reaction conditions to the LiBEt$_3$H reduction reactions described above, did *not* result in formation of Mo$_2$C as determined by X-ray powder diffraction after heating the product to 500 °C.

We have observed that a key feature to the success of these experiments is the purity of the starting materials. When MoCl$_3$(THF)$_3$ is prepared according to the literature method[18] which involves reduction of MoCl$_4$(THF)$_2$ with tin powder, we have found that after reduction and separation, traces of tin were always incorporated in the final product as determined by energy-dispersive spectroscopy. As part of these studies, we have recently reported[19] a single-step method for the preparation of high-purity MoCl$_3$(THF)$_3$ in high yield by the reduction of MoCl$_5$ with 2 equiv of diphenylsilane. Further studies are in progress to unambiguously determine the origin of the carbide in these materials and to explore the generality of this reduction method.

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Registry No. Mo$_2$C, 12069-89-5; W$_2$C, 12070-13-2; MoCl$_2$(THF)$_3$, 31355-55-2; MoCl$_4$(THF)$_4$, 16998-75-7; WCl$_4$, 13470-13-8; LiBEt$_3$H, 22560-16-3.

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Novel Liquid-Crystalline Polymeric Materials via Noncovalent "Grafting"

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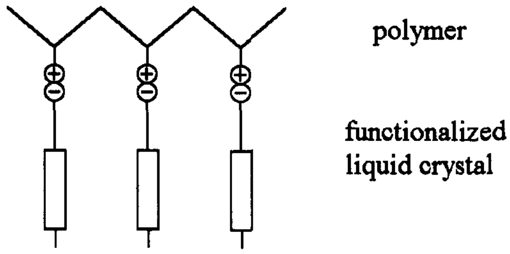
Traditionally, liquid-crystal (LC) polymers have been classified as main-chain or side-chain types.[1,2] In an attempt to better account for the variety in these materials, which now include examples which cannot be classified as strictly side-chain or main-chain, Brostow[3] has proposed a classification scheme based on different architectural arrangements of the structural subunits forming the LC polymer. Twenty classes have been identified.

It is striking that in all cases the structural subunits are connected by covalent bonds. We would like to suggest that the variety in LC polymers can be considerably extended through the use of *noncovalent* bonds of various types. These noncovalent bonds can be formed by hydrogen bonding interactions, electrostatic interactions (e.g., ion–ion, ion–dipole, charge transfer), and coordination complexes or transition-metal ions. An idealized schematic of this concept, illustrated for ion-ion bonding and for a classical side-chain polymer architecture, may be shown as follows:[4]

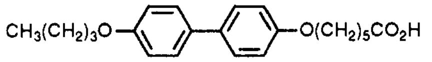


To achieve this end, a typical low molar mass liquid crystal must be functionalized with an ionic or ionizable functional group and mixed with a polymer possessing complementary ionic or ionizable groups.

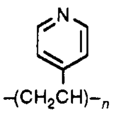
An application of this concept has been published recently by Ujiie et al.[5] They have shown that the mixing of an ammonium cation-functionalized liquid crystal with sulfonate-type anionic polymers, which results in ion–ion interactions, indeed produces a material which exhibits thermotropic liquid-crystalline phases, and that the thermal stability of the phases are enhanced in the mixture. Furthermore, Frêchet and co-workers[6,7] have demonstrated that hydrogen bonding can be effective in forming or in extending mesogen cores, thus creating and stabilizing, respectively, liquid-crystalline phases. In the first case,[6] dimers of alkoxybenzoic acid side chains (attached covalently to the polymer backbone) are formed through hydrogen bonding, thus creating a mesogenic core of sufficient length to allow the formation of liquid-crystalline phases. The second case[7] involves hydrogen bonding between the same alkoxybenzoic acid side chain and a pyridine group which is located at one end of a small-molecule liquid-crystalline rigid core. The last example approaches the idealized schematic illustrated above but with the noncovalent interaction located within the rigid core rather than near the polymer backbone.

