Synthesis and Dilute Solution Properties of Styrene−Isoprene Diblock Copolymers with Mesogenic−Zwitterionic End Groups

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ABSTRACT: Diblock copolymers of styrene and isoprene with an ionic-liquid crystalline end group were synthesized by anionic polymerization high-vacuum techniques. Using (3-dimethylamino)propyllithium as initiator, the dimethylamino group was introduced at either chain end. This group was converted to a zwitterionic-liquid crystalline end group by reaction with 2-{6-[4-(4-methoxyphenylazo)phenoxy]-hexyloxy}-2-oxo-1,3,2λ^5-phospholane. The dilute solution properties of the diblock copolymers, containing ~30 wt % PS, were studied in CCl_4, a nonpolar equally good solvent for both the polymeric blocks, by means of static and dynamic light scattering and viscometry. Static light scattering experiments indicate that dimers are formed in most cases, except for copolymers with $M_w \leq 12\,000$. The estimated aggregation numbers were found to be lower than in the case of sulfozwitterionic end-capped copolymers. It seems that the lower polarity of the nitrogen−phosphorus zwitterion and the increased steric hindrance of the mesogenic group attached to the zwitterionic group are mainly responsible for this behavior. Because of the presence of a liquid crystalline group and the polymeric tail directly bonded to the zwitterion, the formation of elongated aggregate structures is difficult in the studied systems as was observed in sulfozwitterion end-functionalized diblocks. Excluded-volume effects play also some role in the dependence of aggregation number on the molecular weight of the polymeric tails. The results from dynamic light scattering and viscometry agree well with the static light scattering picture if the star model is used to derive aggregation numbers from data on hydrodynamic radii of the end-functionalized copolymers.

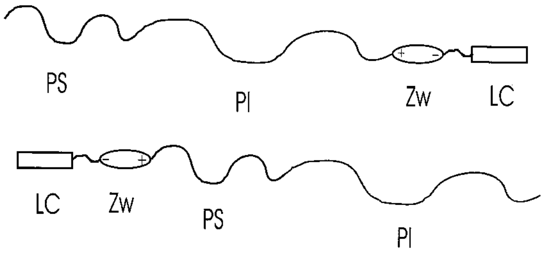
Introduction

For many years an enormous part of basic and applied research has been focused on the synthesis and the properties of polymeric materials (block copolymers, polyelectrolytes, ionomers, liquid crystalline polymers) capable of being highly sensitive and easily responsive to external fields (temperature, nature of solvent, pH, ionic strength, light illumination, electric and magnetic fields). The response of these materials, in the bulk or the diluted state, is associated with changes in their molecular and/or supramolecular structures (changes in chain conformation, chain or side group orientation, association, swelling, new phase formation).[1−6]

The study of the so-called “smart” polymeric materials is of great importance from both basic and technological points of view because it will help in the design of new polymers for interesting applications. Model polymers with well-defined molecular characteristics and architecture, carrying groups able for specific interactions at specific sites of their molecule, can be valuable tools toward this direction.

Many studies have been concerned with the synthesis and properties of liquid-crystalline polymers.[5,7] Recently research has been extended to polymers having ionic and mesogenic sites in their chain.[8−13] By combining these two features in the same polymer molecule, new interesting phase behavior may occur, regarding the formation and stabilization of new morphologies.[8] However, little work has been devoted to the synthesis of model liquid crystalline ionomers, mainly by Jerome and co-workers.[14−17] This group has synthesized linear low molecular weight polystyrenes end-capped, in one or both chain ends with sulfonate and carboxylate groups neutralized with a mesogenic (azobenzene type) quarternary ammonium cation. Their properties in the bulk were studied by DSC, SAXS, and SANS. Microphase separation between the polystyrene chains and the mesogenic counteranions was observed. Peaks corresponding to ionic and mesogenic domains were evident in the SAXS and the SANS profiles. The formation of smectic mesophases was found to depend strongly on the molecular weight of the polymeric chain and the nature of the ionic end groups.

