Macromolecules **1995,** *28,* 8877−8880

Generation of Liquid Crystalline Polymeric Materials from Non Liquid Crystalline Components via Ionic Complexation

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Received July 25, 1995
Revised Manuscript Received October 10, 1995

Introduction. A new concept in the design of polymeric liquid crystalline materials (PLCMs) is based on the use of strong noncovalent, or electrostatic, interactions for holding together molecular components. This has been shown to be a viable option for both side chain[1−4] and main chain[5,6] polymer architectures. Advantageous features of such designs include the increased flexibility in tailoring PLCMs for desired purposes (since the synthesis of smaller components is generally easier and less costly than that of large molecules) and the unique properties that may be introduced by the presence of noncovalent and labile bonds.

A number of side chain-like PLCMs assembled via hydrogen bonds have been reported. Kato and coworkers[1] have published a series of articles on such materials, where hydrogen bonds complex rigid cores (typically containing pyridyl moieties) to polymers containing benzoic acid groups at the extremities of alkyl side chains of variable lengths. The polymers themselves are liquid crystalline due to the extended cores formed by hydrogen-bonded benzoic acid dimers. The low molar mass rigid molecules in neat form (often with alkyl tails) are frequently, but not always, liquid crystalline. Hydrogen-bonded complexes of the two components can possess one or more of the disordered mesophases (nematic and smectics A, B, and C, including chiral), depending on the molecular details. In these systems, the alkyl spacer is covalently part of the polymer component. A system in which the alkyl spacer is part of the functionalized mesogenic molecule, also based on acid−pyridine hydrogen-bonding interactions, was not found to give rise to a disordered liquid crystalline mesophase, although the small molecule studied possesses a monotropic smectic A phase.[7] Recently, it has been reported that liquid crystalline phases (thought to be nematic) can be obtained from simple, functional polymers and rigid aromatic molecules that are not liquid crystalline individually, and which are assembled via hydrogen bonds without the presence of an alkyl spacer.[4]

Assemblies of PLCMs using ionic bonding[2,3] have received little attention to date, compared to those based on hydrogen-bonding. Ujiie and Iimura[2] prepared a side chain-like PLCM of poly(vinylsulfonate) complexed with a liquid crystalline small molecule functionalized at the end of its alkyl chain by an ammonium moiety. Both the ionically functionalized small molecule and its complex with the polymer exhibit an enantiotropic smectic A mesophase, this over a very wide temperature range in the case of the polymer complex.

Ionically complexed assemblies of PLCMs are the subject of the present communication. It will be demonstrated that such assemblies, made up of components neither of which possesses a (disordered) liquid crystalline mesophase, can generate materials which do possess such a mesophase. Furthermore, it will be shown that the mesophase is strongly affected by the nature of the ionic complexation involved. It is also noteworthy that the functional polymers used are simple, commercially available ones.

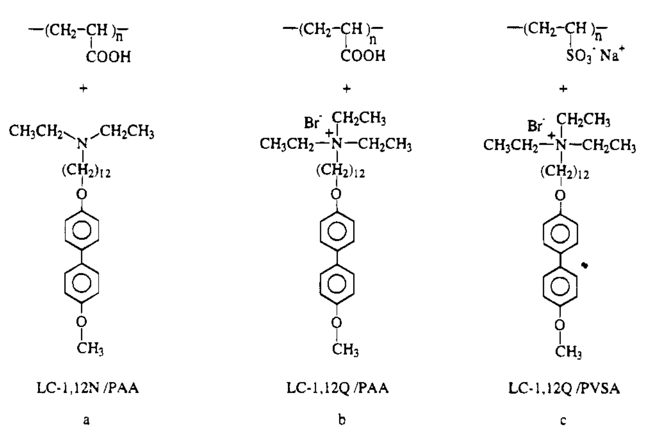

Figure 1. Molecular structures of the components of the three ionically complexed mesogen/polymer mixtures studied. Complex a is formed by proton transfer from the acid to the amine; complexes b and c are formed by ion exchange, with elimination of micro-ions, HBr and NaBr, respectively.

