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End-Functionalized Block Copolymers of Styrene and Isoprene: Synthesis and Association Behavior in Dilute Solution

Stergios Pispas and Nikos Hadjichristidis*

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

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ABSTRACT: The dilute solution properties of di- and triblock copolymers of isoprene and styrene having a highly polar sulfozwitterion group on one or both ends of the chain were studied in the nonpolar solvent carbon tetrachloride (a good solvent for polystyrene and polyisoprene) by low-angle laser light scattering. The copolymers were prepared by anionic polymerization using high-vacuum techniques with [3-(dimethylamino)propyl]lithium as initiator. The dimethylamino end group of the chain was transformed to a zwitterion by reaction with cyclopropanesultone. The monofunctional zwitterion-capped copolymers were found to associate in carbon tetrachloride, whereas the difunctional versions formed gels even below the coil overlap concentration, c^*. The aggregation number was found to decrease with increasing base molecular weight due to the excluded volume repulsions of the copolymeric tails. Comparison with the corresponding ω-zwitterionic polyisoprene homopolymers in cyclohexane and in carbon tetrachloride shows that for the same base molecular weight the materials with the homopolymeric tails aggregate more strongly. Aggregation numbers for the copolymers are of the same order of magnitude as the degree of association measured for a zwitterion-capped polystyrene. The presence of the phenyl rings in the copolymer chain seems to reduce the extent of aggregation. The effect of position and number of the functional groups on the strength of the association is also discussed.

Introduction

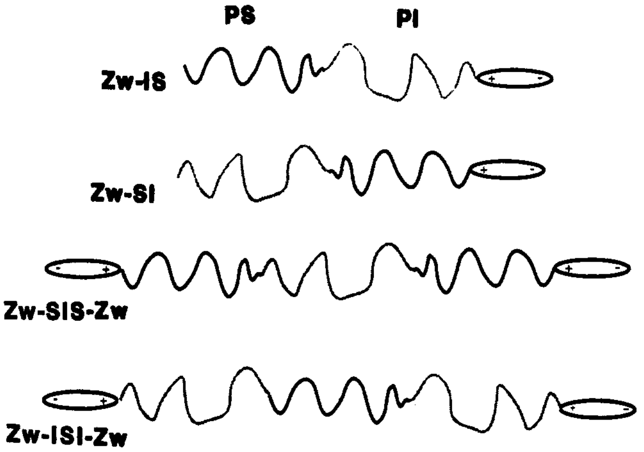
The presence of even a few highly polar groups distributed along[1-7] or fixed at the ends of nonpolar chains[8-14] changes dramatically the properties of polymers. These changes are caused by the association of the polar groups in the nonpolar environment of the hydrocarbon chains in bulk or of the aliphatic solvents in solution.

The least complicated examples of polymeric associating species are chains with only one polar group.[15-21] These simplest systems offer an essential starting point for testing theories and establishing the basic structure-property relationships, which can be used to design associating polymers for applications.

In previous papers the dilute solution[22] and melt state[23] behavior of linear polyisoprenes with a highly polar sulfozwitterion group on one end of the chain was investigated by osmometry, viscometry, light and X-ray scattering, and rheology. A few linear and star polyisoprenes with all ends functionalized were also examined. It was found that the monofunctional species form large aggregates in cyclohexane and the multifunctional versions form gels, which, however, readily dissolved when small amounts of the polar compound 1-heptanol were added. The aggregation strength was found to decrease with increasing base molecular weight. The aggregate lifetimes, geometry of the polar cores, concentration dependence of aggregation, and effects of the solvent medium on the strength of aggregation were discussed.

Strong associations were also found in the melts of the monofunctional zwitterion species while the multifunctional versions behaved like networks at room temperature. It was found by high-resolution synchrotron X-ray scattering that for low molecular weights (<5000) the polymer aggregates into tubular structures with the tubes closely packed on a two-dimensional hexagonal lattice with crystalline order, while for higher molecular weights (>14 000), the starlike aggregates form a body-centered-cubic lattice with long-range order.[24]

Scheme 1



It would be interesting to extent this study in the case of block nonpolar copolymers having the polar groups at one, the other, or both ends. The peculiar behavior of block copolymers in different solvent environments[25-30] and their bulk morphology[31-33] make them attractive for such studies.