Chart 1



In this paper we present the synthesis and molecular characterization of linear block copolymers of styrene and isoprene having a phosphorus zwitterionic group covalently bonded, through a flexible six methylene spacer, with an azobenzene type mesogenic group. A schematic representation of these copolymers is shown in Chart 1. Their association behavior in dilute solutions in CCl_4 was also investigated by static and dynamic light scattering as well as viscometry in order to elucidate some fundamental aspects of self-organization of these new model macromolecules in the supramolecular level.

Experimental Section

Polymer Synthesis. Block copolymers were prepared under high-vacuum conditions in all glass reactors using standard anionic polymerization techniques. [3-(Dimethylamino)propyllithium (DMAPLi) was used as initiator for the

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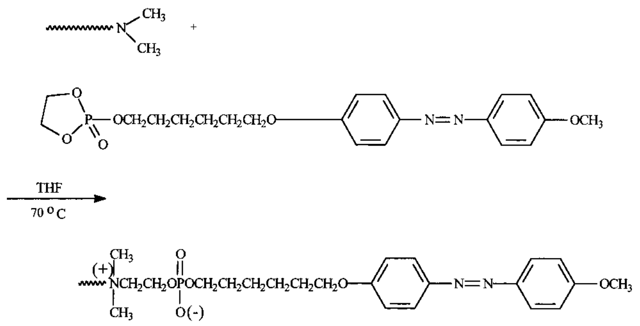
Table 1. Molecular Characteristics of the Amine-Capped Block Copolymer Precursors

sample	$M_w{}^a \times 10^{-4}$	$M_n{}^b \times 10^{-4}$	$A_2{}^c \times 10^3$	wt % PS^d	$M_w/M_n{}^e$	$[\eta]_N{}^f$ (mL/g)	$R_{vN}{}^f$ (nm)	$R_{hN}{}^g$ (nm)
NIS-7	3.74	3.28	1.03	30	1.07	43.3	6.4	6.9
NIS-3	2.44	2.25	1.35	28	1.07	38.8	5.3	6.9
NIS-5	1.41	1.22	1.46	28	1.07	25.5	3.8	3.7
NIS-8	0.91	0.83	1.54	27	1.08	14.8	2.8	3.2
NSI-5F	4.26	3.75	1.18	27	1.07	44.6	6.7	6.9
NSI-3F	1.49	1.34	1.66	32	1.1	23.0	3.8	4.4
NSI-2F	1.14	1.04	3.99	32	1.1	18.3	3.2	3.6

[a] By LALLS in THF at 25 °C. [b] By membrane osmometry in toluene at 37 °C or vapor pressure osmometry in benzene at 50 °C. [c] By LALLS in THF at 25 °C. [d] By ^{1}H NMR in $CDCl_3$ at 30 °C. [e] By SEC in THF at 40 °C. [f] By viscometry in CCl_4 at 25 °C. [g] By dynamic light scattering in CCl_4 at 25 °C.

Scheme 1



introduction of the dimethylamino group at the PS or the PI chain end. All steps of the synthesis of the precursor polymers was monitored by size exclusion chromatography with UV and RI detectors. Extensive molecular characterization of the diblocks by membrane osmometry, low-angle laser light scattering, and ^{1}H NMR spectroscopy proved their high molecular weight and compositional homogeneity. Their molecular characteristics are given in Table 1. Details of the synthesis and the molecular characterization of the materials are given elsewhere.[18]

The conversion of the terminal amine group to a zwitterionic−mesogenic one was achieved by reaction with excess 2-{6-[4-(4-methoxyphenylazo)phenoxy]hexyloxy}-2-oxo-1,3,2λ^5-phospholane (amine/phospholane = 1/10). The latter compound was synthesized by following literature procedures.[19a] A 2% w/v solution of the amine-capped polymer in THF was allowed to react for several days at 70 °C under nitrogen atmosphere according to Scheme 1.[19b] THF was removed at the end of the reaction in a rotor evaporator almost to dryness and the functionalized polymer was precipitated in methanol. After washing with methanol several times the material was dried under vacuum. ^{1}H NMR spectroscopy (Varian Mercury 200 instrument) in $CDCl_3$ at 30 °C was used in order to check the yield of the transformation reaction.

