Association of End-Functionalized Block Copolymers. Light Scattering and Viscometric Studies

Stergios Pispas and Nikos Hadjichristidis*

Department of Chemistry, University of Athens, Panepistimiopolis, 157 71 Athens, Greece, and Institute of Electronic Structure and Laser, 71 110 Heraklion, Crete, Greece

Jimmy W. Mays

Department of Chemistry, University of Alabama at Birmingham, Birmingham, Alabama 35294

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ABSTRACT: The dilute solution properties of diblock and triblock copolymers of styrene and isoprene with one dipolar sulfobetaine group at either or both ends of the chain were examined in carbon tetrachloride by static and dynamic light scattering as well as by viscometry. The copolymers were prepared by anionic polymerization techniques using [3-(dimethylamino)propyl]lithium as initiator. The tertiary amine groups were converted to sulfobetaines by reaction with cyclopropanesultone. Aggregation numbers derived from static and dynamic methods are in good agreement and decrease with increasing molecular weight of the polymeric tail. Aggregates seem to be polydisperse and stable for long periods of time. Although aggregation is reduced when small amounts of 2-methylcyclohexanol are added, in CCl_4 solutions, it persists even at concentrations of alcohol as high as 5% (v/v). Gels, formed by the difunctional species, are also destroyed by addition of alcohol. There is evidence for intramolecular association in very dilute solutions of the difunctional species. The hydrodynamic behavior of the aggregates, formed by the monofunctional species, resembles that of star polymers in general. Comparisons with theoretical predictions show that the behavior of the aggregates is best described by the linear head-packing model.

Introduction

Association of polymer molecules in solution can be created by the incorporation of a relatively few functional groups into the polymer chain.[1–3] These groups have distinctly different polarity as compared to the precursor macromolecule. The phenomenon is observed in water-soluble polymers with hydrophobic groups[4,5] and in hydrocarbon-soluble polymers with hydrophilic groups.[6–10] Solution properties in general can be changed qualitatively by the presence of associating groups whose concentration is so small as to challenge determination or even detection by conventional analytical methods. For example, chain dimensions in dilute solution may be reduced or increased by intramolecular and intermolecular association, respectively.

The behavior of associating polymers is mainly dictated from a combination of factors like (a) the nature of the associating groups, (b) the nature of the solvent, and (c) intrinsically polymeric features (chain length, constitution and microstructure of the polymeric chain, location and number of the associogenic groups, etc.). The control of these factors enables one to study and better understand the polymeric aggregation process and to create a variety of aggregate microstructures. These different microstructures play an important role in the tailoring of the properties of polymer solutions for various applications such as viscosity modifiers and flow improvers.[11] At the same time, these systems also provide unique opportunities for model system studies in complex fluid research.

End-functionalized polymers provide the least complicated examples of polymeric association.[12–15] Although a variety of methods have been used to prepare polymers with functional groups at the chain ends,[16–19] the most attractive approach to the problem seems to be anionic polymerization.[19] By this method the incorporation of many types of functional groups is possible, and functionalized polymers with predictable molecular weights, nearly monodisperse molecular weight distributions, and controllable macromolecular architecture can be obtained.

In a previous paper[20] the synthesis and characterization of block copolymers of styrene and isoprene having dimethylamino and zwitterion groups at the chain ends were described. Some preliminary results on the association behavior of a number of these copolymers in CCl_4 from low-angle laser light scattering were also given.

In this publication we report on the dilute solution properties of a larger number of diblock and triblock samples as examined by static low-angle light scattering, dynamic light scattering, and viscometry in CCl_4 and CCl_4/2-methylcyclohexanol mixtures. Our intention is to study the influence of the polar groups on the solution (association) and solid state (morphology) of block copolymers. These studies are of great technological importance since block copolymers find applications as oil additives, as thermoplastic elastomers, as compatibilizers for polymer blends, and in the modification of surface and interfacial properties. We try to elucidate some aspects of the aggregation process in these systems, such as the molecular weight and concentration dependence of the average aggregation number, aggregate polydispersity, formation of the polar cores, and shape, size, stability, and hydrodynamic behavior of the aggregates. The influence of the chemical structure and architecture of the macromolecular chain and the position and number of the polar groups on the association of the zwitterion groups is studied. Some comparisons with theoretical predictions are also made.

Experimental Section

A. Polymer Synthesis. The polymers were prepared under high-vacuum conditions in all-glass reactors using standard anionic polymerization techniques.[21,22] Block copolymers were obtained by sequential addition of monomers. The dimethylamino functionality was introduced at either the polyisoprene or the polystyrene chain end by polymerizing the appropriate

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monomer first using [3-(dimethylamino)propyl]lithium as initiator.[14,23,24] When styrene was the first monomer and for molecular weights of the polystyrene block lower than 11 000, a small amount of THF was added to the polymerization mixture to accelerate the initiation reaction. Triblock copolymers were prepared by coupling diblock living ends with $(CH_3)_2SiCl_2$. The terminal tertiary amine groups were converted to sulfozwitterionic groups by reaction with cyclopropanesultone. Details are given elsewhere.[14,20]

All stages of polymer synthesis were monitored by size exclusion chromatography (SEC). A Waters Model 510 pump and Waters Model 401 differential refractometer in series with a four μ-Styragel column set having a continuous porosity range from 10^6 to 10^3 Å was used. Tetrahydrofuran was the elution solvent at a flow rate of 1 mL/min at 30 °C. Injection concentrations of about 0.1 g/dL were used.

Composition of the copolymers and microstructure of the polyisoprene blocks were obtained by ^{1}H-NMR spectroscopy (Bruker AC200 instrument) in $CDCl_3$ at 30 °C.

B. Dilute Solution Measurements. Number-averaged molecular weights (M_n) and second virial coefficients (A_2) were determined with a Wescan Model 231 membrane osmometer at 37 °C. RC-51 membranes were used. Toluene, distilled over CaH_2, was the solvent. In all cases, M_n and A_2 values were obtained from the $(\Pi/c)^{1/2}$ vs c plots, where Π is the osmotic pressure.

For the low molecular weight samples (M_n < 11000) a UIC Model 070 vapor pressure osmometer was used. HPLC grade benzene was the solvent at 40 °C. The instrument was calibrated with benzil. The M_n values from VPO were obtained from ($\Delta R/c$) vs c plots (ΔR is the change in resistance of the thermistors), using the relation $(\Delta R/_c)_{c=0} = k_v/M_n$, where k_v is the calibration constant.

Weight-average molecular weights (M_w) and second virial coefficients were obtained from the concentration dependence of the excess Rayleigh ratio ΔR_θ via

$$Kc/\Delta R_\theta = 1/M_w + 2A_2c \qquad (1)$$

where K is a combination of known optical constants including dn/dc, the refractive index increment (measured in THF, carbon tetrachloride, and CCl_4/2-methylcyclohexanol mixtures). 2-Methylcyclohexanol was chosen because it is isorefractive with CCl_4 and its dielectric constant (ϵ = 13.3 at 20 °C) is almost double that of THF (ϵ = 7.6 at 25 °C). Zwitterion-capped block copolymers were not associated in the latter solvent.[20] THF was purified by refluxing over sodium and was distilled just prior to use. Carbon tetrachloride was dried over CaH_2 and fractionally distilled. 2-Methylcyclohexanol was dried over molecular sieves and filtered through 0.22 μm pore size Nylon filters before the preparation of the mixed solvents. Care was taken during the preparation of the solutions to minimize contact with moisture. Solution concentrations were below the coil overlap concentration c^* ($\sim[\eta]^{-1}$). For light scattering measurements solutions were clarified by filtration through 0.22 μm pore size Nylon filters. Fluctuations of the scattered light intensity were considerably larger for Zwitterion-capped samples. $(Kc/\Delta R_\theta)^{1/2}$ vs c plots were used to analyze the data, although $Kc/\Delta R_\theta$ vs c plots gave similar results.

The dn/dc values required for low-angle laser light scattering (LALLS) experiments were measured in all solvents at 25 °C with a Chromatix KMX-16 differential refractometer operating at 633 nm, which was calibrated with aqueous NaCl solutions. For the block copolymers studied here, dn/dc values in all solvents are high enough to permit accurate determination of apparent M_w values[25] which would be close to the true M_w of the copolymers, owing to the molecular weight and compositional homogeneity of the samples. It was shown earlier[26] that the equations derived for copolymers in single solvents[25] hold also for copolymers in binary solvent mixtures. In the case where the solvents comprising the mixtures are isorefractive, the dn/dc value can be determined by constant chemical composition of the mixture instead of constant chemical potential.[27]

Dynamic light scattering (DLS) experiments were carried out using a Brookhaven BI200SM goniometer and a ca. 28 mW Ar^+ laser operating at λ = 488 nm. Correlation functions were analyzed to second order by the method of cumulants[28] using a Brookhaven Model BI2030 correlator with 72 channels. Temperature was controlled to 25 ± 0.1 °C. Measurements were confined to an angle of 45° for the amine-capped copolymers, whereas for the zwitterion-capped samples measurements were taken at 45, 90, and 135°. A small angular dependence of the Γ/q^2 was observed for the solutions of the zwitterion samples with the higher precursor (amine-capped polymer) and aggregate molecular weights. Second moments μ_2/Γ^2 were larger than 0.2 for zwitterion-capped copolymers in many cases.

