polydispersity index cannot be determined.

As part of an investigation of block ionomers, it was of interest to look at the whole range of possible block lengths, including the very shortest, i.e., a single ionic group. In addition, however, it is worth recalling that the presence of a single ionic group at the end of a polymer chain confers on the material a number of unique properties. The ionomer with one ionic group at one end is believed to form starlike aggregates in nonpolar solvents, a special case of spherical micelles of block ionomers. Such systems have received only very little attention, in contrast to the difunctionally terminated telechelics.[33] Möller et al.[34] studied lithium monosulfonate terminated polystyrenes in cyclohexane, THF, and cyclohexanol/cyclohexane. The aggregation number was found to be 12 in cyclohexane and to decrease with addition of cyclohexanol. No aggregation was found in THF. Aluminum, barium, magnesium, and zinc monocarboxylate terminated polystyrenes in toluene have been studied by Duplessix and Jalal.[35] Anomalous aggregation behavior was found.

It is evident that the monochelic polymers resemble, in some ways, the low molecular mass amphiphiles, e.g., Aerosol OT (alkali-metal 2-(diethylhexyl)sulfosuccinates), alkylammonium propionate, the alkali-metal dialkylnaphthalenesulfonates, etc. It is not unreasonable to expect, therefore, that the monochelic polymers should have a well-defined aggregation number, critical micelle concentration, etc. Various methods have been used to determine the aggregation number and the critical micelle concentration of the low molecular mass amphiphiles in nonpolar solvents, which include vapor pressure osmometry (VPO), light scattering, ultracentrifugation, viscometry, photocorrelation spectroscopy, fluorescence spectroscopy, nuclear magnetic resonance (NMR) spectroscopy, etc.[36]

This article describes a detailed and systematic study of the aggregation behavior of monocarboxylate polystyrenes by viscometry and light-scattering measurements. Specifically, the effects of the polystyrene molecular weight, the counterions, and the solvents will be discussed. The results are of interest not only because the materials represent block ionomers of the shortest possible ionic block length but also because the materials provide a bridge between the behavior of block ionomers and that of low molecular mass amphiphiles.

Experimental Section

Reagents and Solvents. Styrene and α-methylstyrene (Aldrich) were dried over calcium hydride (Aldrich) for 24 h, distilled under vacuum, and stored under nitrogen at -20 °C. They were then treated with fluorenyllithium for 15 min and distilled under vacuum just before polymerization. *sec*-Butyllithium (1.3 M) in cyclohexane (Aldrich) was used without further purification. Tetrahydrofuran (BDH) was distilled under nitrogen over sodium benzophenone complex, which yielded a blue-violet color, indicating a solvent free of oxygen and moisture. High-purity CO_2 was purchased from Linde/Union Carbide.

Polymerization and Functionalization. The anionic polymerization of styrene and the polymer functionalization were carried out under a nitrogen atmosphere in a previously flamed glass reactor. The freshly distilled THF and a few drops of purified α-methylstyrene were first transferred into the reactor under nitrogen with a double-ended needle. After the reactor had been cooled to -20 °C, *sec*-butyllithium was added dropwise with a syringe until a light red color appeared and persisted. A predetermined volume of *sec*-butyllithium was then added, and the solution became dark red. After 15 min, the solution was cooled to -78 °C in a dry ice/acetone bath; a predetermined amount of styrene was added dropwise by means of a stainless steel capillary and accompanied by vigorous stirring. The dark red color of the initiator solution changed quickly to an orange-red color. A few minutes after the last drop of styrene was added, the color changed back to dark red, indicating the end of the styrene polymerization. However, the polymerization was allowed to proceed for 10 min beyond that point. An aliquot of the reaction medium was withdrawn as unfunctionalized polystyrene for SEC characterization. In order to functionalize the polystyrene, CO_2 was introduced to the reactor through a needle. The solution changed quickly from dark red to violet, to blue, and finally became colorless. The polystyrene was thus terminated with a carboxylate group. The polymer solution was added dropwise to a 5–10-fold excess of acidic methanol (HCl/MeOH). The precipitated polymer was filtered and dried under vacuum at 70–80 °C for 24 h.

Titration. The functionality of the polymers was determined by titration with 1.083 M NaOH/MeOH. A known weight of PS-COOH was dissolved in toluene/MeOH (95:5 v/v), and a few drops of phenolphthalein solution were added to the indicator. The end point was reached when the solution turned from colorless to pink. The functionality was calculated from the obtained acid content and the molecular weight determined by SEC. It was found to vary between 0.98 and 1.02.

Neutralization. The dried polymers of PS-COOH were dissolved in benzene/methanol (95:5 v/v). The acid content was neutralized by adding excess basic solution. The bases used were LiOH, NaOH, KOH, RbOH, CsOH, NMe_4OH, NEt_4OH, and NBu_4OH, depending on the desired cations. The polymer solution was stirred for 30 min, and the methanol was stripped off under vacuum. The material was recovered by freeze-drying. It was subsequently washed with methanol several times to remove any extra base. The polymer was filtered and dried under vacuum at 80 °C for 24 h.