Results and Discussion. Three related complexes, shown in Figure 1, were investigated. All involve a biphenyl mesogen substituted in the 4,4′ positions by a methoxy tail and a 12-carbon alkoxy spacer; the latter is functionalized at its extremity by an amine (LC-1, 12N) or an ammonium (LC-1,12Q) moiety. The synthesis of the compounds is described in detail elsewhere.[8,9] It involves three steps: monosubstitution of 4,4′-biphenol by a methoxy group using dimethyl sulfate, substitution of the remaining phenol by a bromoalkoxy group using 1,11-dibromoundecane, and amination of the bromo moiety by either diethylamine or triethylamine to obtain LC-1,12N and LC-1,12Q, respectively. All starting products were obtained from Aldrich. The purity of the products was assured by NMR (Bruker, 300 MHz, $CDCl_3$). The functional polymers are poly(acrylic acid) (PAA) and poly(vinylsulfonate), sodium salt (PVSA), both obtained from Aldrich. The complexes were prepared by dissolution of the components in equimolar acid/amine proportions in a common solvent or solvent mixture, followed by precipitation and/or solvent evaporation (in the case of the LC-1,12N/PAA complex, both precipitation and evaporation recovery were tested and gave essentially the same results[9]). Complexation is achieved in system a by proton transfer from the acid to the amine, and in systems b and c by ion exchange and possible elimination of the micro-ions, HBr and NaBr, respectively.

That complexation takes place was verified by infrared spectroscopy (Mattson Sirius 100). For both complexes a and b, the strong decrease in the acid carbonyl absorption near 1700 cm^{-1} and the appearance of the asymmetric COO$^-$ absorption near 1550 cm^{-1} are diagnostic, as shown in Figure 2; residual carbonyl absorption remains, indicating that complexation is not quite 100%. (This is currently being investigated in detail, as a function of spacer length, and will be published separately.[9]) It is noteworthy that the spectra of the two complexes are very similar, as are those for complex a prepared by solvent evaporation and by precipitation. It should be mentioned that no indication of phase separation was observed. Evidence for complexation in the spectrum of system c is more difficult

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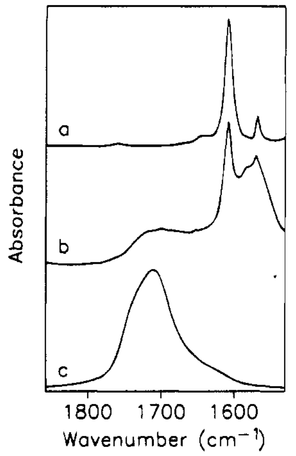

Figure 2. Infrared spectra of (a) the LC-1,12N/PAA complex, (b) LC-1,12N, and (c) PAA.

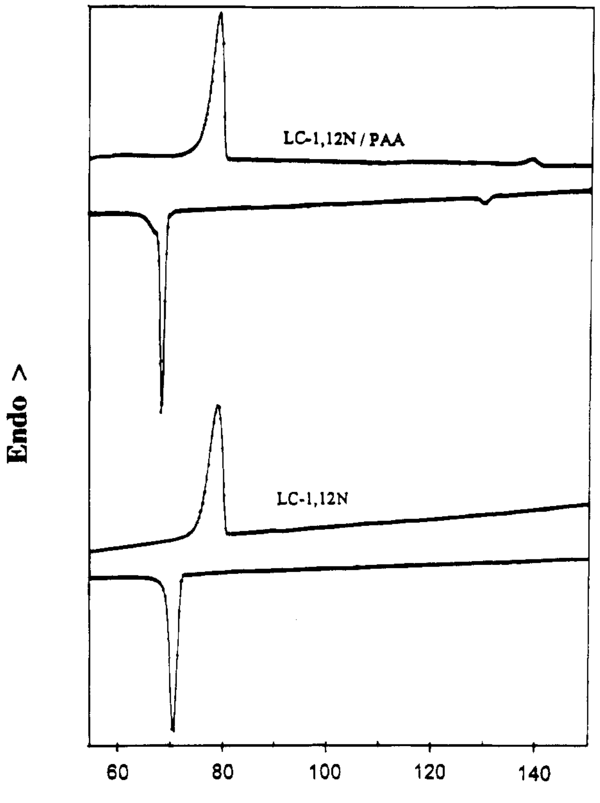

Figure 3. DSC heating and cooling curves (5 °C/min, DSC-4) of neat LC-1,12N and its complex with PAA.

