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Toward Supramolecular Side-Chain Liquid Crystal Polymers. 5. The Template Receptor Approach†

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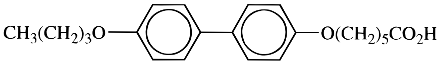
ABSTRACT: Three series of copolymers have been prepared by the reaction of a mesogenic methacrylate, 6-((4-((4-methoxyphenyl)azo)phenyl)oxy)hexyl methacrylate, with either 4-vinylpyridine, 2-vinylpyridine or styrene. These copolymers were blended with either a mesogenic acid, 6-((4-((4-methoxyphenyl)azo)phenyl)oxy)hexanoic acid, or a nonpolar low molar mass liquid crystal, 4-(hexyloxy)-4′-methoxyazobenzene. The blends were prepared such that the low molar mass component was in an equimolar ratio to the nonmesogenic units in the copolymer. The acid was essentially immiscible in the styrene-based copolymers, while the nonpolar mesogen was miscible providing the mole fraction of mesogenic side chains exceeded 0.27. This miscibility was attributed to the mesogen−mesogen interactions and resulted in a linear dependence of the nematic−isotropic transition temperature on composition. By contrast the miscibility of the mesogenic acid is greater than that of the nonpolar mesogen with the vinyl pyridine-based copolymers and for the acid mixtures results in the observation of either induced or enhanced liquid crystalline behavior; these effects were more pronounced for the 4-vinylpyridine-based copolymers. This nonlinear dependence of the nematic−isotropic transition temperatures on composition was attributed to the formation of hydrogen bonds between the carboxylic acid and pyridyl units. Thus the vinylpyridine-based copolymers are described in terms of template polymers, *i.e.*, preformed receptors, for the low molar mass acid substrates.

Introduction

Supramolecular chemistry is a new and exciting branch of chemistry encompassing systems held together by noncovalent bonds,[1] and such complexes have considerable application potential in the rapidly developing field of molecular electronics.[2] More recently, the concepts of supramolecular chemistry have been applied in the design of liquid crystal polymers in the expectation that a molecular interaction may be amplified into a macroscopically observable phenomenon, *i.e.*, liquid crystallinity.[3−5] A conventional side-chain liquid crystal polymer comprises three structural elements: a polymer backbone, a flexible spacer, and a mesogenic group.[6,7] The mesogenic unit is covalently attached as a pendant to the polymer backbone via the spacer. The role of the spacer is to decouple the tendencies of the mesogenic units to self-assemble from those of the backbones to adopt random coil configurations and endows upon the material a unique combination of polymeric properties with the electro-optic characteristics of low molar mass mesogens. In consequence, side-chain liquid crystal polymers are candidates for use in advanced electro-optic technologies.[8,9]

Recently a novel class of supramolecular side-chain liquid crystal polymers has been described in which the novelty arises from the use of a noncovalent linkage to connect the spacer to the backbone; see Figure 1a.[3] Ujiie and his co-workers described the first example of such polymers using an ionic bond to connect bis(2-hydroxyethyl)ethyl(6-((4-((4-nitrophenyl)azo)phenyl)oxy)hexyl)ammonium to poly(vinyl sulfonate).[10−12] Bazuin and Brandys suggested that a much weaker interaction, the hydrogen bond, could be used to achieve the same goal, citing the liquid crystalline properties of mixtures of the mesogenic acid **1** with poly(4-vinylpyridine).[13,14]



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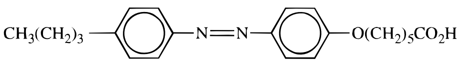
In order to investigate the generality of this proposal, we characterized the thermal properties of mixtures of the mesogenic acid **2** not only with poly(4-vinylpyridine) (P4VP) but also with poly(2-vinylpyridine) (P2VP) and polystyrene (PS).[15] The strong similarity in the thermal behavior of mixtures of **2** with either P4VP or P2VP suggested that supramolecular side-chain liquid crystal polymers as shown in Figure 1a do not form.



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It was evident from these results, however, that **2** was miscible to a limited degree with P4VP and P2VP and that miscibility was driven by hydrogen bond formation. The infrared spectra of the blends revealed that the coverage of the backbone by the side chain was not complete, but instead a dynamic equilibrium between acid dimers and acid−pyridine complexes was established. We termed these complexes supramolecular copolymers in which a given fraction of pyridine units remain uncomplexed and these suppress the formation of liquid crystallinity.[16] Our investigation of the thermal behavior of **1** with P4VP confirmed that supramolecular liquid crystal polymers do not in fact form,[17] a view now shared by Brandys and Bazuin.[18] This general approach does, however, appear to give rise to mesomorphic behavior in mixtures of poly(4-vinylpyridine) and a surfactant, 3-pentadecylphenol.[19]

Here we describe a modified approach to the design of supramolecular side-chain liquid crystal polymers in

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† For part 4 in this series, see: Stewart, D.; Paterson, B. J. A.; Imrie, C. T. *Eur. Polym. J.* **1996**, in press.