Aggregation Studies. The aggregation behavior of the zwitterion−mesogenic end-functionalized block copolymers was investigated in CCl_4, a nonpolar solvent good for both the polymeric chains. CCl_4 was dried by reflux over CaH_2 for several hours and fractionally distilled just prior to use. Stock solutions were prepared by direct dissolution of the solid samples in dried CCl_4. Solutions of lower concentration were obtained by subsequent dilution of the stock solutions. For light scattering measurements the solutions were filtered through 0.22 μm nylon filters whereas for viscosity measurements 1.2 μm nylon filters were used.

Static light scattering measurements were performed at 25 °C with a Chromatix KMX-6 low-angle laser light scattering photometer, equipped with a 2 mW He−Ne laser operating at $\lambda = 633$ nm. Apparent weight-average molecular weights, M_w, and second virial coefficients, A_2, were obtained from the concentration dependence of the reduced scattering intensity using the equation

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

where $K = (2\pi n_0)^2(dn/dc)^2(N_A\lambda_0{}^4)^{-1}$, c is the polymer concentration, ΔR_θ is the excess Rayleigh ratio, and dn/dc is the specific refractive index increment determined by a KMX-16 laser differential refractometer operating at the same wavelength and calibrated with NaCl standards.

Dynamic light scattering experiments were carried out at 25 °C, using a series 4700 Malvern system composed of a PCS5101 goniometer interfaced with a PCS7 stepper motor controller, a Cyonics variable power Ar^+ laser, operating at 488 nm, a PCS8 temperature control unit, and a RR98 pump/filtering unit. A 192-channel correlator was used for accumulation of the data. Correlation functions were analyzed by the cumulant method and the Contin software provided by the manufacturer. The correlation function was collected at angles between 45° and 135°. At the concentration range studied for each sample Contin analysis revealed only one distribution of diffusing species. The ratio μ_2/Γ^2, where μ_2 is the second cumulant and Γ the decay rate, derived from cumulant analysis was <0.15 for all angles and concentrations, indicating not a very wide size distribution of the aggregates. No variation of the diffusion coefficient with scattering angle was observed within experimental error. Apparent diffusion coefficients at zero concentration, $D_{0,\ app}$, were obtained after extrapolation to zero angle by the use of eq 2:

$$D_{app} = D_{0,app}(1 + k_Dc) \qquad (2)$$

where D_{app} is the diffusion coefficient measured at each concentration and k_D the coefficient at the concentration dependence of D_{app}. Apparent hydrodynamic radii, R_h, were determined by equation

$$R_h = k_BT/6\pi\eta_0D_{0,app} \qquad (3)$$

where k_B is the Boltzmann constant, T the absolute temperature, and η_0 the viscosity of the solvent at the temperature of measurement ($\eta_0 = 0.91$ cP was used for CCl_4 at 25 °C).

For the viscosity measurements Cannon-Ubbelohde dilution viscometers were used in a temperature-controlled bath ($\Theta = 25 \pm 0.01$ °C). Flow times for the solvent and the micellar solutions were measured with a Scott-Gerate AVS 410 automatic flow timer. Data were analyzed by aid of the Huggins (4) and Kraemer (5) equations

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

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

where $[\eta]$ is the intrinsic viscosity and k_H and k_K are the Huggins and Kraemer coefficients, respectively. Viscometric radii, R_v, were calculated from the equation

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

where $M_{w,app}$ is the weight-average molecular weight determined by light scattering.

