Synthesis and Preliminary Characterization of Model Liquid Crystalline Ionomers

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Received September 1, 1995; Revised Manuscript Received February 13, 1996[⊗]

ABSTRACT: Model liquid crystalline ionomers have been synthesized that consist of low molecular weight linear chains selectively end-capped at one or both end(s) with an ionic mesogenic group. ω- and α,ω-carboxylato and sulfonato polystyrene chains have been prepared by living anionic polymerization and associated with mesogenic counterions, the structure of which is a rigid azobenzene moiety attached to a quaternary ammonium halide through a flexible spacer. The thermotropic behavior of the liquid crystalline halato(semi)telechelic polymers (LC H(S)TP's) has been studied by differential scanning calorimetry and optical microscopy. Some of them show smectic mesophases in a large temperature range. Actually, the liquid crystalline properties of the LC H(S)TP's depend on the molecular weight and the nature of the ionic end groups. A model, based on a crystal close packing approach, shows that the bulkiness of the sulfonato end groups can prevent the formation of smectic mesophases. The supramolecular organization of the LC H(S)TP's has also been studied by small angle neutron scattering, which agrees with a microphase separation between the polymer chains and the mesogenic counterions.

Introduction

The noncovalent bonding of mesogens to polymer chains has recently been proposed as a new concept in the design of liquid crystalline polymers (LCP's).[1] This type of ionic LCP's deserves interest from both the academic and applied points of view due to an interesting combination of the characteristic features of both LCP's and ionomers in the same material. It is also a pertinent approach to the role of ions in the formation and stability of mesophases.[2]

LCP's are currently prepared either from mesogenic monomers, the polymerization of which is usually cumbersome, or by grafting LC moieties onto preformed polymers, which is a high cost solution process that often results in poor yields. In contrast, ionic LCP's can be made available by reaction of a traditional ionomer bearing metal carboxylate or metal sulfonate groups with a low molar mass mesogen bearing a mutually reactive group, e.g., a quaternary ammonium halide. The final cost might be significantly reduced compared to the conventional methods.

Until now, very few ionic LCP's have been reported in the scientific literature. The first known example has been published by Ujiie and co-workers.[1,3,4,5] These authors have shown that a thermotropic LCP was formed upon the mixing of a liquid crystal substituted by an ammonium cation with an anionic polymer of the sulfonate type. Bazuin and co-workers[6,7,8] have studied the electrostatic interactions between poly(4-vinylpyridine) and a carboxylic acid group terminated mesogen, and they have emphasized that noncovalent interaction between functional mesogens and mutually reactive polymers is indeed a promising route toward creating a novel family of polymeric liquid crystalline materials.

Another class of liquid crystalline ionomers can also be formed from classical covalently bonded LCP's where ionic moieties replace some of the mesogenic units. Zentel et al. have studied liquid crystalline ionomers prepared from ferrocene containing liquid crystalline polymers by a redox reaction,[9] and they have shown that blends of these compounds with partially sulfonated polystyrene combine the properties of the constitutive components.[10,11] Zhang and Weiss have synthesized liquid crystalline ionomers containing sodium sulfonate pendant groups by an interfacial condensation reaction.[12]

In the line of this concept, our laboratory has been interested in the synthesis of model LC ionomers, i.e., linear chains of a well-defined molecular weight (MW) and a narrow MW distribution, end-capped with a mesogen through an ionic bonding, at one or both end(s). They are referred to as liquid crystalline halato(semi)telechelic polymers (LC H(S)TP's). Actually, they are model ionomers, in which the mesogen is the counterion of the ionic end groups. They are thus ideal candidates for morphological studies of liquid crystalline ionomers.

In this paper, we report the synthesis of a series of LC H(S)TP's, consisting of low molecular weight polystyrene chains end-capped with sulfonate or carboxylate groups associated with a mesogenic quaternary ammonium cation.

Experimental Part

Polymer Synthesis. ω- and α,ω-sulfonato and carboxylato polystyrenes were synthesized by living anionic polymerization of styrene, as reported elsewhere.[13,14]

The end sulfonation of the living chains was carried out according to the slightly modified Quirk's procedure.[15] The living chains were first capped with 1,1-diphenylethylene, before being deactivated with a 2-fold molar excess of freshly distilled 1,3-propanesultone. The polymer was twice precipitated in methanol.[16]

ω- and α,ω-carboxylato polystyrenes were obtained by deactivation of the living anionic species by bubbling dry CO_2 into the reaction medium kept at −78 °C. Bubbling was maintained for 15 min, and the polymer was twice precipitated in acidified methanol. α,ω-Carboxylic acid polystyrene was converted into the corresponding sodium salt by end neutralization with the stoichiometric amount of sodium methoxide in anhydrous toluene.

Molecular weight and molecular weight distribution were measured by size exclusion chromatography (calibrated with polystyrene standards), in THF, of a polymer sample picked out before deactivation of the living chains. Functionality was calculated from the molecular weight and potentiometric

[⊗] Abstract published in *Advance ACS Abstracts,* April 1, 1996.

S0024-9297(95)01303-9 CCC: $12.00

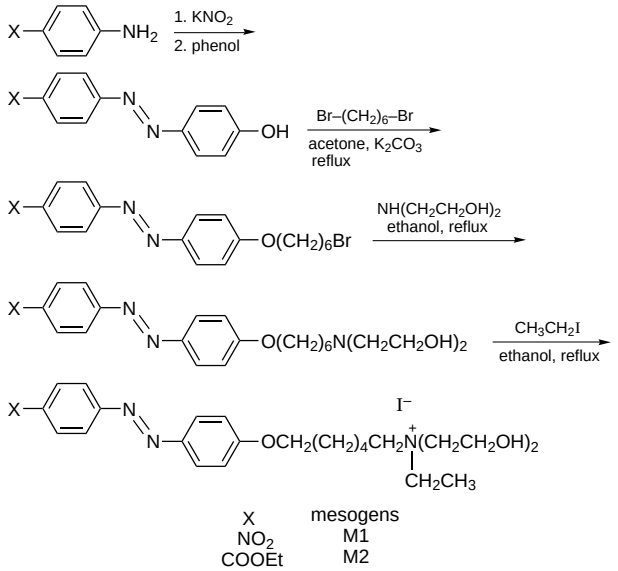
Table 1. Molecular Characteristics of H(S)TP's