In this communication, we present our first results for a mixture of a simple low molar mass liquid crystal, functionalized at the end of the alkyl chain spacer by a carboxylic acid group, with poly(4-vinylpyridine) (P4VP). Hydrogen bonding interactions are expected between the acid and the vinylpyridine groups. These interactions are weaker than those exploited by Ujiie and co-workers; this has been illustrated, for instance, by the large difference in the effectiveness, in compatibilizing ionomer blends, of interactions between sulfonic acid and pyridine (where ion pairs are formed due to proton transfer) compared to those between methacrylic acid and pyridine.[8]

The functionalized liquid crystal (compound I), which we synthesized, and mixed with poly(4-vinylpyridine) (compound II), is based on a biphenyl core. This is disubstituted by two *n*-alkoxy groups, one of which is terminated by the carboxylic acid group. To obtain the mixtures, the two compounds were dissolved and blended



(I)



(II)

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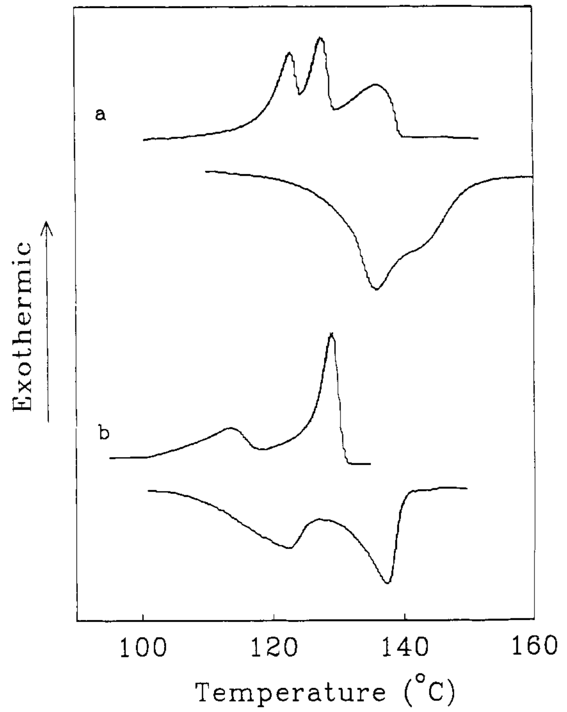

Figure 1. DSC thermograms (5 °C/min) of (a) the functionalized liquid crystal and (b) its mixture with poly(4-vinylpyridine) at 0.5 molar ratio.

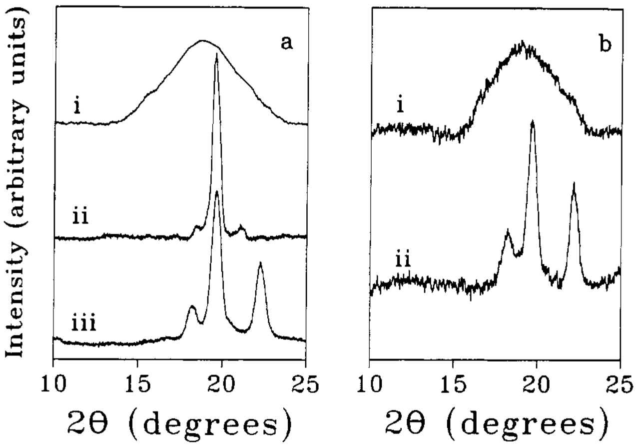

Figure 2. Wide-angle X-ray scattering curves of (a) the functionalized liquid crystal and (b) its mixture with poly(4-vinylpyridine) at 0.5 molar ratio; i, ii, and iii designate the curves obtained for each phase in order of decreasing temperature, beginning with the disordered smectic phase.