In this paper we present the synthesis and characterization of block copolymers of isoprene and styrene having the dimethylamino and zwitterion groups at the polyisoprene or polystyrene end (Scheme 1). We also present the results found by low-angle laser light scattering (LALLS) in dilute solutions in the nonpolar solvent carbon tetrachloride, which is a good solvent for both blocks. To our knowledge there is no other work dealing with the synthesis of end-functionalized block copolymers and their dilute solution behavior. Some work has been done on block ionomers with short polar blocks where the exact number of end groups per chain is not well defined.[13,14]

Experimental Section

In all polymerizations [3-(dimethylamino)propyl]lithium (DMAPLi) was used as the initiator. The synthesis of this functional initiator was carried out in hexane under vacuum in an all-glass sealed apparatus. 3-(Dimethylamino)propyl chloride (DMAPCl) was reacted with a lithium dispersion containing ~2

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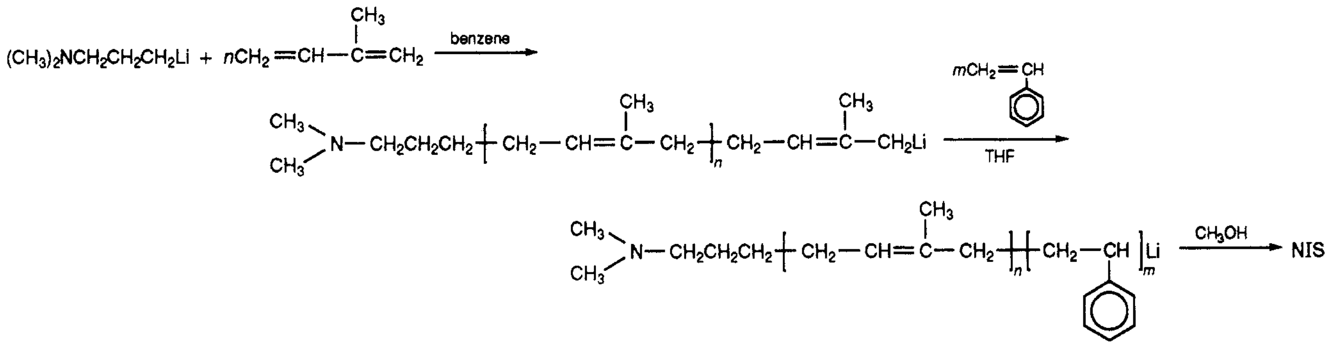
Scheme 2



wt % sodium[34,35] according to the following scheme:

$$\underset{\text{DMAPCl}}{(CH_3)_2NCH_2CH_2CH_2Cl} + 2Li^0 \xrightarrow[\text{hexane}]{20\,°C} \underset{\text{DMAPLi}}{(CH_3)_2NCH_2CH_2CH_2Li} + LiCl$$

After completion of the reaction the insoluble initiator was separated from the polar byproducts, mainly Wurtz coupling products, by filtration. Benzene was then introduced into the reactor to dissolve the initiator. More details on the synthesis and analysis of DMAPLi by GC–MS will be given in a forthcoming note.[36] A known amount of the solution of DMAPLi in benzene was used to polymerize a known amount of purified styrene, according to the standards required for anionic polymerization. The effective concentration of the organolithium initiator was then determined by using the stoichiometric ratio:

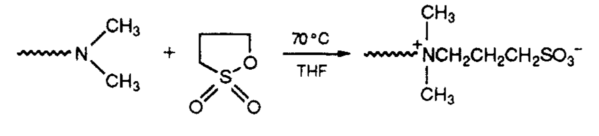
$$\text{moles of DMAPLi} = (\text{grams of monomer})/M_n$$

where M_n is the number-average molecular weight of the resulting polymer which was determined by SEC, calibrated with polystyrene standards. In some cases a known amount of the initiator's solution was hydrolyzed and the resulting amine was removed by distillation. The remaining solution was titrated with aqueous HCl solution to a phenolphthalein end point. Good agreement was obtained between the two methods.