type of H(S)TP	acronym	M_n	polydispersity	functionality (%)
monosulfonato polystyrene	P1-SO_3Li	700	1.1	90
monosulfonato polystyrene	P2-SO_3Li	1000	1.05	97
monosulfonato polystyrene	P3-SO_3Li	5500	1.1	100
disulfonato polystyrene	P4-$(SO_3Na)_2$	5500	1.1	195
dicarboxylato polystyrene	P5-$(COONa)_2$	4700	1.15	190
dicarboxylato polystyrene	P6-$(COONa)_2$	16000	1.05	94
monocarboxylato polystyrene	P7-COOLi	2000	1.15	84
monocarboxylato polystyrene	P8-COOLi	5200	1.05	90
monocarboxylato polystyrene	P9-COOLi	6500	1.05	92
monocarboxylato polystyrene	P10-COOLi	10000	1.05	100

titration of the acid end groups with a standard tetramethylammonium hydroxide solution in a toluene/methanol 9/1 mixture.

The acronyms and molecular characteristics of the synthesized telechelic polystyrenes are listed in Table 1.

Synthesis of the Mesogenic Counterions. Two ionic mesogens, M1 and M2, were prepared according to a procedure known in the scientific literature.[1,4] The synthetic pathway is schematized by the following equations:



The final products were recrystallized from ethanol. Nonionic mesogenic compounds were removed by preparative chromatography on a silica gel column.

The molecular structure of M1 and M2 was ascertained by IR spectroscopy of chloroform-cast films with a Perkin Elmer FT-IR spectrometer and by ^{1}H NMR spectroscopy (solvent: CD_3OD) with a Bruker 400 MHz spectrometer. Spectroscopic data were consistent with the expected structures. Representatives IR and ^{1}H NMR data are shown in Table 2.

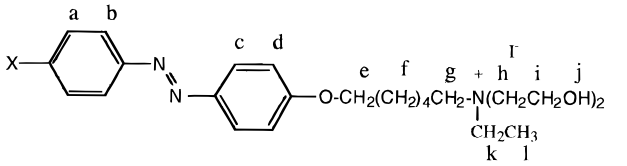
Synthesis of LC H(S)TP's. LC H(S)TP's were prepared by an ion exchange reaction as shown by the following equation:

$$P^-M^+ + A^+I^- \rightarrow P^-A^+ + M^+I^-$$

where $P^- = P1\text{-}SO_3^-$, ..., $P10\text{-}COO^-$; $M^+ = Li^+, Na^+$; and $A^+ = M1^+, M2^+$.

The mesogenic compounds M1 and M2 (0.5 mmol) were dissolved in 20 mL of chloroform. These solutions were added dropwise to a stoichiometric amount of ω- and α,ω-sulfonato (carboxylato) polystyrene, respectively, dissolved in 20 mL of chloroform. The mixed solutions were refluxed for 2 h and then cooled down to room temperature. Sodium (lithium) iodide was extracted from the reaction mixture by repeated washing with 10 mL of water. Silver nitrate was added to the water phases to verify that sodium (lithium) iodide was removed. LC H(S)TP's were recovered by chloroform evaporation and then carefully dried in a vacuum oven at 80 °C for 2 days. Functionality of the LC H(S)TP's was checked by ^{1}H NMR by comparing the relative intensities of the polystyrene and mesogen signals in the aromatic region and was found systematically better than 95%.

Table 2. Spectroscopic Data for M1 and M2



X	δ (ppm)	ν (cm^{-1})
NO_2	1.3−1.8 (m, 8H, Hf), 2.6 (m, 3H, H1), 2.8 (s, 2H, Hj), 3.4 (m, 8H, Hg, Hk, Hh), 3.6 (m, 4H, Hi), 4.2 (t, 2H, He), 7 (d, 2H, Hd), 7.9 (d, 4H, Hc, Hb), 8.35 (d, 2H, Ha)	1344 (NO_2 stretch)
$COOCH_2CH_3$ *m n*	1.4−1.8 (m, 8H, Hf), 1.9 (t, 3H, Hn), 2.2 (s, 2H, Hj), 2.5 (t, 3H, H1), 2.7 (m, 8H, Hg, Hk, Hh), 3.6 (t, 4H, Hi), 4 (t, 2H, He), 4.4 (q, 2H, Hm), 7 (d, 2H, Hd), 7.9 (d, 4H, Hc, Hb), 8.1 (d, 2H, Ha)	1735 (C=O ester)

LC H(S)TP Characterization. The liquid crystalline properties of LC H(S)TP's were investigated by polarized-light microscopy (Leitz polarizing microscope equipped with a Mettler FP52 hot stage) and differential scanning calorimetry (Dupont 9000 apparatus calibrated with an indium standard).

SANS. The SANS experiments were performed with the spectrometer PACE in the reactor Orphée at the Laboratoire Léon Brillouin (CEA-CNRS), Saclay, France. The incident wavelength, λ, isolated by a mechanical selector, was 5 Å ± 10%. The q range of the collimated beam was 0.03 to 0.3 $Å^{-1}$. The cells were held in the neutron beam in an appropriately designed aluminium block, the temperature of which was controlled by circulating a thermostated ethylene glycol−water mixture. The samples were annealed at 100 °C during 1 day and then rapidly cooled to room temperature. This procedure is able to freeze-in the smectic mesophase at room temperature.

The "raw intensity", $I_r(q,T)$, was corrected in a standard manner[17] for the scattering from the empty cell walls and scaled as $I'(q,T)$ by the scattering cross section of 1 mm of water. This corrected and scaled $I'(q,T)$ value still comprised the incoherent background scattering. The background scattered intensity $I_b(q,T)$ was thus substracted from $I'(q,T)$ to provide the final $I(q,T)$ value. An amorphous mixture of polystyrene and mesogen methanesulfonate was used to estimate the $I_b(q,T)$ value.

