

Communications to the Editor

Poly(*p*-phenyleneethynylene)s Are Thermotropic Liquid Crystalline†

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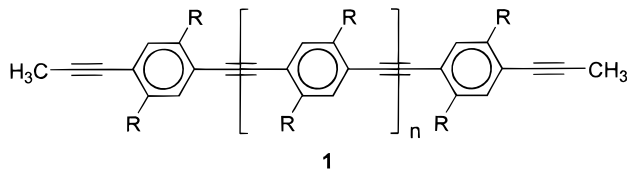
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Poly(*p*-phenyleneethynylene)s (PPEs)^{1,2} are conjugated polymers and organic semiconductors.³ Alkyl-substituted derivatives are stable up to at least 150 °C in air and dissolve easily in halogenated organics. Their high fluorescence quantum yields make them promising candidates as active layers in light-emitting diodes (LEDs),³ “plastic lasers”,⁴ and as polarizers in LC displays.⁵ However, we have only limited knowledge about their thermal phase behavior with concomitant changes in morphology.^{1,5,6} Neher^{7a} pointed out that morphology plays a crucial role in the manipulation of physical properties of conjugated polymers, its knowledge being of utmost importance in any application: “The existence of (thermotropic) liquid-crystalline (LC) phases offers the possibility to manipulate molecular order by means of external...forces”,^{7a} such as magnetic fields.⁸ Thermotropic liquid-crystalline phases of PPEs would offer the entry point into PPE-based optical devices, including LEDs exhibiting polarized emission.

Thermotropic nematic behavior is reported for polyphenylenevinylenes,^{7,9} polythiophenes,⁹ and some polyphenylenes.⁶ Thermotropic liquid-crystalline behavior has always been proposed but has never been detected in PPEs^{1c,g,h,i,2,10} and only in 1997 Weder observed well-defined *lyotropic*–nematic LC phases in alkoxy-substituted PPEs.¹⁰ Our recently published synthesis of *alkyl*-substituted PPEs via alkyne metathesis provides access to material of unprecedented high molecular weight, solubility, and purity.^{1a,h,i,11b} These factors all facilitate formation of LC phases.

In a first experiment we studied the thermal behavior of **1a**.¹¹ It exhibits one endothermic transition in the



differential scanning calorimetry trace (DSC; 280 °C) followed by a strong exotherm >300 °C, indicating cross-linking. Because of the proximity of this transition to

† Dedicated to Helmut Ringsdorf.

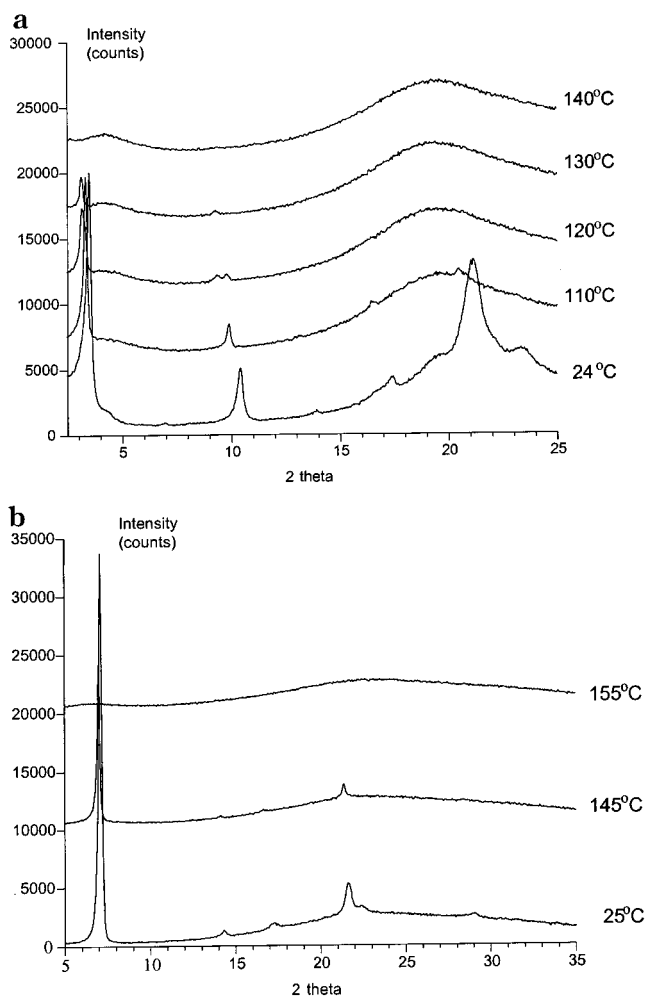


Figure 1. (a) X-ray powder diffraction of polymer **1b** (R = dodecyl) at different temperatures. (b) X-ray powder diffraction of polymer **1c** (R = 2-(ethyl)hexyl) at different temperatures.