All polymerizations were carried out under high-vacuum conditions in all-glass reactors at room temperature. Purification of the solvents [benzene, tetrahydrofuran (THF)], monomers (isoprene, styrene), and terminating (methanol) and linking (dichlorodimethylsilane) agents was achieved using standard anionic polymerization techniques.[37,38] Block copolymers were obtained by sequential addition of monomers. The dimethylamino functionality was introduced either to the polyisoprene or the polystyrene chain end by polymerizing the appropriate monomer first. When isoprene was the first monomer, after the completion of the polymerization a small amount of purified THF (~1 mL) was introduced to the mixture followed by the addition of styrene to accelerate the crossover reaction.[39,40] Living ends were terminated with degassed methanol at the end of the polymerization (Scheme 2).

Triblock copolymers were prepared by coupling diblock living chains with $(CH_3)_2SiCl_2$. In these cases the desired product was isolated by fractionation of a ~1% w/v polymer solution in benzene using methanol as nonsolvent. The polymers were precipitated in excess methanol, dried under vacuum, and stored in vacuum desiccators.

The conversion of the amine-capped polymers to the sulfozwitterion ones was achieved by reaction of the tertiary amine moiety with excess cyclopropanesultone (amine/sultone = 1/10). A 2% w/v solution of polymer in THF was reacted for several days at 70 °C according to the following scheme:



THF was evaporated almost to dryness, and the resulting polymer was washed several times with acetone to remove unreacted sultone. Polymers were dried and stored in a vacuum desiccator.

Preparation and fractionation procedures 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 were used. Tetrahydrofuran and chloroform with a flow rate of 1 mL/min at 30 °C were the elution solvents. Injection concentrations of ~0.1 g/dL were used.

The 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.

Number-average 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. The M_n values were obtained from the corresponding $(\pi/c)^{1/2}$ vs c plots, where π is the osmotic presssure.

Weight-average molecular weights (M_w) and second virial coefficients were obtained from the concentration dependence of the excess Rayleigh ratio measured with a Chromatix KMX-6 low-angle laser light scattering photometer at 25 °C for $\lambda = 633$ nm in THF and carbon tetrachloride. THF was purified by reflux over sodium and was distilled just prior to use. Carbon tetrachloride was dried over CaH_2 and fractionally distilled. Care was taken during the preparation of the solutions to minimize contact with moisture. Solution concentrations were below the coil overlap concentration c^* ($\sim[\eta]^{-1}$). The lowest concentrations were selected in such a way that the value of the excess Rayleigh ratio could be determined with reasonable accuracy (typically, the R_θ values for the lowest concentrations were 1.5–2 times larger than the R_θ of the solvent). Difunctional zwitterion-capped polymers formed stable gels in CCl_4 at 1 wt % concentration ($c^* \sim 1.5$ wt %). When these solutions were further diluted with dry solvent, gelation disappeared at ~0.5 wt % concentration. For light scattering measurements, solutions were clarified by filtration through 0.22-μm pore size Nylon filters. Plugging of the filters was a frequent phenomenon with the high-concentration solutions of zwitterion-capped polymers in CCl_4. Also fluctuations of the scattered light intensity were considerably larger for these samples. $(Kc/\Delta R_\theta)^{1/2}$ vs c plots were used to analyze the data, where ΔR_θ is the excess Rayleigh ratio and K is a combination of known optical constants including dn/dc, the refractive index increment. In all cases $Kc/\Delta R_\theta$ vs c plots give similar results for the values of M_w and the second virial coefficient.

The dn/dc values required for light scattering experiments were measured in THF and CCl_4 at 25 °C with a Chromatix KMX-16 differential refractometer operating at 633 nm and calibrated with NaCl solutions. For the block copolymers studied here, dn/dc values in both solvents are fairly high enough to permit accurate determination of apparent M_w values which would be close to the true M_w of the copolymers[41] due to the molecular weight and compositional homogeneity of the samples (see next section). For CCl_4 solutions the values are between 0.093 and 0.098 mL/g, depending on composition. The dn/dc values in CCl_4 for polystyrene and polyisoprene homopolymers were also