Translational diffusion coefficients D_0[29] at infinite dilution were determined for amine- and zwitterion-capped copolymers in CCl_4 from the concentration dependence of the apparent diffusion coefficient

$$D_{app} = D_0(1 + k_Dc + ...) \qquad (2)$$

where k_D is the coefficient of the concentration dependence of the diffusion coefficient ($k_D = 2A_2M - k_f - u_2$, where A_2 is the second virial coefficient, M is the molecular weight, k_f is the coefficient in the concentration dependence of the friction coefficient, and u_2 is the partial specific volume of the polymer).

The average hydrodynamic radius at infinite dilution was calculated from

$$R_h = kT/6\pi\eta_sD_0 \qquad (3)$$

where k is Boltzmann's constant and η_s is the solvent viscosity. Equation 3 was also used for calculating the apparent hydrodynamic radius at each concentration when the variation of R_h with concentration was nonlinear. In these cases, the value of D_{app} was used for each concentration.

Intrinsic viscosities and Huggins coefficients for the amine- and zwitterion-capped block copolymers were obtained from the concentration dependence of the specific viscosity, η_{sp} ($=\eta_r - 1$), where the relative viscosity η_r is the ratio of solution to solvent flow times

$$\eta_{sp}/c = [\eta] + k_H[\eta]^2c + ... \qquad (4)$$

in CCl_4 and CCl_4/2-methylcyclohexanol mixtures at 25 °C. Kraemer plots

$$\ln \eta_r/c = [\eta] + k_K[\eta]^2c + ... \qquad (5)$$

where k_K is the Kraemer coefficient, were also used in all cases. Cannon-Ubbelohde dilution viscometers with a Scott-Gerate automatic flow timer were used. Solvent flow times were greater than 200 s. The average viscometric radius was calculated by aid of the equation

$$R_v = (3/10\pi N_A)^{1/3}([\eta]M_w)^{1/3} \qquad (6)$$

where N_A is the Avogadro number and M_w is the weight-average molecular weight from light scattering.

Results and Discussion

The molecular characteristics of amine precursors of the samples used in this study are given in Table 1. Samples are designated with the letter corresponding to the type of the terminal group (N for the amine-capped copolymers and Zw for the zwitterion-capped samples) followed by the sequence of the blocks starting with the block at which the group is attached (I for polyisoprene and S for polystyrene) and a number showing the order of sample preparation. In this way NSI-1 denotes a diblock copolymer having the dimethylamine group at the end of the polystyrene block, the first prepared. The corresponding zwitterion-capped diblock is designated ZwSI-1. The notation NSISN-1 corresponds to a triblock copolymer with polystyrene end blocks and amine end groups. The zwitterionic triblock is designated ZwSISZw-1. The letter F after the order number denotes that THF

Table 1. Molecular Characteristics of End-Functionalized Block Copolymers

sample	M_w[a] × 10^{-4}	A_2[a] × 10^3 (mol mL g^{-2})	M_n[b] × 10^{-4}	A_2[b] × 10^3(mol mL g^{-2})	% PS[c] (wt)	% 3,4-vinyl[c]	% 1,2-vinyl[c]
NIS-2[e]	5.49	1.20	5.38	1.08	29		
NI-2[e]			3.82	1.22		15	
NIS-7	3.74	1.03	3.28	1.07	30		
NI-7			2.37	1.60		16	
NIS-3[e]	2.44	1.35	2.25	1.26	28		
NI-3[e]			1.66	1.84		17	
NIS-4[e]	1.79	1.40	1.57	1.51	29		
NI-4[e]			1.15	1.85		18.5	
NIS-5[e]	1.41	1.46	1.22	1.27	28		
NI-5[e]	0.89	3.10	0.88[d]			20	
NIS-8	0.91	1.54	0.83[d]		27		
NI-8			0.60[d]			28	
NIS-6	0.62	2.16	0.51[d]		16		
NI-6			0.43[d]			38	3
NSI-1[e]	6.96	0.93	6.12	1.04	30	15	
NS-1[e]			1.97	0.44			
NSI-5F	4.26	1.18	3.75	1.24	27	58	16
NS-5F			1.07[d]				
NSI-4F	1.88	1.40	1.70	1.31	30	59	13
NS-4F			0.50[d]				
NSI-3F	1.49[f]		1.34	1.66	32	63	12
NS-3F			0.44[d]				
NSI-2F	1.14[f]		1.04	3.99	32	57	6
NS-2F			0.35[d]				
NSISN-1[e]	7.63	0.81	7.02	1.18	36	21	
NS[e]	1.65	0.42					
NISIN-1[e]	6.98	1.10	6.27	1.08	27		
NI[e]			2.29	1.69		18	

[a] By LALLS in THF at 25 °C. [b] By membrane osmometry in toluene at 37 °C. [c] By ^{1}H-NMR. [d] By VPO in benzene at 40 °C. [e] Data from ref 20. [f] Calculated from M_n (membrane osmometry) and $I = M_w/M_n$ (SEC).

was added to the polymerization mixture before the initiation of styrene polymerization by DMAPLi. The agreement between M_w and M_n is good, implying low heterogeneity of the copolymers with respect to molecular weight and chemical composition. There are some differences of microstructure of the polyisoprene block on the one hand because of the use of an initiator with a polar amine group (in the case of the NIS type copolymers) and on the other hand because of the use of THF to accelerate the initiation reaction (in the case of the NSI type samples). This is a result of the limitations imposed by the synthesis. It is unlikely that these differences affect the solution properties in any significant way within the same series. Conclusions will be drawn for groups of samples with similar composition and microstructure.

The results from static low-angle light scattering for the zwitterion-capped block copolymers in CCl_4 are given in Table 2. The samples are clearly aggregated in this nonpolar solvent in contrast to the amine-capped precursors. The measured M_w values are markedly increased and A_2 values are decreased almost by an order of magnitude. A decrease of the average aggregation number N_w with increasing molecular weight of the precursor polymer is evident. This phenomenon is observed for both types of monofunctional copolymers. Also the N_w values are in the same range for the two different types of samples. The average degree of association seems to depend only on the overall molecular weight of the polymer chain and not on the sequence of blocks. However, the average aggregation numbers for the copolymers are lower than those determined for zwitterion-capped polyisoprenes in cyclohexane and CCl_4 and close to the value determined for a zwitterion-capped polystyrene in CCl_4 for reasons explained before.[20] It seems that the factor which, in some way, dictates the aggregation process is the nature of the comonomers incorporated in the macromolecules chain and their specific interactions with polar heads and not the detailed architecture of the nonpolar tail. The influence of stereochemical restrictions (or differences) in the neighborhood of the groups, which tend to associate producing a hydrophilic core with defined dimensions, also seems to be negligible, at least in dilute solutions.

Table 2. Aggregation Results for End-Functionalized Block Copolymers in CCl_4

sample	M_w × 10^{-4}	A_2 × 10^4 (mol mL g^{-2})	N_w
NIS-3	2.53	11.7	1.0_4
NIS-4[a]	2.0	11.8	1.1
NIS-5[a]	1.46	12.8	1.0_4
NIS-8	0.96	13.2	1.0_5
NIS-6	0.84	20.2	1.4
NSI-1[a]	7.15	7.2	1.0_3
NSISN-1[a]	7.83	5.4	1.0_3
ZwIS-2[a]	12.0	3.3	2.2
ZwIS-7	17.9	3.6	4.8
ZwIS-3[a]	19.1	3.4	7.8
ZwIS-4[a]	20.0	8.2	11.2
ZwIS-5[a]	11.2	−1.4	7.9
ZwIS-8	14.1	6.7	15.5
ZwIS-6	9.28	9.5	15.0
ZwSI-1[a]	40.5	2.4	5.8
ZwSI-5F	17.1	4.0	4.0
ZwSI-4F	21.3	5.8	11.3
ZwSI-3F	18.1	−4.5	12.1
ZwSI-2F	12.2	2.6	10.7
ZwSISZw-1[a]	39.1	4.0	5.1
ZwISIZ-1[a]	43.2	2.8	6.2

[a] Data from ref 20.