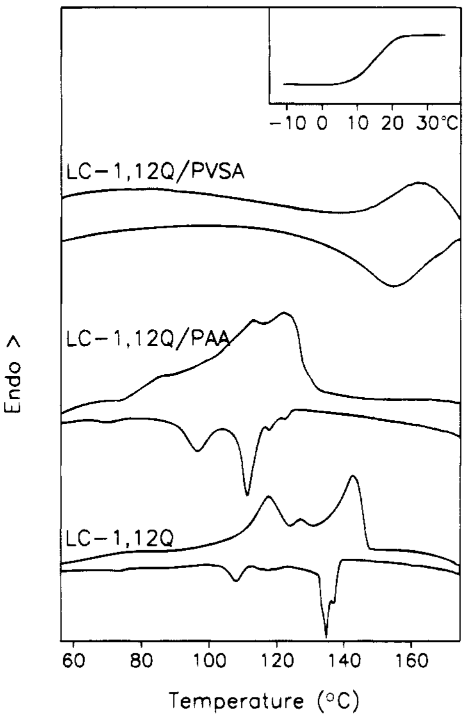

Figure 4. DSC heating and cooling curves (5 °C/min, DSC-7) of neat LC-1,12Q and its complexes with PAA and with PVSA. The inset shows the glass transition of the LC-1,12Q/PVSA complex (20 °C/min).

to determine, since it simply involves ion exchange; nevertheless, the results presented below are strong indirect evidence that complexation of the two components does indeed take place.

The mesogenic molecule, whether functionalized by the tertiary amine or by the ammonium bromide moiety, does not display a disordered liquid crystalline phase. This was concluded from DSC (differential scanning calorimetry; Perkin-Elmer DSC-4 and DSC-7), POM (polarizing optical microscopy; Zeiss microscope with Leica objective), and X-ray diffraction (Rigaku rotating anode) analyses. Figure 3 shows that LC-1,12N has a single transition near 80 °C (with moderate supercooling of about 10 °C and an enthalpy of 73 J/g), between a highly ordered or crystalline phase and an isotropic phase, according to POM and X-ray analyses (see the lowest two profiles of Figure 5a). When capped with the quaternized moiety, the mesogenic molecule, LC-1,12Q, displays multiple transitions in a higher temperature range (Figure 4), becoming isotropic near 145 °C and crystallizing into an apparently highly ordered phase (Figure 5b) near 140 °C (with the possibility of an intermediate monotropic disordered phase over a very short temperature range).

When the two mesogenic molecules are complexed with appropriate polymers, disordered liquid crystalline phases are generated. Of the three complexes studied, such a phase was clearly obtained for LC-1,12N/PAA and for LC-1,12Q/PVSA, although with major differences in their characteristics.

As shown in Figure 3, the LC-1,12N/PAA complex has a major transition at about the same temperature as neat LC-1,12N (with an enthalpy of 37 J/g), but in addition, it has a weak transition near 140 °C (with an enthalpy of about 1 J/g and 8 °C supercooling). In POM, the material is birefringent, and relatively fluid, in the 80–140 °C temperature range, although the small-scale texture observed is difficult to define. It is optically isotropic above 140 °C. X-ray analysis (Figure 5a) shows that the mesophase is a disordered smectic, with a broad peak at wide angles and a sharp peak at small angles. The latter, at $2\theta = 4°$, indicates a lamellar thickness of 22 Å, but profiles obtained with a small-angle camera indicate that it is a second-order diffraction peak and that the lamellar thickness is actually 44 Å. This thickness is between one and two (extended) molecular lengths of LC-1,12N, even with the acrylate moiety added. The type of molecular arrangement that this corresponds to (for instance, an interdigitated smectic A partial bilayer or an tilted smectic C bilayer) will be dealt with in a future article.[9] It is noteworthy that the lower temperature phase of the complex, in particular at wide angles where the molecular arrangement within lamellae is reflected, strongly resembles that of neat LC-1,12N.