Size Exclusion Chromatography. The SEC measurements were performed at room temperature on a Varian 5010 liquid chromatography apparatus equipped with a refractive index detector. THF was used as the eluent at a flow rate of 1 mL/min. The columns were progel-TSK G4000 HXL and 2000 HXL from Supelco, Inc. The system was calibrated with polystyrene standards. The concentration of injected polymer solution was about 2 mg/mL. The solution was filtered through membrane filters before injection. The molecular weight and the polydispersity index were calculated by a Varian DS-604 computer with SEC application software.

Viscometry. The viscosity measurements were carried out at 25 °C on an Ubbelohde viscometer with a solvent flow time of over 100 s. The polymer solution and the molecular sieve

Table 1. d*n*/d*c* Values of Several Samples in Cyclohexane at 25 °C

samples	d*n*/d*c*
PS(43)	0.167
PS(43)-COONa	0.166
PS(100)-COONa	0.166
PS(100)-COOCs	0.164
PS(208)-COONa	0.165

dried solvents were filtered with 0.5-μm membrane filters. The measurements started with the most concentrated polymer solution, followed by dilution with known amounts of filtered solvent.

Light-Scattering Measurement. The light-scattering measurements were performed at 25 °C on a DAWN instrument from Wyatt Technology Corp. The wavelength of the laser beam was 632.8 nm. Fifteen detectors were situated at different angles ranging from 26.57 to 128.66°. At the beginning of the measurement, the solvent offset was recorded. Cyclohexane, CCl_4, $CHCl_3$, and dioxane were dried with molecular sieves. Toluene and THF were distilled over CaH_2 and sodium benzophenone complex, respectively. The polymer solution and the solvents were filtered through 0.5-μm Millipore filters. The measurement vials from Kimble Glass Inc. were rinsed 3 times with filtered methanol and dried under protection from dust. The initial polymer solution was prepared in a 10-mL volumetric flask and diluted in a vial. After the first measurement by light scattering, the solution was further diluted to a lower concentration. Each dilution was followed by a light-scattering measurement. Alternating measurement and dilution were continued until the scattering intensity at 90° was down to 50 mV. The polymer concentration at each measurement was calculated from the previous polymer concentration and the dilution factor as determined by weighing.

The d*n*/d*c* value from the literature for homopolystyrene in cyclohexane was 0.168.[43] We have measured the d*n*/d*c* values of several samples in cyclohexane at 25 °C. These values are in Table 1. It is clear that the presence of an ionic group as well as changes in the polystyrene chain length or in the counterions does not have any significant effect on d*n*/d*c*. The value of d*n*/d*c* from the literature was very close to those shown above. Therefore, we used the literature values. The values of d*n*/d*c* from the literature for polystyrene in other solvents are 0.110 in toluene, 0.194 in THF, 0.158 in chloroform, and 0.146 in carbon tetrachloride, and these were also utilized in this work.

Nomenclature. In this article, the sample names are given in the form of PS(*x*)-COOM, which stands for a carboxylate-terminated monochelic polystyrene of *x* units with the counterion of M^+.

Results and Discussion

Size Exclusion Chromatography. All the unfunctionalized polystyrenes gave a narrow peak. The calculated molecular weights correspond to the ratio of the weight of the added monomer per mole of initiator during the synthesis. The polydispersity index varies between 1.03 and 1.10. The functionalized polystyrenes PS-COOH and PS-COOM also eluted as a narrow peak in THF at the same position as the unfunctionalized polystyrenes, indicating the absence of coupling reactions during the functionalization. Since THF is a polar solvent and the cmc is quite high, as will be described later, no aggregation was observed in THF by SEC.

Intrinsic Viscosity. As shown in Figure 1, the viscosity of PS(100)-COONa is significantly higher than that of PS(100), which indicates clearly the formation of multimers in the sodium carboxylate terminated polystyrene. The extrapolation to zero concentration gives an intrinsic viscosity of 17.1 and 9.3 mL/g for PS(100)-COONa and PS(100), respectively, and a ratio of 1.84. This ratio is consistent with that found for star polymers, which is reasonable, since the aggregates of monochelic ionomers in solution are expected to be starlike reverse micelles, as mentioned in the Introduction section.

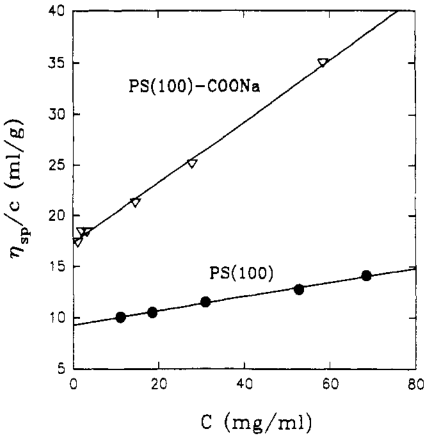

Figure 1. Plot of the reduced viscosity vs the concentration for PS(100) (●) and PS(100)-COONa (▽) in toluene at 25 °C.

