Variable Composition Mixtures of a Tertiary Amine-Functionalized Mesogen and Poly(acrylic acid)

C. Geraldine Bazuin,* Julie Boivin, Amir Tork,† Hugues Tremblay,‡ and Elda Bravo-Grimaldo

Centre de Recherche en Sciences et Ingénierie des Macromolécules (CERSIM), Dépertement de chimie, Université Laval, Cité universitaire, Québec, Canada G1K 7P4

Received January 22, 2002; Revised Manuscript Received May 6, 2002

ABSTRACT: Mixtures of a diethylamine-functionalized dodecyloxy methoxy biphenyl mesogen and poly(acrylic acid) (PAA) were investigated as a function of composition by infrared spectroscopy, differential scanning calorimetry, polarizing optical microscopy, and X-ray diffraction. The data obtained indicate that the components form a monophasic supramolecular complex for amine/acid molar ratios below about 0.5 and a biphasic system composed of the supramolecular complex and a mesogen-pure phase for higher molar ratios. The complex gives rise to a smectic A mesophase that becomes isotropic at 147 °C for molar ratios down to about 0.3. An E-like phase is detected in the complexes of 0.4 and 0.5 molar ratios after lengthy annealing. The complex in the biphasic mixtures may also tend to E-like order below the melting point (crystal E-like−isotropic transition) of the mesogen-pure phase. The thermotropic transformation from E-like to smectic A order in the complex appears to be slow.

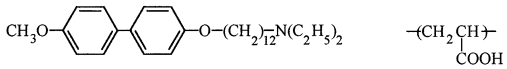
Introduction

The formation of liquid crystalline polymers (LCPs) using principles of supramolecular chemistry has been well established within the past decade.[1,2] Among the side-chain supramolecular LCP's that have received particular attention are those obtained by proton-transfer interactions between poly(acrylic acid) (PAA) and (non-liquid crystalline) amine-functionalized amphiphiles. One of the simplest such systems studied involves long-chain linear alkyl- and dialkylamines (primary and secondary, respectively).[3] Equimolar proton-transfer complexes of these compounds with PAA were obtained, and they give smectic A mesophases in all the cases studied (even-numbered 12- to 18-carbon chains) as well as smectic B and E phases for the longest alkyl- and dialkylamines, respectively.

Tertiary amine-functionalized amphiphiles, incorporating (short) mesogenic moieties in these cases, have also been associated with PAA, giving LC smectic mesophases.[4,5] Dimethylamine functions are reported to lead to 2:1 acid:amine complexation,[6] so that any excess amphiphile results in phase separation. We have previously presented the results of our investigations of equimolar mixtures of diethylamine-functionalized alkoxy biphenyl mesogens and PAA.[7] They form biphasic systems composed of a mesogen-pure E-like phase and a supramolecular PLC phase whose isotropization temperature was observed to increase strongly as a function of the spacer length (7−12 methylene units). Examination of the melting point enthalpies of the mesogen-pure phase in the mixtures, which were found to be roughly half of those measured for the mesogens alone, suggested that diethylamine functions, despite their greater bulkiness, give 2:1 acid:amine complexes similar to the dimethylamine systems.

In this paper, we present thermal, spectroscopic, and structural investigations of mixtures of PAA and the diethylamine-functionalized mesogen with the 12-methylene spacer (termed LC-1,12N; see Scheme 1), where the molar composition is varied. It will be shown that the evolution of the properties with composition strongly supports the existence of a 2:1 complex. Variations in the structure of the supramolecular complex as a function of composition and after long annealing times are also shown and lead to new insights.

Scheme 1



LC-1,12N PAA

Experimental Part

Materials. The synthesis and characterization of LC-1,12N and its bromine-terminated precursor, LC-1,12Br, are described elsewhere.[7] Atactic poly(acrylic acid) (PAA) in powder form, obtained from Aldrich and reported to have a molar mass (M_w) of 250 000, was used as received. To prepare each mixture, accurately weighed components in the desired proportions were first dissolved separately in hot anhydrous ethanol (about 70 °C), giving transparent solutions (1% concentration). After 30 min of stirring, the LC-1,12N (or LC-1,12Br) solution was added all at once to the PAA solution, which immediately became somewhat milky or cloudy. This solution was stirred for 12 h at about 50 °C. After evaporation of the solvent at ambient temperature using a rotary evaporator, the recuperated product was finely ground and then further dried in a vacuum oven at about 60 °C for at least 4 days. The products were stored in this same vacuum oven until all measurements were made, in some cases months later (specified in the Results section).

Techniques of Analysis. Differential scanning calorimetry (DSC) was performed with a Perkin-Elmer DSC-7 calorimeter, calibrated with indium and flushed with helium. About 5−15 mg of sample (the higher the PAA content, the greater the amount of sample) was packed into standard aluminum pans. Depending on the composition, the samples were scanned at either 5 °C/min (higher LC-1,12N content) or 20 °C/min (lower LC-1,12N content), to detect the first-order and glass transitions, respectively. First-order transition temperatures are

† Current address: Photonic Innovative Technology (PhotInTech) Inc., 1245 ch. Ste-Foy, Québec (QC), Canada G1S 4P2.