the cross-linking temperature, **1a**¹¹ is not a good choice for studying thermotropic LC behavior in PPEs. Longer and/or branched side chains should lower the transition temperature of PPEs into a more manageable region and allow the examination of the phase behavior by polarizing microscopy, DSC, and powder X-ray diffraction (XRD).

DSC. The dodecyl-substituted **1b**¹¹ displays one transition in the DSC at 105 °C upon cooling (from 250 °C, 10 °C min⁻¹). This transition is not observed when heating the sample from ambient temperature, even upon repetition of the heating/cooling cycle. The second polymer we investigated was the 2,5-bis-2-(ethyl)hexyl-PPE **1c**¹¹ which shows two distinct transitions (142 °C, 160 °C) in the DSC upon heating, but only one during the cooling cycle. We have studied the thermal behavior of several other alkyl-substituted PPE derivatives by DSC (see Table 1). All display one phase transition in

Table 1. Thermal Behavior of Substituted PPEs; Phase Transitions of 1a–f¹¹

entry	1	substituent	transition temperatures measured by				P_n^d (GPC)
			DSC, P_1^a/P_2^b	upon cooling, P_2/i^c	polarizing microscopy, analogous transition	XRD	
1	a	hexyl		280			597
2	b	dodecyl		105	105, 140 iso	120, 140 iso	140
3	c	2-(ethyl)hexyl	142	160	140, 160 iso	155	200
4	c	2-(ethyl)hexyl		—	126 iso	130	100
5	d	nonyl		210	218 iso	—	710
6	e	copolymer dodecyl/hexyl		190	198 iso	—	360
7	f	2,5,5-trimethylhexyl		277	>250 iso	300	420

^a P_1 sanidic phase. ^b P_2 nematic or sanidic phase. ^c i clearing point. ^d P_n degree of polymerization.