The aggregation number for the difunctional samples is also of the same order as that determined for monofunctional samples. These relatively low degrees of association are a bit surprising considering the fact that triblocks having zwitterion groups at both ends of the chain form stable gels at concentrations below c^* ($c_{gel} \approx 0.5c^*$). Measurements in CCl_4 were confined to concentrations

Table 3. DLS Results for End-Functionalized Block Copolymers in CCl_4[a]

sample	$D_0 \times 10^7$ ($cm^2\ s^{-1}$)	k_D ($mL\ g^{-1}$)	R_h (nm)	R_{hZw}/R_{hN}
NIS-2	2.78	96	8.7	
NIS-7	3.52	44	6.9	
NIS-3	4.08	−7.3	6.9	
NIS-4	6.06	−2.9	4.0	
NIS-5	6.55	−10.6	3.7	
NIS-8	7.58	−14.8	3.2	
NIS-6	10.1	−6.2	2.4	
NSI-1	2.34	59	10.4	
NSI-5F	3.52	37	6.9	
NSI-4F	5.00	2.1	4.8	
NSI-3F	5.49	0.9	4.4	
NSI-2F	6.73	−4.4	3.6	
NSISN-1	2.96	29	8.2	
NISIN-1	2.47	45	9.8	
ZwIS-2	2.0 (1.48)	−105 (−11)	12.1 (16.5)	1.4 (1.9)
ZwIS-7	1.93 (1.67)	−113 (39)	12.6 (14.5)	1.8 (2.1)
ZwIS-3	1.84	6.5	13.3	2.3
ZwIS-4	2.25	1.8	10.7	2.7
ZwIS-5	3.04	−69	8.0	2.2
ZwIS-8	2.97	−5.7	8.2	2.6
ZwIS-6	3.47	−76	7.0	2.9
ZwSI-1	1.02 (0.95)	−20	23.7 (25.5)	2.3 (2.5)
ZwSI-5F	1.84	0.8	13.2	1.9
ZwSI-4F	2.00	4.3	12.1	2.5
ZwSI-3F	1.82	−237	13.3	3.0
ZwSI-2F	2.56	9.8	9.5	2.6
ZwSISZw-1	1.91 (1.48)	−569 (−57)	12.7 (16.3)	1.5 (2.0)
ZwISIZw-1	1.25 (1.18)	−79 (−0.9)	19.4 (20.5)	2.0 (2.1)

[a] Values for D_0 and k_D in parentheses were obtained from linear extrapolation from high concentrations when there was curvature in the plots of D vs c. Results given in parentheses in the other columns were calculated using the values of D_0 obtained as mentioned previously.

lower than c_{gel}. This result can be seen as evidence of intramolecular association in dilute solutions.

To determine the size of the aggregates formed by the zwitterion-capped block copolymers and to complement the static light scattering measurements, dynamic light scattering experiments were also carried out in CCl_4. Since the dimensions of the polymer chain in dilute solutions depend strongly on the nature of the solvent,[30] the amine-capped precursors were also studied in CCl_4 to allow direct comparison. The results are given in Table 3. The DLS results support the conclusions drawn from LALLS. The behavior of amine-capped samples is similar to that expected for unfunctionalized polymers in good solvents. D_0 values decrease and R_h increases as the molecular weight of the copolymeric chain increases. k_D values decrease as the molecular weight decreases but below a certain M_w (which is different for the two kinds of polymers studied) become negative. The k_D dependence on molecular weight resembles that of a homologous molecular weight series of nonassociating polymers in a thermodynamically moderate solvent.[31,32]

We do not believe that the k_D dependence can be attributed to some kind of association of the amine-capped copolymers since LALLS measurements showed no evidence for the existence of aggregates (weight-average molecular weights for the amine-capped copolymers in CCl_4 were similar to those obtained in THF). We believe that the dependence arises from the fact that CCl_4 is not an equally good solvent for polystyrene and polyisoprene (it seems that it is a better solvent for polyisoprene[33,34]). Additionally, in the low molecular weight region, where it has been shown that the exponent a in the Mark–Houwink–Sakurada relationship is diminished,[35,36] the frictional contribution to the magnitude of k_D dominates. The difference in the M_w values where k_D changes sign for the two different types of samples may be a result of the differences in the microstructure of the polyisoprene block and subsequently differences in solvent quality. Unfortunately, there is no systematic work on the dependence of k_D on the molecular weight of copolymers of the same composition in different solvents.

For the analysis that follows we consider the D_0 and R_h values determined for the amine-capped copolymers as values characteristic for the isolated block copolymer chain. In any case, comparisons are made between the zwitterion copolymer and the corresponding amine precursor so the conclusions drawn are direct and unambiguous.

The behavior of the zwitterion-capped copolymers is substantially different from that of their precursors. D_0 values are considerably lower and R_h higher. For samples with higher molecular weight of the precursor, a slight dependence of the Γ/q^2 values on the angle of measurement was observed. These values are lower for the lower angle used (45°) and almost identical for the other two angles (90 and 135°). This angular dependence results from the presence of aggregates with dimensions comparable to 1/20 of the laser wavelength used. Additionally, it reflects the polydispersity in size of the micelles, a conclusion that is also supported by the relatively high values for μ_2/Γ^2 (>0.2) observed in several cases. For the samples with lower precursor M_w, no angular dependence was observed.

The dependence of the measured diffusion coefficient (and correspondingly that of the hydrodynamic radius) on concentration shows some interesting features. For the samples with the shorter chains, D depends linearly on c. For longer precursor chains (including the samples with both ends functionalized), D decreases (R_h increases) exponentially for increasing polymer concentration and in the case of monofunctional samples attains an almost constant value; but in the case of difunctional species D continues to decrease with a smaller slope (Figures 1 and 2). The values of D_0, k_D, and R_h determined from extrapolation from high concentrations are given in Table 3 in parentheses. For the last cases it seems that the aggregation number increases with concentration, arriving at a constant value (monofunctional samples) but the increase is sharper at low concentrations. The phenomenon is more pronounced in the difunctional zwitterionic copolymers where the increase in aggregation number (and aggregate dimensions) persists until the formation of gel. Regardless of the concentration range used for extrapolation, the values of k_D are erratic. There is no regular trend with respect to the molecular weight of precursor or of aggregates. In most cases, k_D is negative, a consequence of the aggregation process taking place in the solutions which also decreases the observed second virial coefficient. Similar behavior was observed in other aggregating systems.[37,38]

In Table 3 the ratios of the hydrodynamic radius of the zwitterion aggregates, R_{hZw}, to that of the amine precursor, R_{hN}, are also given. This ratio gives an estimate of the increase of the dimensions of the polymeric entities in solution after association and also an estimate of the average degree of aggregation derived by aid of the star model. In star polymers the ratio of the viscometric radius of the star, $R_{v,star}$, to the viscometric radius of the arm, $R_{v,arm}$, depends only on the number of arms and is independent of the arm molecular weight. These ratios are the same for star polystyrenes and polyisoprenes of the same functionality in good solvents and Θ solvents[39]

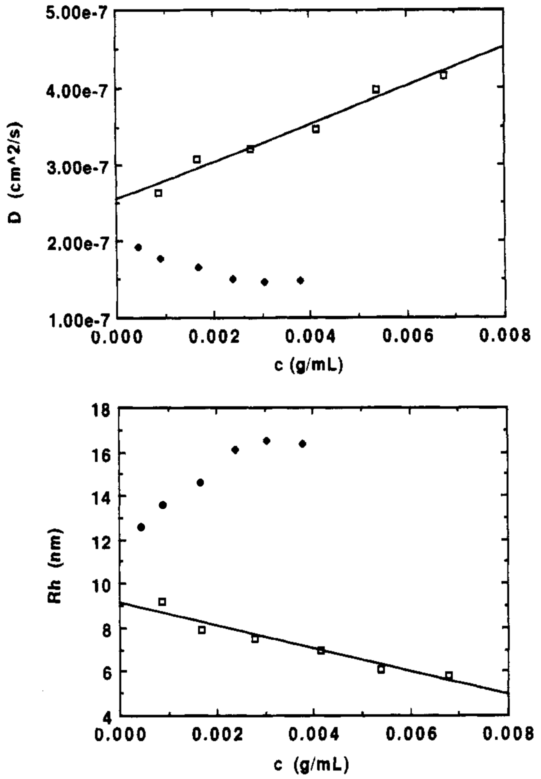

Figure 1. Diffusion coefficient and hydrodynamic radius vs concentration for samples NIS-2 (□) and ZwIS-2 (◆) in CCl_4 at 25 °C.