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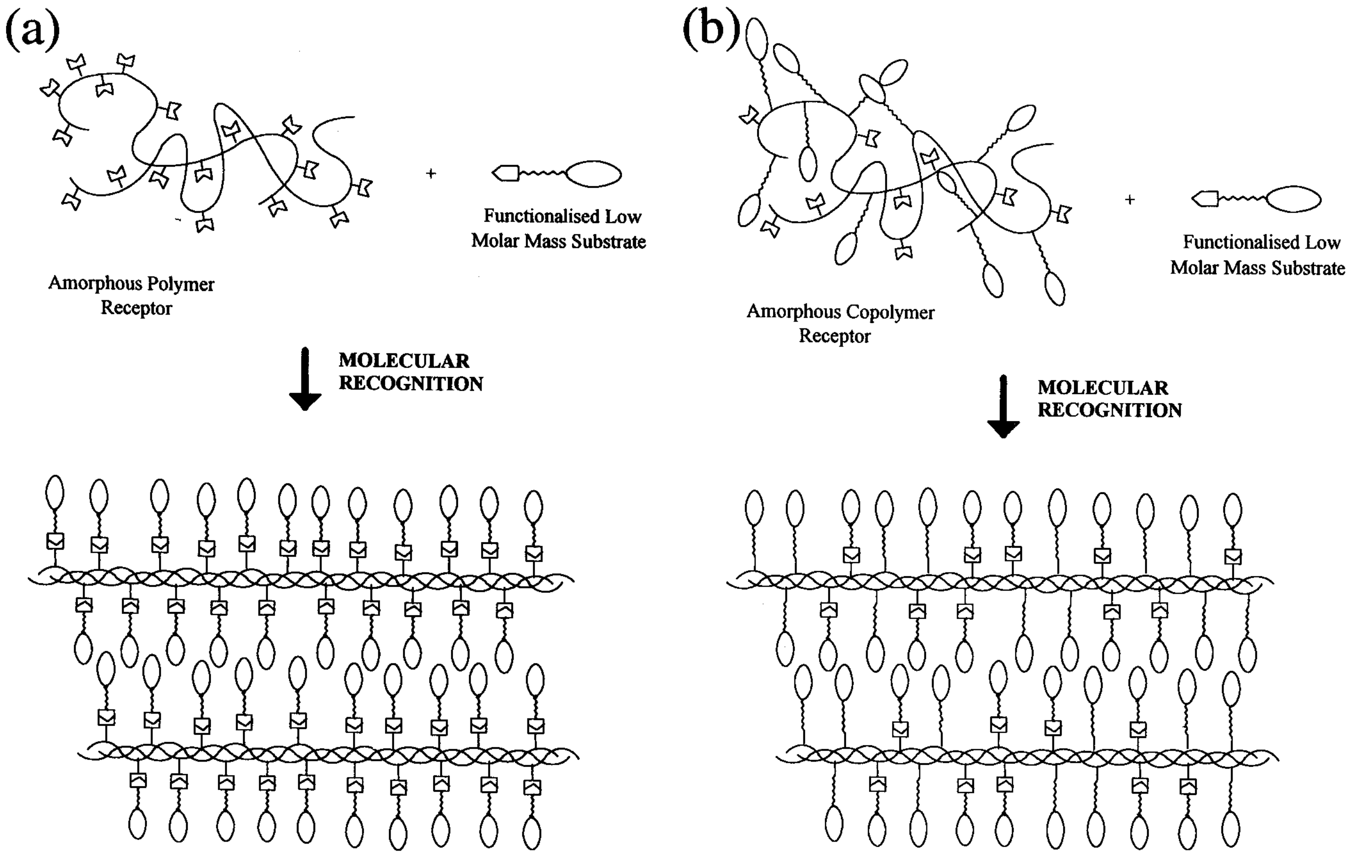
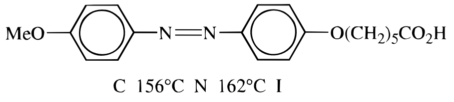


Figure 1. Schematic representations of (a) an idealized supramolecular side-chain liquid crystal polymer and (b) the use of a template polymer in complex formation.

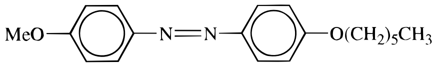
which mixtures between a mesogenic acid (**3**) and copolymers containing both complementary binding sites, *i.e.*, pyridine groups, and covalently attached mesogenic side chains; see Figure 1b. We term these copolymers templates in the expectation that they will serve as preformed receptors for the low molar mass substrate. The structures of the copolymers used in these studies are shown in Figure 2; also shown are the acronyms used to describe the polymers. We note that Kato *et al.* have recently described a similar design approach.[20]



C 156°C N 162°C I

3

In order to establish the importance of hydrogen bonding in determining the thermal behavior of these blends, we have characterized also two quite different control systems: (i) blends of acid **3** with copolymers containing styrene and (ii) blends of the mesogen **4** with the copolymers (see Figure 2). In both these systems no significant interactions between the differing components are expected to occur. In all the mixtures the low molar mass compound has been added in an equimolar ratio to the nonmesogenic units in the backbone.



C 96°C N 104°C I

4

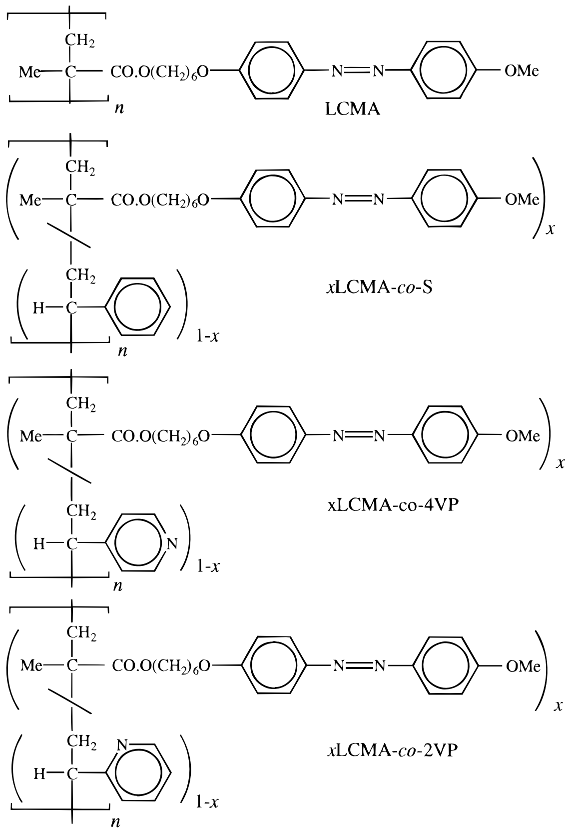
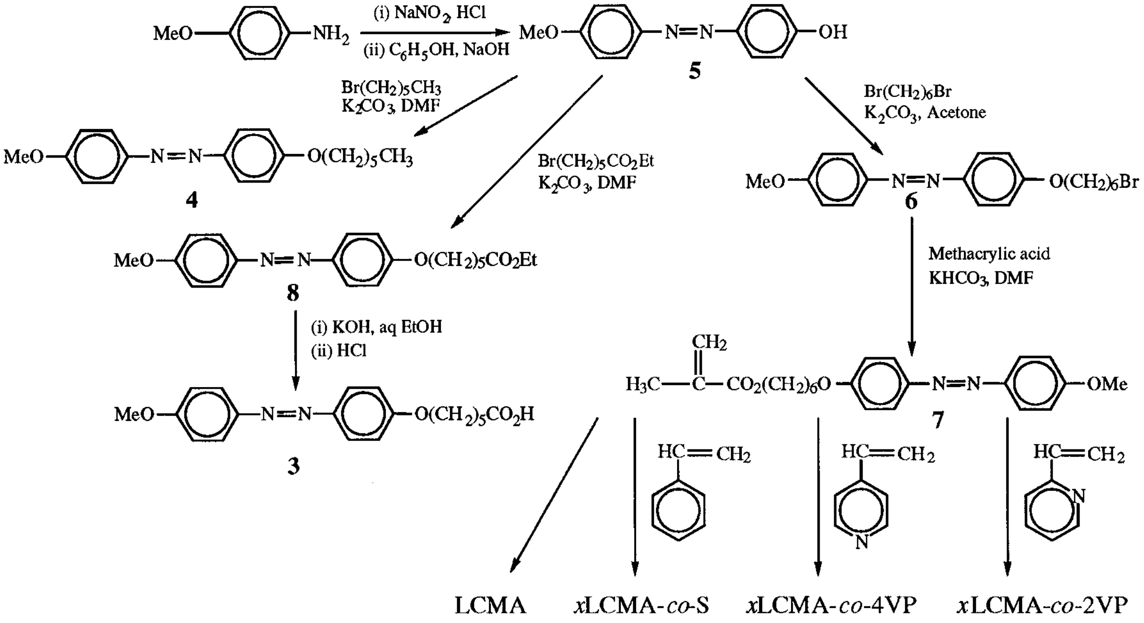