Zilliox[37] has measured the intrinsic viscosity of star polystyrenes, $[\eta]_*$, in benzene at 25 °C and related it to that of the polystyrene branch, $[\eta]_{br}$. When the length of the PS branch is kept constant, the intrinsic viscosity increases with the number of branches and eventually levels off. For the number of branches $p \geq 10$, it was found that the intrinsic viscosity is independent of the number of branches with $[\eta]_* = 1.95[\eta]_{br}$. Since the ratio obtained here for the ionomer system is close to but below 1.95, it is believed that the number of branches, or the aggregation number, is close to 10, where the intrinsic viscosity becomes independent of the aggregation number. From the above results, it can be seen that viscometry provides a simple way proving that the aggregation of the functionalized polystyrene has indeed taken place and also suggests an approximate aggregation number. Unfortunately, the precision of the viscometric method so close to the limiting ratio for $[\eta]_*/[\eta]_{br}$ is not precise enough to yield a reliable aggregation number.

From the plot in Figure 1, the Huggins constant (k_H) was found to be 0.81 for PS(100) and 1.04 for PS(100)-COONa. The increased value of k_H for PS(100)-COONa results from the aggregation. According to the hydrodynamic theory of Riseman and Ullman,[38] the value of k_H would be 3/5 for coils and 11/15 for rods. For spherical particles, $k_H \geq 1$. This is in good agreement with the present finding.

Aggregation Number and cmc Determined by Light Scattering. Light scattering is an absolute method for the determination of the molar mass and the size of particles in solution. In the present systems, the aggregation number can be calculated from the molar mass of the aggregates determined by light scattering, combined with the results for the unfunctionalized polystyrenes determined by size exclusion chromatography. This technique becomes necessary for the molecular weight measurements of short single chains of the polystyrenes, since light scattering is not sensitive enough for species of low molecular weight. In addition, however, light scattering can be used to determine the cmc if its value is not too low.

Figure 2 shows the angular dependence of the reduced light-scattering intensity of PS(208)-COONa in cyclohexane at 25 °C for $c = 8.4 \times 10^{-4}$ g/mL. *K* is the optical constant as defined in the next few paragraphs, and $R(\Theta)$ is the Rayleigh ratio. A straight line with a very small slope (8×10^{-8}) is obtained. This means that the radius of gyration of the aggregates is so small ($<\lambda/20$) that its

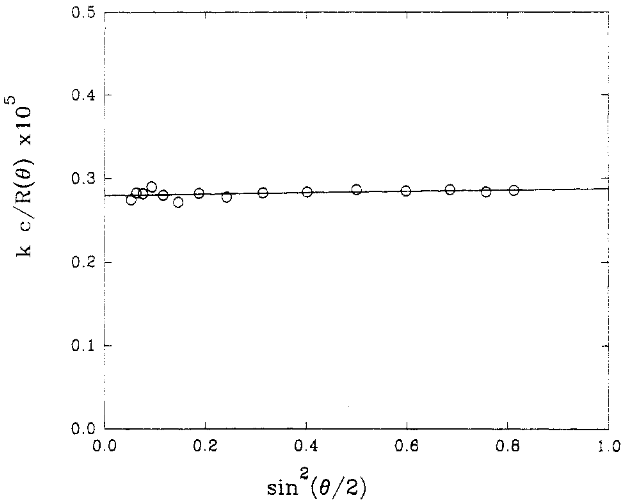

Figure 2. Angular dependence of the reduced light scattering intensity of PS(208)-COONa in cyclohexane at 25 °C ($c = 8.4 \times 10^{-4}$ g/mL).

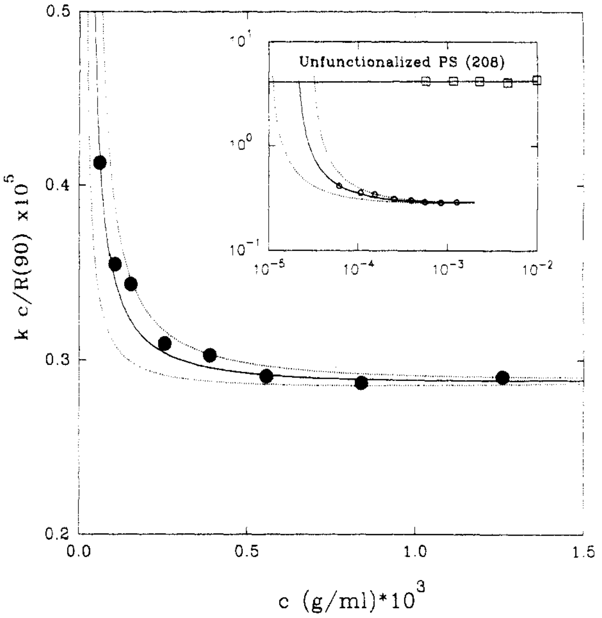

Figure 3. Light scattering of PS(208)-COONa in cyclohexane at 25 °C. Fitting parameters: $f = 16.6$, cmc $= 2.2 \times 10^{-5}$ g/mL $= 1.0 \times 10^{-6}$ M, $A_2 = 2 \times 10^{-5}$ mol mL/g^2. The discontinuous lines were obtained by using cmc = 5×10^{-7} and 1.5×10^{-6} M.