‡ Current address: Bio Syntech Canada Inc., 475 blvd. Armand-Frappier, Laval (QC), Canada H7V 4B3.

10.1021/ma020096c CCC: $22.00
Published on Web 07/27/2002

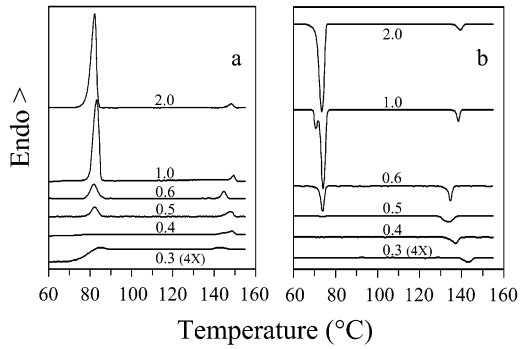


Figure 1. DSC thermograms (at 5 °C/min) of LC-1,12N/PAA mixtures on (a) first heating followed by (b) first cooling (baseline-adjusted). The intensities of the thermograms are weight-adjusted, with that of the 0.3 sample increased by a factor of 4 relative to the others.

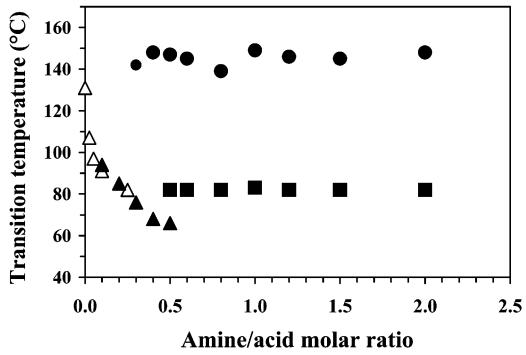


Figure 2. Transition temperatures of the LC-1,12N/PAA mixtures as a function of composition. The first-order transitions are obtained from 5 °C/min first heating scans (rectangles, circles) and the glass transitions from 20 °C/min second heating scans (triangles, open and closed indicating different sets of samples studied by different researchers). The small circle designates a very weak transition.

given by the peak values and glass transitions by the midpoint of the heat capacity jump. Polarizing optical microscopy (POM) was performed using a Zeiss Axioskop microscope, equipped with a 25× Leica objective, a Mettler FP52 hot plate, and a FP5 temperature controller.

Fourier transform infrared (FTIR) spectra were obtained from an accumulation of 100 interferograms at a resolution of 2 cm^{-1}, using a Nicolet Magna 560 FTIR spectrometer equipped with a MCT detector. All samples including pure PAA were prepared in the form of KBr pellets.

X-ray diffraction studies were carried out with a Bruker diffractometer (Siemens Kristalloflex 760 generator), operated at 40 kV and 40 mA, using sealed tube Cu Kα (1.542 Å) radiation collimated by a graphite monochromator and 0.8 mm pinhole; the diffraction pattern was captured by an AXS two-dimensional wire-grid detector. The temperature was controlled fairly crudely (in terms of absolute temperatures and rates, but was constant during the isothermal measurements) by a Watlow 988 controller and oven supplied by Bruker or by a homemade water-cooled copper block oven (except for the data in Figure 9, where the temperature was well controlled with an Instec HCS400 hot stage and STC200D temperature controller). Powder samples were packed into 1.0 mm diameter glass capillary tubes (Charles Supper).

Results

Thermograms of representative LC-1,12N/PAA mixtures studied are shown in Figure 1. The transition temperatures and enthalpies are plotted as a function of composition in Figures 2 and 3, respectively. Between molar ratios of 0.5 and 2.0, the mixtures are characterized by two transition peaks that are both constant in temperature as a function of composition. The first one, at 82 ± 1 °C on heating and 74 °C on cooling, is identical to the melting temperature of pure LC-1,12N (previously identified as a transition between a crystal E-like phase and the isotropic phase[7]) and can be associated with phase-separated LC-1,12N in the mixtures. The second one, at 147 ± 2 °C (a little lower for the 0.8 and 0.3 samples) on first heating and 136 ± 3 °C on first cooling,[8] was identified in equimolar mixtures as a transition from a disordered lamellar (smectic) phase to the isotropic phase and was associated with the supramolecular LC-1,12N/PAA complex.[7] The enthalpies of the latter transition are low for all compositions where it appears (1−2 kJ/mol of LC on heating, −1 to −3 kJ/mol of LC on cooling, where mol of LC indicates mole of LC-1,12N), which concords with the nature of the transition involved. The enthalpies of the lower temperature transition are similar at about 16 kJ/mol of LC for molar ratios between 2 and 1 and then decrease rapidly until the transition is no longer visible below 0.5 molar ratio. For the 0.5 sample, this transition is clearly evident only on the first heating curve (ΔH = 2.7 kJ/mol of LC), with just a hint left on the first cooling and second heating curves ($\Delta H \sim 0.2$ kJ/mol of LC).