Results and Discussion

Thermal and orientational properties of the mesogenic compound M1 have previously been reported by Ujiie et al. M1 is known to form a smectic A mesophase in the temperature range from 40.5 to 170.2 °C,[1] whereas fan-shaped textures[18] are observed by polarized optical microscopy. Furthermore, the ammonium group is at the origin of the alignment of the smectic phase, which explains the homeotropic structure observed upon an-

Table 3. Phase Transition Temperatures for M1 and M2

sample	phase transition temperature,[a] °C[(b)]
M1	S $41_{(43.2)}$ Sa $170_{(5.7)}$ I
M2	S $62_{(33.1)}$ Sa $105_{(4.4)}$ I

[a] S, solid phase; Sa, smectic A phase; I, isotropic phase. [b] Transition enthalpy in kJ/mol.

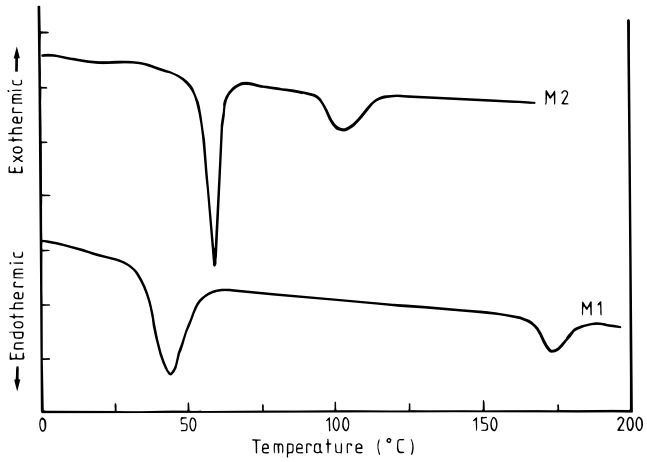


Figure 1. DSC traces for M1 and M2 on heating (heating rate: 10 °C/min).

nealing. All these characteristic features of the cationic liquid crystal M1 have been confirmed in this study.

The mesogenic properties of M1 and M2 are quite comparable, since they show two first-order transitions, i.e., a solid−smectic transition and a smectic−isotropic transition, respectively. The thermal properties of M1 and M2 are summarized in Table 3, and the DSC traces on heating are shown in Figure 1. The efficiency of the terminal group in stabilizing the liquid crystalline phase is found to be R−NO_2 > R−COOEt, in complete agreement with the general behavior of low molar mass mesogens.[19]

Quite similarly to M1, optical microscopy observation of M2 between crossed polarizers shows a fan-shaped texture and a homeotropic structure upon annealing. Furthermore, the cationic liquid crystals M1 and M2 are totally miscible and show the same texture in the whole composition range. These results confirm that M2 forms a smectic A mesophase.[18]

The cationic liquid crystals M1 and M2 can be associated with various types of counteranions such as low molecular weight anionic compounds and polyanions. In this study, halato(semi)telechelic polymers (H(S)TP's) have been selected as counteranions, the chain length and terminal anion of which can be easily changed. Furthermore, these polymeric counteranions are expected to freeze in liquid crystalline structures in the solid state. This study will mainly focus on the ionic mesogen M1 because of a larger smectic mesophase stability range compared to M2.

Carboxylato LC H(S)TP's. DSC and polarization microscopy support that liquid crystalline mesophases are formed for most of the carboxylato LC H(S)TP's under consideration. The thermal properties of these compounds are listed in Table 4.

Except for the P10-COOM1 sample, the carboxylato LC H(S)TP's form a smectic mesophase in a quite comparable T_s-T_i temperature range. The solid−smectic transition is observed at T_s close to 50 °C, in complete agreement with Ujiie et al.,[5] who have studied the liquid crystalline properties of LCP's prepared from poly-

Table 4. Thermal Properties of Carboxylato LC H(S)TP's and Their H(S)TP's Precursors (Heating Rate: 20 °C/min)

sample	M_n	phase transition temperatures,[a] °C[(c)]	T_g of precursors, °C
P5-$(COOM1)_2$	4700	G $50.2_{(3.65)}$ Sa $155_{(1.36)}$ I	98
P6-$(COOM1)_2$	16000	G $52_{(1.56)}$ G and Sa 87 (T_g) Sa $150^b_{(0.15)}$ I	103
P7-COOM1	2000	G $49.5_{(4.2)}$ Sa $157_{(1.7)}$ I	61
P8-COOM1	5200	G $50_{(2.87)}$ Sa $155_{(0.85)}$ I	99
P9-COOM1	6500	G $50.1_{(2.1)}$ G and Sa 85 (T_g) Sa $153^b_{(0.42)}$ I	98
P10-COOM1	10000	$T_g = 90$	100

[a] G, glassy phase; G and Sa, coexistence of glassy and smectic A phases; Sa, smectic A phase; I, isotropic phase; T_g, glass transition. [b] Transition not detected by DSC but observed by optical microscopy. [c] Transition enthalpy in kJ/mol.

(sodium styrenesulfonate) and the mesogenic cation M1. Although it may be a problem to detect the smectic−isotropic transition by DSC because of a low enthalpy change, T_i has been observed by optical microscopy at ca. 155 °C for all the mesogenic carboxylato LC H(S)-TP's. Therefore, the polystyrene molecular weight seems to have no effect on T_i, in contrast to the usual observation of an increase in the mesomorphic−isotropic transition temperature with molecular weight in conventional LCP's. In the systems studied in this paper, the situation is completely different, since molecular weight of the polystyrene carrier does not perturb the formation and stability of the mesophases, at least until a critical molecular weight is reached. Beyond this value, concentration of the ionic mesogens in the polymer matrix is no longer high enough for the mesophases to be formed, as shown by the P10-COOM1 sample. Determination of this critical molecular weight is currently in progress, and the preliminary results indicate that this critical molecular weight is ca. 8000 for the monofunctional polystyrene chains and 16 000 for the difunctional analogues.[20] As this critical molecular weight is approached, e.g., in P6-$(COOM1)_2$ and P9-COOM1 samples a glass transition temperature becomes detectable, which may be assigned to the glass transition of the polystyrene chains and is the signature of a phase separation between the mesogenic counterion and the polymer backbone. Compared to the polymer precursor H(S)TP's, T_g of the LC components occurs at lower temperature, indicating that the mesogenic group has an effect on the mobility of the polystyrene chains.