accurate measurement is not possible, although the molar mass is quite high (3.6×10^5), as indicated later in this section. This is due to the starlike conformation of the aggregates, which are more compact than random coils of unbranched homopolystyrene.

Since the scattering intensity is almost independent of the observation angle, it is sufficient to take the value at 90° for different concentrations. The reduced light-scattering intensity at 90° is plotted as a function of the polymer concentration in Figure 3. The reduced light-scattering intensity $Kc/R(90)$ increases with decreasing polymer concentration below 0.5×10^{-3} g/mL, which indicates that the apparent weight-average molar mass of the particles decreases significantly with decreasing polymer concentration below that point. This phenomenon is undoubtedly related to the proximity of the critical micelle concentration, in the vicinity of which the fraction of the aggregates decreases rapidly with concentration. In the higher concentration range, $Kc/R(90)$ is nearly constant. This means that the molar mass or the aggregation number of the particles does not change with concentration in that range. Since cyclohexane is a Θ solvent for polystyrene at 34.5 °C, the second virial coefficient (A_2) is expected to be close to 0 for PS(208)-COONa in that solvent at 25 °C.

In order to obtain the aggregation number, cmc, and A_2 from light scattering, the experimental points are fitted with a theoretical line by using the phase separation model of micellization. A similar approach was used for block ionomer solutions of polystyrene-*b*-poly(sodium acrylate).[39] In this model, it is assumed that there is a cmc below which only single chains are present and above which the concentration of the single chains remains constant at the value of the cmc, with the concentration of aggregates equal to the total concentration minus the cmc. The light-scattering intensity is a sum of both the single chain and the aggregate scattering. This model is a good approximation for the systems which have high enough aggregation number (probably >5). This is true for most of our studies. For the systems with low aggregation numbers, the cmc concept breaks down. However, for the sake of comparison, we used this model for all our systems. The derivation of the relevant equations is given below.

The general equation for light scattering from a micellar system in the absence of single chains is

$$\frac{Kc_m}{R_m(90)} = \frac{1}{M_m}(1 + 2A_2M_mc_m) \qquad (1)$$

where M_m is the molar mass of the micelles, c_m is their concentration, A_2 is the second virial coefficient, $R_m(90)$ is the Rayleigh ratio for the micellar particles at 90°, and K is the optical constant for the particular scattering system given by

$$K = 2\pi^2n_0^{\,2}(\mathrm{d}n/\mathrm{d}c)^2\lambda_0^{-4}N^{-1}$$

Here n_0 is the refractive index of the solvent, dn/dc is the specific refractive index increment, λ_0 is the wavelength of light in vacuo, and N is Avogadro's number.

Setting $m_m = fM_1$ where f is the aggregation number and M_1 is the molar mass of the single chains, we obtain

$$\frac{Kc_m}{R_m(90)} = \frac{1}{fM_1}(1 + 2A_2fM_1c_m) \qquad (2)$$

Thus, $R_m(90)$ for the micelles becomes

$$R_m(90) = \frac{Kc_mfM_1}{1 + 2A_2fM_1c_m} \qquad (3)$$

For single chains alone, it is

$$R_1(90) = Kc_1M_1 \qquad (4)$$

where $R_1(90)$ is the Rayleigh ratio for single chains and c_1 is the concentration of the single chains.

A combination of eq 3 and eq 4 gives the result for total scattering:

$$R(90) = R_m(90) + R_1(90) = \frac{Kc_mfM_1}{1 + 2A_2fM_1c_m} + Kc_1M_1 \qquad (5)$$

Letting

$$c_1 = \text{cmc } (=c_x) \qquad (6)$$

we obtain, from conservation of mass,

$$c_m = c - c_x \qquad (7)$$

Substituting eqs 6 and 7 into eq 5, we obtain

$$R(90) = \frac{K(c - c_x)fM_1}{1 + 2A_2fM_1(c - c_x)} + Kc_xM_1 \qquad (8)$$

By a simple arrangement, this equation becomes

$$\frac{Kc}{R(90)} = \frac{c}{M_1c_x + \dfrac{fM_1(c - c_x)}{1 + 2A_2fM_1(c - c_x)}} \qquad (9)$$

Since the cmc is usually low and A_2 is very small, the second virial term for the light scattering from the single chains was neglected for the sake of simplicity in the development of the model. Also the angular term of $\sin^2(\Theta/2)$ was not included since the particle size is small, as mentioned earlier.