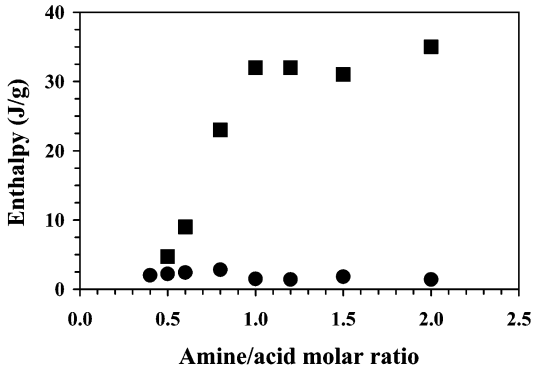


Figure 3. Enthalpies of the first-order transitions of the LC-1,12N/PAA mixtures as a function of composition, obtained from 5 °C/min first heating thermograms: rectangles, lower temperature transition; circles, higher temperature transition.

These data are consistent with the formation of a 2:1 acid:amine complex, such that it is only for compositions below 0.5 amine/acid molar ratio that a monophasic system formed of the supramolecular complex is obtained. For higher molar ratios, the mixtures are biphasic, with one phase composed of the supramolecular complex (responsible for the higher temperature transition) and the other phase composed of excess uncomplexed LC-1,12N (responsible for the lower temperature transition). At the borderline molar ratio of 0.5, the LC-1,12N phase is still detectable by DSC if barely, suggesting complexation of a little less than 50%. This is not really surprising, since it is quite conceivable that, like for chemical reactions on polymers, it is difficult to "react" *all* of the potential sites; for example, if strictly 2:1 acid:amine complexes are formed, then it is probable that there are trapped single acid sites with which free amines cannot interact.

The constancy of the melting point of the LC-1,12N phase in the biphasic mixtures indicates that this phase is not perturbed by the presence of the supramolecular complex or excess uncomplexed acrylic acid units and must therefore be essentially pure. This contrasts with mixtures of carboxylic acid-functionalized biphenyl me-

sogens with poly(4-vinylpyridine), where the melting point of the mesogen (or mesogen-rich) phase is decreased significantly compared to the mesogen alone despite a maximal complexation to the polymer of only about 20%.[9] This may be related in part to the fact that the amine groups do not self-associate, whereas the carboxylic acid groups are extensively hydrogen-bonded in the form of acid dimers that may be easily perturbed by interfacial effects or by a small amount of mixed polymer complex.

The LC smectic−isotropic transition of the complex is clearly visible in DSC down to a molar ratio of about 0.4 (with a hint remaining for the 0.3 sample, as shown in Figure 1). On the other hand, the samples appear to maintain birefringence between crossed polarizers to lower molar ratios (at least 0.1 albeit weakly).[10] Similar observations were made for analogous ion-containing liquid crystalline copolymers obtained by partial quaternization of poly(4-vinylpyridine) with alkoxy methyloxy biphenyl derivatives.[11] (These are covalently bonded analogues of the ionically bonded complexes of the present study by virtue of the similar placement of the ion pair and the identical mesogenic moiety.) In comparison, analogous nonionic, covalently bonded random side chain liquid crystalline copolymers, formed from a mesogenic and a small nonmesogenic comonomer, can also maintain liquid crystallinity to as low as 20 mol % mesogenic comonomer content.[12,13]

A glass transition is clearly observed in the thermograms (20 °C/min) for amine/acid molar ratios of 0.5 and below. The decrease in T_g from that of PAA[14,15] as the amine/acid ratio is increased (Figure 2) can be attributed to the increasing plasticization of PAA by the complexed mesogens acting as long, flexible effective side chains. Similar behavior was noted for the hydrogen-bonded acid-functionalized mesogen/poly(4-vinylpyridine) system mentioned above[16] and provides additional evidence that the mesogens are actually complexed to the polymer at the compositions involved. The T_g appears to approach a constant value near the composition range where phase separation of crystalline LC-1,12N sets in. (A T_g-like transition, whose temperature is difficult to define precisely, is detectable in the thermogram of the 0.6 sample in the same region as for the 0.5 and 0.4 samples.)

Infrared spectra of various mixtures, compared with those of PAA, LC-1,12N, and an equimolar reference mixture (LC-1,12Br/PAA, where no proton transfer can take place), are shown in Figure 4. The intensities of the spectra of the LC-1,12N/PAA mixtures are adjusted relative to the intensities of the two biphenyl bands at 1600 and 1500 cm^{-1} in the reference mixture. In previously studied equimolar mixtures as a function of spacer length,[7] the decrease in the acid carbonyl stretch band compared to that in the reference mixture and the appearance of a new band near 1550 cm^{-1} attributed to the asymmetric carboxylate stretch (generally weak and broad, appearing as a shoulder to a LC-1,12N band at 1569 cm^{-1}) were taken as strong indicators that there was acid-to-amine proton transfer. In the spectra of Figure 4, the 1550 cm^{-1} band is most evident for molar ratios of 0.6 and less, although it can be equally evident for higher (i.e., equimolar) molar ratios as shown and discussed in ref 7. Two bands related to the amine moiety, an ethyl band at 2798 cm^{-1} and a C−N band at 1200 cm^{-1}, have almost disappeared for the 0.6 and 0.5 molar ratios, with no trace remaining for molar ratios