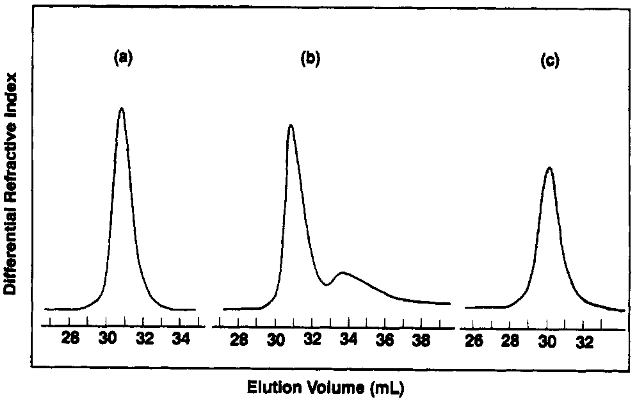


Figure 1. SEC chromatograms of sample NIS-3 in THF (a), sample ZwIS-3 in THF (b), and sample ZwIS-3 in $CHCl_3$ (c).

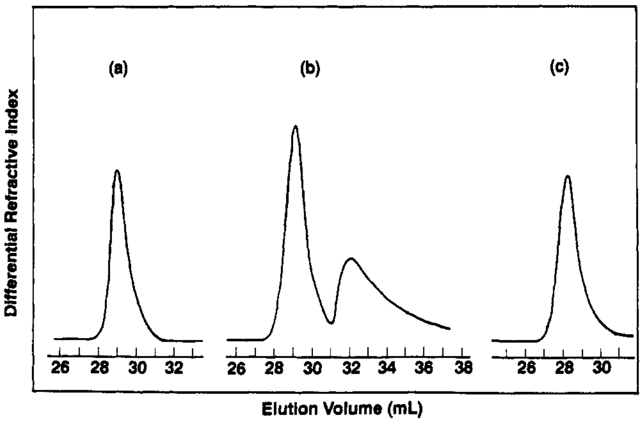


Figure 2. SEC chromatograms of sample NISIN-1 in THF (a), sample ZwISIZw-1 in THF (b), and sample ZwISIZw-1 in $CHCl_3$ (c).

measured and found to be 0.145 mL/g (for $M_w = 4.2 \times 10^4$) and 0.081 mL/g (for $M_w = 5.0 \times 10^4$), respectively.

The molecular weights of a few zwitterion-capped polyisoprenes and a zwitterion-capped polystyrene were also measured in CCl_4 for a more direct comparison.

Results and Discussion

SEC chromatograms of the synthesized block copolymers are given in Figures 1 and 2. The amine-capped polymes in THF show narrow molecular weight distributions ($M_w/M_n < 1.1$) as expected for anionically prepared samples (Figures 1a and 2a). After the sultone reaction, zwitterion polymers show shoulders or peaks at the higher elution volume regions of the chromatograms. The position and shape of these peaks change from run to run. Generally, the second peaks are more diffuse and have long tails compared to the first, which are sharp and obviously correspond to the same elution volume as for the amine precursor. These phenomena can be attributed to adsorption, which seems to be more pronounced for the difunctional samples (Figures 1b and 2b).

When chloroform was used as the carrier solvent, these effects were suppressed and SEC chromatograms were similar to those from amine polymers in THF (Figures 1c and 2c). $CHCl_3$, on one hand, seems to be polar enough to break down any aggregation of the polar groups (the dielectric constant ϵ for $CHCl_3$ is 4.8) and, on the other hand, is preferentially adsorbed instead of polymers with polar groups.

If is difficult to determine the extent of conversion of amine groups to sulfobetaine because of the low concentration of these groups on the polymer chain. Nevertheless, a qualitative picture can be drawn from NMR experiments. The ^{1}H-NMR spectra of the lowest molecular weight sample are given as an example in Figure 3. The first spectrum (Figure 3a), from the amine-capped polymer shows a peak at 2.2 ppm, which is assigned to the methyl protons of the carbons attached to nitrogen. The second spectrum (Figure 3b) was taken after the completion of the reaction with cyclopropanesultone. The peak at 2.2 ppm has disappeared and two new peaks at 3.15 (singlet) and 2.95 ppm (triplet) are present. They were assigned to methyl protons attached to the positively charged nitrogen of the zwitterion group and methylene protons of the carbon attached to sulfur, respectively.[42-44]