The fitting was performed on a PC by using the Sigmaplot 5.0 program. At first, the aggregation number (f) was adjusted to match the level of experimental points in the higher concentration range. Then the second virial coefficient (A_2) was changed so that the theoretical line in the higher concentration range fits the experimental points in terms of the slope. The value of cmc was finally adjusted to fit the experimental points in the lower concentration range. In the case of PS(208)-COONa in cyclohexane at 25 °C, as is shown in Figure 3, the best fit was obtained with $f = 16.6$, cmc = 1.0×10^{-6} M, and $A_2 = 2 \times 10^{-5}$ mol mL/g^2. By comparison, the results of the unfunctionalized polystyrene PS(208) were also plotted, which gave the expected value of molecular weight as determined by SEC. In order to have an idea about the accuracy of the cmc determination, the value of the cmc which gave the best fit was changed by ±50%, yielding the dotted lines, which obviously did not fit the experimental points in the lower concentration range. The best fitting parameters obtained for PS(208)-COONa are comparable to those of the lithium sulfonate terminated polystyrene PS(385)-SO_3Li in cyclohexane at 27.5 °C studied by Möller et al.,[34] who found $f = 12$, cmc = 6×10^{-6} M, and $A_2 = 0$ mol mL/g^2.

Effect of Polystyrene Chain Length. In reverse micelles of low molecular weight amphiphiles, the length of the hydrophobic segment is known to influence the aggregation number and the cmc.[36] Therefore, it was thought to be of interest to determine the polystyrene chain length dependence of the aggregation number and the cmc in the present system also. For this purpose, the sodium carboxylate terminated polystyrenes of different lengths (43, 52, 100, and 208 repeating units) were prepared, and their aggregation was studied by light scattering. Figure 4 shows the aggregation number and the cmc in cyclohexane at 25 °C as a function of the polystyrene chain length. It is seen that with increasing polystyrene chain length, the aggregation number increases and the cmc decreases. Initially, it was thought that these effects might be due to solvent quality. As the molecular weight of polystyrene increases, the solvent quality of the cyclohexane for polystyrene becomes worse, which is expected to lower the cmc. If the solvent quality were the only important factor, the effects of polystyrene chain length would be eliminated by using a nonpolar solvent good for polystyrene, such as benzene or CCl_4. In fact, two samples of different polystyrene chain length, PS(100)-COONa and PS(208)-COONa, were measured in CCl_4 at 25 °C. It was found, however, that the effects were similar to those in cyclohexane. The results are shown in Table 2.

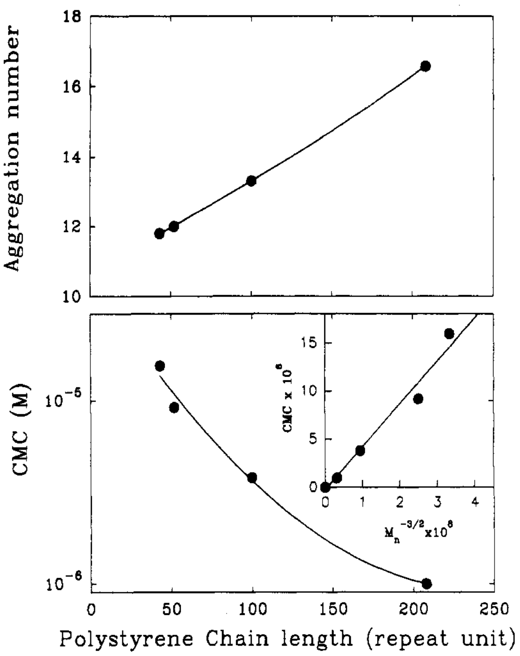

Figure 4. Aggregation number and cmc of sodium carboxylate terminated polystyrene PS-COONa in cyclohexane at 25 °C as a function of the polystyrene chain length. The lines represent a second-order fit to the points. The insert plots the cmc as a function of $M_n^{-3/2}$, and the line is the best linear fit.

Table 2. Aggregation Number (f) and Critical Micelle Concentration (cmc) of Two Samples of Different Polystyrene Chain Length

solvent	samples	f	CMC, M
cyclohexane	PS(100)-COONa	13.5	3.8×10^{-6}
cyclohexane	PS(208)-COONa	16.6	1.0×10^{-6}
CCl_4	PS(100)-COONa	10.0	1.4×10^{-6}
CCl_4	PS(208)-COONa	13.5	0.9×10^{-6}

Therefore, the solvent quality cannot explain the effects of polystyrene chain length. Jérôme[40] has studied the gelation of halato telechelic polymers including α,ω-dicarboxylates. He found that the gelation point, C_{gel} (g/L), is inversely proportional to the square root of the polymer molecular weight:

$$C_{gel} = k\bar{M}_n^{-1/2} \text{ (g/L)} = k\bar{M}_n^{-3/2} \text{ (mol/L)} \qquad (10)$$

The authors suggested that this observation was related to the overlap concentration (C^*), which decreases as the molecular weight increases. Since the micellization or aggregation of carboxylate-terminated monochelic polystyrenes is, in some respects, analogous to the gelation of α,ω-dicarboxylate polystyrene, one should be able to relate the cmc of monochelic polystyrene of n units (PS(n)-COONa) to the C_{gel} of telechelic polystyrene of $2n$ units, NaOOC-PS($2n$)-COONa, in a given nonpolar solvent at the same temperature.