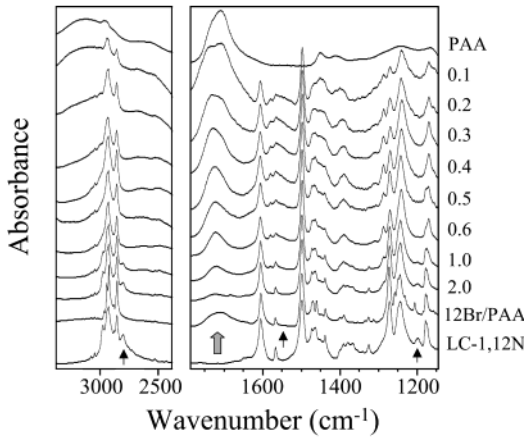


Figure 4. Infrared spectra of LC-1,12N/PAA mixtures at the amine/acid molar ratios indicated, in comparison to those of the pure components and the reference mixture, LC-1,12Br/PAA (labeled 12Br/PAA), where there is no proton transfer. The arrows indicate the bands mentioned in the text.

of 0.4 and less. This is direct evidence that all amine groups are effectively protonated below molar ratios of 0.5, confirming what was deduced from the DSC data, namely, that all of the LC-1,12N molecules are complexed to PAA for those molar ratios.

Figure 4 also shows that the acid carbonyl stretch changes not only in intensity but also in shape. In PAA, it is composed of two main bands at about 1740 and 1700 cm^{-1} for the free and hydrogen-bonded carbonyls, respectively.[6,17] The latter band is clearly more intense than the former in the spectra of both PAA and LC-1,12Br/PAA. In contrast, when small amounts of LC-1,12N are added to PAA, the relative intensities of the two carbonyl bands invert (note the spectra for 0.1 and 0.2 molar ratios in particular) and then, above molar ratios near 0.4, appear to be dominated by a band at about 1730 cm^{-1}. This corresponds once again to a maximum complexation near the 0.5 acid/amine molar ratio. The band at about 1730 cm^{-1} can be attributed to free carbonyls in acid groups whose OH moiety is hydrogen-bonded;[9,18] this may involve the formation of a complexed local structure of one amine and two acid groups where the proton of one of the acid groups is transferred to the amine.[6,19]

Ambient temperature X-ray diffractograms of LC-1,12N/PAA mixtures of various compositions are shown in Figures 5 and 6. Prior to measurement, the samples of Figure 5, denoted "fresh", were dried and stored in a 60 °C vacuum oven for 3 months (except the equimolar mixture, which is a very fresh sample that was dried for 4 days) and those of Figure 6, denoted "well-aged", for 8 months. A very fresh 0.4 molar ratio sample (dried for 4 days) gave an essentially identical profile to the "fresh" sample shown in Figure 5. The diffractogram of the equimolar mixture (Figure 5), as described previously,[7] is similar to that of pure LC-1,12N: the two prominent wide-angle peaks, the very intense first-order peak at 1.75° accompanied by three weak higher-order peaks with reciprocal spacings in the ratio 1:2:3:4 (marked by lines in the figure) and a layer spacing of 50 Å compared to a calculated extended molecular length for the mesogen of 32 Å, are indicative of an E-like partial bilayer phase. On this is superposed an additional peak at 4.6° (marked by an asterisk) that is related to the supramolecular complex, as will be shown below.

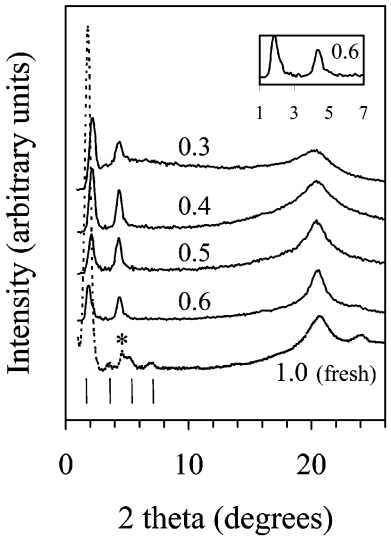


Figure 5. X-ray diffractograms of "fresh" (see text for details) LC-1,12N/PAA mixtures at ambient temperature, with amine/acid molar ratios indicated.