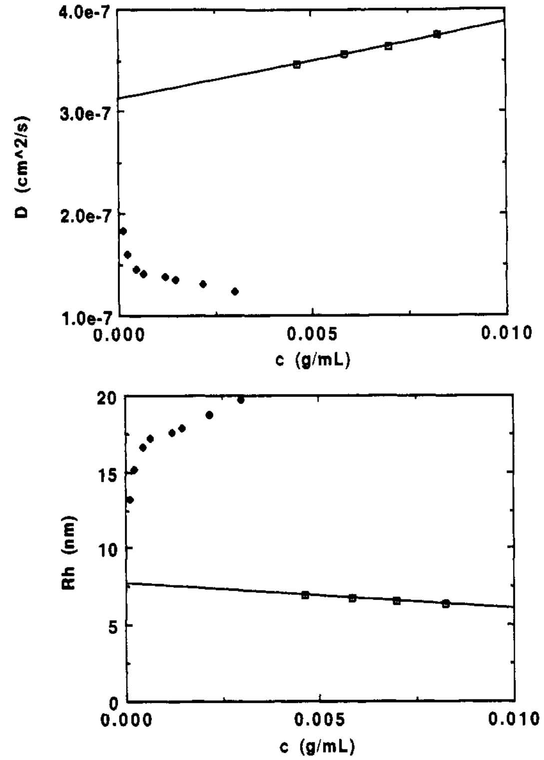

Figure 2. Diffusion coefficient and hydrodynamic radius vs concentration for samples NSISN-1 (□) and ZwSISZw-1 (◆) in CCl_4 at 25 °C.

and presumably for star block copolymers derived from these monomers. Additionally, it has been shown that R_v/R_h is very close to unity for linear and star polymers,[40–43] so $R_{h,star}/R_{h,arm}$ will be close to the ratio of the viscometric radii and would also depend in the same way on the functionality of the star. We used the values of R_{hZw}/R_{hN} for each sample and the data of ref 39 for the variation of $R_{v,star}/R_{v,arm}$ with the functionality f of chlorosilane-linked polystyrene and polyisoprene stars with 2–18 arms to calculate the aggregation number from dynamic light scattering measurements.

The assumption that the aggregates produced by association of the end-functionalized block copolymers can be visualized as star polymers, having a number of arms equal to the average aggregation number, is supported, at least for the case of the monofunctional versions, by the relatively low aggregation numbers obtained for these polymers ($N_w < 16$). The presence of only one group at the chain end leads to the formation of a polar core of small dimensions compared to that of the polymer chain, irrespective of the detailed geometry of the core. In this way the chains are anchored at the periphery of a small core (a cluster of ionic groups) and behave like the arms of a star polymer.

The above approach is not so straightforward in the case of the difunctional samples. The possibility of closed loop formation by the incorporation of two dipoles that belong to the same chain into the same cluster or formation of intermicellar connections when the end groups of the same chain belong to different clusters cannot be ruled out. The first structure can be observed in very dilute solutions and results in smaller dimensions. The second may be abundant in more concentrated solutions and lead eventually to the formation of gels. Of course, the parallel existence of structures with closed loops, interconnections, or even aggregates with chains having one group participating in the core of an aggregate and the other one floating free in the hostile environment of the nonpolar solvent and aggregates of mixed type is another possibility (which seems more realistic).

Loop formation is not entropically favored since the chains lose configurational entropy, and the presence of free polar groups in a nonpolar environment increases the free energy of the system (due to unfavorable thermodynamic interactions). The factors mentioned before in combination with those acting in the case of the monofunctional species determine the situation in the solutions of the difunctional block copolymers. The case of difunctional zwitterionic triblock copolymers in a good solvent for the polymeric chain is analogous to the case of unfunctionalized ABA triblock copolymers in solvents selective for the middle block.[44]

Comparison of the results from static low-angle light scattering (where the average aggregation number N_w is obtained from the ratio of the weight-average molecular weights) with the results from dynamic light scattering or viscometry (where the aggregation number is obtained through the ratio of the hydrodynamic radii) can give some answers to the problem of the configuration of the difunctional chains when they are participating in the association process. In the limiting case where only one group per chain is associated and the other is free the chain behaves as the arm of a star polymer, and the ratio R_{hZw}/R_{hN} (or the equivalent R_{vZw}/R_{vN}) will correspond to that of a star polymer with functionality equal to N_w. In the other limiting case, where only closed loops exist in the aggregates, the structure is more compact and the apparent aggregation number derived from the ratio of the hydrodynamic radii will be lower than the value determined by the ratio of the molecular weights. When many different types of aggregates exist in solution, the analysis is more complicated and quantitative evaluations are not readily made.

For a more direct comparison viscosity measurements were also conducted on solutions of amine-capped and zwitterion-capped block copolymers in CCl_4. Results are

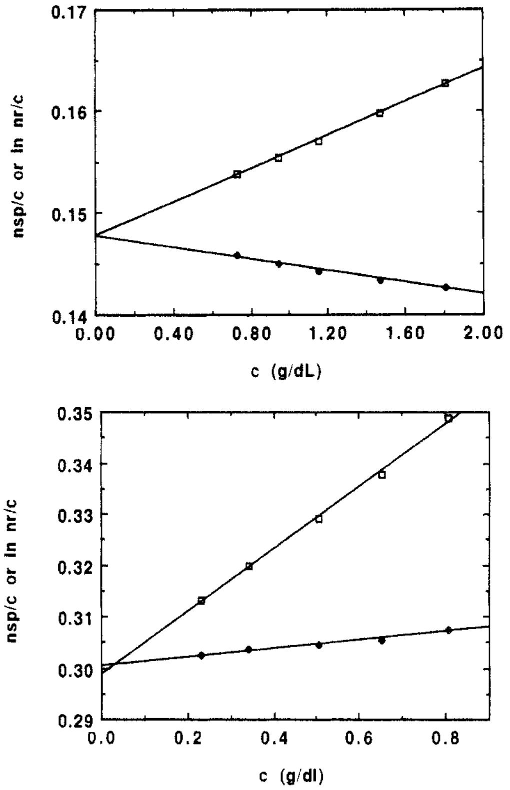

Figure 3. η_{sp}/c or $\ln \eta_r/c$ vs c for samples NIS-8 (□) and ZwIS-8 (◆) in CCl_4 at 25 °C.

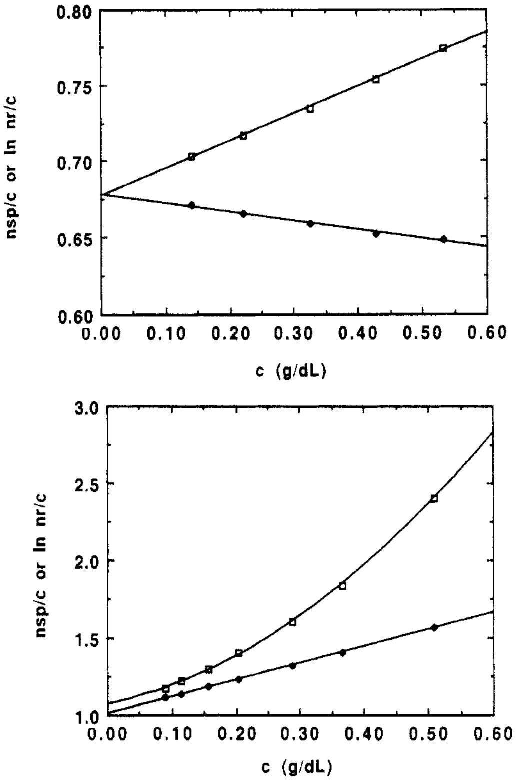

Figure 4. η_{sp}/c or $\ln \eta_r/c$ vs c for samples NISIN-1 (□) and ZwISIZw-1 (◆) in CCl_4 at 25 °C.