As shown in the insert of Figure 4, the cmc is proportional to $M_n^{-3/2}$, where M_n is the number-average molecular weight of polystyrene. Therefore, the cmc and C_{gel} show the same molecular weight dependence. This is not unreasonable. However, it should be pointed out that the cmc is much lower than C_{gel} (10^{-6}–10^{-5} vs 10^{-3}–10^{-2} M). This phenomenon requires some discussion. It should be recalled that the cmc is a true thermodynamic number determined by light scattering, which gives time-averaged values of the aggregation properties of the system. On the other hand, gelation is a phenomenon which is determined by some mechanical property, which therefore is a function of kinetics of the system. For example, if the

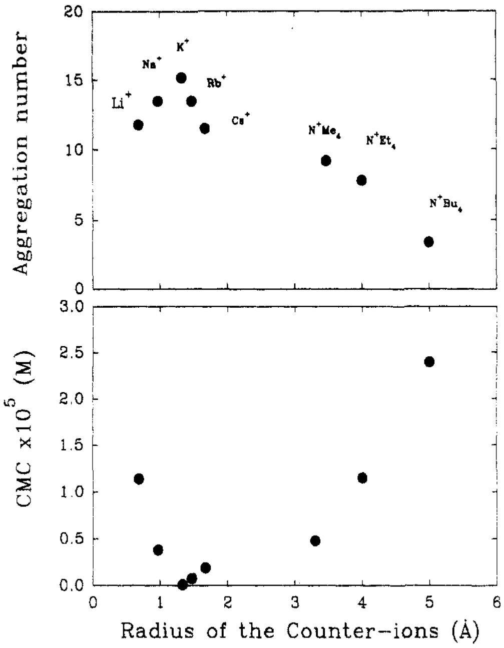

Figure 5. Aggregation number and cmc of PS(100)-COOM in cyclohexane at 25 °C as a function of the radius of the counterions.

frequency at some temperature is more rapid than the rate at which the ions move out of the ionic aggregates (ion hopping rate), the material would be perceived as a gel. On the other hand, if the rate of hopping is faster, the material would be perceived as a liquid. The viscosity measurements of Jérôme, therefore, imply that the gel is studied at frequency or time scale consistent with the viscosity measurements. Naturally, the C_{gel} has to be higher than the cmc, because, for ions to hop from one aggregate to another, the aggregates have to exist. Thus, while the C_{gel} and the cmc are related, they should not be expected to have identical values, since in one case thermodynamic phenomena are probed, while in the other case the phenomena are based on kinetics.

Möller et al.[34] studied two lithium sulfonate terminated polystyrenes of different chain lengths, i.e., PS(380)-SO_3Li and PS(770)-SO_3Li, in cyclohexane at 27.5 °C. The same aggregation number, $f = 12$, was found for both polymers. It is worth noting that the molecular weights of both polymers investigated by Möller et al. are higher than those of the present study; this means that behavior found in these two investigations may not be inconsistent since it is possible that as the molecular weight increases, the effect of the molecular weight levels off. It should also be recalled that the interactions of alkali-metal sulfonate ion pairs with each other are stronger than those between alkali-metal carboxylates. Both of these factors may influence the aggregation number as a function of polystyrene chain length.

Effect of Counterions. Since the aggregation of the carboxylate-terminated polystyrenes is due to ionic interactions, the counterions of the carboxylates are expected to play an important role in the process. To explore this aspect, the carboxylic acid terminated polystyrene PS(100)-COOH was neutralized with different alkali-metal hydroxides as well as tetraalkylammonium hydroxides. In parallel with the measurements described above, the aggregation numbers and cmc's of these neutralized samples in cyclohexane at 25 °C were determined by light scattering. The plots of the data as a function of the radii of the counterions are presented in Figure 5. The values of the radii of the metal cations and those of the tetraalkylammonium ions were taken from *Handbook of Chemistry and Physics* and the article of Gregor and Greff,[41] respectively.