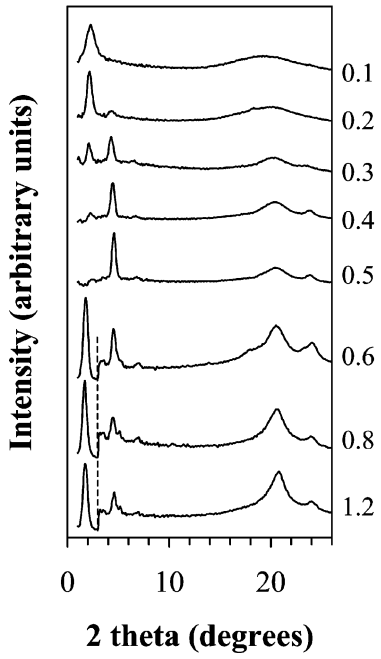


Figure 6. X-ray diffractograms of "well-aged" (see text for details) LC-1,12N/PAA mixtures at ambient temperature, with amine/acid molar ratios indicated. The dashed line indicates the angle above which the intensities were tripled relative to the lower angle points. The inset shows an enlargement of the small-angle portion of the diffractogram of the 0.6 sample.

The diffractograms of the "fresh" samples in Figure 5 indicate that the ordered LC-1,12N phase is weakly present for the 0.6 molar ratio sample and is undetectable for molar ratios of 0.5 and below, in accordance with the above DSC and IR data. In the 0.6 sample, this is shown by the relatively weak first-order, small-angle peak (at about 1.9°), by the weak wide-angle peak near 24°, and by the relative sharpness of the peak at 20.5°, all weak expressions of the features associated with the mesogen-pure phase. Another peak is located at 4.4°. For molar ratios of 0.5, 0.4, and 0.3, there are two small-angle peaks at 2.2° and 4.4° and a single wide-angle peak at 20.4° whose broadness increases with decreasing molar ratio. This profile is very similar to what was

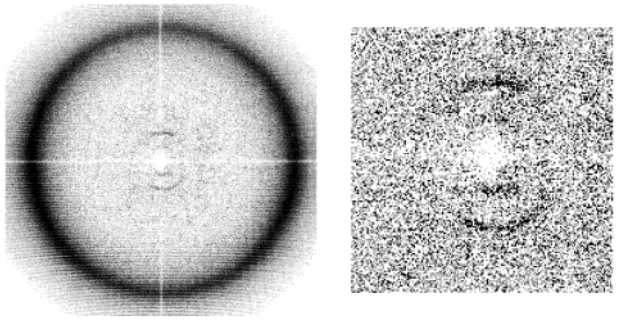


Figure 7. 2D X-ray diffractogram of a uniaxially stretched 0.4 molar ratio LC-1,12N/PAA compression-molded film. The stretch direction is vertical. The right image is an enlargement of the small-angle center of the left image, with the contrast optimized differently for the two images.

observed for the equimolar mixture at temperatures between the mesogen melting point and the complex clearing point and attributed to the complex mesophase with a disordered lamellar morphology of the smectic A or C type.[7] It is therefore concluded that the supramolecular complex in the monophasic 0.3−0.5 samples has the same morphology. Moreover, the 4.4° reflection in the diffractogram of the 0.6 sample must also be due to this complex. In this case, the shoulder that can be perceived on the higher-angle side of the 1.9° reflection (see inset in Figure 5) may correspond to the 2.2° reflection, albeit at reduced intensity compared to the 4.4° reflection (to be addressed below); this shoulder could account for the small increase in position of the lowest-angle peak in this sample compared to the samples of higher molar ratio.

To determine whether the smectic mesophase is A or C, a film made by compression molding a 0.4 molar ratio sample was manually stretched in one direction above its T_g. The resulting 2D diffractogram is shown in Figure 7. The small-angle peaks, which are located at the same angles as in the unoriented samples, clearly have greater intensity around the axis parallel to the stretch direction and the wide-angle halo around the axis perpendicular to the stretch direction; this shows that the long axis of the mesogens is oriented orthogonally to the lamellar plane. The layer thickness determined from the small-angle peaks in both the oriented and nonoriented samples is about 40 Å, which is between one and two extended molecular lengths. It can thus be concluded that the supramolecular complex in the "fresh" monophasic samples of intermediate molar ratio is structurally organized as an interdigitated or partial bilayer smectic A mesophase.

For the "well-aged" samples (Figure 6), no significant changes are observed in the diffractograms of the higher molar ratio samples compared to that of the very fresh equimolar sample. They all show the very intense first-order reflection and three weak higher-order reflections at small angles and the two wide-angle peaks indicative of the E-like mesogen-pure phase, along with the additional reflection at 4.6°. In contrast, those for intermediate molar ratios are clearly modified compared to the "fresh" samples. First, the profile for the 0.6 mixture now strongly resembles those for the higher molar ratios, indicating a better ordered mesogen-pure phase. (There does not appear to be increased phase separation of the mesogen, as indicated by the lack of increase in enthalpy of the corresponding transition in the thermogram of a well-aged sample.) Second, the two

wide-angle peaks indicative of E-like order are clearly present also in the 0.5 and 0.4 samples and even, more weakly, in the 0.3 sample. At smaller angles, these three samples show three equidistant reflections, of which the second one is much more intense than the other two in the 0.4 and 0.5 samples. In the 0.3 sample, the first peak is nearly as intense as the second one, and in the 0.2 sample, it is much more intense, giving a profile that resembles that for the "fresh" 0.3 sample. For the 0.1 sample, there is just a single, much broader peak at small angles (as often observed for so-called cybotactic structures[20]), suggesting that any lamellar organization now extends over very short correlation lengths; thus, this mixture can be considered as essentially isotropic, which is consistent with its weak birefringence. It is also noted that the wide-angle peak near 20° not only broadens, but its maximum decreases from about 20.5° to about 19.5° with decreasing molar ratio, especially from 0.3 to 0.1.