Results and Discussion

Polymer Synthesis. It is difficult to determine the extent of conversion of the dimethylamine groups to the

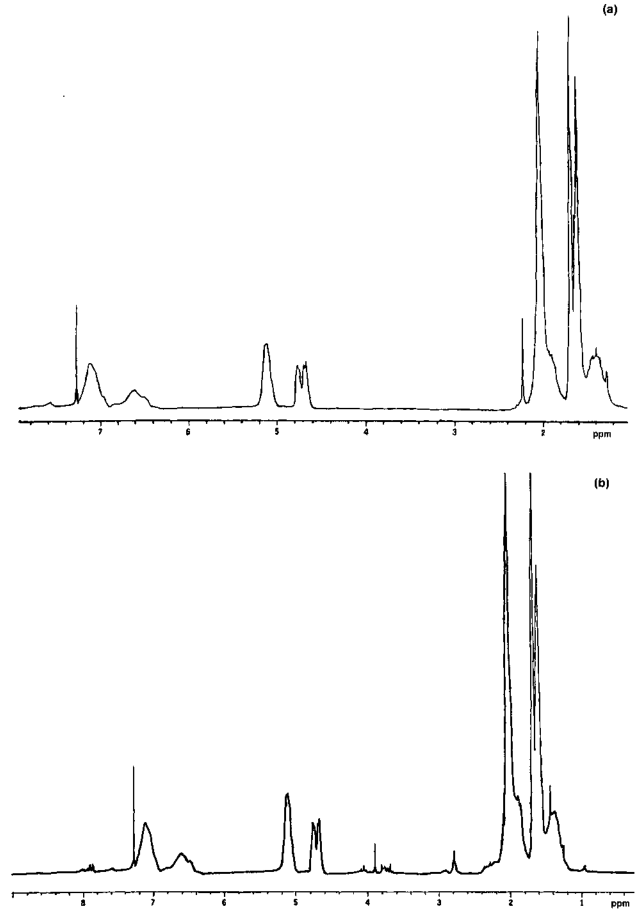


Figure 1. ^{1}H NMR spectra of samples NIS-8 (a) and LCZwIS-8 (b) in $CDCl_3$.

zwitterionic−mesogenic form due to their low concentration. However, some semiquantitative results can be obtained by the use of ^{1}H NMR. In Figure 1 the ^{1}H NMR spectra of sample NIS-8 and its zwitterionic−mesogenic derivative (LCZwIS-8) are shown. The spectrum of NIS-8 (Figure 1a) shows a single peak at 2.2 ppm which is assigned to the methyl protons of the carbons directly attached to the nitrogen.[20] In the spectrum of LCZwIS-8 (Figure 1b) this peak has disappeared and a new one at 2.8 ppm has appeared, indicating transformation of the nitrogen atom of the end group to a positively charged nitrogen. Furthermore, new peaks have appeared which are assigned to protons of the mesogenic group (i.e., $-OCH_3$ protons: singlet at 3.9 ppm, $-(CH_2)_2-$ protons: at 4.0−4.2 ppm, aromatic protons: at 7.8−8.1 ppm).[19] Due to the low intensity of the peaks, only semiquantitative conclusions can be drawn. For the higher molecular weights the intensity of the aforementioned peaks becomes very low, making quantitative interpretation of the spectra even more difficult. We followed the course of the reaction to completion by judging from the disappearance of the peak at 2.2 ppm. By the procedure followed i.e., use of excess of phospholane and long reaction times, the conversion of the end groups is high. We estimate that the reaction proceeded to a conversion of more than 90% for all cases. (There is some background at around 2.2 ppm which can also been seen in the spectra of the amine precursors which makes quantitative determinations of the area under the peak difficult.)

Aggregation Behavior in CCl_4. It has been previously shown that the amine-capped diblocks do not aggregate in CCl_4.[18] The results from static low-angle laser light scattering (LALLS) for the zwitterionic−mesogenic diblock copolymers in the same solvent are given in Table 2. A representative plot demonstrating the variation of reduced scattering intensity with concentration is shown in Figure 2. Linear plots were obtained in all cases at the concentrations studied, indicating that the equilibrium is shifted toward the formation of aggregates and properties of the solutions are dominated by the presence of aggregates. The critical micelle concentration for these systems, if it exists, must be very low and outside the experimentally accessible concentration range. The weight-average molecular weights are elevated. Also the values of the second virial coefficient have decreased considerably compared to the values in a good solvent (Table 1) almost by 1 order in magnitude, and in one case a negative A_2 has been obtained. It is obvious that the mesogenic−zwitterionic end-functionalized samples aggregate in CCl_4. This must be a result of the fact that ionic dipoles are not soluble in nonpolar solvents such as CCl_4. It has to be noted that the mesogenic end group has a small solubility in CCl_4. The weight-average aggregation number, N_w, defined as the ratio of the $M_{w,app}$ in CCl_4 to M_w of the amine precursor in THF, remains constant, within experimental error, and equal to 2 for molecular weights higher than 12 000. For $M <$ 12 000 higher aggregation numbers are derived which increase more steeply with decreasing molecular weight of the precursor diblock. The behavior is similar irrespective of the position of the mesogenic−zwitterionic end group as was found in the case of sulfobetaine end-functionalized polymers. The variation of N_w with weight-average molecular weight of the precursor can be seen in Figure 3. In comparison to the zwitterion