At high temperature (>200 °C), a thermal degradation occurs, which is more likely due to the limited thermal stability of the ammonium groups.[21]

Figure 2 illustrates the optical texture for the P7-COOM1 sample observed at 120 °C in a sandwich cell under crossed polarizers. Actually, mesophases have been assigned on the basis of the optical textures. For this purpose, each polymer has been heated up to approximately 10 °C above the clearing point and then allowed to cool down slowly through the phase transition. For the low molar mass LC H(S)TP's (i.e., P5-$(COOM1)_2$, P7-COOM1, and P8-COOM1), rods are formed at the transition to yield a fan-shaped texture (Figure 2a) indicative of a layered organization.[18,22] In addition, regions of a homeotropic texture are visible, which indicates that the director of the phase is oriented perpendicular to the cell windows. The tendency for ionically functionalized liquid crystals to align perpendicularly to the glass substrate has already been observed by other research groups.[1,23] This homeotropic alignment is disrupted by shearing the sample between the glass plates, promoting a shimmering aspect. The

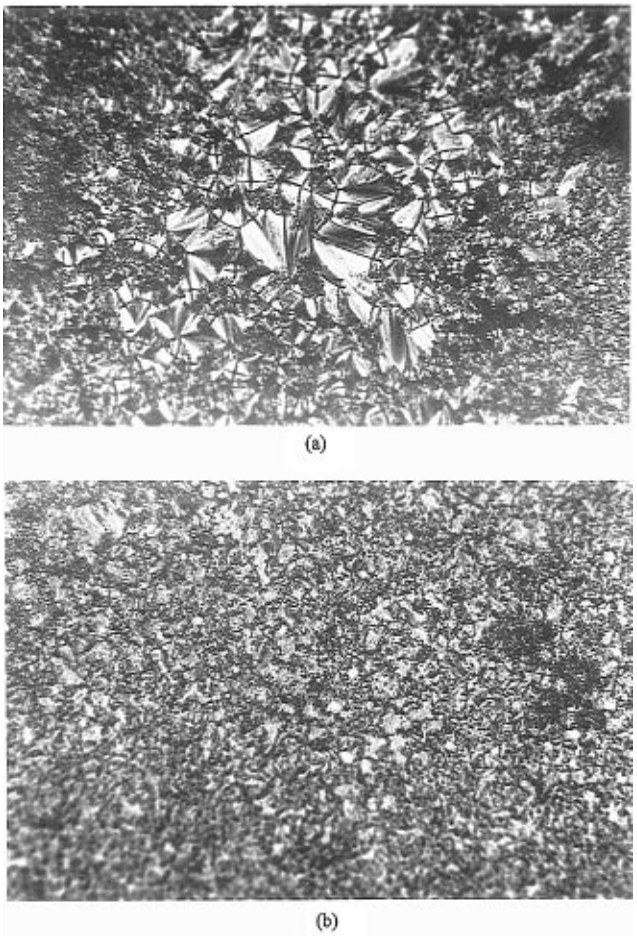


Figure 2. Optical textures observed for carboxylato LC H(S)TP's: (a) fan-shaped texture in P7COO-M1, (b) texture observed in P9-COOM1 (crossed polarizers, observation temperature = 120 °C; original magnification = 400×, reduced to 60% of original for publication).

observed phase has been assigned to a smectic A phase, in agreement with the surface alignment of amphiphilic alkylammonium mesogens, the ionic group of which acts as a smectogen.[1] The adsorption of ammonium ions on the glass plates triggers the perpendicular alignment of the LC molecules and the formation of a homeotropic structure in which the nitroazobenzene mesogenic groups are able to overlap as a result of the strong mutual interaction of the nitro terminal groups. The homeotropic structure formed in the smectic phase remains unaltered on cooling below T_g. The oriented domains can accordingly be frozen in the solid state. This feature is of great interest for many applications such as nonlinear optics and data storage.[24] For the higher molecular mass carboxylato LC H(S)TP's (i.e., P6-$(COOM1)_2$ and P9-COOM1), the optical texture consists of small domains as shown in Figure 2b. This texture remains essentially unchanged even after annealing for several hours, which is in favor of a less ordered mesophase. Actually, the mesophase would be the same as for lower mass analogue, but perturbed by some defects, in agreement with the low enthalpy of the smectic−isotropic phase transition as observed by DSC.

The phase separation observed in some of the carboxylato LC H(S)TP's used in this study suggests that these compounds might act as interfacial agents in immiscible polymer/LC blends. Thus, an interfacial agent might consist of a chain identical to the polymer matrix to which is ionically bonded a component miscible or strongly interacting with the LC to be dispersed.

Table 5. Thermal Properties of Sulfonato LC H(S)TP's (Heating Rate: 20 °C/min)

sample	M_n	phase transition temperatures,[b] °C$_{(b)}$	T_g of precursors, °C
P1-SO_3M1	700	G 49.5$_{(4.9)}$ Sa 155$_{(1.85)}$ I	19
P2-SO_3M1	1000	$T_g = 60$	74
P3-SO_3M1	5500	$T_g = 101$	85
P4-$(SO_3M1)_2$	5500	$T_g = 103$	85

[a] G, glassy phase; Sa, smectic A phase; I, isotropic phase; T_g, glass transition. [b] Transition enthalpy in kJ/mol.