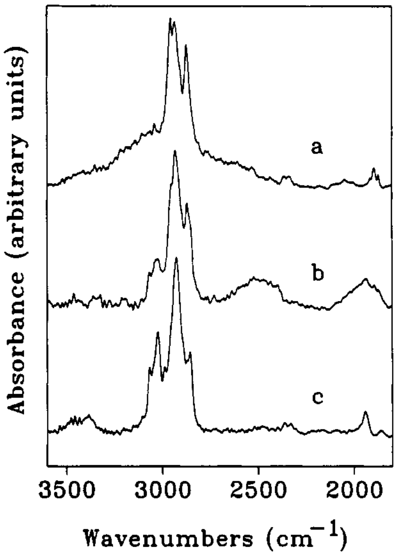

Figure 3. Room-temperature FTIR spectra of (a) the functionalized liquid crystal, (b) its 0.5 molar ratio mixture with poly(4-vinylpyridine), and (c) poly(4-vinylpyridine).

in pyridine, which was then removed by evaporation. Thermal treatment of the dried mixture in its melt region was applied to maximize the interactions.

Differential scanning calorimetry (DSC) of the functionalized liquid crystal by itself (Figure 1a) shows overlapping transitions on heating, and three distinguishable transitions on cooling (5 °C/min). When observed through a polarizing optical microscope, the highest temperature phase develops a focal conic texture when cooled from the isotropic liquid, suggesting a disordered smectic A or C phase. A single, broad peak centered at $2\theta = 19°$ (Figure 2a), which corresponds to a Bragg spacing of 4.7 Å, is observed from wide-angle X-ray diffraction. Small-angle X-ray scattering (using a photographic film) gives a single sharp ring at an angle which corresponds to a Bragg spacing of 21.4 Å. This spacing is less than 10% shorter than the calculated length of the liquid crystal in its most extended configuration, 23.3 Å. Thus it can be concluded that the phase is a single-layered smectic A phase. Further cooling of the compound results in two successive ordered or crystalline phases, as indicated by the X-ray scattering curves (Figure 2a) as well as polarizing optical microscopy. The Bragg spacing corresponding to the single, sharp ring at small angles remains constant at 21.4 Å in both ordered phases, as in the disordered phase.

FTIR measurements of the compound at room temperature indicate that there is a significant amount of hydrogen-bonded pairing of the acid groups, as is clear from the broad band centered around 3000 cm^{-1} (Figure 3a), attributed to the OH dimer stretch.[9] When it is mixed with P4VP at a molar ratio of one LC molecule for every two polymer repeat units (0.5:1 LC:4VP), the OH dimer stretch is no longer visible (though possibly masked by the other absorption bands in this region), and two new broad bands centered at 2500 and 1950 cm^{-1} have appeared (Figure 3b). The latter are indicative of strong H-bonding between the carboxylic acid and pyridine groups.[9,10] Preliminary measurements indicate that these bands remain essentially unchanged at temperatures up to at least 160 °C. There are also significant changes in the carbonyl region of the spectra in going from the pure LC to the mixture. In particular, two carbonyl bands are visible in the spectrum of the pure LC, a weak band due to free carbonyl (ca. 1730 cm^{-1}) and a strong one due to H-bonded carbonyl (ca. 1700 cm^{-1}), indicating that dimerized acid groups are the predominant species in the pure LC. In the mixture, the spectrum in this region is dominated by a broad band centered at 1710–1715 cm^{-1}; this can be related to association of the acid hydroxyl group with the pyridine nitrogen group, which "frees" the carbonyl.[9] Further study is in progress to analyze these and other changes in the spectra of the mixtures compared to the pure compounds. The most important point, presently, is the clear evidence that there is a significant association between the LC and the polymer.

The DSC curves of the mixture (Figure 1b), in contrast to those for the pure LC, show two distinct transitions on

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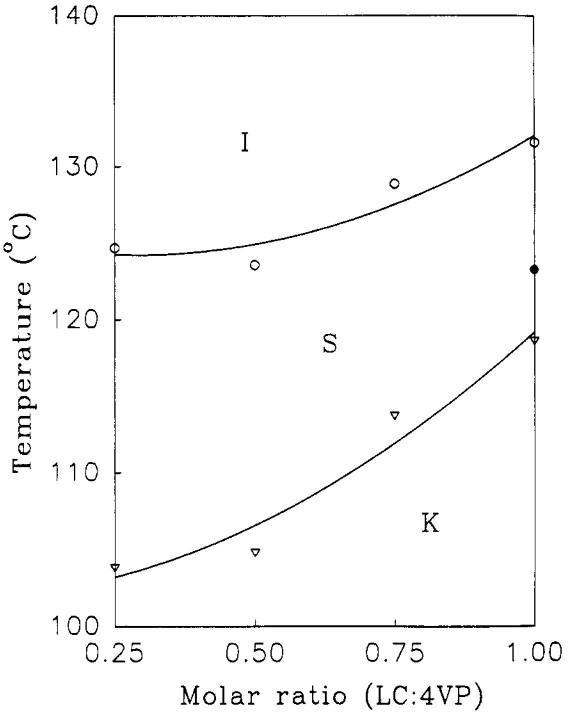