Figure 2. Structures and acronyms of the polymers.

Experimental Section

The polymers, see Figure 2, and the low molar mass materials, **3** and **4,** were prepared via the synthetic routes shown in Scheme 1. Detailed synthetic procedures have been given elsewhere for the preparation of 4′-hydroxy-4-methoxy-

Scheme 1



azobenzene (**5** in Scheme 1),[21] 1-bromo-6-((4-((4-methoxyphenyl)azo)phenyl)oxy)hexane (**6**),[21] 6-((4-((4-methoxyphenylazo)-phenyl)oxy)hexyl methacrylate (**7**),[21] ethyl 6-((4-((4-methoxyphenyl)azo(phenyl)oxy)hexanoate (**8**),[22] 6-((4-((4-methoxyphenyl)azo(phenyl)oxy)hexanoic acid (**3**),[22] and 4-(hexyloxy)-4′-methoxyazobenzene (**4**).[22]

Polymerizations. 2-Vinylpyridine (Aldrich) and 4-vinylpyridine (Aldrich) were purified by distillation under reduced pressure immediately prior to use. Styrene (Aldrich) was dissolved in dichloromethane and washed twice with 5% aqueous sodium hydroxide solution and twice with water. The organic layer was collected and dried with magnesium sulfate and the solvent removed under vacuum. The styrene was then distilled from calcium hydride under reduced pressure. AIBN (Aldrich) was recrystallized from toluene (dissolved at 35 °C and crystallized at −70 °C), washed with petroleum spirit (80−100 °C), and dried under vacuum.

Appropriate amounts of the two comonomers, *i.e.*, **7** and either styrene, 2-vinylpyridine or 4-vinylpyridine, were dissolved in benzene, and 1 mol % AIBN was added as initiator. The reaction mixture was flushed with argon for 20 min and then heated in a water bath at 60 °C to initiate the polymerization. After 48 h the polymerization was terminated by precipitation into petroleum spirit (40−60 °C). The copolymer was collected and purified by repeated dissolution in chloroform and precipitation into petroleum spirit (40−60 °C).

Blends. The blends of each copolymer with **3** or **4** were prepared by codissolution in either pyridine (4-vinylpyridine-containing copolymers) or THF (styrene- and 2-vinylpyridine-containing copolymers). The solvent was allowed to evaporate slowly, and the blends were dried under vacuum at ambient temperature for at least 48 h. In all the blends the low molar mass compound, *i.e.*, **3** or **4**, was mixed in an equimolar ratio to the nonmesogenic component of the copolymer.

General. The proposed structures of all products were verified by ^{1}H-NMR spectroscopy using a Bruker AC-F 250 MHz NMR spectrometer and by infrared spectroscopy using a Nicolet 205 FTIR spectrometer. The actual compositions of the copolymers were determined by ^{1}H NMR spectroscopy. The molecular weights of LCMA and the copolymers containing styrene were determined by gel permeation chromatography using a Knauer Instruments chromatograph equipped with two PL gel 10 μm mixed columns and controlled by PL GPC SEC V5.1 software. Chloroform was used as the eluent and the chromatograph was calibrated against polystyrene standards. Tables 1−3 summarise the characterization data for the *x*LCMA-*co*-S, −4VP, and −2VP series, respectively.

Table 1. Copolymerization of Styrene (S) and the Mesogenic Methacrylate 7

feed (mol fraction)		conversion	copolymer (mol fraction)		M_n/	M_w/
S	7	(%)	S	7	(g mol^{-1})	M_n
0.79	0.21	53	0.86	0.14	8600	1.5
0.61	0.39	55	0.73	0.27	5000	1.6
0.42	0.58	49	0.57	0.43	9300	1.6
0.24	0.76	32	0.37	0.63	6800	1.6
0.23	0.77	45	0.36	0.64	7800	1.7

Table 2. Copolymerization of 4-Vinylpyridine (4-VP) and the Mesogenic Methacrylate 7

feed (mol fraction)		conversion	copolymer (mol fraction)	
4-VP	7	(%)	4-VP	7
0.80	0.20	72	0.83	0.17
0.60	0.40	53	0.79	0.21
0.59	0.41	76	0.67	0.33
0.39	0.61	68	0.54	0.46
0.21	0.79	78	0.29	0.71

Table 3. Copolymerization of 2-Vinylpyridine (2-VP) and the Mesogenic Methacrylate 7

feed (mol fraction)		conversion	copolymer (mol fraction)	
2-VP	7	(%)	2-VP	7
0.79	0.21	91	0.89	0.11
0.60	0.40	44	0.77	0.23
0.40	0.60	34	0.66	0.34
0.21	0.79	64	0.48	0.52
0.20	0.80	43	0.26	0.74
0.13	0.87	87	0.12	0.88