This two-component chain is expected to be located at the polymer/LC interface and thus to control the size and shape of the dispersed phase. Indeed, blending a LC with an immiscible polymer, in the presence of an interfacial agent, has been shown to be a promising route for the production of well-defined polymer-dispersed liquid crystals.[25]

Sulfonato LC H(S)TP's. The thermal properties of the sulfonato LC H(S)TP's and H(S)TP's precursors are listed in Table 5. Except for the very low molar mass P1-SO_3M1, the sulfonato LC H(S)TP's show only one T_g as the lithium precursor does. No transition attributable to a clearing transition is observed, in agreement with a lack of liquid crystalline properties. Nevertheless, temperature and broadness of the glass transition are deeply modified by the substitution of the mesogen cation for lithium. A decrease in T_g from ca. 100 °C down to 85 °C is observed for the P3-SO_3M1 and P4-$(SO_3M1)_2$ samples. This modification is consistent with a plasticizing effect of the ionic mesogen. Plasticization has already been reported for noncovalent side-chain LCP's of a low mesogen content.[6] In contrast, the DSC trace of the lower molar mass P1-SO_3M1 sample shows an increase in T_g from 60 to 74 °C. It thus appears that the effect of an ammonium liquid crystalline counterion on T_g of a sulfonate-ended polystyrene critically depends on the polystyrene molecular weight, i.e., on the mesogen content. At a low content, the ionic mesogen acts as a plasticizer, although an anti-plasticization is observed at higher mesogen contents.

Sulfonato LC H(S)TP's have been observed by optical microscopy under crossed polarizers. Chloroform-cast films appear to be homogeneous at room temperature. When the samples are heated above T_g between two glass plates, the observed texture consists of a dark region, in which there is no homeotropic alignment since no texture appears upon shearing the sample. Upon cooling down to the solid state (cooling rate = 1 °C/min), a uniform dispersion of submicrometer size point-like birefringent domains is observed below T_g, in agreement with a phase separation (Figure 3). Although no mesogen-like transition is observed in these systems, those tiny birefringent points could be LC domains dispersed in the immiscible polystyrene matrix.

In contrast to the other sulfonato LC H(S)TP's, the P1-SO_3M1 sample which is of a very low molecular weight ($M_n = 700$) exhibits liquid crystalline properties. DSC and optical microscopy studies agree with the formation of a smectic A phase in the temperature range from 50 to 155 °C. The optical texture is quite similar to that observed for the low molecular weight carboxylato LC H(S)TP's. Thus substitution of sulfonate anions for carboxylates dramatically shifts toward a very small value the critical molecular weight of the polystyrene chains above which no liquid crystalline properties are observed.

Liquid crystallinity can however be triggered above the critical molecular weight when sulfonato LC H(S)-

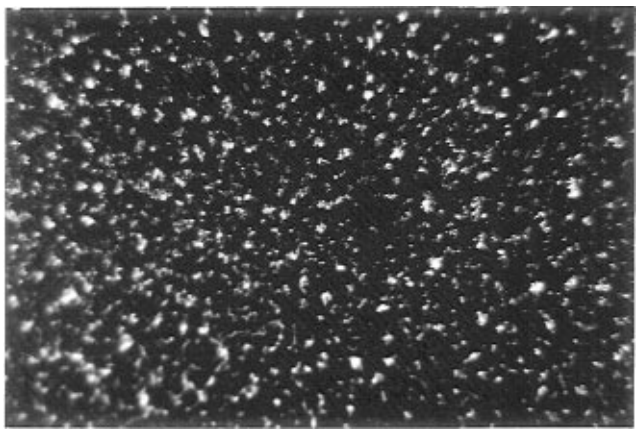


Figure 3. Optical microscopy of birefringent domains in the P3-SO_3M1 sample at 20 °C (crossed polarizers, magnification = 400×, reduced to 60% of original for publication).

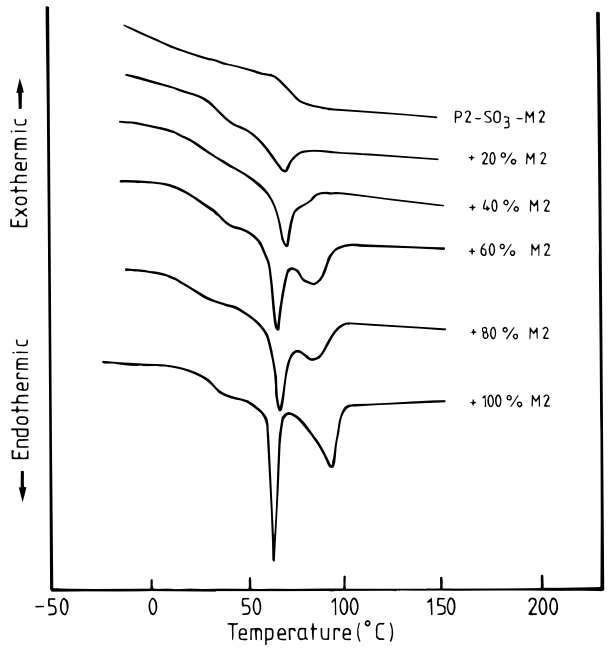


Figure 4. DSC traces for P2-SO_3M2 added with a molar excess of M2.

TP's are added with an excess of mesogen molecules compared to the available sulfonate groups. DSC and optical microscopy confirm the emergence of mesogenic properties in P2-SO_3M2, when an excess as small as 5 mol % of M2 is added. The change in the thermal properties of P2-SO_3M2 upon addition of M2 excess is shown in Figure 4. The T_g of P2-SO_3M2 is split into two first-order transitions respectively assigned to a solid−smectic (T_s) and a smectic−isotropic (T_i) transition. As confirmed by fan-shaped texture observed by optical microscopy, a smectic mesophase forms in the $T_i - T_s$ temperature range. This stability temperature range for the smectic mesophase actually increases with the M2 excess. At 100% M2 excess, the smectic mesophase extends over the same range as in pure M2. The same observation holds when an M1 excess is added to P2-SO_3M1; the T_g of P2-SO_3M1 is split into two first-order transitions that correspond, at high M1 excess, to the same transitions as in pure M1.