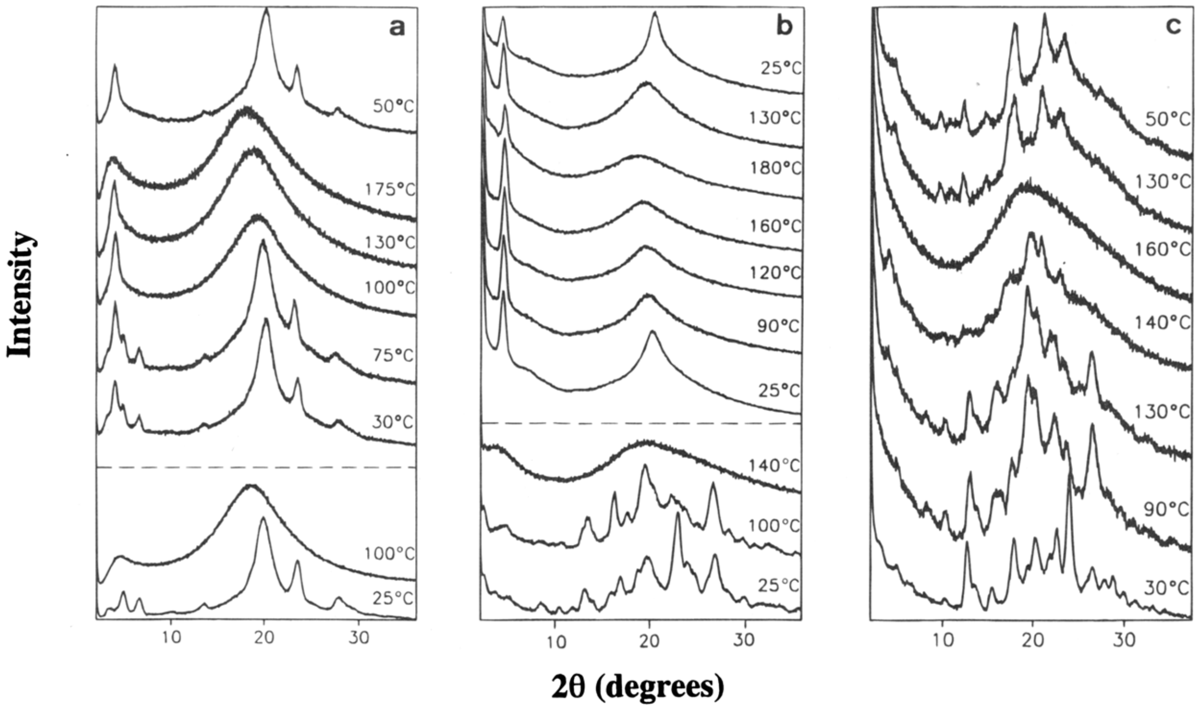

Figure 5. X-ray diffraction profiles of (a) neat LC-1,12N (lowest two curves) and its complex with PAA, (b) neat LC-1,12Q (lowest three curves) and its complex with PVSA, and (c) the LC-1,12Q/PAA complex, at the nominal temperatures indicated. Profiles for a given material were recorded in the order of lowest to uppermost curves.