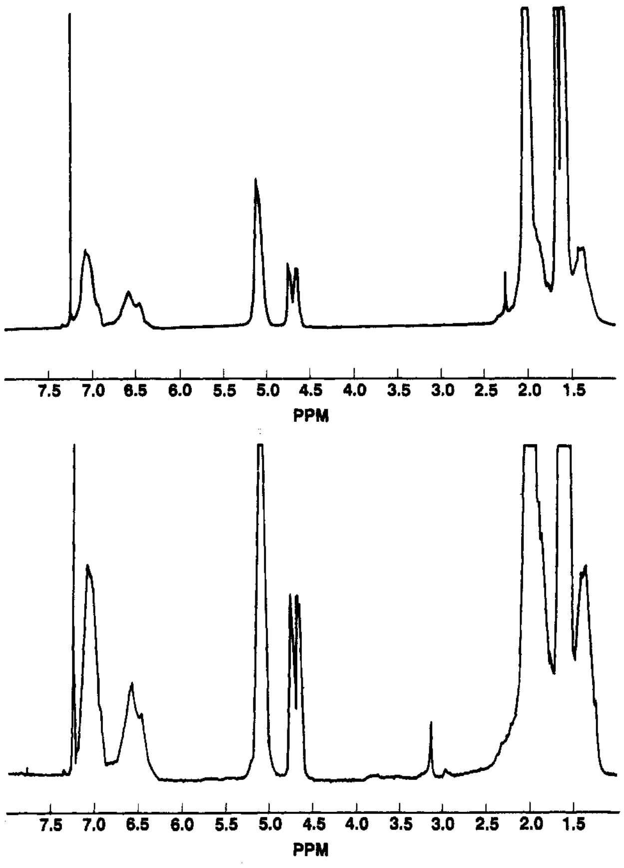


Figure 3. ^{1}H-NMR spectra of samples NIS-5 (top) and ZwIS-5 (bottom) in $CDCl_3$.

Unfortunately, the low intensity of the peaks and the noisy base line do not permit quantitative interpretation. Additionally, no characteristic peaks of the sultone could be detected. It seems that, by the procedure followed, the reaction proceeded to high conversion and all unreacted sultone was eliminated.

In Table 1 results on composition for the block copolymers are presented together with the analysis of the chain microstructure of the polyisoprene blocks. The tertiary amine group on the initiator alters the microstructure of the polyisoprene produced.[45] There is an increase of 3,4 content with decreasing molecular weight of the block, as anticipated from the use of higher initiator concentration for the synthesis of low molecular weight polymers. No 1,2 enchainment was detected. These findings are in agreement with those reported by Davidson et al.[22a]

We assume that 3,4 content increases at the end of the isoprene polymerization as the monomer to amine ratio at that stage decreases, resembling the conditions of preparing low molecular weight polymers (the amine to lithium ratio is always equal to 1).

Molecular characteristics of the amine-capped copolymers in THF and toluene are given in Table 1. Representative $(\pi/c)^{1/2}$ vs c plots for the end-functionalized diblocks are shown in Figure 4. Weight-average molecular

Table 1. Molecular Characteristics of End-Functionalized Block Copolymers in THF and Toluene

	THF[a]		toluene[b]			
sample	$M_w \times 10^{-4}$	$A_2 \times 10^3$	$M_n \times 10^{-4}$	$A_2 \times 10^3$	% wt PS[c]	% vinyl PI[c]
NIS-2	5.49	1.20	5.38	1.08	29	
NI-2			3.82	1.22		15
NIS-3	2.44	1.35	2.25	1.26	28	
NI-3			1.66	1.84		17
NIS-4	1.79	1.40	1.57	1.51	29	
NI-4			1.15	1.85		18.5
NIS-5	1.41	1.46	1.22	1.27	28	
NI-5	0.89	4.10	0.88[d]			20
NSI-1	6.96	0.93	6.12	1.04	30	15
NS-1			1.97	0.44		
NSISN-1	7.63	0.81	7.02	1.18	36	21
NS	1.65	0.42				
NISIN-1	6.98	1.10	6.27	1.08	27	
NI			2.29	1.69		18
ZwIS-2	5.55	1.0				
ZwSISZw-1	8.01	0.58				

[a] By LALLS. [b] By membrane osmometry. [c] By ^{1}H-NMR. [d] By VPO in benzene.