Dependence of the Liquid Crystalline Properties on the Anionic Group of the Model Liquid Crystalline Ionomers. From the previously discussed observations, it appears that the liquid crystalline properties of the LC H(S)TP's do not depend on the

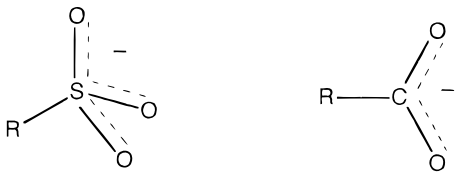


Figure 5. Structure of carboxylate and sulfonate anions.

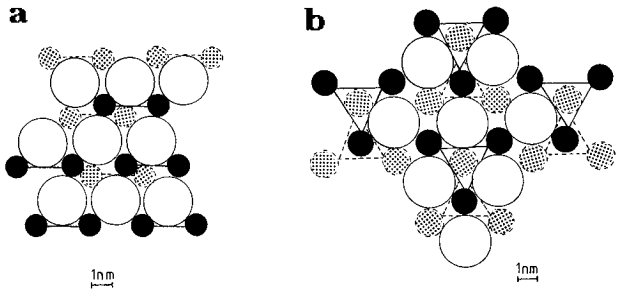


Figure 6. Close packing in carboxylate (a) and sulfonate LC H(S)TP's (b). Large open circles are ammonium cations; small shaded circles are oxygen atoms below the cation plane. Small filled circles are oxygen atoms above the cation plane. Lines connect oxygen atoms from the same carboxylate or sulfonate anion.

polymer functionality, i.e., mono- or difunctional. In contrast, the ion pair, of the ammonium carboxylate or ammonium sulfonate type, that links the mesogen to the polystyrene chain ends has a deep effect on the liquid crystalline properties of the LC H(S)TP's. Would it be recalled that the liquid crystalline properties are no longer observed above a critical MW value of 8000 for the monofunctional carboxylato LC H(S)TP's, whereas this upper limit is only 700 for the monofunctional sulfonato LC H(S)TP's samples. The origin of this deeply different behavior should be found in the structure and polarity of the ammonium sulfonates and ammonium carboxylates, respectively. It is well-known from the literature on ionomers that the mutual dipolar interactions of metal sulfonates largely exceed the interactions of metal carboxylates, all the other conditions being the same. For instance, Lundberg and Makowski[26] and Rigdahl and Eisenberg[27] have concluded from rheological studies that the effect on physical properties is several orders of magnitude larger for sulfonate ions than for carboxylate ions. Indeed, the softening behavior of the metal sulfonate ionomer suggests that strong ionic association persists at temperatures higher by 50−100 °C compared to the carboxylate ionomer. Similarly, the melt viscosity of the sulfonate ionomers is 2 or 3 orders of magnitude larger than the carboxylate analogues (same ion pair content).

From the molecular point of view, Lefelar and Weiss[28] have proposed models for the structure of metal sulfonate and metal carboxylate ion pairs on the basis of a crystal close packing approach. These models show that the anion packing of carboxylates depends on the counterion, in sharp contrast to the packing of the sulfonate anions which is completely independent of the cation. Figure 5 compares the planar structure of the carboxylate anion with only one edge available for the cation bonding and the tetrahedral geometry of sulfonate anion with two cation binding sites, i.e., one edge and one face. Figure 6 is another comparison of the ionic close packing of the sulfonate and the carboxylate anions associated with a monovalent cation, in this case a mesogenic quaternary ammonium cation. Figure 6a shows how the oxygen atoms of the carboxylate anions are packed in two parallel hexagonally packed layers,

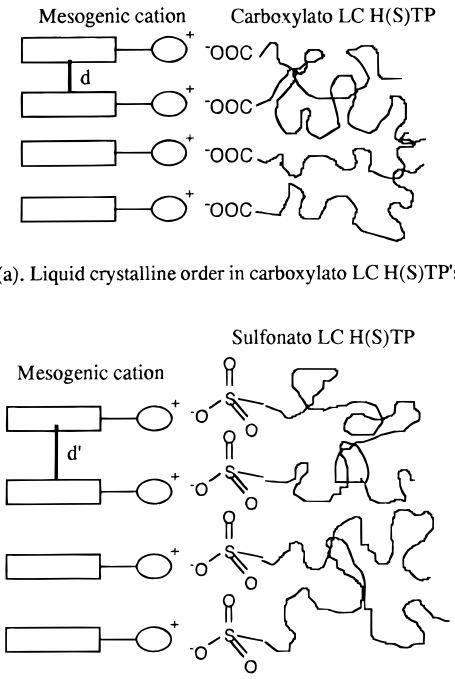


Figure 7. Sketch of the comparative packing for the carboxylato (a) and sulfonato (b) LC H(S)TP's.

with one layer slightly displaced compared to the other one. In Figure 6a, the mesogenic cations fit into the six-coordinated trigonal−bipyramidal holes between the anion layers, as it occurs in $NaH(CH_3CO_2)$.[29] This packing scheme is consistent with the structure of a smectic mesophase. Ions can be further added possibly in any direction of this planar array, so as to form long-range ordered layers of densely packed mesogen molecules as shown in Figure 7a. In this situation, the distance between two near neighbor mesogen molecules is small enough for the liquid crystalline order to be stabilized by intermolecular interactions. Figure 6b shows the antiparallel overlapping of layers of hexagonally packed sulfonate anions with the mesogenic cations fitting the octahedral holes limited by the anion edges, in agreement with the published structure of $Na_2(CH_2(SO_3)_2)$.[29] As for the case of the carboxylate analogues, additional ion pairs can approach in any direction. The distance between two adjacent mesogens is however larger compared to the carboxylate anion array. Furthermore, the mesogenic cations are more strongly associated with the sulfonato H(S)TP's, which restricts their mobility and accordingly their ability to form a mesophase. The combination of these two effects can prevent the sulfonato LC H(S)TP's from being organized in a smectic mesophase, as illustrated in Figure 7b.