Table 2. LALLS Results on Block Copolymers with Mesogenic−Zwitterionic End Group in CCl_4 at 25 °C

sample	$M_w \times 10^{-4}$	$A_2 \times 10^4$	N_w[a]
LCZwIS-7	6.23	4.7	1.7
LCZwIS-3	6.00	3.2	2.5
LCZwIS-5	2.49	−2.9	1.8
LCZwIS-8	5.51	3.32	6.0
LCZwSI-5F	8.75	1.7	2.0
LCZwSI-3F	4.02	0.16	2.7
LCZwSI-2F	4.75	0.20	4.2

[a] N_w is the weight-average aggregation number defined as the ratio of M_w determined for the mesogenic−zwitterion end-functionalized diblocks in CCl_4 to the M_w of the amine precursors ($N_w = (M_w)_{LCZw}/(M_w)_N$).

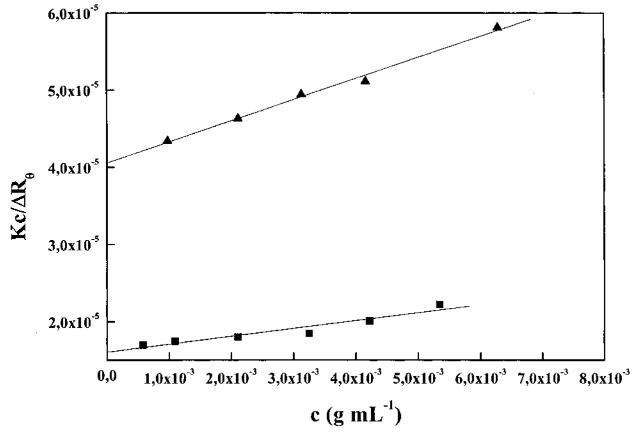


Figure 2. Comparison low-angle light scattering plots of $Kc/\Delta R$ vs concentration for samples NIS-3 in THF (▲) and LCZwIS-3 in CCl_4 (■) at 25 °C.

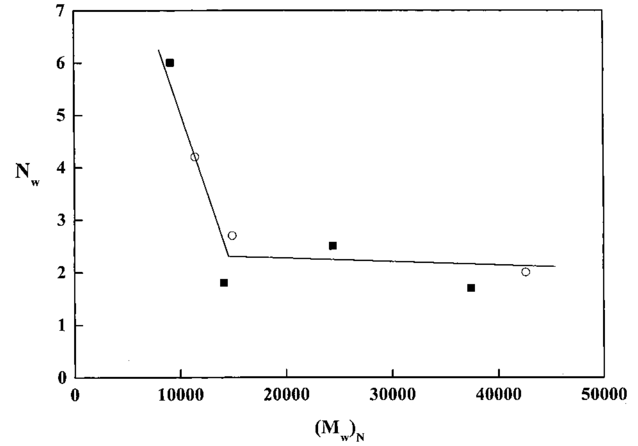


Figure 3. Dependence of weight-average aggregation number, N_w, of mesogenic−zwitterionic end-functionalized diblocks on molecular weight of the precursor amine-capped copolymers in the nonpolar solvent CCl_4 ((■) LCZwIS diblocks, (○) LCZwSI diblocks). The lines are a guide for the eye.