Table 3. Trends of the Melting Points of Alkali-Metal Halides

	T_m, °C			
	fluoride	chloride	bromide	iodide
Li^+	845	605	550	449
Na^+	**993**	**801**	**747**	661
K^+	858	770	734	**681**
Rb^+	795	718	693	647
Cs^+	682	645	636	626

An inspection of Figure 5 shows that the two graphs, i.e., aggregation number as a function of the counterion radius and the cmc as a function of the counterion radius, are almost mirror images of each other. Potassium carboxylate terminated monochelic polystyrene, which has the highest aggregation number, shows the lowest cmc. Conversely, the tetrabutylammonium salt, which has the lowest aggregation number, shows the highest cmc.

In the case of the metal carboxylate terminated polystyrene, the aggregation number increases with increasing size of cation from Li^+ to Na^+ and K^+. It passes through a maximum for K^+ and decreases from K^+ to Rb^+ and Cs^+. The cmc decreases from Li^+ to Na^+ and K^+, it passes through a minimum for K^+, and then increases slightly from K^+ to Rb^+ and Cs^+.

At the critical micelle concentration, the micelle falls apart while maintaining ion pairing; therefore, the main contribution to the free energy of micellization is the interaction between ion pairs. This interaction energy is undoubtedly related not only to sizes of individual ions but also to the relative sizes of the anion and cation.

The maximum in the aggregation number and the minimum in the cmc for K^+ for probably due to the match in sizes between K^+ and COO^-, which suggests that the packing is probably optimized for those ion sizes. Thus, if a cation is larger than K^+, the strength of interaction will decrease in the case of multiple chain aggregates. Conversely, the smaller the cation relative to K^+, the worse the mismatch in sizes of ions, the less efficient the packing, and the weaker the interaction. In the Li^+ case, the difference in sizes between the very small Li^+ and the considerably larger carboxylate anion will make the packing efficiency poor and possibly even result in contacts between the negative carboxylate ions. Similar phenomena are observed in the lattice energy of salts as a function of ion sizes. These manifest themselves, for example, in the trend of the melting points of alkali-metal halides, listed in Table 3, which also exhibit maxima.

It is clear that Na^+ or K^+ gives the maximum melting point, depending on the size of the anion. In the case of fluoride and chloride, Na^+ gives the maximum value of T_m, while KI has the highest melting point in the series of iodides. The melting point of NaBr and that of KBr are very close. By comparing this to our observation for PS-COOM, it appears that the effective size of carboxylate anion is close to that of I^-, the radius of which is 2.2 Å. It is evident that for the highest stability of the micelles or the minimum free energy of micellization, the size of the counterions should match that of carboxylate anion. In the present case, K^+ matches the carboxylate anion most closely, giving the most stable micelles and the highest aggregation number.

In the case of the tetraalkylammonium carboxylate terminated polystyrene, the aggregation number was found to decrease with increasing radius of the counterions. The opposite effect was observed for the cmc. The trend is consistent with the observation discussed above. The

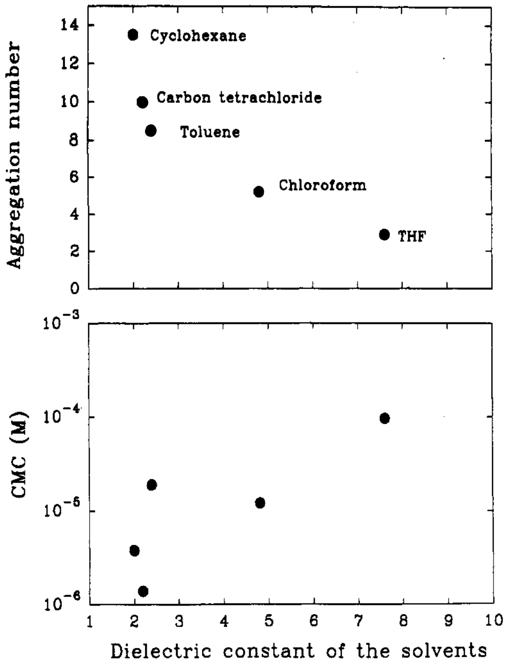

Figure 6. Aggregation number and cmc of PS(100)-COONa in cyclohexane at 25 °C as a function of the dielectric constant of the solvents.

dependence of the cmc on the size of the tetraalkylammonium parallels the dependence observed in the dodecylammonium alkanoates investigated by Muto et al.,[42] who found that the cmc increases linearly with the hydrocarbon chain length of carboxylate counterions. Given the substantial mismatch in ion sizes, the phenomena in both systems can be understood simply by invoking Coulomb's law, which states that the ionic interaction energy, W, is inversely proportional to the distance (r) between the ions, i.e., $W = -e^2/\epsilon r$, where e is the unit charge and ϵ is the dielectric constant of the medium. In the ionic aggregates, the species may not yield individual ions but ion pairs; the qualitative reasoning, however, applies equally to both, since the distance between ions or between ion pairs increases with increasing size of the counterions. Therefore, the larger the size of the counterion, the weaker the interaction between the ionic groups or between the ion pairs and the easier the separation which leads to a breakup of the micelle and thus the higher the cmc. Naturally, in parallel, the solubility of tetrabutylammonium carboxylate is expected to be higher than that of tetramethylammonium carboxylate. All these are the manifestation of the same underlying electrostatics. Conversely, the smaller the size of the counterion, the stronger the interaction, the larger the number of molecules that can get together to form the micelle by overcoming whatever steric effects need to be overcome to form aggregates, and the lower the critical micelle concentration.