Figure 4. Maxima of the DSC transitions in the cooling thermograms (5 °C/min) of the mixtures of functionalized liquid crystal with poly(4-vinylpyridine) as a function of molar ratio. I, S, and K represent the isotropic, disordered smectic, and crystalline phases, respectively.

both heating and cooling. The temperatures of their maxima are somewhat lower than those for the pure LC. Furthermore, the transition to and from the isotropic liquid is the predominant transition, and it is very sharp compared to that for the pure LC. X-ray scattering results (Figure 2b) show that the phase between the two transitions has the same structure as the disordered phase of the pure LC; only the small-angle Bragg spacing, at 19.3 Å, is somewhat smaller for the mixture than it is for the LC by itself. It is also evident from the X-ray measurements that the phase which exists on cooling in the pure LC, and which has disappeared in the mixture, is the higher temperature ordered phase.

When the molar ratio of the mixture is varied, DSC results (Figure 4) demonstrate that the disordered phase is extended over a significantly wider temperature region with decrease in the molar ratio of LC to 4VP (P4VP repeat unit) from 1:1 to 0.25:1. This is in contrast to our preliminary results of mixtures of the same LC with poly(acrylic acid). In the latter case, the thermal stability of the disordered phase *decreases* considerably, to less than 2 °C between the maxima of the two transitions at a molar ratio of 0.25:1. In these mixtures, hydrogen-bonded acid pairs involving the functionalized LC and the polymer are not expected to be favored as in the LC/P4VP mixture. It is also to be noted that, for the mixtures with P4VP, the intermediate phase in the pure LC is absent in all mixtures of molar ratios less than 1:1. Distinct glass transition temperatures were not detected by DSC; this phenomenon has been noted previously in side-chain LC polymers.[11]

In conclusion, the results described above indicate that the H-bonding interactions between the acid group of the functionalized LC and the pyridine group of the polymer are sufficient to thermally stabilize the disordered phase which is existent in the LC alone. The stabilization increases as the molar ratio of LC to 4VP is diminished, in the range studied. We are currently completing our studies of the LC/P4VP mixtures at various molar ratios, as well as investigating their dynamic mechanical properties.

Acknowledgment. We thank NSERC (Canada) and FCAR (Québec) for financial support.

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Second Order Optical Nonlinearity on a Modified Sol–Gel System at 100 °C

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Second-order nonlinear optical (NLO) properties of polymeric materials have been widely studied.[1] Polymeric materials have become competitive with inorganics for nonlinear optical applications such as fast waveguide electrooptic modulation and frequency-doubling devices provided the nonlinearity shows reasonable stability at ambient temperatures. The noncentrosymmetric alignment of the NLO chromophores that results from the poling process is not in a state of thermodynamic equilibrium. Therefore, the alignment would relax to a random configuration in the absence of a poling field. To prevent the randomization of the poled molecules, the NLO chromophores are usually incorporated in a polymer which has a high glass transition temperature (T_g). This is due to the fact that the molecular orientational motion is closely associated with the T_g of the polymer. Moreover, enhanced temporal stability of second-order NLO properties in a poled polymer system can be obtained when a certain degree of cross-linking is introduced. In the cross-linked polymer, the NLO moieties are either incorporated or covalently bound into a rigid polymer network and are much less likely to relax to random orientation. The polymers can be cross-linked by thermal means[1e,f,2] or by photochemical means.[3]

Sol–gel technology provides an attractive route to the preparation of a three-dimensional inorganic network.[4] The basic sol–gel process involves the sequential hydrolysis

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