Table 4. Viscometric Results for End-Functionalized Block Copolymers in CCl_4

sample	$[\eta]$ (mL g^{-1})	k_H	R_v (nm)	$[\eta]_{Zw}/[\eta]_N$	$(R_v)_{Zw}/(R_v)_N$
NIS-2	67.1	0.30	8.4		
NIS-7	43.3	0.36	6.4		
NIS-3	38.8	0.36	5.3		
NIS-4	26.7	0.32	4.2		
NIS-5	25.5	0.33	3.8		
NIS-8	14.8	0.38	2.8		
NIS-6	11.2	0.44	2.2		
NSI-1	77.4	0.37	9.5		
NSI-5F	44.6	0.36	6.7		
NSI-4F	29.4	0.33	4.4		
NSI-3F	23.0	0.45	3.8		
NSI-2F	18.3	0.50	3.2		
NSISN-1	63.0	0.32	9.1		
NISIN-1	67.7	0.39	9.1		
NwIS-2	74.8	0.44	11.2	1.11	1.3
ZwIS-7	68.4	0.43	12.5	1.58	2.0
ZwIS-3	60.4	0.62	12.2	1.56	2.3
ZwIS-4	45.2	0.51	11.3	1.69	2.7
ZwIS-5	31.7	0.71	8.2	1.24	2.2
ZwIS-8	29.9	0.68	8.7	2.02	3.1
ZwIS-6	23.0	0.55	7.0	2.05	3.2
ZwSI-1	106.0	0.55	18.9	1.37	2.0
ZwSI-5F	60.9	0.62	11.8	1.36	1.8
ZwSI-4F	47.6	0.61	11.7	1.62	2.7
ZwSI-3F	43.9	0.72	10.8	1.91	2.8
ZwSI-2F	32.6	0.63	8.6	1.78	2.7
ZwSISZw-1	85.0	1.45	17.4	1.35	1.9
ZwISIZw-1	101.3	0.76	19.1	1.50	2.1

shown in Table 4. Representative diagrams for copolymers with different numbers of zwitterion groups are given in Figures 3 and 4. Again the behavior of the amine precursors was normal. The $[\eta]$ values were the ones expected for the molecular weight range used, and k_H values were positive and around 1/3. The viscometric radii calculated from $[\eta]$ and M_w from LALLS in THF are in good agreement with the hydrodynamic radii determined from DLS experiments.

In contrast to the amine precursors, the $[\eta]$ values for the solutions of the zwitterion-capped copolymers are considerably higher even though lower concentrations were used in the latter case. The dependence of η_{sp}/c or $\ln \eta_r/c$ on concentration is not always linear. Huggins plots show, in some cases, upward curvature at high concentrations,[45] and the effect is more pronounced in the case of the difunctional samples. The Huggins coefficient, determined from the initial slope, is very high ($k_H > 0.5$) in most cases. The viscometric radii determined from $[\eta]$ and M_w in CCl_4 for the same samples are higher than those determined for the amine precursors and close to that obtained by dynamic light scattering.

The above results support the conclusion drawn from light scattering measurements that the zwitterion-capped block copolymers associate in CCl_4. The increased $[\eta]$ values result from the increase of mass and consequently in the dimensions of the dispersed species due to the association. The increased values of the Huggins coefficient indicate increased hydrodynamic interactions between polymer chains due to the incorporation of the polymer molecules in the aggregates. An analogous increase in k_H is also observed in the case of star polymers relative to the linear homologs.[35] Increased k_H values were reported before for associating systems.[46-48] The nonlinear dependence of the specific viscosity on concentration may be an indication of changes in the aggregation number by increasing concentration of polymer in solution,[45] a phenomenon that is expected to be more pronounced in the case of the difunctional triblocks.

To study the stability of the aggregrates formed by the zwitterionic copolymers and extract, indirectly, information about the whole association process, static low-angle light scattering and viscometry experiments were made in mixtures of CCl_4 and 2-methylcyclohexanol (at 1 and 5% (v/v) alcohol content). Before conducting the measurements, it was established that solvent quality, with respect

Table 5. LALLS Results for Polystyrene and Polyisoprene Homopolymers in CCl_4 and CCl_4/2-Methylcyclohexanol (2MeCHOH) Mixtures

	CCl_4		1% 2MeCHOH/CCl_4 mixture		5% 2MeCHOH/CCl_4 mixture	
sample	$M_w \times 10^{-4}$	$A_2 \times 10^4$ (mol mL g^{-2})	$M_w \times 10^{-4}$	$A_2 \times 10^{-4}$ (mol mL g^{-2})	$M_w \times 10^4$	$A_2 \times 10^4$ (mol mL g^{-2})
PS-40K	4.14	6.33	3.86	6.34	3.82	5.91
PI-50K	5.07	16.3	4.8	16.9	4.54	16.1

Table 6. Aggregation Results for Zwitterion-Capped Block Copolymers in CCl_4/2-Methylcyclohexanol Mixtures

	CCl_4/1% 2-methylcyclohexanol mixture		CCl_4/5% 2-methylcyclohexanol mixture	
sample	$M_w \times 10^{-4}$	$A_2 \times 10^3$ (mol mL g^{-2})	$M_w \times 10^{-4}$	$A_2 \times 10^3$ (mol mL g^{-2})
ZwIS-2	11.3	0.78	6.44	0.78
ZwIS-7	16.9	0.37	6.68	0.49
ZwIS-3	14.0	0.51	5.58	0.22
ZwIS-4	12.3	0.51	6.19	0.25
ZwIS-5	6.49	0.70	5.63	~0
ZwIS-8	8.43	0.33	4.52	0.34
ZwIS-6	9.02	0.70	2.89	0.20
ZwSI-1	31.9	0.28	26.4	0.43
ZwSI-5F	16.6	0.54	8.05	0.82
ZwSI-4F	15.6	0.47	4.87	−0.26
ZwSI-3F	16.0	0.27	6.58	~0
ZwSI-2F	11.4	0.49	5.68	0.38
ZwSISZw-1	24.6	0.18	11.4	0.43
ZwISIZw-1	28.4	0.34	10.6	0.66

Table 7. Viscometric Results for Zwitterion-Capped Block Copolymers in CCl_4/1% 2-Methylcyclohexanol Mixture

sample	$[\eta]$ (mL g^{-1})	k_H	R_v (nm)	$[\eta]_{Zw}/[\eta]_N$	$(R_v)_{Zw}/(R_v)_N$
ZwIS-2	77.1	0.41	11.1	1.15	1.3
ZwIS-7	68.5	0.55	12.2	1.58	1.9
ZwIS-3	59.8	0.55	10.9	1.54	2.1
ZwIS-4	42.2	0.85	9.4	1.58	2.2
ZwIS-5	26.0	1.33	6.4	1.02	1.6
ZwIS-8	28.7	0.84	7.3	1.94	2.6
ZwIS-6	22.8	0.72	6.9	2.04	3.1
ZwSI-1	98.0	1.90	17.0	1.27	1.8
ZwSI-5F	57.3	0.92	11.5	1.28	1.7
ZwSI-4F	47.7	0.65	10.6	1.62	2.4
ZwSI-3F	44.0	0.71	10.4	1.91	2.7
ZwSI-2F	31.6	0.90	8.3	1.73	2.6
ZwSISZw-1	79.1	2.55	14.6	1.26	1.6
ZwISIZw-2	94.7	2.06	16.2	1.40	1.8

Table 8. Viscometric Results for Zwitterion-Capped Block Copolymers in CCl_4/5% 2-Methylcyclohexanol Mixture

sample	$[\eta]$ (mL g^{-1})	k_H	R_v (nm)	$[\eta]_{Zw}/[\eta]_N$	$(R_v)_{Zw}/(R_v)_N$
ZwIS-2	69.2	0.36	8.9	1.03	1.1
ZwIS-7	54.3	0.88	8.3	1.25	1.3
ZwIS-3	47.7	1.19	7.5	1.23	1.4
ZwIS-4	38.8	0.64	7.2	1.45	1.7
ZwIS-5	26.1	1.9	6.2	1.02	1.6
ZwIS-8	20.9	2.1	5.3	1.41	1.9
ZwIS-6	20.5	1.1	4.5	1.83	2.0
ZwSI-1	89.0	1.0	15.5	1.15	1.6
ZwSI-5F	49.7	0.65	8.6	1.11	1.3
ZwSI-4F	40.8	0.83	6.8	1.39	1.5
ZwSI-3F	37.4	0.94	7.3	1.63	1.9
ZwSI-2F	32.4	1.51	6.7	1.77	2.1
ZwSISZw-1	67.1	2.2	10.6	1.06	1.2
ZwISIZw-1	79.3	1.5	11.0	1.17	1.2

to polystyrene and polyisoprene, does not change appreciably by addition of alcohol, as can be seen from the A_2 values in Table 5. Therefore direct comparisons on aggegate dimensions can be made safely between pure CCl_4 and mixtures. The results on the zwitterionic samples are shown in Tables 6–8. Representative plots for monofunctional samples in different solvents are given in Figures 5 and 6.

The first conclusion that can be drawn is that association is reduced in the presence of alcohol, as expected, but some samples remain aggregated even at 5% alcohol. In the 1% alcohol mixture, the aggregates having aggregation numbers equal to or lower than 4 remain in the same state of aggregation, whereas in others, with higher degrees of association, the number of chains per aggregate is reduced substantially. This may be an indication that the aggregates with a small number of chains are more stable than larger associates and the forces which hold the polar heads together in the cores are weakened as the size of the aggregate becomes larger. In other words, the unimers in the larger micelles are loosely tied together. This observation supports theoretical predictions that the dimers of the zwitterion groups are the first multimers that can be formed, and consequently are the most stable, and that the formation of large clusters is accomplished through the formation of dimers, tetramers, etc., with decreasing stability.[49] The values of the second virial coefficient remain low but a small increase with respect to those determined in pure CCl_4 is evident in some cases.