The distinctness of the small-angle profile in the "well-aged" 0.5 and 0.4 samples from both the E-like mesogen-pure phase and the smectic A complex mesophase—notably, the second small-angle peak having a much higher intensity than the first and third peaks—suggests that it arises from increased (E-like lamellar) order in the complex (and not from a small amount of phase-separated mesogen) as a result of lengthy aging or annealing. This order appears to be more weakly present in the 0.3 mixture and not at all in the 0.2 mixture. [It may also be noted that the angular position of the second small-angle peak in these samples is slightly higher, and thus the derived lamellar thickness slightly smaller, when the E-like wide-angle peaks are simultaneously present than when a single wide-angle halo is present (the decrease in angle from 4.6° for the 0.5 sample to 4.3° for the 0.3 sample is perceptible in Figure 6).] It is noteworthy that others have reported fairly slow development of more ordered phases in complexes of PAA with primary alkylamines (2 days in this case).[3] The sluggish kinetics could be related to the proximity of the T_g and the high viscosity of the samples (related, in turn, to their polymeric character and extensive ionic interactions).

The small-angle intensity profile associated with the E-like complex phase in the "well-aged" 0.5 and 0.4 samples also sheds light on the source of the 4.6° reflection in the biphasic mixtures. In particular, it clarifies that this peak must originate from the complex phase, and it rationalizes the apparent absence of a corresponding peak at 2.3°. Furthermore, it suggests that the complex in these mixtures also has E-like order. That this appears to be the case even in fresh biphasic samples may be related to stabilization of E-like order in the complex phase by that of the mesogen-pure phase, possibly through some kind of epitaxial or nucleation mechanism.

Selected mixtures were investigated by X-ray diffraction as a function of temperature. It was already noted above and in ref 7 that the equimolar mixture at temperatures between the mesogen melting point and the complex clearing point gives a diffraction profile very similar to those shown for the "fresh" 0.4 and 0.5 mixtures at ambient temperature, with two equidistant small-angle peaks and a single broad halo at wide angles. In more detailed studies (Figure 8), it is now noted that, just above the melting point, the second small-angle peak is significantly more intense than the first one but that as the temperature is further raised the relative intensities gradually become inverted (along with a small decrease in position) and that this is reversible. The same behavior was observed for the 0.8 mixture. This corroborates the above identification of the 4.6° reflection in the biphasic mixtures.

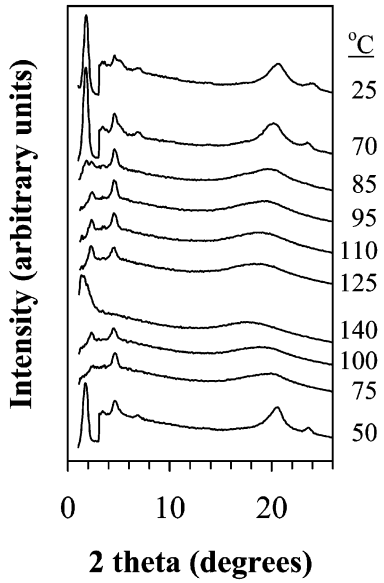


Figure 8. X-ray diffractograms of the 1.0 molar ratio LC-1,-12N/PAA mixture at various temperatures (taken in order from top to bottom). Nominal temperatures are indicated. The very intense peak between $2\theta = 1°$ and 3° for the lowest temperatures is decreased by a factor of 3 relative to the rest.

On the other hand, the wide-angle peak near 24° is not visible in the profiles at temperatures above the LC-1,12N melting point, even when the second small-angle peak is more intense than the first one. A possible explanation is that the in-plane correlation lengths giving rise to the 24° peak (which are probably quite short, in any case) are lost before there is sufficient change in the electron density profile normal to the lamellar plane from one that gives rise to a more intense second-order peak to one that gives rise to a more intense first-order peak. In other words, the transformation from effective E-like order to smectic A order may also be fairly slow on heating (besides being extremely slow on cooling, as shown above), possibly related again to high viscosity.