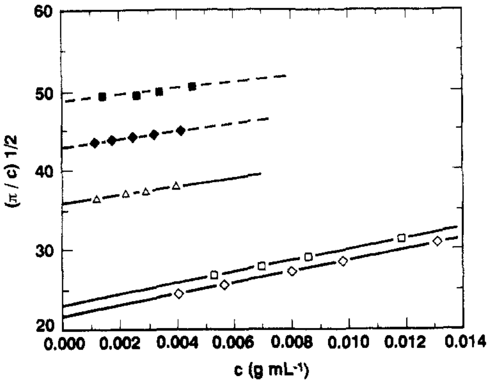


Figure 4. $(\pi/c)^{1/2}$ vs c plots for amine-capped diblocks in toluene at 37 °C. From top to bottom: samples NIS-5, NIS-4, NIS-3, NIS-2, and NSI-1.

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

sample	$M_w \times 10^{-4}$	$A_2 \times 10^3$	N_w
ZwIS-2	12.0	0.33	2.2
ZwIS-3	19.1	0.34	7.8
ZwIS-4	20.0	0.82	11.2
ZwIS-5	11.2	−0.14	7.9
ZwSI-1	40.5	0.24	5.8
ZwSISZw-1	39.1	0.40	5.1
ZwISIZw-1	43.2	0.28	6.2
NIS-4	2.00	1.18	1.1
NIS-5	1.46	1.28	1.04
NSI-1	7.15	0.72	1.03
NSISN-1	7.83	0.54	1.03

weights are close to number-average values and are in good agreement with M_s (stoichiometric molecular weight), indicating low polydispersity in molecular weight and composition in accordance with SEC analysis. LALLS results in CCl_4 (Table 2) give no real evidence of association of these polymers in this solvent. Weight-average molecular weights are essentially the same as the ones measured in THF, although a small decrease in the values of the second virial coefficient is observed. It seems that the tertiary amine group is not polar enough to promote aggregation.

The results for the zwitterion-capped samples show that these groups are not associated in THF (Table 1). In contrast, weight-average molecular weights are elevated in CCl_4 (Table 2). The low dielectric constant ($\epsilon = 2.24$) of this solvent, a good one for both polyisoprene and polystyrene chains, seems to support aggregation of the zwitterion groups. The values of the second virial coefficients are also dramatically diminished relative to those obtained in THF or toluene for the amine precursors. This is due mainly to the increase in molecular weight and in part to the starlike structure[46,47] of the aggregates as a result of the relatively small aggregation number.[22] Representative $(Kc/\Delta R_\theta)^{1/2}$ vs c plots in THF and CCl_4 for samples differing in molecular weight and architecture are given in Figures 5–7.

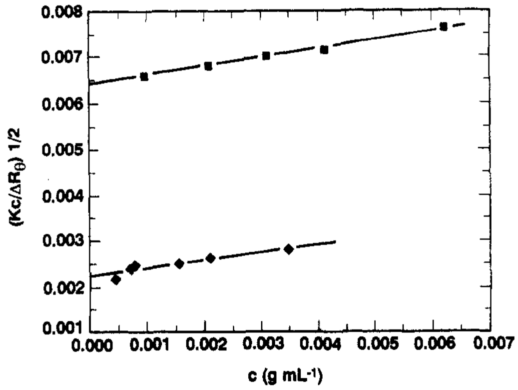


Figure 5. LALLS square-root plot for samples NIS-3 (■) in THF and ZwIS-3 (◆) in CCl_4 at 25 °C.

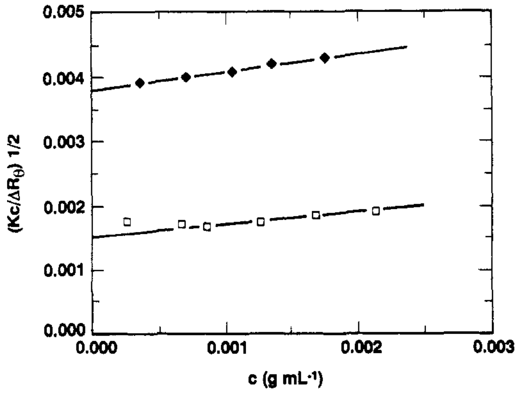


Figure 6. LALLS square-root plot for samples NISIN-1 (◆) in THF and ZwISIZw-1 (□) in CCl_4 at 25 °C.