The changes in the intrinsic viscosity are not so dramatic, at least for the monofunctional samples. This can be expected when the aggregation number remains constant, but it is also observed when the degree of association is reduced. The Huggins coefficient approaches values higher than unity, especially for the difunctional samples.

In the mixture having 5% alcohol content, the aggregation number is reduced in all cases, approaching unity for some samples. The A_2 values remain in the range observed for the previous mixture. No definite trends can be identified for the changes of A_2 in the cases discussed so far, and the variations seem to be sample dependent. The decrease in intrinsic viscosity is larger but there are a few exceptions. Samples that still have aggregation numbers close to 5 show a smaller decrease in $[\eta]$. This result seems to support the assumption made before that the aggregates have a starlike structure. Previous viscometric studies in good solvents[50] on star block copolymers of styrene and dienes having six or more arms have shown that the intrinsic viscosity does not change appreciably on changing the number of arms for samples with the same composition and arm molecular weight. The variation of the aggregation number by changing the composition of the mixture simulates an analogous situation for the aggregating block copolymers.

The k_H values decrease toward the values determined for the amine-capped precursors in the case where a drastic decrease of the aggregation number occurs, while they are still high where appreciable aggregation is observed. The difunctional samples are an exception, showing high values for the Huggins coefficient although the aggregation number from light scattering is close to unity.

The aggregation numbers obtained by different methods for the zwitterion-capped block copolymers in CCl_4 and the mixtures are shown for comparison in Table 9. Aggregation numbers from viscometric measurements were calculated from the ratio R_{vZw}/R_{vN} assuming the star model,

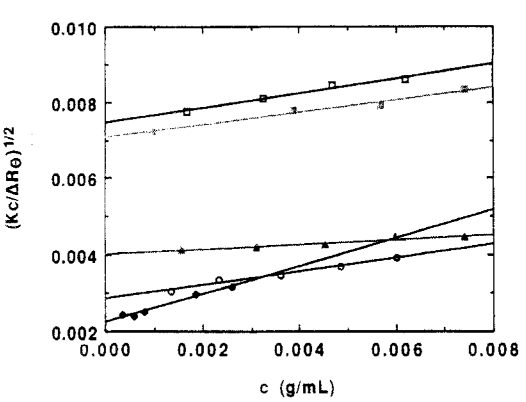

Figure 5. LALLS square root plots for samples NIS-4 and ZwIS-4 in several solvents. The symbols denote sample NIS-4 in THF (□), sample NIS-4 in CCl_4 (■), sample ZwIS-4 in CCl_4 (◆), and sample ZwIS-4 in CCl_4/2-methylcyclohexanol mixtures (1% alcohol (○) and 5% alcohol (▲)).

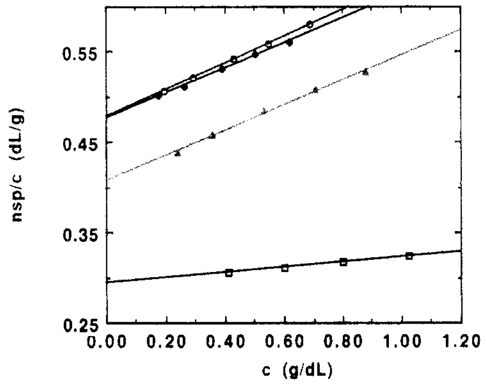

Figure 6. Viscosity measurements for samples NSI-4F and ZwSI-4F in several solvents. The symbols denote sample NSI-4F in CCl_4 (□), sample ZwSI-4F in CCl_4 (○), and sample ZwSI-4F in CCl_4/2-methylcyclohexanol mixtures (1% alcohol (◆) and 5% alcohol (▲)).

as in the case of dynamic light scattering. The calculated degrees of association from viscometry and DLS are almost identical, except for the samples with the lower molecular weight of the precursor polymer where the DLS measurements are not so accurate as far as the value of the R_{hN} is concerned. The agreement between the aggregation numbers derived from the equilibrium method and those from the dynamic methods is reasonably good.

The star model seems to describe the hydrodynamic behavior of the aggregates fairly well in all the solvents used, even in the case of the difunctional species. This may be a consequence of the fact that all the methods used weight predominantly the larger entities in solution (the molecular weights derived by static light scattering are weight average, the diffusion coefficient derived from dynamic light scattering is a z average, and $[\eta]$ is related closely with M_w). However, one must have always in mind that static methods measure time-averaged properties of the system under investigation while the dynamic methods are influenced by the variations of the measured quantity during the characteristic time period of the experiment. As far as viscometry is concerned, one also has to take into account that shear forces are developed on the sample, forces which, no matter how small or controllable they may be, can possibly disrupt the equilibrium state of a delicate microscopic process. Nevertheless, the individual characteristics of a method can become a tool for extraction of information on systems that change with time.

A closer inspection of the results in Table 9 reveals that the aggregation numbers derived from the dynamic methods are slightly lower than those obtained by static light scattering. This implies that the characteristic time of the method plays a substantial role on whether processes taking place in dilute solution will be determined by the method used or not. However, the differences are relatively small and this means that the aggregates exist in the solution long enough to be detected by the dynamic methods (their lifetime must be longer than the characteristic times of both methods used, $t = 2 \times 10^{-4}$ s for dynamic light scattering and $t = 2 \times 10^{-3}$ s for viscometry). If the lifetime of the aggregates were smaller than the characteristic time, the properties measured by the method would be characteristic of the free chains, because unimers would exist in solution for longer periods and they would have a stronger influence on the properties of the solution. In this way the aggregation numbers derived from the dynamic methods would be distinctly lower than those determined by a static method, which is not the case here. Additionally, because of the good agreement between the results of viscometry and the other methods used, we can conclude that aggregates are stable against the shear forces developed in the capillary viscometers ($\dot{\gamma} \approx 5 \times 10^2$ s^{-1}).

Another point that must be elucidated is whether the properties of the solutions of these associating polymers change in long time periods after the dissolution from the solid state. This point connects with the question of the time scale of the structural relaxation time τ_s, which characterizes the time needed for the aggregates in the solid state to equilibrate in the environment of the nonpolar solvent and, additionally, the time required for the aggregates to return to an equilibrium state after dilution of a stock solution. The measurements reported so far were made in freshly prepared solutions (<1 week after dilution of the sample). If τ_s is very large, the properties measured in these solutions would reflect the situation in the solid state. Additionally, comparison of the mesured properties in different time periods can give information on the thermodynamic identity of the association process. In other words, if the aggregates are metastable structures and not supramolecular entities which are produced from an equilibrium between free chains and micelles, the properties of the solutions are expected to decay with time, acquiring the values characteristic for the free chains after a specific period. In the opposite case, the properties must be almost unchanged by aging the solution, the conditions under which this aging occurs maintained constant and similar to those of the initial state.

For this reason stock solutions of preselected samples were prepared in CCl_4 and low-angle light scattering measurements were conducted in a series of solutions made by dilution shortly after the preparation of the stock solution. Portions of these stock solutions were preserved in stoppered vials in desiccators at room temperature to prevent contact with moisture. After 1.5 years the same dilutions were made from the aged solutions and the molecular weight and the second virial coefficient were determined by LALLS. The results from the measurements on the aged solutions are given in Table 10. Comparison with the results in Table 2 for the same samples reveals that the weight-average molecular weight and consequently the average aggregation number do not change appreciably over this period. Since total rejection of moisture from the solutions for such long periods of time cannot be achieved, the decrease in N_w for sample ZwIS-4 can be expected; but even in this case, the average degree of aggregation remains at the same order of magnitude. The A_2 values are still small and in the range determined in the previous cases.