The gradual change in complex order was verified at more closely spaced temperatures in a very well-aged 0.6 sample (stored in a 60 °C vacuum oven for a year and a half). The diffractograms are shown in Figure 9. The (weak) first-order complex-phase reflection is clearly visible at lower temperatures as a shoulder on the high-angle side of the first-order mesogen-phase reflection and becomes prominent near the mesogen melting point. After melting, the wide-angle peak near 24° remains visible, indicating that the complex phase indeed shows E-like order up to these temperatures in this sample. With increasing temperature, it decreases gradually in intensity in parallel with the gradual intensity increase of the first small-angle reflection. On cooling, however, while the intensity profile of the small-angle peaks is reversible, the 24° peak does not reappear until the mesogen phase crystallizes (and even then remains weak, giving a profile that is more similar to that of the "fresh" sample). This is consistent with the results above for the 1.0 and 0.8 samples.

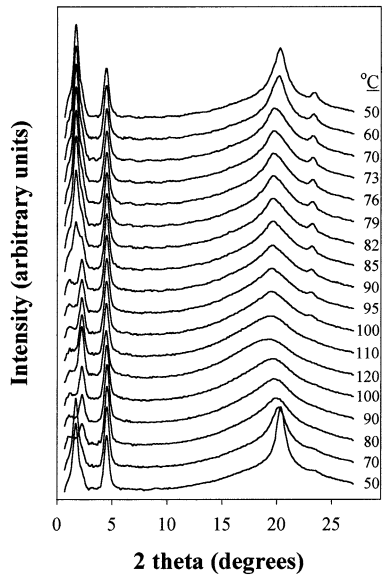


Figure 9. X-ray diffractograms of a very well-aged 0.6 molar ratio LC-1,12N/PAA sample at the various temperatures indicated (taken in order from top to bottom).

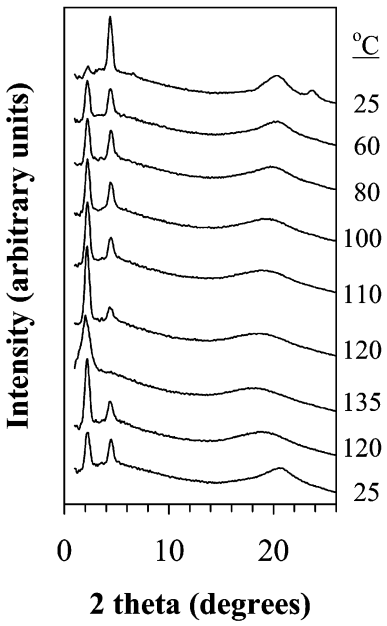


Figure 10. X-ray diffractograms of a "well-aged" 0.4 molar ratio LC-1,12N/PAA sample at various temperatures (taken in order from top to bottom). Nominal temperatures are indicated. The very intense peak between $2\theta = 1°$ and 3° for the lowest temperatures is decreased by a factor of 3 relative to the rest.

In the "well-aged" 0.4 mixture (Figure 10), where there is no phase-separated LC-1,12N, the intensity inversion of the two small-angle peaks and disappearance of E-like order appears to occur at low temperatures (not determined precisely). As the temperature is further raised, the second small-angle peak decreases continuously in intensity compared to the first one. It disappears near the isotropization temperature and reappears on cooling; however, on the return to ambient temperature, it remains of comparable intensity to the first-order peak, with no change 2 weeks later, suggesting again the possible role of ordered, phase-separated mesogen in accelerating the kinetics of the complex-phase transition from smectic A to E-like order. The wide-angle halo for all samples also broadens and decreases in angle with increasing temperature. The same experiment was repeated on a very freshly prepared 0.4 sample, with identical results except for the initial ambient-temperature profile. In the (well-aged) 0.2 sample, it is simply observed that the already weak second-order peak gradually disappears with increasing temperature and reappears with decreasing temperature, again with no change in position of the peaks (the wide-angle halo behaving as in the 0.4 sample).

Finally, it should be added that no tell-tale differences could be detected between the infrared spectra of "fresh" and "well-aged" samples (checked for 0.4, 0.5, and 0.6 molar ratios), nor was any clearly defined transition that may correspond to a change from E-like to smectic A order in the complexes observed in the DSC thermograms of well-aged samples. This absence of a DSC transition would be consistent with the apparently slow transformation from E-like to smectic A order in the complex mesophase as observed in the X-ray studies.

Conclusions

The thermal, spectroscopic, and structural data obtained as a function of composition for mixtures of poly(acrylic acid) and a diethylamine-functionalized alkoxy biphenyl mesogen, LC-1,12N, support the existence of an ionic 2:1 acid:amine complex involving proton-transfer interactions, as observed previously for PAA and dimethylamine-functionalized complexes.[4,6] This results in biphasic systems composed of a supramolecular complex phase and a mesogen-pure phase for mixtures of amine/acid molar ratios greater than 0.5. The mesogen-pure phase is characterized by crystal E-like order that melts into an isotropic phase at 82 °C. The supramolecular LC-1,12N/PAA complex, with an isotropization temperature of 147 °C, is structurally organized as a (partial bilayer or interdigitated) smectic A mesophase down to an amine/acid molar ratio of about 0.3. Lengthy annealing leads to the development of E-like order at low temperatures in the 0.4 and 0.5 complexes. The distinctive small-angle X-ray diffractogram of the E-like complex phase provides an explanation for the complex-related peak at 4.6° in the diffractograms of the biphasic mixtures. Furthermore, there is evidence that the complex phase in the latter is likewise characterized by E-like order below the melting point of the crystal E mesogen phase. The thermotropic transformation from E-like to smectic A order in the complexes appears to occur gradually.