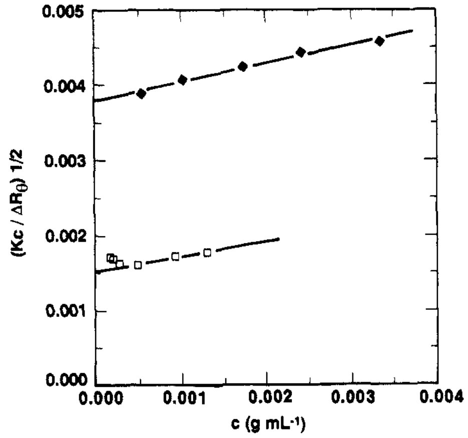


Figure 7. LALLS square-root plot for samples NSI-1 (◆) in THF and ZwSI-1 (□) in CCl_4 at 25 °C.

The weight-average aggregation number, N_w, i.e., the ratio of M_w of zwitterion aggregates in CCl_4 to M_w of amine polymers in THF (where aggregation does not occur), increases as the base polymer molecular weight decreases, a phenomenon that can be explained by excluded volume repulsions of the polymeric tails. In the case of end association, two factors have a strong influence on the whole process. The first is the attractive forces between the polar groups which tend to aggregate in the nonpolar

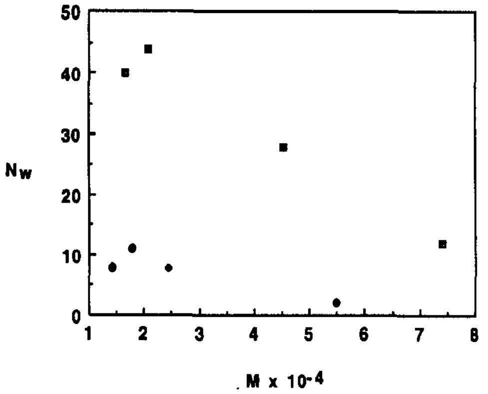


Figure 8. N_w vs base molecular weight of polymeric tail: (□) zwitterion-capped polyisoprenes in cyclohexane (results from ref 22); (◆) zwitterion-capped block copolymers of the type ZwIS in CCl_4 (this study).

environment of the solvent. The second is the excluded volume repulsions between the polymeric tails which, due to the clustering of the heads, are forced to be crowded in the area around the core. These factors have opposite effects, the latter acting toward destruction of the aggregates. The size of the aggregates is defined by the balance between the above tendencies. The higher the molecular weight, the larger the dimensions of the chain, and restrictions become more and more unbearable. The aggregate has to decrease in size to be in a state of equilibrium (minimum free energy). In other words, by association the chains reduce their free energy but lose configurational entropy.

The degree of association depends on concentration. At infinite dilution it is expected to be zero. Measurements in CCl_4 were extended to lower concentrations in an attempt to find an indication of the existence of some "critical micelle concentration" (cmc) for these associating polymers. In general, the variation of $(Kc/\Delta R_\theta)^{1/2}$ with concentration was linear, and extrapolation to zero concentration gives an estimation of the molecular weight of the aggregates in the lower limit of the concentration range studied.[48] Only in one case (Figure 7) do the $(Kc/\Delta R_\theta)^{1/2}$ values show a systematic increase by lowering the polymer concentration below 3×10^{-4} g/mL, revealing dissociation and an approach to some kind of cmc. The increase seems to be larger than the typical statistical error of the measurements but still measurements at so low concentrations are subject to larger error. Molecular weight determination in this case was accomplished by extrapolation from the linear part of the graph as in the other cases.