Small Angle Neutron Scattering (SANS) of Sulfonato LC HSTP's. The phase morphology of halatotelechelic polymers is dictated by the microphase separation of the ionic groups from the polymer matrix.[30] The ionic microdomains, known as "multiplets", act as thermoreversible cross-links which greatly improve the mechanical properties. Generally, these multiplets are spherical and contain roughly 10 ion pairs.[31] The ion pairs in a multiplet effectively anchor the polymer chains at the point to which they are attached. Therefore, the mobility of the polymer chain in the immediate vicinity of a multiplet is greatly reduced compared to that of a chain in the bulk polymer.[32] The firmness of the ion pair anchoring is expected to control the restriction on the chain mobility. The phase morphology of H(S)TP's has been studied by small angle scattering of either X-rays (SAXS)[16,32] or neutrons (SANS).[33] Typical scattering profiles display a broad peak, designated as the "ionic" peak, in the range of 0.07−1 nm^{-1} s values corresponding to 1−15 nm Bragg distances. Furthermore, a strong upturn in the scattered intensity is observed at very small angles (typically below 0.08 nm^{-1}). Figure 8 shows the SANS profile for the P1-SO_3Li sample. The so-called ionic peak is observed at a Bragg distance of 3.3 nm, which has been assigned to interparticle interferences.[31]

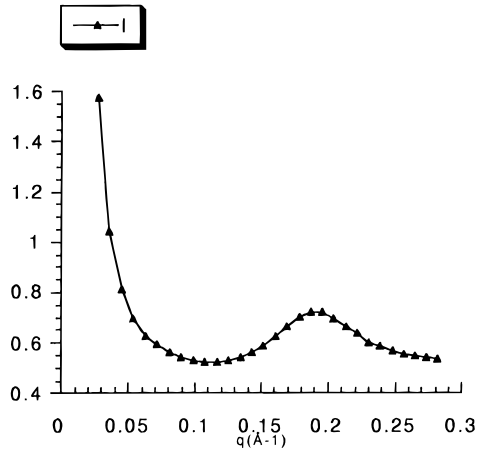


Figure 8. SANS profile for P1-SO_3Li (intensity in arbitrary units, T = 20 °C).

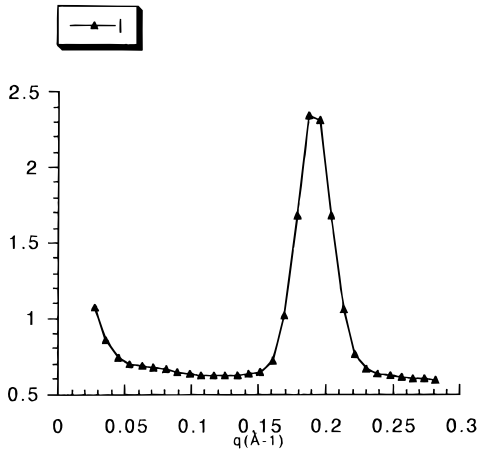


Figure 9. SANS profile for M1 (intensity in arbitrary units).

In LC H(S)TP's, a mesogenic counterion is substituted for the metal one. In contrast to metal counterions, the mesogenic counterions are able to organize themselves with formation of mesophases. Furthermore, since the mesogenic ion pairs are densely packed in layers, the shape and size of the multiplets are expected to be strongly modified. The mobility and possibly the local extension of the polymer chains in the vicinity of the mesogenic ion pairs should also be affected. Therefore, the question of the phase morphology of LC H(S)TP's must be addressed. The SANS profile for the mesogenic cation M1 is shown in Figure 9. The peak at 3.5 nm corresponds to the smectic layer spacing. This result is consistent with the data published by Ujiie et al. for the same compound analyzed by wide angle X-ray scattering.[1]

The SANS analysis clearly emphasizes a deep modification in the supramolecular organization of the original HSTP's when a mesogenic counterion is sub-

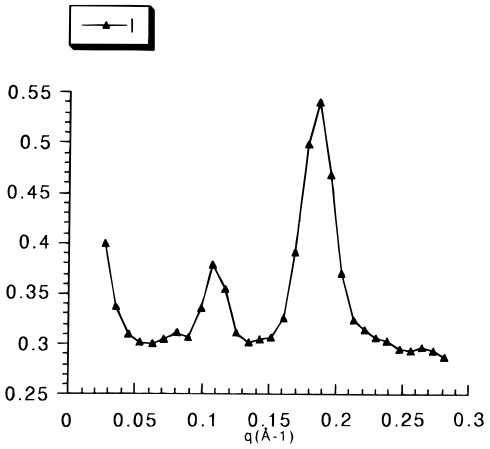


Figure 10. SANS profile for P1-SO_3M1 (intensity in arbitrary units).

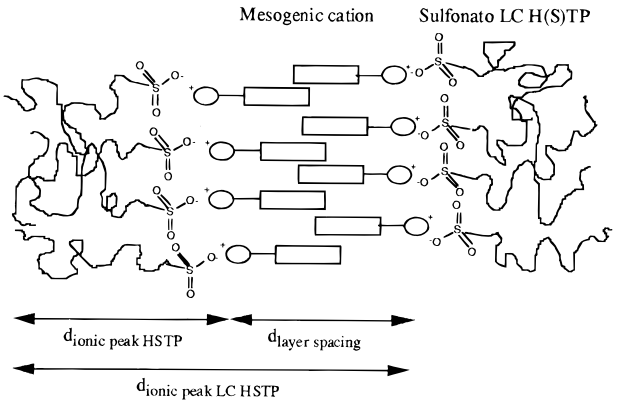


Figure 11. Model for the supramolecular organization of LC HSTP's in the solid state.