The thermal behavior of the materials was characterized by differential scanning calorimetry using a Polymer Laboratories PL-DSC equipped with an autocool accessory and calibrated using an indium standard. The time-temperature profile was identical in each case. Thus, each sample was heated from 25 to 200 °C, isothermed at 200 °C for 3 min, cooled from 200 to −50 °C, isothermed at −50 °C for 3 min, and, finally, reheated from −50 to 200°C. The heating and cooling rates in all cases were 10 °Cmin^{-1}. Phase identification was performed by polarized light microscopy using an Olympus BH-2 optical microscope equipped with a Linkam THMS 600 heating stage and TMS 91 control unit. Clear, characteristic optical textures from which phase assignments were possible were obtained by cooling at either 0.2 or 0.1 °C min^{-1} from *ca.* 10 °C above the clearing temperature to below the glass transition temperature or, in the absence of glassy behavior, to room temperature.

Results and Discussion

LCMA. The DSC trace obtained on the second heating of LCMA exhibited two endothermic peaks (see Figure 3). On cooling from the isotropic phase a characteristic schlieren nematic texture was obtained at 133 °C. On further cooling a well-defined focal conic fan texture was observed at 93 °C. Thus the phase sequence is assigned as smectic A—nematic—isotropic. The transition temperatures are in good agreement with those reported by Muzzalupo *et al.* but we found no evidence for the nematic—nematic transition proposed by the authors.[23] The glass transition temperature of LCMA estimated from the DSC trace is 73 °C.

***x*LCMA-*co*-S.** Figure 3a shows the second-heating DSC traces for the *x*LCMA-*co*-S copolymers, and the transition temperatures are listed in Table 4. The polystyrene used in these investigations exhibited a glass transition at 102 °C. The copolymers containing 0.14, 0.27, and 0.43 mol fraction of mesogenic sidechains formed isotropic glasses on cooling. The copolymers containing 0.63 and 0.64 mol fraction of mesogenic side chains exhibited a glass transition and a nematic—isotropic transition. The nematic phase was identified on the basis of the characteristic schlieren texture observed using polarized light microscopy: such textures were observed for all the nematic phases assigned for the copolymers and their blends. The dilution of the mesogenic units in the liquid crystalline copolymers accounts for both the reduction in the clearing temperature and the suppression of smectic behavior as compared with LCMA.[24] The initial decrease in T_g on increasing *x* reflects the plasticization of the polymer backbone by the side chains, while the subsequent increase in T_g concurrent with the observation of liquid crystallinity can be rationalized in terms of the reduction in the free volume on passing from the isotropic to a liquid crystal phase.

***x*LCMA-*co*-4VP.** The DSC traces obtained on the second heating of the *x*LCMA-*co*-4VP copolymers are shown in Figure 4a, and the transition temperatures are listed in Table 4. The poly(4-vinylpyridine) used in these investigations exhibited a glass transition at 155 °C. The copolymers containing 0.17, 0.21, 0.33, and 0.46 mol fraction of mesogenic side chains exhibited only a glass transition (see Figure 4); as would be expected, the T_gs are higher than those of the corresponding *x*LCMA-*co*-S. The DSC trace for 0.46LCMA-*co*-4VP contains a broad endothermic peak centred at *ca.* 115 °C; this was not accompanied by a change in optical texture, *i.e.*, the sample remained isotropic over the whole temperature range. The molecular relevance of this peak is, therefore, unclear. 0.71LCMA-*co*-4VP exhibited a glass transition and a nematic—isotropic transition. The reduction in T_{NI} and the suppression of smectic behavior compared to LCMA again reflect the dilution of the mesogenic side chains.[24]

***x*LCMA-*co*-2VP.** The DSC traces obtained on the reheating cycle for the *x*LCMA-*co*-2VP copolymers are shown in Figure 5a, and the transition temperatures are listed in Table 4. The poly(2-vinylpyridine) exhibited a glass transition at 102 °C. The copolymers containing 0.11, 0.23, 0.34, and 0.52 mol fraction of mesogenic side chains exhibited only glass transitions, while the copolymers containing 0.74 and 0.88 mol fraction of mesogenic side chains also exhibited nematic behavior. The DSC traces for the copolymers containing 0.52, 0.74, and 0.88 mol fraction of mesogenic side chains appear to contain a weak transition at temperatures slightly higher than T_g. No change in the optical