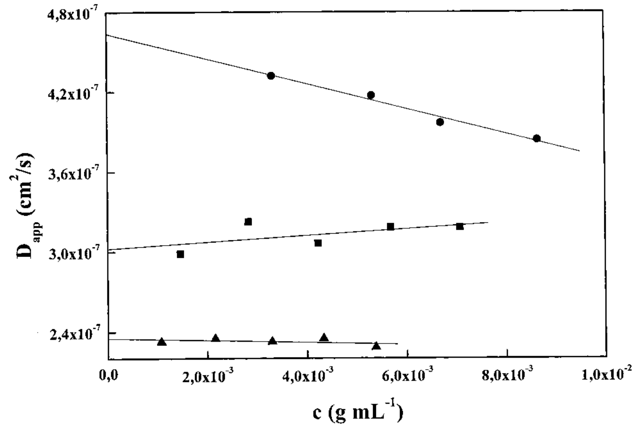


Figure 4. D_{app} vs concentration for samples LCZwIS-7 (■), LCZwIS-8 (●), and LCZwSI-5F (▲) in CCl_4 at 25 °C.

Table 3. DLS Results on Block Copolymers with Mesogenic−Zwitterionic End Group in CCl_4 at 25 °C

sample	D_0 (cm²/s) × 10^7	k_D	R_{hLCZw} (nm)	R_{hLCZw}/R_{hN}
LCZwIS-7	3.02	8	8.0	1.16
LCZwIS-3	3.10	1	7.8	1.13
LCZwIS-5	4.17	−41	5.8	1.6
LCZwIS-8	4.64	−20	5.2	1.6
LCZwSI-5F	2.35	−3	10.3	1.5
LCZwSI-3F	3.60	−32	6.7	1.5
LCZwSI-2F	3.88	−19	6.2	1.7

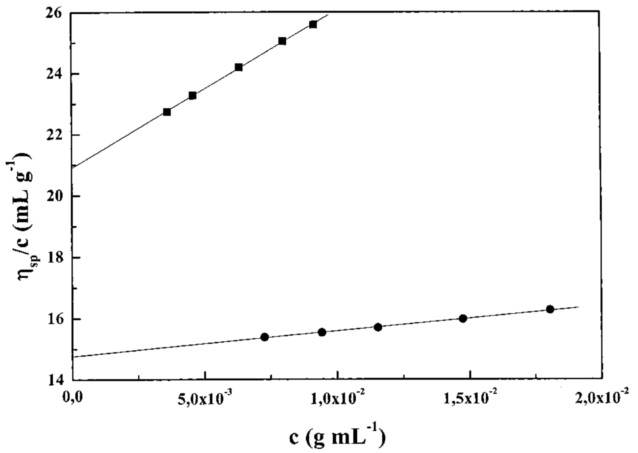


Figure 5. Comparison η_{sp}/c vs concentration plots for samples NIS-8 (●) and LCZwIS-8 (■) in CCl_4 at 25 °C.

Table 4. Viscometric Results on Block Copolymers with Mesogenic−Zwitterionic End Group in CCl_4 at 25 °C

sample	$[\eta]$ (mL/g)	k_H	R_{vLCZw} (nm)	$[\eta]_{LCZw}/[\eta]_N$	R_{vLCZw}/R_{vN}
LCZwIS-7	48.6	0.73	7.8	1.12	1.22
LCZwIS-3	44.5	0.61	7.5	1.15	1.49
LCZwIS-5	28.0	1.3	4.8	1.10	1.26
LCZwIS-8	20.9	1.18	5.7	1.41	2.0
LCZwSI-5F	48.3	0.54	8.7	1.08	1.30
LCZwSI-3F	29.1	0.90	5.7	1.26	1.50
LCZwSI-2F	21.4	1.16	5.4	1.17	1.69

capped diblocks,[18] the aggregation numbers of the mesogenic−phosphorus zwitterionic diblocks in the same solvent are lower. In the present case the dependence of aggregation number on precursor molecular weight is less pronounced. We will return to this point later.