Acknowledgment. Financial support of this research was provided by NSERC (Canada) and FCAR (Québec). A.T. thanks the Ministry of Science and Higher Education of the Islamic Republic of Iran for a Ph.D. scholarship. We are grateful to Carmen M. Tibirna for careful DSC measurements of PAA.

References and Notes

(1) Bazuin, C. G. In *Mechanical and Thermophysical Properties of Polymer Liquid Crystals*; Brostow, W., Ed.; Chapman and Hall: London, 1998; Vol. 3, Chapter 3.
(2) Kato, T. In *Handbook of Liquid Crystals*; Demus, D., Goodby, J. W., Gray, G. W., Spiess, H. W., Vill, V., Eds.; Wiley-VCH: Weinheim, 1998; Vol. 2B, p 969.
(3) Tsiourvas, D.; Paleos, C. M.; Skoulios, A. *Macromolecules* **1997**, *30*, 7191.
(4) Tal'roze, R. V.; Kuptsov, S. A.; Sycheva, T. I.; Bezborodov, V. S.; Platé, N. A. *Macromolecules* **1995**, *28*, 8689.

(5) Bazuin, C. G.; Tork, A. *Macromolecules* **1995**, *28*, 8877.
(6) Kornienko, E. V.; Sycheva, T. I.; Kuptsov, S. A.; Bezborodov, V. S.; Lebedeva, T. L.; Tal'roze, R. V.; Platé, N. A. *Polym. Sci.* **1992**, *34*, 997.
(7) Tork, A.; Bazuin, C. G. *Macromolecules* **2001**, *34*, 7699.
(8) The higher temperature transition tended to decrease in temperature with each subsequent scan, usually by about 2−3 °C per scan for scans to 155 °C and 5 min at 155 °C before cooling (the lower temperature transition was unaffected). This is probably related to anhydride formation in PAA, as discussed elsewhere.[7] This implies that the clearing temperatures recorded during the first heating scans are accurate, whereas those recorded during the first cooling scans are slightly underestimated.
(9) Brandys, F. A.; Bazuin, C. G. *Chem. Mater.* **1996**, *8*, 81.
(10) The high viscosity and elasticity of the samples, PAA degradation at high temperatures,[8] and the insolubility of the complexes in common solvents, all of which prevent preparation of the sample into thin films, precludes being precise about the composition where birefringence can be considered to no longer be visible in POM.
(11) Navarro-Rodriguez, D.; Guillon, D.; Skoulios, A.; Frère, Y.; Gramain, Ph. *Makromol. Chem.* **1992**, *193*, 3117.
(12) (a) Percec, V.; Pugh, C. In *Side Chain Liquid Crystal Polymers*; McArdle, C. B., Ed.; Blackie: Glasgow, 1989; p 89. (b) Pugh, C.; Kiste, A. L. In *Handbook of Liquid Crystals*; Demus, D., Goodby, J. W., Gray, G. W., Spiess, H. W., Vill, V., Eds.; Wiley-VCH: Weinheim, 1998; Vol. 3, pp 192−193.
(13) Donald, A. M.; Windle, A. H. *Liquid Crystalline Polymers*; Cambridge University Press: Cambridge, 1992; p 90.
(14) Glass transition values reported in the literature for PAA are confusing, as a result of being determined in various ways and possibly not always under conditions where there is insignificant anhydride formation.[15] The T_g of the PAA used in this study is reported by the supplier to be 106 °C. However, we consistently observe a T_g of 131 °C for both dried and as-received PAA exempt of anhydride formation (as verified by infrared spectroscopy), when taken as the midpoint of the heat capacity jump in DSC thermograms obtained at a heating rate of 20 °C/min after first scanning to a maximum of 135 °C.
(15) See, for example: Maurer, J. J.; Eustace, D. J.; Ratcliffe, C. T. *Macromolecules* **1987**, *20*, 196.
(16) Brandys, F. A.; Bazuin, C. G. *Chem. Mater.* **1996**, *8*, 81.
(17) Dong, J.; Ozaki, Y.; Nakashima, K. *Macromolecules* **1997**, *30*, 1111.
(18) See, for example: Lee, J. Y.; Painter, P. C.; Coleman, M. M. *Macromolecules* **1988**, *21*, 346.
(19) The carbonyl band is discussed in more detail in a separate publication involving quantitative analysis of the carbonyl region for these kinds of mixtures. Tremblay, H.; Pézolet, M.; Bazuin, C. G., manuscript in preparation.
(20) De Vries, A. *J. Phys. Suppl.* **1975**, *Fasc. 3*, C-1. De Vries, A. *Pramana, Suppl.* **1975**, *1*, 93.

MA020096C