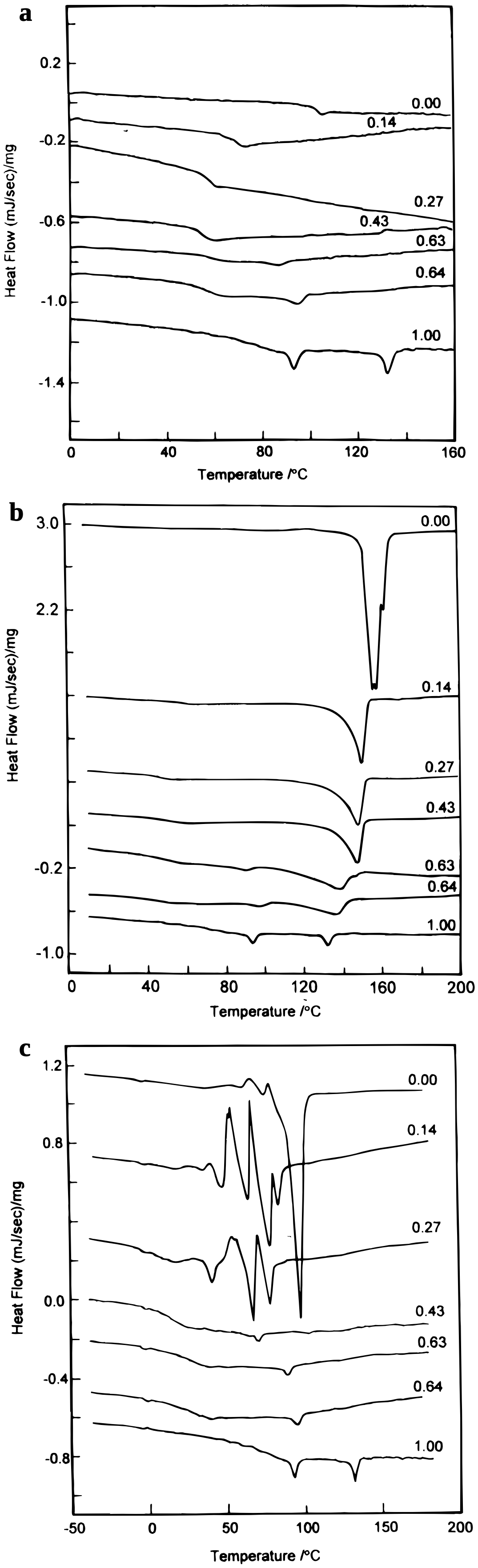


Figure 3. Normalized DSC traces obtained on the second heating for (a) the *x*LCMA-*co*-S copolymers, (b) the blends of *x*LCMA-*co*-S copolymers and the mesogenic acid **3**, and (c) the blends of *x*LCMA-*co*-S copolymers and the mesogen **4**. *x* denotes the mole fraction of mesogenic side chain and is given on each trace.

Table 4. Transition Temperatures of the Copolymers and Their Blends with Mesogenic Acid 3 and Mesogen 4[a]

	unblended			blends with acid **3**			blends with mesogen **4**		
copolymer	T_g (°C)	T_{CI} (°C)	T_{NI} (°C)	T_g (°C)	T_{CI} (°C)	T_{NI} (°C)	T_g (°C)	T_{CI} (°C)	T_{NI} (°C)
0.14LCMA-*co*-S	68			60	151			85	
0.27LCMA-*co*-S	56			47	149			79	
0.43LCMA-*co*-S	55			48	148		16		72
0.63LCMA-*co*-S	58		83	46	138		26		90
0.64LCMA-*co*-S	57		91	47	135		26		95
0.17LCMA-*co*-4VP	100			50				96	
0.21LCMA-*co*-4VP	84			54				94	
0.33LCMA-*co*-4VP	66			47		81		96	
0.46LCMA-*co*-4VP	70			47		103		75	
0.71LCMA-*co*-4VP	62		104	60		117	35		109
0.11LCMA-*co*-2VP	73			35	124			82	
0.23LCMA-*co*-2VP	59			39	128			80	
0.34LCMA-*co*-2VP	52			40	128		6	80	
0.52LCMA-*co*-2VP	54			44	131		13	76	
0.74LCMA-*co*-2VP	55		93	51		103	37		94
0.88LCMA-*co*-2VP	59		105	55		108	49		104

[a] The peak temperatures are assigned as the transition temperatures.

texture accompanied this peak, and its molecular significance is uncertain. The glass transition temperatures exhibited by the *x*LCMA-*co*-2VP series are comparable with those of the corresponding *x*LMCA-*co*-S series but are lower than those of the *x*LCMA-*co*-4VP series.

***x*LCMA-*co*-S Blends.** The DSC traces for the blends of the *x*LCMA-*co*-S copolymers and the mesogenic acid **3** are shown in Figure 3b, and the transition temperatures are listed in Table 4. The equimolar blend of polystyrene and **3** is essentially immiscible;[22] thus, the transition temperatures for the blend are the same as for the pure acid, while the isotropic phase exhibits a two-phase morphology. The blends of the *x*LCMA-*co*-S copolymers with **3** each exhibited a glass transition and a crystal−isotropic transition; see Figure 3b. The isotropic phases were homogeneous. In each mixture the reduction in T_g of the copolymer is small, *ca.* 6 °C. Similarly for the blends containing 0.14-, 0.27-, and 0.43LCMA-*co*-S, the reduction in the melting point of the acid was also small, *ca.* 9 °C. Thus for these blends the two components appear to be essentially immiscible although the destruction of the nematic phase exhibited by **3** reveals that some degree of molecular mixing must be occurring. The nematic−isotropic transition is a thermodynamically weak transition, however, and therefore particularly sensitive to the presence of a second component, *i.e.*, small amounts of the copolymer.

Quite different behavior is observed for the mixtures containing 0.63- and 0.64LCMA-*co*-S, for which the reduction in the melting point of the acid is greater, *ca.* 20 °C, and the nematic behavior of both the copolymer and acid has been extinguished. This indicates a higher degree of miscibility between the two components, and this is presumably driven by the interaction between the mesogenic units. The acid exists in a dimeric form,[15,22] however, and this will limit the extent to which it is miscible with the side chains of the copolymer.

The DSC traces obtained, on the second heating of the *x*LCMA-*co*-S/**4** blends are shown as Figure 3c, and the transition temperatures are listed in Table 4. The equimolar mixture of polystyrene and **4** exhibits transitional behavior identical with that of pure **4**, *i.e.*, the components are essentially immiscible.[22] For the blends containing 0.14- and 0.27LCMA-*co*-S, a complex crystallization and melting sequence is observed; see Figure 6. The mixtures containing 0.43-, 0.63-, and 0.64LCMA-*co*-S exhibit a glass transition and a nematic phase. The T_{NI}s exhibited by the latter two blends correspond to the arithmetic mean of those of the individual components and are, therefore, indicative of molecular mixing. If this is assumed, also, to be the case for the mixture containing 0.43LCMA-*co*-S, then the virtual T_{NI} for the copolymer is *ca.* 30 °C. Thus, the *x*LCMA-*co*-S/**4** mixtures are miscible if the mole fraction of mesogenic side chain is above a critical value, and the miscibility is presumably driven by the interaction of the mesogenic units.