Dynamic light scattering experiments were conducted in the same solvent in order to obtain information about the hydrodynamic size of the aggregates. The results are shown in Table 3. The variation of apparent diffusion coefficient, D_{app}, on concentration was linear in all cases. A representative plot is given in Figure 4. No variation of D_{app} with scattering angle was observed, indicating a small size for the aggregates in comparison to the wavelength used for the measurements and also a rather low polydispersity of the entities in the solution. These last conclusion is supported by the rather low values of μ_2/Γ^2 (<0.15) obtained from cumulant analysis and the monomodal distribution obtained by Contin analysis. The $D_{0,app}$ values are lower for the mesogenic−zwitterionic block copolymers than for the amine precursors in CCl_4. The k_D values are negative in most cases as a consequence of the decrease of A_2 due to the aggregation process. The hydrodynamic radii are also increased relative to the amine precursors, suggesting aggregation of the mesogenic−zwitterionic end-functionalized diblocks. These findings are in accord with the static light scattering picture of the systems, which implies that in the concentration range studied the majority of diblock chains must be incorporated into aggregates.

To complement the light scattering measurements and to gain more insight into the aggregation process and the properties of the aggregates, viscosity measurements were also performed in CCl_4 on solutions of the mesogenic−zwitterionic diblock samples. The results are given in Table 4. The variation of the η_{sp}/c or ln η_r/c vs concentration was linear as can be seen in Figure 5. Extrapolated intrinsic viscosities are higher than those of the amine precursors. The k_H values are also much higher and in some cases larger than 0.99, the limit for hard spheres, as a result of increased hydrodynamic interactions coming from the incorporation of chains in an aggregate. Large values of k_H have been observed in many other aggregating systems. Viscometric radii calculated from $[\eta]$ and $M_{w,app}$ values in CCl_4 or the mesogenic−zwitterionic copolymers are larger than the amine-capped diblocks. The viscometric results support the conclusions drawn from light scattering measurements that the end-functionalized diblocks under investigation aggregate in CCl_4.

It is reasonable to assume that aggregates formed by polymers with only one associating group at the chain end, as in the present case, are starlike. To check this assumption, dilute solution data can be used. For star

Table 5. Aggregation Numbers Derived by Different Methods for Block Copolymers with Mesogenic−Zwitterionic End Group in CCl_4 at 25 °C

sample	N_{LALLS}	N_{DLS}[a]	N_{VIS}[a]
LCZwIS-7	1.7	1.2	1.3
LCZwIS-3	2.5	1.2	1.8
LCZwIS-5	1.8	2.3	1.4
LCZwIS-8	6.0	2.3	4.0
LCZwSI-5F	2.0	2.0	1.5
LCZwSI-3F	2.7	2.0	2.3
LCZwSI-2F	4.2	2.7	2.7

[a] Assuming the star model.

polymers the ratio of hydrodynamic radius of the star to that of the arm depends only on the number of arms.[21,22] Stars with up to 256 arms have been studied.[22] For starlike aggregates one can calculate the aggregation number (number of arms) by comparison of the aggregates radius to that of the monomeric chain.[18] The ratios of the hydrodynamic radii estimated by dynamic light scattering and viscometry, R_{hLCZw} and R_{vLCZw}, for the aggregates to that of the precursors, R_{hN} and R_{vN}, respectively, are tabulated in Tables 3 and 4. The calculated aggregation numbers by different methods are given in Table 5. There seems to be good agreement, within experimental error, between the different methods. Therefore, the star model can well describe the behavior of the aggregates formed by the mesogenic−zwitterionic diblock copolymers in CCl_4. It has to be added that the increased k_H values are also indicative of a starlike structure for the aggregates.

The fact that the aggregation numbers derived by viscometry, where the system is perturbed by shear, are close to those estimated by LALLS and DLS, where the system feels no perturbation, leads to the conclusion that the aggregates are stable under the shear forces developed in a capillary (shear rate was lower than 5×10^2 s^{-1}). Additionally, the lifetime of these aggregates is long enough since both static (LALLS) and dynamic (DLS, viscometry) methods detect almost the same aggregation number (at least longer than the characteristic time of DLS, 2×10^{-4} s, and viscometry, 2×10^{-3} s).