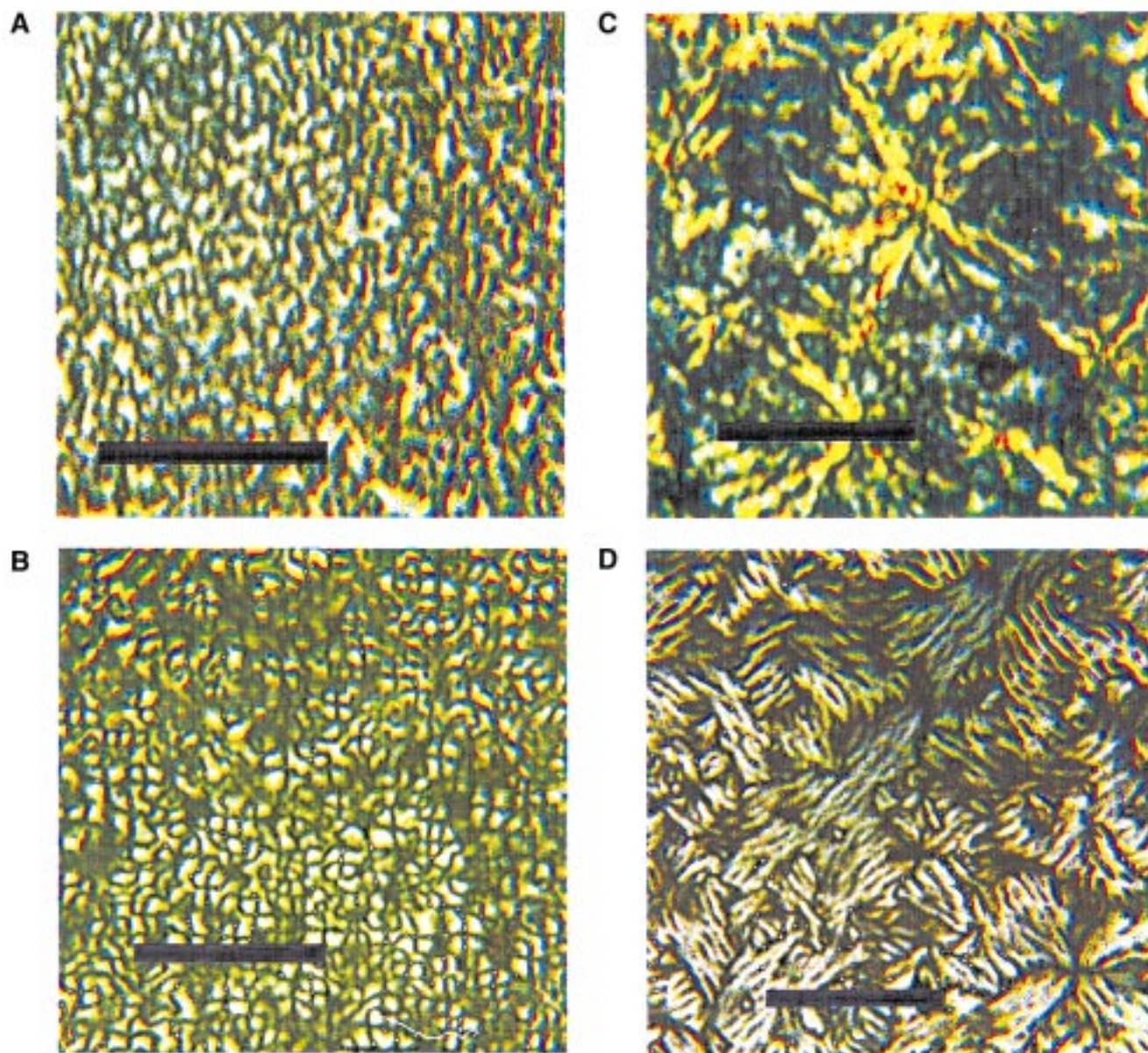


Figure 2. (A) Schlieren texture of **1b**. Bar represents 20 μm . (B) Maltese crosses of **1b**. Bar represents 20 μm . (C) Fused batons of **1c**. Bar represents 20 μm . (D) Flower or brush-type textures of **1c** upon shearing. Bar represents 20 μm .

the range of 160–277 $^{\circ}\text{C}$ upon cooling, above which they are isotropic liquids based on polarizing optical microscopy (*vide infra*). The clearing temperatures (liquid crystalline to isotropic) depend on the degree of polymerization (P_n) and choice of the solubilizing group, with higher clearing temperatures (i.e., reaching the isotropic state) being observed for shorter side chains and longer

polymer main chains (i.e., increasing aspect ratio; see Table 1).

XRD. Figure 1a shows the thermally reversible X-ray pattern of **1b** (heating curve). At ambient temperature two sets of peaks are detected.^{11c} The first set ($2\theta = 3.48^{\circ}$, 6.96° , 10.40° , 13.92° , and 17.43° , $\text{CuK}\alpha$ radiation) is consistent with an interlayer spacing of 25.5 \AA . This

distance represents the separation of the polymer main chains by the dodecyl groups.^{11c} The monomeric unit with fully extended lateral dodecyl groups would give a *d*-spacing of approximately 36 Å according to simple geometric considerations. The assumption of a decreased angle between the side chains and the main chain will lead to the reduced *d*-spacing. The remaining broad peaks at $2\theta > 15^\circ$, dominated by a feature at $\sim 4^\circ$, reflect the aromatic π - π -stacking of the polymer rods in a boardlike, sanidic^{11c,12a} fashion. Upon heating, the overall intensity decreases and the peaks broaden. The interlayer spacing increases to 27.1 Å (120 °C) and a second phase with a larger *d*- or interlayer spacing of 28.3 Å appears. At 130 °C only the second phase is observed. PPE **1b** is an isotropic liquid at 140 °C. The temperature dependence of the *d*-spacing in **1b** is readily explained by the increased movement of the soft dodecyl chains at enhanced temperatures. Figure 1b shows the (fully reversible) X-ray diffraction pattern of **1c**. The diffraction pattern of **1c** at ambient temperature exhibits a prominent series of Bragg peaks consistent with an interlayer spacing of 12.4 Å and several broad peaks at $2\theta > 15^\circ$, again dominated by a feature at $\sim 4^\circ$. The distance between polymer main chains must be 12.4 Å if slightly interdigitated ethylhexyl side groups (fully extended side chains ca. 18 Å) are assumed, while the 4 Å distance reflects the aromatic π - π -stacking of the polymer rods. Ordering in the third dimension cannot be inferred from the diffraction data.^{11c} The thermal behavior of **1c** is also similar to that of **1b**; however, the change of the interlayer spacing as a function of temperature is much smaller (12.5 Å at 150 °C, $\Delta d = 0.1$ Å) and no second phase is detected upon heating. Above 155 °C the material appears isotropic. The two phases of **1c** observed by DSC therefore must be quite close in structure, due to their indiscernible diffraction patterns.