***x*LCMA-*co*-4VP Blends.** The DSC traces obtained on the second heating for the *x*LCMA-*co*-4VP/**3** blends are shown in Figure 4b, and the transition temperatures are listed in Table 4. The equimolar mixture of poly(4-vinylpyridine) and mesogenic acid **3** exhibits limited miscibility.[22] Specifically, the nematic phase exhibited by the pure acid is extinguished in the blend, and a crystal−isotropic transition is observed at 133 °C. For the mixtures containing 0.17- and 0.21LCMA-*co*-4VP, amorphous glasses are obtained on cooling from the isotropic phase, indicating molecular mixing between the two components. Crystallization was also suppressed in the remaining mixtures, and each exhibited a glass and a nematic−isotropic transition. The DSC trace for 0.71LCMA-*co*-4VP appears to contain a weak transition which overlaps the glass transition and is similar to that described for members of the *x*LCMA-*co*-2VP series: again, however, no change in the optical texture accompanied the transition. For the amorphous 0.33- and 0.46LCMA-*co*-4VP copolymers, blending with the acid **3** has induced liquid crystallinity. The miscibility of **3** with the copolymers is presumably driven by the hydrogen bond formation between the acid group and the pyridyl unit. Such an interaction is normally confirmed using infrared spectroscopy; specifically, a modification of the carbonyl region of the spectrum is observed, and new bands appear at *ca.* 2650 and 1930 cm^{-1} if the self-associated acid dimers are destroyed and acid−pyridyl complexes are formed.[25] The infrared spectrum of **3** contains strong bands at approximately 3000 cm^{-1} (OH stretch) and 1699 cm^{-1} (carbonyl stretch); these frequencies are characteristic of self-associated carboxylic acid dimers.[22] The infrared spectra of all the copolymers contain a strong carbonyl stretching band at approximately 1723 cm^{-1}, indicative of a saturated ester. For polymers containing a high mesogenic content (x > 0.6), this band masked any possible changes in the carbonyl region on blending with the low molar mass component. For copolymers containing lower mesogenic contents, however, infrared spectroscopy did confirm the existence of hydrogen bonding. For example, for blends containing either

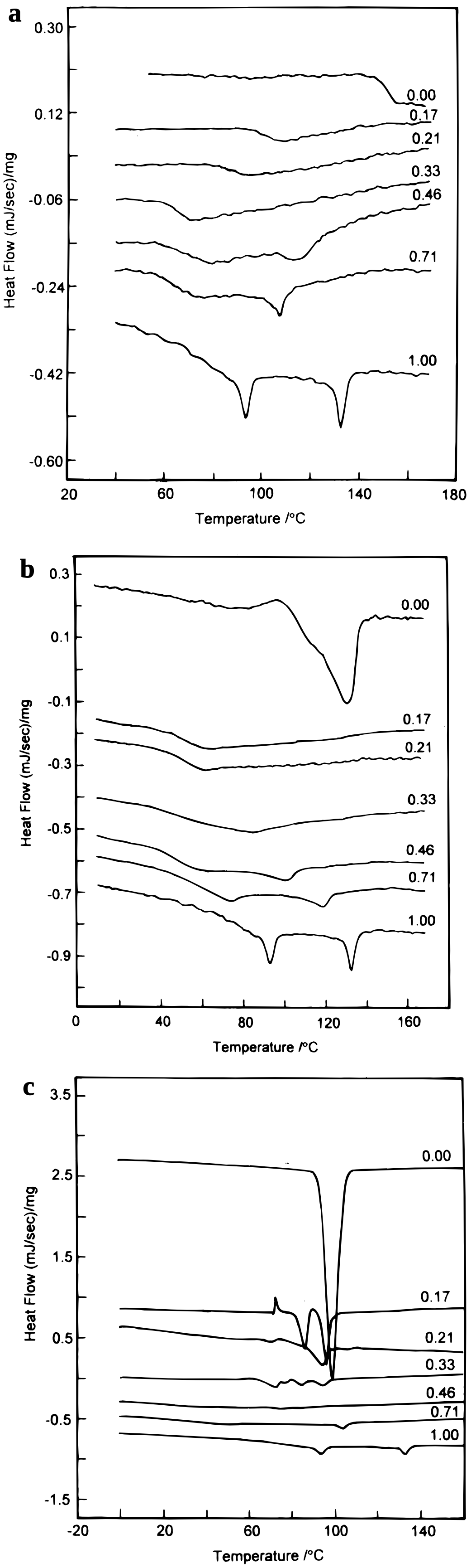


Figure 4. Normalized DSC traces obtained on the second heating for (a) the *x*LCMA-*co*-4VP copolymers, (b) the blends of *x*LCMA-*co*-4VP copolymers and the mesogenic acid **3**, and (c) the blends of *x*LCMA-*co*-4VP copolymers and the mesogen **4**. *x* denotes the mole fraction of mesogenic side chain and is given on each trace.

0.17LCMA-*co*-4VP or 0.11LCMA-*co*-2VP with **3**, the carbonyl region in the infrared spectrum contains additional bands at *ca.* 1713 cm^{-1}, indicating the presence of acid groups hydrogen bonded to pyridyl units,[18,25] and at *ca.* 2650 and 1930 cm^{-1}. By contrast no modification of the infrared spectrum is observed on blending 0.14LCMA-*co*-S with **3**. Thus, the infrared spectra of the mixtures cannot be used to unambiguously confirm the formation of hydrogen bonds for high mesogenic side chain contents. However, the greatly enhanced miscibility of **3** with the *x*LCMA-*co*-4VP copolymers compared to that with the *x*LCMA-*co*-S copolymers strongly supports the view that hydrogen bonds are formed. The high T_{NI} exhibited by the acid **3** can be attributed to the formation of hydrogen-bonded dimers.[15] On complexation with the backbone pyridyl units, these dimers are necessarily destroyed resulting in a decreased T_{NI}. In order to assess the effect on the T_{NI} of **3** on blending with the *x*LCMA-*co*-4VP copolymers, we must consider therefore the virtual T_{NI} of the free acid which, to a first approximation, is likely to be comparable to that of **4**. More realistically the bulky carboxylic acid group is likely to reduce the clearing temperature of the free acid to lie below that of **4**. If we calculate the T_{NI} of the mixture containing 0.71LCMA-*co*-4VP assuming that T_{NI} varies linearly with composition and that the T_{NI} of **4** is a reasonable approximation, then the value obtained is 106 °C. This lies below that observed for the blend. The addition of a monomer to a polymer backbone invariably increases the clearing temperature of the monomer, and this provides further evidence to support the view that a specific interaction exists between the pyridyl units and **3**.