The observed variation of aggregation number with molecular weight of the precursor deserves some comments. Presumably the decrease in the aggregation number with increasing molecular weight originates from the increase in the steric repulsions (excluded-volume interactions) as the polymeric chains become longer, and it was observed in the case of sulfozwitterionic end-functionalized polymers. However, another factor that determines aggregation number is the association of the end groups and furthermore the way they are arranged in the core of the aggregates. It has been proposed and demonstrated by theoretical calculations that in zwitterionic end-capped polymers the headgroups prefer to be aligned in an antiparallel fashion in order to minimize electrostatic repulsions in the core.[23] Several theoretical models have been proposed in order to describe the behavior of polymers having associating end groups. In the spherical head packing model[24] the headgroups are arranged in a liquid drop like core, and the aggregates have a narrow size distribution, a conclusion that does not always coincide with low polydispersity in the aggregation number, and are characterized by a very low cmc. In the preferred head-packing model[24] the aggregation number is almost constant (low polydispersity) and independent of the chain molecular weight. This model also predicts a low cmc, a narrow size distribution, and a critical molecular weight above which no aggregation exists. In the linear head-packing model[25] the dipolar heads are placed antiparallel to each other, forming a one-dimensional core which can grow infinitely. The model predicts no cmc but an increase in the aggregation number by decreasing chain molecular weight together with a rather broad size distribution of the aggregates.

It is difficult to resolve which model describes the situation at hand. In our case there is variation of the aggregation number with molecular weight of the chain which can also be attributed in the antiparallel placement of the zwitterionic part of headgroups as the linear head-packing model predicts. On the other hand, the aggregate polydispersity is not so large as in the case of sulfobetaine end-capped polymers.[18] Of course, the low polydispersity may be a result of the low aggregation numbers.

However, in the mesogenic−zwitterionic copolymers the zwitterionic part is connected from one end with a large polymeric tail and from the other with a rigid aromatic group, through a flexible spacer. The new factor in this system is the possible existence of steric and solvating interactions between the phosphorus zwitterion and the aromatic rings and nitrogen atoms of the mesogenic group. Although their specific nature cannot be conceived in detail, one can assume that the electrostatic forces between dipoles can be somehow mediated or altered by the mesogenic groups leading to weaker dipole−dipole interaction. Steric effects in the core coming from the interactions described above and other between the mesogenic groups also play a role in determining core dimensions. The interplay between core interactions and tail excluded-volume repulsions determine the size and shape of the aggregate as a whole. Core interactions are expected to be active in all cases whereas the excluded-volume interactions between copolymeric tails are becoming more and more important as the molecular weight of the chain increases. The two regimes in the dependence of aggregation number on chain molecular weight may be a result of tail steric effects dominating over core interactions as the high molecular weight limit is reached.

In any case differences in behavior, in comparison to sulfozwitterionic end-functionalized diblocks, do exist when the main chain and solvent chemical nature remain unchanged and only the end group has been changed. This is another definite illustration of how solution properties of associating polymers can be altered by a change in the end group.

Conclusions

The dimethylamino end group of styrene−isoprene block copolymers can be transformed to a mesogenic−zwitterionic one by reaction with excess 2-{6-[4-(4-methoxyphenylazo)phenoxy]hexyloxy}-2-oxo-1,3,2λ^5-phospholane. The conversion of the end groups is almost quantitative.

In dilute solutions in CCl_4 aggregates of relatively low polydispersity are formed due to the dipole−dipole interactions as evidenced by different methods. These aggregates could be well described by the star model. The absolute values of the aggregation numbers were almost constant and equal to 2 for high molecular weights and increase steeply for $M_w \leq 12\,000$. On the other hand, experimentally determined N_w's are lower compared with the case of sulfozwitterionic block copolymers.

The observed behavior can be understood if the lower polarity of the phosphorus zwitterion relative to the sulfobetaine one and the increased steric hindrance experienced by the aggregated zwitterions in the core are taken into account. Because of the presence of a liquid crystalline group and the polymeric tail directly bonded to the zwitterion, elongated aggregate structures are difficult to be formed in the studied systems.

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