Table 9. Aggregation Numbers for Zwitterion-Capped Block Copolymers in CCl_4 and 2-Methylcyclohexanol/CCl_4 Mixtures Obtained by Different Methods

	CCl_4			1% 2-methylcyclohexanol/CCl_4 mixture		5% 2-methylcyclohexanol/CCl_4 mixture	
sample	N_w(LALLS)	N(DLS)[a]	N(VIS)	N_w(LALLS)	N(VIS)	N_w(LALLS)	N(VIS)
ZwIS-2	2.2	2.3 (3.4)	1.7	2.0	1.7	1.2	1.3
ZwIS-7	4.8	3.0 (4.4)	3.9	4.5	3.4	1.8	1.7
ZwIS-3	7.8	5.6	5.6	5.7	4.4	2.3	1.9
ZwIS-4	11.2	9.1	9.1	6.9	4.9	3.4	2.7
ZwIS-5	7.9	4.9	4.9	4.6	2.4	4.0	2.4
ZwIS-8	15.5	8.0	14.7	8.8	8.0	5.0	3.4
ZwIS-6	15	11.2	16.6	14.5	14.7	4.7	3.9
ZwSI-1	5.8	5.6 (7.1)	3.9	4.6	3.0	3.8	2.4
ZwSI-5F	4.0	3.4	3.0	3.9	2.7	1.9	1.7
ZwSI-4F	11.3	7.1	9.1	8.3	6.3	2.6	2.1
ZwSI-3F	12.1	13.0	10.2	10.7	9.0	4.4	3.4
ZwSI-2F	10.7	8.0	9.1	10.0	8.0	5.0	4.4
ZwSISZw-1	5.1	2.6 (4.8)	3.4	3.2	2.4	1.5	1.5
ZwISIZw-1	6.2	4.8 (5.7)	4.4	4.1	3.0	1.5	1.5

[a] Values in parentheses are calculated from D_0 obtained by extrapolation from high concentrations.

Table 10. LALLS Results for Zwitterion-Capped Block Copolymers in CCl_4[a]

sample	$M_w \times 10^{-5}$	$A_2 \times 10^4$ (mol mL g^{-2})	N_w
ZwIS-3	1.73	4.1	7.1
ZwIS-4	1.39	4.0	7.8
ZwSI-1	3.92	4.0	5.6

[a] Measurements were made 1.5 years after the preparation of stock solutions.

The above results, in combination with the results from dynamic methods, lead to the conclusion that the aggregates continue to exist in solution for long periods of time, a fact that can be attributed to the existence of an equilibrium association process between unimers and multimers in CCl_4. The existence of a very long τ_s, although it cannot be ruled out, does not seem likely. The case of such a long structural relaxation time, of the order of years, does not differ, from a practical point of view, from the case of an equilibrium process. On the contrary, it could be stated that τ_s is small enough that an equilibrium state is attained shortly after dissolution or dilution and the measurements reflect this equilibrium state. The high k_H and the low A_2 in the solutions of the zwitterion-capped copolymers in CCl_4 and the mixtures indicate that a partial reduction of the aggregation number of the aggregates may take place after dilution of the stock solution, supporting a small value for the structure relaxation time. Measurements of the flow time for the same solutions (viscometry measurements) are stable a few minutes after dilution in the viscometer, and the same happens for the light scattering measurements. On the other hand, the almost instant destruction of the gels, formed by the difunctional samples and which are stable also for very long periods (years), by addition of alcohol cannot be compatible with a completely frozen state in solution similar to that in the solid state.

The variation of the aggregation number by increasing concentration is supported by the high values for the Huggins coefficient. k_H values are higher for the mixtures. The aggregation number is expected to increase with concentration, as the dynamic light scattering experiments imply together with the formation of gels in solutions of the difunctional samples. This results in an analogous increase of the specific viscosity with concentration and the observed large values of k_H. The effect is more pronounced when alcohol is present in the system in a constant proportion with respect to the primary solvent but in a continuously decreasing ratio relative to the polar groups, as the concentration of polymer increases. In this way the initial slope of the η_{sp}/c vs c plot is large. The aggregation numbers derived by extrapolation to zero concentration, where only free chains are expected to exist, are in fact a measure of the degree of association at the lower limits of the concentration range studied.

The situation in the case of the solutions of the difunctional triblocks remains somewhat unclear. The aggregation numbers determined by dynamic methods, assuming the star model, are actually smaller than the ones determined by static light scattering. However, differences are not great and can be compared with those obtained for the monofunctional samples. It has to be mentioned that the variations of the diffusion coefficient, the hydrodynamic radius, and the specific viscosity with concentration are more dramatic. The relatively low aggregation numbers obtained in dilute solutions ($c < c_{gel} < c^*$) for these polymers, which also form gels at relatively low concentrations, support the assumption that intramolecular association exists in CCl_4. The larger decrease of $[\eta]$ values in solution in mixed solvents and the high k_H values imply changes in the configuration of the chain for the difunctional species relative to the monofunctional species, as different possibilities exist for the incorporation of the two types of copolymers in an aggregate. These changes, which can surely result from an intramolecular association of the end groups, reduce the dimensions of the aggregate (and the isolated chain) and because of the more compact structure the hydrodynamic interactions between chains increase.

At this point a comparison of the experimental results with the expectations of theoretical models for polymers having associating end groups is in order. From what was mentioned above, the spherical head-packing model[51] can be ruled out as a possible model for describing this kind of association process. Taking into account the nature of the associating groups (dipoles), their incorporation into a core which resembles a liquid drop does not seem probable. In the sulfozwitterionic group, different charges (positive and negative) exist at specific sites relative to each other and relative to the polymeric chain. They are connected together by covalent carbon–carbon and carbon–heteroatom bonds with constant bond lengths and predescribed rotational freedom. Any packing of the polar heads must be done in such a way that restrictions are taken into account. This fact decreases the possibility of liquid drop packing since this structure is very variable and has high intrinsic mobility. This kind of packing seems more probable in the case of the polar groups of the classical

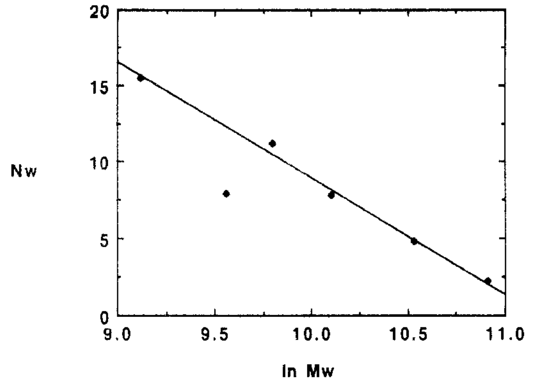

Figure 7. N_w vs ln M_w plot for zwitterion-capped block copolymers of the type ZwIS in CCl_4 at 25 °C.

ionomers where the charges are tied together by pure electrostatic forces and the counterions are allowed to move freely. However, the model's prediction of a very low critical micelle concentration (cmc), the concentration of first appearance of the aggregates, agrees with the failure of determination of any kind of cmc for these systems in the concentration range studied and the indication in one case[20] that, if there exists a cmc, this must be of the order of 10^{-5} g/mL or even lower. The last result also implies a very large equilibrium constant for the association process.

The preferred head-packing model[51] predicts the existence of a specific aggregation number per aggregate, independent of the molecular weight of the polymer chain, and very low polydispersity for the aggregates. Both predictions are inconsistent with the experimental findings since in both series of samples the aggregation number depends on the molecular weight of the precursor, and the dynamic light scattering measurements suggest a relatively broad size distribution for the aggregates. Here it must be noted that the liquid drop model also predicts a narrow size distribution for the micelles.

The experimental results seem to be in better agreement with the linear head-packing model[52] (where the dipoles are coordinated in an antiparallel fashion side by side, producing a linear array of polar heads), at least as far as the decrease of the aggregation number with increasing molecular weight of the polymeric chain and the polydispersity of the aggregates are concerned. In Figure 7 the variation of N_w with M_w is given for the ZwIS type diblock copolymers for samples having similar chemical composition and polyisoprene microstructure. Because of the aforementioned interaction between the aromatic rings of the polystyrene block and the polar groups,[20] N_w falls in the range of small aggregation numbers. The plot is given in the form $N_w = f(\ln M_w)$ since the molecular weight is a function of the degree of polymerization. The variation of N_w is linear ($N_w \sim M^{-1}$) for both classes of samples, in contrast to the $M^{-2/3}$ ($\sim N^{-2/3}$, where N is the degree of polymerization) which is predicted by the model, with almost the same coefficients. There is definitely a stronger experimental dependence of the average degree of aggregation on the molecular weight of the chain as it was observed for zwitterion-capped polyisoprenes[14] (of course, the preexponential term is different for the homopolymeric chains dissolved in a different solvent). This variation must result from the intrinsic features of the associating group and not from the chemical nature of the chain.

The observed dependence may be a result of the mixed structure of the aggregates (linear packing of the polar heads and a behavior similar to the arms of a star for the chains). It must be stressed that the model does not take into account the interrelations and interactions between the two factors that determine the size and shape of the aggregates (free energy of the polar heads and of the nonpolar chains) and, of course, specific interactions that can arise between the dipoles and the monomers incorporated in the polymeric chain.