We now turn our attention to the behavior of the *x*LCMA-*co*-4VP/**4** mixtures (see Figure 4c) in which hydrogen bond formation is not possible. The poly(4-vinylpyridine) / **4** equimolar mixture is essentially immiscible. For the mixture containing 0.17-, 0.21-, and 0.33LCMA-*co*-4VP complexes melting behavior is observed and the components are largely immiscible, although the destruction of the liquid crystalline phase exhibited by **4** does imply limited interaction between the components. The mixture containing 0.46LCMA-*co*-4VP exhibits similar behavior to that containing 0.33LCMA-*co*-4VP, although the transitions are weak and difficult to see on the scale used in Figure 4c; the larger depression in the melting point (see Table 4) indicates a greater degree of miscibility between the components. The 0.71LCMA-*co*-4VP mixture exhibits a glass transition and a nematic phase; the T_{NI} is in good agreement with that predicted assuming a linear dependence of T_{NI} on composition. Thus increasing the concentration of mesogenic side chain promotes miscibility with **4**. It is interesting to note that **4** exhibits a higher degree of miscibility with the polystyrene-based copolymers than with the poly(4-vinylpyridine)-based materials. This is in accord with our previous observation that the miscibility of **4** decreases as the polarity of the backbone increases.[22]

***x*LCMA-*co*-2VP Blends.** The DSC traces obtained on the second heating for the *x*LCMA-*co*-2VP/**3** blends are shown in Figure 5b, and the transition temperatures are given in Table 4. The equimolar mixture of poly(2-vinylpyridine) and **3** is essentially immiscible, although the modification of the transition temperatures of the individual components indicates a limited degree of mixing. The mixtures containing 0.11-, 0.23-, 0.34-, and 0.52LCMA-*co*-2VP each exhibit a glass transition and a crystal−isotropic transition. The similarity in behavior across this composition range indicates a high degree of phase separation; see Table 4. By contrast,

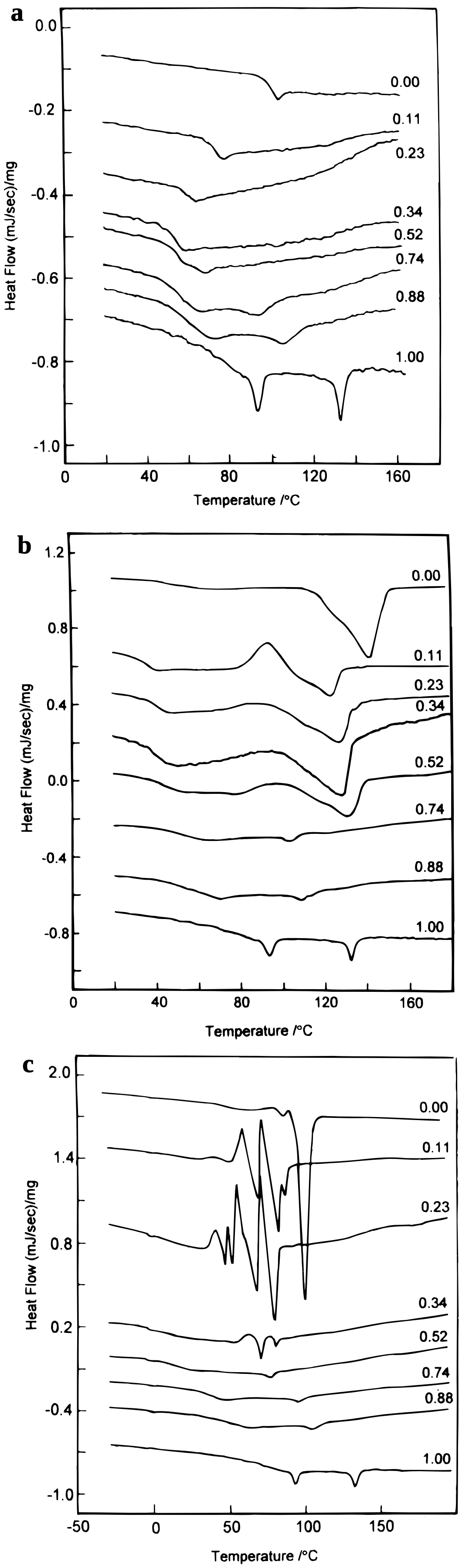


Figure 5. Normalized DSC traces obtained on the second heating for (a) the *x*LCMA-*co*-2VP copolymers, (b) the blends of *x*LCMA-*co*-2VP copolymers and the mesogenic acid **3**, and (c) the blends of *x*LCMA-*co*-2VP copolymers and the mesogen **4**. *x* denotes the mole fraction of mesogenic side chain and is given on each trace.

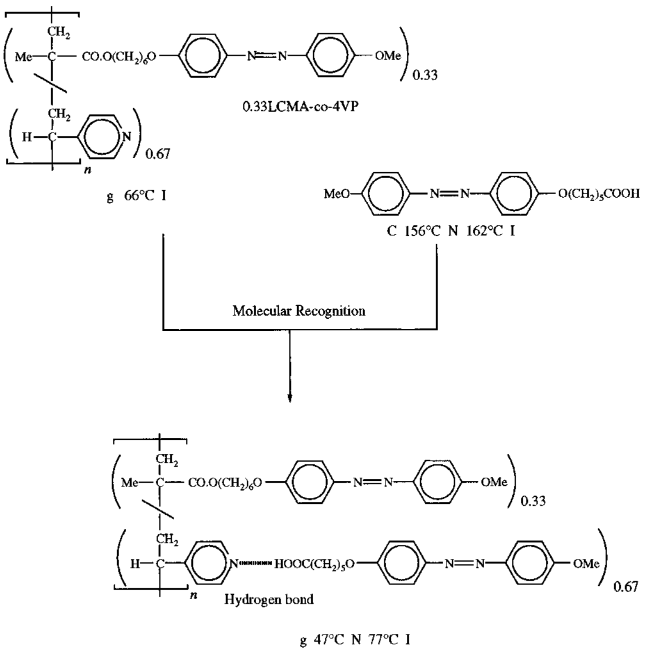


Figure 6. Formation of a supramolecular liquid crystal side-chain polymer.

the 0.74- and 0.88LCMA-*co*-2VP-based blends are miscible and exhibit a glass transition and nematic behavior. The T_{NI}s are slightly higher, *ca.* 6 °C, than predicted on the basis of a linear dependence of T_{NI} on composition and that **4** serves as a model for unassociated **3**. As with the *x*LCMA-*co*-4VP/**3** blends this enhancement of T_{NI} is probably an underestimation. It is clear, however, that the induction and enhancement of liquid crystallinity is greater in the *x*LCMA-*co*-4VP/**3** blends than in the *x*LCMA-*co*-2VP/**3** mixtures. The presence of hydrogen bonding in these blends was verified using IR spectroscopy; the spectra were essentially identical with those described for blends containing *x*LCMA-*co*-4VP and **3**.