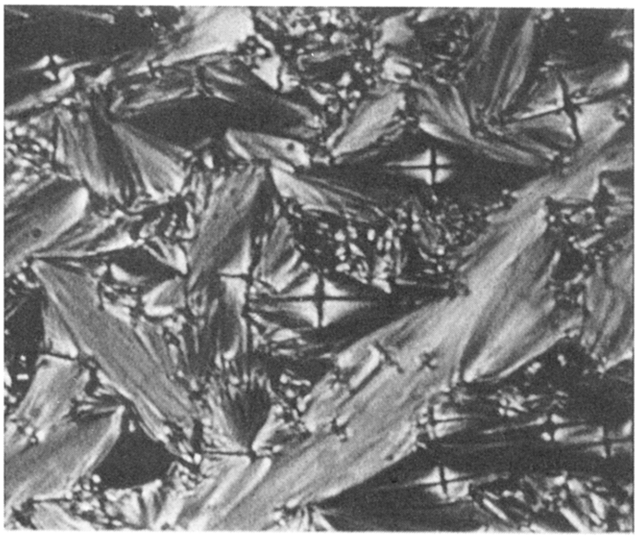

Figure 6. Focal conic texture of the LC-1,12Q/PVSA complex, as observed in the polarizing optical microscope at 50 °C.

When the acid type is changed to a much stronger acid, as in complex c, the results obtained are particularly striking. In order to build complex c, which involves sodium-neutralized PVSA, the functional group was changed to a quaternized form in order to facilitate production and removal of the (NaBr) micro-ions. Figure 4 shows that this complex possesses only a single, weak, broad transition near 160 °C, with an enthalpy of about 10 J/g. POM observations indicate that this is a transition between a disordered smectic mesophase and an optically isotropic phase: on slow cooling, there is the distinct formation of bâtonnets during the transition and the gradual development of a focal conic texture (Figure 6), and the material is quite fluid. It slowly becomes more viscous on further cooling and is gum-like at room temperature, suggesting a glass transition temperature somewhat below room temperature [confirmed by DSC to be at 15 °C (midpoint, 20 °C/min), as shown in the inset of Figure 4], where the liquid crystalline phase is frozen into the glassy state. X-ray analysis (Figure 5b) confirms the disordered nature of the mesophase. The sharp peak at low angles is again a second-order diffraction and indicates a lamellar spacing of 36.8 Å. At the highest temperature recorded (nominal, about 10−15 deg above the true sample temperature), this peak clearly is beginning to fade, in parallel with significant broadening of the wide-angle peak. The lamellar spacing is comparable to the molecular length of LC-1,12Q (about 34 Å in its most extended configuration) to which about 4 Å may be added to take into account the sulfonate moiety. It can be concluded from the various observations that the LC-1,12Q/PVSA complex possesses a single-layered smectic A mesophase.[10] The wide temperature range over which it exists and the freezing-in of the mesophase into the glassy state was also observed by Ujiie and Iimura[2] for a complex involving almost identical ionic moieties (although, in that case, the functionalized small molecule also displays a distinct smectic A phase).

Finally, it is noteworthy that the same mesogenic molecule in quaternized form, when complexed with PAA (system b), apparently does not generate a distinct disordered liquid crystalline mesophase (except possibly over a very short temperature range). It has multiple transitions similar to that of neat LC-1,12Q, although at depressed temperatures (Figure 4), and X-ray profiles are indicative of highly ordered phases (Figure 5c). The main difference between complexes a and b is that the first is quaternized by a proton, so that hydrogen-bonded ion pairing may take place, whereas the second is quaternized by an ethyl group, eliminating any H-bonding. Whether or not this is responsible for the striking differences in the behavior of the two complexes or whether other factors may also play a role (such as the presence or absence of micro-ions, or other details in the preparation methods) is undergoing further investigation.

The study described above clearly illustrates that mixtures of simple, amorphous, commercially available polymers with appropriately functionalized low molar mass mesogens which do **not** possess disordered liquid crystalline mesophases can generate such mesophases, including over a very wide temperature range, through ionic complexation. This phenomenon was shown to be considerably more pronounced for complexes involving sulfonate rather than carboxylate moieties. This may be compared to the stronger miscibility enhancement observed in ionomer blends involving sulfonate–pyridinium pairs compared to that in carboxylate–pyridinium pairs,[11] and to the stronger effects of amine-terminated small molecules on sulfonic acid-containing copolymers than on carboxylic acid-containing copolymers, both of which involve proton transfer from the acid to the amine.[12]

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. We are also grateful to NSERC (Canada) and FCAR (Québec) for additional financial support. A. T. thanks the Ministry of Science and Higher Education of the Islamic Republic of Iran for a Ph.D. scholarship.

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MA9510799