Conclusions

Diblock copolymers of isoprene and styrene with one sulfobetaine group at either end of the polymeric chain associated in CCl_4, a nonpolar nonselective solvent for the macromolecular tails. Triblocks with both ends functionalized form stable gels at low concentrations, which are destroyed by small amounts of 2-methylcyclohexanol. Addition of the alcohol also reduces the degree of aggregation in solutions of the monofunctional samples but some aggregation persists even at 5% alcohol.

Static and dynamic light scattering and viscometry measurements show that the aggregation number decreases as the precursor molecular weight increases due to excluded volume repulsions. Aggregation numbers derived from the static method are in good agreement with the ones derived from dynamic methods. Aggregates are polydisperse. Dynamic light scattering measurements show that the aggregation number shifts with concentration.

The hydrodynamic behavior of the micelles is well described by the star model. Increased k_H values, combined with low $[\eta]$ values, for the difunctional species indicate the existence of intramolecular association in dilute solution.

The aggregation process seems to be an equilibrium between free chains and aggregates. The properties of aged solutions of these aggregating polymers remain almost unchanged for long periods of time (years).

Experimental results agree in general with the predictions of the linear packing model, although specific interactions between polar groups and the aromatic rings on the polymeric chain are not accounted for by the model.

References and Notes

(1) Wilson, A. D.; Prosser, H. J., Eds.; *Developments in Ionic Polymers*; Applied Science Publishers: London, 1983; Vol. 1.
(2) Tsuchida, E.; Abe, K. *Adv. Polym. Sci.* **1982**, *45*, 1.
(3) MacKnight, W. J.; Earnest, P. R. *J. Polym. Sci., Macromol. Rev.* **1981**, *16*, 41.
(4) Ikemi, M.; Odagiri, N.; Tanaka, S.; Shinohara, I.; Chiba, A. *Macromolecules* **1981**, *14*, 34.
(5) (a) Selb, J.; Gallot, Y. *Makromol. Chem.* **1981**, *182*, 1513. (b) Valint, P. L.; Bock, J. *Macromolecules* **1988**, *21*, 175.
(6) Lundberg, R. D.; Phillips, R. R. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 1143.
(7) Lantman, C. W.; MacKnight, W. J.; Peiffer, D. G.; Sinha, S. K.; Lundberg, R. D. *Macromolecules* **1987**, *20*, 1096.
(8) Kim, M. W.; Peiffer, D. G. *J. Chem. Phys.* **1985**, *83*, 4159.
(9) Hara, M.; Wu, J. L. *Macromolecules* **1988**, *21*, 402.
(10) Desjardins, A.; van de Ven, T. G. M.; Eisenberg, A. *Macromolecules* **1992**, *25*, 2412.
(11) Schulz, D. N.; Glass, J. E., Eds. *Polymers as Rheology Modifiers*; ACS Symposium Series 462; American Chemical Society: Washington, DC, 1991.
(12) Broze, G.; Jerome, R.; Teyssie, P. *Macromolecules* **1982**, *15*, 920.
(13) Worsfold, D. J. *J. Polym. Sci., Polym. Chem. Ed.* **1983**, *21*, 2237.
(14) Davidson, N. S.; Fetters, L. J.; Funk, W. G.; Graessley, W. W.; Hadjichristidis, N. *Macromolecules* **1988**, *21*, 112.
(15) Moller, M.; Omeis, J.; Muhleisen, E. In *Reversible Polymeric Gels and Related Systems*; Russo, P. S., Ed.; ACS Symposium Series 350; American Chemical Society: Washington, DC, 1987.
(16) Lenz, R. W. *Organic Chemistry of Synthetic High Polymers*, Interscience: New York, 1967.
(17) Kennedy, J. P. *Rubber Chem. Technol., Rubber Rev.* **1983**, *56*, 639.
(18) Sogah, D. Y.; Webster, O. W. *J. Polym. Sci., Polym. Lett. Ed.* **1983**, *21*, 927.

(19) Young, R. N.; Quirk, R. P.; Fetters, L. J. *Adv. Polym. Sci.* **1984**, *56*, 1.

(20) Pispas, S.; Hadjichristidis, N. *Macromolecules* **1994**, *27*, 1891.

(21) Morton, M.; Fetters, L. J. *Rubber Chem. Technol.* **1975**, *48*, 359.

(22) Roovers, J.; Toporowski, P. *Macromolecules* **1983**, *16*, 843.

(23) Stewart, M. J.; Shepherd, N.; Service, D. *Br. Polym. J.* **1990**, *22*, 319.

(24) Eisenbach, C. D.; Schnecko, H.; Kern, W. *Eur. Polym. J.* **1975**, *11*, 699.

(25) Bushuk, W.; Benoit, H. *Can. J. Chem.* **1958**, *36*, 1616.

(26) Tuzar, Z.; Kratochvil, P.; Strakova, D. *Eur. Polym. J.* **1970**, *6*, 1113.

(27) Huglin, M. B., Ed. *Light Scattering from Polymer Solutions*; Academic: New York, 1972; Chapters 6 and 15.

(28) Koppel, D. E. *J. Chem. Phys.* **1972**, *57*, 4814.

(29) Burchard, W.; Kajiwara, K.; Nerger, D.; Stockmayer, W. H. *Macromolecules* **1984**, *17*, 222.

(30) Berry, G. C.; Casassa, E. F. *J. Polym. Sci., Part D* **1970**, *4*, 1.

(31) King, T. A.; Knox, A.; McAdam, J. D. G. *Polymer* **1973**, *14*, 293.

(32) (a) Lewis, M. E.; Nan, S.; Mays, J. W. *Macromolecules* **1991**, *24*, 197. (b) Lewis, M. E.; Nan, S.; Wan, Y.; Li, J.; Mays, J. W.; Hadjichristidis, N. *Macromolecules* **1991**, *24*, 6686.

(33) von Meerwall, E.; Tomich, D. H.; Grigsby, J.; Pennisi, R. W.; Fetters, L. J.; Hadjichristidis, N. *Macromolecules* **1983**, *16*, 1715.

(34) Chen, X.; Xu, Z.; von Meerwall, E.; Seung, N.; Hadjichristidis, N.; Fetters, L. J. *Macromolecules* **1984**, *17*, 1343.

(35) Altares, T.; Wyman, D. P.; Allen, V. R. *J. Polym. Sci.* **1964**, *A2*, 4533.

(36) Kow, C. Synthesis of Uniform and Non-Uniform Polymer Networks. Ph.D. Thesis, University of Akron, 1982, p 121.

(37) Stock, J.; Burchard, W.; Stadler, R. *Macromolecules* **1992**, *25*, 6885.

(38) Xu, R.; Winnik, M. A.; Hallet, F. R.; Riess, G.; Croucher, M. D. *Macromolecules* **1991**, *24*, 87.

(39) Bauer, B. J.; Fetters, L. J.; Graessley, W. W.; Hadjichristidis, N.; Quack, G. F. *Macromolecules* **1989**, *22*, 2337.

(40) Davidson, N. S.; Fetters, L. J.; Funk, W. G.; Hadjichristidis, N.; Graessley, W. W. *Macromolecules* **1987**, *20*, 2614.

(41) Lindner, J. S.; Wilson, W. W.; Mays, J. W. *Macromolecules* **1988**, *21*, 3304.

(42) (a) Roovers, J.; Toporowski, P. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 1907. (b) Roovers, J.; Hadjichristidis, N.; Fetters, L. J. *Macromolecules* **1983**, *16*, 214.

(43) Roovers, J.; Martin, J. F. *J. Polym. Sci., Polym. Phys. Ed.* **1989**, *27*, 2513.

(44) Balsara, N. P.; Tirrell, M.; Lodge, T. P. *Macromolecules* **1991**, *24*, 1975.

(45) Wolff, C.; Silberberg, A.; Priel, Z.; Layec-Raphalen, M. N. *Polymer* **1979**, *20*, 281.

(46) Otocka, E. P.; Hellman, M. Y.; Blyler, L. L. *J. Appl. Phys.* **1969**, *40*, 4221.

(47) Misra, N.; Mandal, B. M. *Macromolecules* **1984**, *17*, 495.

(48) Bitsch, B.; Reiss, G.; Banderet, A. *J. Chim. Phys.-Chim. Biol.* **1970**, *67*, 1977.

(49) Bredas, J. L.; Chance, R. R.; Silbey, R. *Macromolecules* **1988**, *21*, 1633.

(50) Bi, L.-K.; Fetters, L. J. *Macromolecules* **1976**, *9*, 732.

(51) Bug, A. L. R.; Cates, M. E.; Safran, S. A.; Witten, T. A. *J. Chem. Phys.* **1987**, *87*, 1824.

(52) Wang, Z.-G.; Safran, S. A. *J. Chem. Phys.* **1988**, *89*, 5323.