Figure 5c shows the DSC traces obtained on the second heating of the *x*LCMA-*co*-2VP/**4** blends. The equimolar mixture of poly(2-vinylpyridine) and **4** is essentially immiscible. The mixtures containing 0.11- and 0.23LCMA-*co*-2VP exhibit complex melting behavior. The 0.34- and 0.52LCMA-*co*-2VP mixtures exhibit glass and crystal—isotropic transitions; the modification of the transition temperatures of the individual components indicates a limited degree of mixing; see Table 4. By comparison the blends containing 0.74- and 0.88LCMA-*co*-2VP are miscible and exhibit glass transitions and nematic phases; the T_{NI}s correspond to the arithmetic mean of those of the individual components. The miscibility of **4** with the *x*LCMA-*co*-2VP copolymers was similar to that observed for the *x*LCMA-*co*-4VP-based systems but less than that observed for the styrene-based materials.

Comparison of the Systems. The insertion of nonmesogenic units into a side-chain liquid crystal polymer results in a decrease in the clearing temperature, the magnitude of which is related to the flexibility of the backbone of the resulting copolymer.[24] The more flexible the backbone then the more nonmesogenic units may be inserted without the destruction of liquid crystallinity. For example, for polysiloxane-based materials, as little as 10% of the repeat units need to have mesogens attached in order for liquid crystallinity to be observed. This value rises to *ca.* 50% for polymethacrylate-based materials. The dependence of the transition temperatures on composition for the new copolymer series reported here is in accord with this view. For the styrene-based series liquid crystallinity is observed for 0.63 mol fraction of side chains but not for 0.43; the 2-vinylpyridine-based material containing 0.52 mol fraction of side chains is amorphous while that containing 0.74 is mesogenic, and for 4-vinylpyridine-containing materials at 0.46 mol fraction of side chains the copolymer is amorphous but at 0.71 liquid crystallinity is observed. This dependence of the clearing temperature on composition is thought to reflect the ease at which the backbone can be distorted to ensure a sufficient packing density of the mesogens for liquid crystallinity to be observed.[24]

The addition of mesogenic side chains to polystyrene, poly(2-vinylpyridine), and poly(4-vinylpyridine) has enhanced the miscibility of the polymer with the low molar mass mesogen, *i.e.*, **3** or **4**. Indeed, molecular mixing is now observed in all the systems with the exception of the *x*LCMA-*co*-S/**3** mixtures, for which the miscibility of the self-associated acid dimers and the side chains is insufficient to drive molecular mixing. The extent of miscibility of **4** with the copolymer systems is dependent on the polarity of the backbone, and the highest degree of miscibility is observed for the least polar backbone, *i.e.*, the *x*LCMA-*co*-S series. These control studies using **4** revealed that the T_{NI} observed in the molecularly mixed blends corresponded to the arithmetic mean of those of the individual components. This linear dependence of T_{NI} is normally referred to as ideal behavior and may be rationalized within the framework of molecular field theory developed to predict phase diagrams for binary mixtures of low molar mass nematogens.[26,27] In this theory three interaction parameters are defined as follows: the interaction parameters between the like components, ϵ_{AA} and ϵ_{BB}, and the mixed interaction parameter between the unlike components, ϵ_{AB}. ϵ_{AA} and ϵ_{BB} are proportional to the clearing temperatures of the pure components. If ϵ_{AB} is assumed to be the geometric mean of ϵ_{AA} and ϵ_{BB}, then the predicted transition temperatures of the mixtures are the weighted averages of those of the pure components, *i.e.*, T_{NI} varies in a linear fashion with composition. This has been experimentally verified for many low molar mass systems,[26,27] and hence, the geometric mean approximation appears to be valid. It is not surprising that ideal behavior is observed for mixtures containing **4** because the interacting groups are identical.

In contrast, the molecularly mixed *x*LCMA-*co*-4VP/**3** and *x*LCMA-*co*-2VP/**3** mixtures exhibit a positive deviation from ideal behavior, *i.e.*, T_{NI} is greater than that of the arithmetic mean of the individual components. Such behavior is often observed in binary mixtures of low molar mass mesogens containing differing mesogenic groups.[28] At the root of the deviation is a specific favorable interaction between the unlike groups such that ϵ_{AB} is greater than the geometric mean of the like interaction parameters. This interpretation does not account for the positive deviation observed for the *x*LCMA-*co*-4VP/**3** and *x*LCMA-*co*-2VP/**3** mixtures in which the mesogenic units attached to the differing species are identical. Instead these data strongly suggest the formation of a supramolecular side chain liquid crystal polymer in which hydrogen bond formation occurs between the carboxylic acid and pyridyl units. This results in a greater coverage of the backbone by mesogenic side chains and hence higher clearing temperatures;[24] see Figure 6. It is more difficult sterically for such complexes to form between **3** and 2-VP subunits, and hence, lower T_{NI}s would be predicted. Experimentally it is indeed observed that the *x*LCMA-*co*-2VP/**3** blends exhibit lower T_{NI}s than the corresponding *x*LCMA-*co*-4VP/**3** mixture. It is interesting to note, however, that studies of the thermal behavior of mesogenic acids with poly(2-vinylpyridine) and poly(4-vinylpyridine) revealed no significant steric influence.[15−17,22] Thus the addition of mesogenic side chain has enhanced the selectivity of the polymeric receptor toward the low molar mass substrate, and the polymer does indeed act as a template for the formation of the mesogenic supramolecular complex.

Conclusions

A template approach has been adopted in order to realize supramolecular side chain liquid crystal polymers. The key structural factor is the introduction of mesogenic side chains to the polymeric receptor which not only assist in miscibilizing the low molar mass substrate but also enhance the selectivity of the receptor. The degree of induction or enhancement of the liquid crystallinity is modest in the systems described here, but no attempt has been made to control the microstructure of the polymeric receptor. The comparison of the 4- and 2-vinylpyridine-based systems shows that this is an important feature, and future work will focus on this issue.

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