In Figure 8 a comparison plot of N_w vs base molecular weight for zwitterion-capped polyisoprene homopolymers[22] and diblock copolymers is given. It is clear that for the same base molecular weight the degree of association is much higher for zwitterion-capped polyisoprenes in cyclohexane than for the corresponding end-functionalized block copolymers in CCl_4. Such a comparison is justified if the main interest is focused on the association behavior of the same zwitterionic group attached to different polymeric tails, which are dissolved in a good solvent, without changing the environment in the near proximity of the polar group. Unfortunately, for a more direct comparison it would be necessary to make measurements on the functionalized diblocks in cyclohexane, which is a θ solvent for the polystyrene block, and this would probably complicate the interpretation of the results. The dielectric constant of CCl_4 (ϵ = 2.24) is very close to that of cyclohexane (ϵ = 2.02) and the difference is not so large to explain the reduction in aggregation number. However, the polarizability of CCl_4 must be higher than that of cyclohexane as can be seen from the values of the Rayleigh factor for these solvents ($R_\theta = 6.2 \times 10^{-6}$ cm^{-1} for CCl_4 and $R_\theta = 5.1 \times 10^{-6}$ cm^{-1} for cyclohexane at λ = 633 nm). Also, excluded volume effects between polymeric tails may be more pronounced in the case of block copolymers, where the chain consists of two different and highly incompatible segments which tend to repel each other more strongly than in the case of homopolymers, and the effect may play a significant role in situations like the chain end association.

Table 3. Aggregation Results for Zwitterion-Capped Polyisoprenes and Polystyrene in Cyclohexane and CCl_4

		cyclohexane[a]			carbon tetrachloride		
sample	$M_0 \times 10^{-4}$	$M_w \times 10^{-4}$	$A_2 \times 10^4$	N_w	$M_w \times 10^{-4}$	$A_2 \times 10^{-4}$	N_w
R-Zw	0.48[a]	11.1	3.9	23	13.2	9.6	28
G-Zw	1.65[a]	71.7	3.4	40	49.6	3.7	30
I-Zw	10.7[a]	116	2.8	10	67.8	4.6	6.3
ZwPS-1	3.93				20.2	1.8	5.1

[a] Data from ref 22.

To elucidate this point LALLS measurements on three zwitterion-capped polyisoprenes and one zwitterion-capped polystyrene were undertaken in CCl_4. The results are given in Table 3 together with the results in cyclohexane for comparison. For the zwitterionic polyisoprenes aggregation numbers in CCl_4 are lower than in cyclohexane but essentially of the same order of magnitude. The differences may be due to the difference in polarizability. On the other hand, the degree of association for the polystyrene sample is considerably lower and of the same order of magnitude as N_w for the zwitterionic diblocks. It seems that the phenyl rings on the polystyrene chain play a role similar to that of toluene.[22] Due to the high polarizability of the aromatic rings, present in the vicinity of the polar groups since both species are attached to the same chain, some kind of solvation can take place, leading to a lower aggregation number.

It seems also that the degree of association is not significantly different when the zwitterion group is at the polystyrene or at the polyisoprene side, at constant base molecular weight. At least differences are not so pronounced as in the case of homopolymers. In the case of the two triblock copolymers which have both ends functionalized, N_w is about the same. Further experiments, including dynamic light scattering and intrinsic viscosity measurements, are in progress to gain some insight on the shape and the hydrodynamic properties of these associating polymers. Preliminary results from these methods are in agreement with LALLS results. A detailed study on the hydrodynamic behavior of the aggregates will be presented in a forthcoming paper.[49]

Conclusions

Well-defined and near-monodisperse ω-dimethylamino diblock and triblock copolymers of styrene and isoprene can be prepared by using [3-(dimethylamino)propyl]lithium as initiator. The dimethylamino group can be converted to the corresponding highly polar sulfobetaine group by reaction with cyclopropanesultone. The monofunctional zwitterion block copolymers were found, by LALLS to aggregate in CCl_4, a nonpolar good solvent for PS and PI, and the difunctional triblock copolymers were found to form gels at concentrations even below c^*. The aggregation number of the functionalized diblocks decreases with increasing base molecular weight, as in the case of the ω-zwitterion-capped PI in cyclohexane. However, the ω-functionalized polyisoprenes aggregate much more strongly than the corresponding diblock copolymers and polystyrene homopolymers due to the polarizability of the aromatic rings. Finally, it seems that the degree of association does not change appreciably when the functional group is at either the PS or the PI side.

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