stituted for the metal one. Figure 10 shows the SANS profile for the liquid crystalline P1-SO_3M1 sample. Two peaks are observed, which have been assigned to the ionic peak at 6.8 nm and the layer spacing at 3.5 nm, respectively. The characteristic distance associated to the ionic peak is much larger in the LC HSTP (6.8 nm) compared to the HSTP precursor (3.3 nm). The second peak for the LC compound is observed at the same q value as M1, which confirms the persistency of the layer spacing. On the basis of these observations, the model shown in Figure 11 is proposed for the morphology of ω-sulfonato LC polymers at room temperature. This model is consistent with a microphase separation of the polystyrene chains and the mesogen layers, which nicely explains the shift of the ionic peak of the LC HSTP's as an additive combination of the Bragg distance associated to the ionic multiplets and the layer spacing typical of the mesogen moieties. A similar effect has already been observed by Poths and Zentel in side-chain liquid crystalline copolysiloxanes, in which only part of the monomer units are substituted with a mesogenic group ("diluted" polysiloxanes).[34] X-ray diffraction experiments on these compounds have shown a linear increase in the smectic layer spacing by "dilution" of the mesogenic side groups, similarly to the sulfonato LC H(S)TP's. At very small scattering angles, an important intensity upturn is observed, the origin of which can be attributed to large scale heterogeneities in the material.[35,36]

The SANS profile for the P7-COOM1 mesogenic carboxylato polystyrene is shown in Figure 12. The intensity of the ionic peak is weak compared to the sulfonato parent compounds, which would reflect a

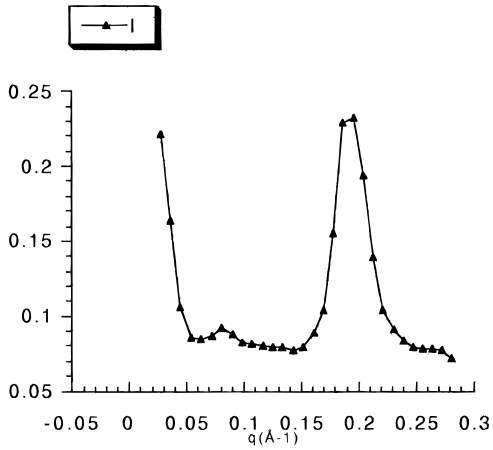


Figure 12. SANS profile for P7-COOM1 (intensity in arbitrary units).

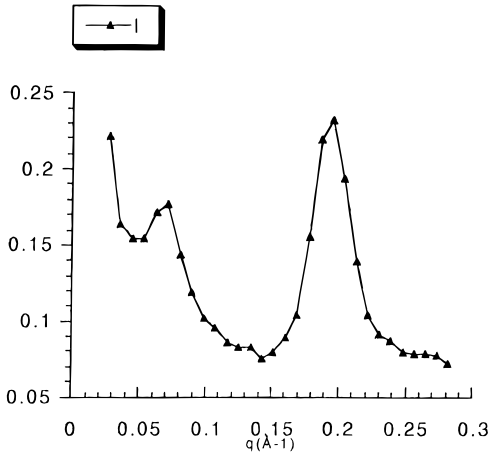


Figure 13. SANS profile for P2-SO_3M1 (intensity in arbitrary units).

weaker neutronic contrast for the carboxylato ammonium ion pairs compared to the sulfonato−ammonium ion pairs. The hereabove proposed microphase separation model matches the experimental data: d(ionic peak P7-COOM1) (7.6 nm) = d(ionic peak P7-COOLi) (4.1 nm)[32] + d(layer spacing (3.5 nm)). The microphase separation model is thus readily applicable to the liquid crystalline P1-SO_3M1 and P7-COOM1 samples.

The SANS curve for the P2-SO_3M1 nonmesogenic sulfonato polystyrene is shown in Figure 13. This curve is very similar to the P1-SO_3M1 curve of Figure 10. From the microphase separation model of Figure 11 it comes up: d(ionic peak P2-SO_3M1) (8.3 nm) = d(ionic peak P2-SO_3Li) + d(layer spacing) (3.5 nm). As a result, the d(ionic peak P2-SO_3Li) value should be 4.8 nm, which is larger that the experimental value (4.3 nm).[16] Therefore, the model of Figure 11 is not applicable to the non-liquid crystalline P2-SO_3M1 sample. Very tentatively, the packed layer structure of the mesogen−sulfonate ion pairs of the P2-SO_3M1 sample might induce a local extension of the polymer chain, which would be of 5 Å in this case. Hence, this extension is believed to enhance the restriction of mobility experienced by the chains in the close proximity of their attachment to the mesogen layers. Furthermore, if the regions of reduced mobility overlap each other, an increase in T_g should be observed, as it is for the P2-SO_3M1 sample (T_g = 74 °C) compared to the P2-SO_3Li precursor (T_g = 60 °C). The mesogenic moieties linked to the sulfonate groups experience also this restriction

of mobility. As a result, no liquid crystalline order is observed in the P2-SO_3M1 sample.

Conclusion

A novel type of ionic liquid crystalline polymers, referred to as liquid crystalline halato(semi)telechelic polymers, has been synthesized, in which a mesogenic cation is associated with the terminal sulfonate or carboxylate group(s) of low molecular weight linear polystyrene. These compounds form a smectic mesophase in a large temperature range (50−150 °C) when the molecular weight does not exceed a critical value which strongly depends on the nature of the ionic end group(s), either ammonium carboxylate or sulfonate. A model, based on a crystal close packing, can explain why ammonium sulfonato end groups have a detrimental effect on the liquid crystalline properties. SANS studies of LC H(S)TP's are in agreement with a microphase separation between the polystyrene chains and the mesogenic counterions.

Acknowledgment. The authors are indebted to the "Services Fédéraux des Affaires Scientifiques, Techniques et Culturelles" for financial support in the frame of the "Pôles d'attraction Interuniversitaires: Polymères". J.F.G. is grateful to I.R.S.I.A. for a fellowship. Special thanks are due to Dr. F. Boué (CEA-CNRS Saclay) for his invaluable help during SANS measurements and to Dr. R. Sobry (University of Liège) and Dr. M. Stamm (MPIP Mainz) for helpful discussions.

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