Effects of Solvents. It has been recognized that the stability of reverse micelles is solvent dependent.[36] The tendency to form micelles decreases, in general, with increasing polarity of the solvent. In order to explore the effects of solvents on the polymeric reverse micelles, measurements were carried out on a sodium carboxylate terminated polystyrene of 100 repeating units, PS(100)-COONa, in different solvents, i.e., cyclohexane, carbon tetrachloride, toluene, chloroform, and THF at 25 °C. The aggregation numbers and the cmc's are plotted as a function of the dielectric constant of the solvent in Figure 6. As expected, the aggregation number decreases and the cmc increases with increasing dielectric constant.

These effects are simply due to the fact that the free energy of micellization in a solvent of higher dielectric constant is smaller than in that of a lower dielectric constant, resulting in a higher cmc. On the other hand, in the solvent of higher dielectric constant, the ionic interactions are weaker, which make it easier for polymer chains to move out from aggregates, resulting in lower aggregation number.

Table 4. Values of Aggregation Number (f) and Second Virial Coefficient (A_2) for Different Solvents and Counterions

solvent	PS chain length[a]	counterion	f	$10^4 A_2$,[b] mol mL/g^2
cyclohexane	43	Na^+	11.8	0.3
	52		12.0	0.2
	100		13.5	0.01
	208		16.6	0.20
cyclohexane	100	Li^+	11.8	0.01
		Na^+	13.5	0.01
		K^+	15.2	0.01
		Rb^+	13.5	0.4
		Cs^+	11.5	0.01
		NMe_4^+	9.2	−1.0
		NEt_4^+	7.8	−1.5
		NBu_4^+	3.4	−0.8
cyclohexane	100	Na^+	13.5	0.01
CCl_4			10.0	2.9
toluene			8.5	2.5
$CHCl_3$			5.2	4.8
THF			2.9	8.5
CCl_4	208	Na^+	13.5	1.9

[a] Repeating unit. [b] The second virial coefficient A_2 is very close to zero in cyclohexane, which makes it difficult to determine accurately. The experimental error is estimated to be ca. $\pm 0.2 \times 10^{-4}$ mol mL/g^2. Thus, for A_2 values below 0.5×10^{-4}, the low sensitivity of the measurement does not allow us to compare the different values in a meaningful way.

Second Virial Coefficients. The values of A_2 are listed in Table 4. It can be seen that A_2 is very small ($<10^{-4}$) but positive in cyclohexane at 25 °C except for the tetraalkylammonium cvarboxylate terminated polystyrenes. The Θ temperature is, therefore, close to and below 25 °C for the alkali-metal carboxylate terminated polystyrenes in cyclohexane. By contrast, A_2 is negative for linear polystyrene of similar molecular weight under the same conditions, and the Θ temperature is 34–35 °C for the linear polystyrene in cyclohexane.[43] The depression of the Θ temperature compared to that of linear polystyrene has also been reported for star-type polystyrene[37] and lithium sulfonate terminated polystyrene[34] in cyclohexane. The drop is due to the expansion of the chains near the core.[37] In the case of tetraalkylammonium carboxylate terminated polystyrene, A_2 is negative and close to that of linear polystyrene, since the aggregation number is low.

In the other solvents, A_2 is positive but lower than that of linear polystyrene of similar molecular weight. For example, A_2 is equal to 2.5×10^{-4} mol mL/g^2 for PS(100)-COONa in toluene, where it has an aggregation number of 8.5 and an apparent molecular weight of 88 400, while A_2 is 10^{-3} mol mL/g^2 for a linear polystyrene of molecular weight of 95 400.[44] The decrease in A_2 compared to linear polystyrene was also found in 12- and 18-arm-star polystyrenes.[45]

Conclusions

The present study has explored the aggregation behavior of carboxylate-terminated monochelic polystyrene in solvents of low dielectric constant. It was found that the aggregation number increases with increasing polystyrene chain length between 43 and 208 units and with decreasing dielectric constant of the solvents. Conversely, the critical micelle concentration decreases with increasing polystyrene chain length and decreasing dielectric constant of the solvents. By contrast to this monotonous change, the aggregation number passes through a maximum and the cmc passes through a minimum if the size of counterion is varied. These phenomena were interpreted in light of the gelation of telechelic ionomers, Coulomb's law of ionic interaction, and size matching between cation and anion. On the other hand, the Θ temperature is reduced in cyclohexane, and the second virial coefficient is depressed in the other solvents as expected for the starlike aggregates.

Acknowledgment. This work was supported, in part, by NSERC (Canada) and in part by FCAR (Quebec).

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