The complete reversibility of the thermal properties of the PPEs is of importance. It shows that (a) no cross-linking occurs during the heating cycles, i.e., the PPEs are stable at the employed conditions, and (b) the reversibility should allow orientation of the LC phase by a strong field or simple rubbing, while it forms during cooling of the isotropic melt. This is of relevance for any application of PPEs such as for polarized emission.

Polarizing Optical Microscopy. A thin film of **1b** corroborates that this polymer is completely isotropic (black) under crossed polarizers above 145 °C. Upon cooling to 130 °C, coexisting isotropic and birefringent domains are observed. These domains transform at 105 °C into a fully developed Schlieren texture (Figure 2a), confirming the transition observed in the DSC.^{12b} The texture does not change any further when cooling the sample to ambient temperature and is characteristic of a nematic phase. In some samples of **1b** we find Maltese crosses,^{12b} transforming into banded textures by annealing^{12b} which are characteristic of lamellar-nematic or sanidic phases (Figure 2b).¹³ Sanidic phases are boardlike phases of rigid-rod polymers investigated by Ringsdorf and Voigt-Martin.¹² At temperatures between 90 and 130 °C, **1b** is a birefringent fluid that can be sheared. Polarizing microscopy reveals that **1c** forms an isotropic melt above 160 °C which upon cooling gives rise to a Schlieren texture^{12b} (similar to the one observed in **1b** shown in Figure 2a) or to crossed and annealed batons (Figure 2c). If a thin film of **1c** is produced by shearing an isotropic drop of polymer with a cold glass

slide, the flower-like texture shown in Figure 2d forms. The striations found in these preparations are uniformly 1.4 μm apart and corroborate a lamellar ordering in these phases.^{11c} The other examined PPEs (see Table 1) exhibit Schlieren textures, analogous to those observed for **1b**, which points strongly to the occurrence of a nematic phase in these polymers. An exception is the highly branched **1f**, which forms batons^{12b} similar to **1c**. Its neohexyl group improves solid-state packing and thus gives rise to a much higher clearing point. The clearing temperature of the PPEs decreases generally with increasing side-chain length and branching. The statistic PPE copolymer **1e** with hexyl and dodecyl side chains displays behavior similar to the nonyl-substituted **1d**. The herein-described trends are expected and are in accord with the thermotropic behavior of other rigid-rod polymeric LCs.

The occurrence of Bragg peaks in both **1b** and **1c** almost certainly excludes a purely nematic¹³ phase in which only the observation of a broad feature ("nematic streak")¹⁴ in the X-ray patterns would be expected. In the hitherto known thermotropic conjugated polymers such as Wegner's PPPs,⁶ Yu's PPVs,⁹ the organometallic (phenyleneethynylene)cyclobutadienylene copolymers,^{15a} and the polythiophenes^{8,9,16} textures and X-ray powder data suggest the formation of nematic phases. Alkyl-substituted PPEs are different. While we *do* observe nematic Schlieren textures, the birefringent melt of **1c** forms textures (batons, flowers; Figure 2c,d) which point to a higher degree of order in these thermotropic phases, and X-ray powder data strongly support this view. A classic example for this type of order is found in Lieser's wormlike *lyotropic* polydiacylene, which according to electron microscopy forms a highly ordered lamellar phase, but displays nematic textures by polarizing microscopy.¹⁷ Similarly, lyotropic thiophene-ethynylene-cyclobutadiene copolymers display brushlike textures reminiscent of the ones shown in Figure 2d.^{15b} The thermotropic PPEs **1** have to be put into perspective with respect to morphologies of the known conjugated polymers. By comparison of PPEs with the other conjugated LC main-chain polymers and polymeric rigid-rod polyesters,^{12a,c} we infer that our phases are sanidic and show a boardlike lamellar structure. In a low-molecular mesogen this packing behavior would correspond to a smectic A phase.

In conclusion, we have demonstrated by DSC, XRD, and polarizing microscopy that PPEs (**1**) are thermotropic liquid crystalline and we presently attempt to obtain uniaxially aligned samples for application in polarized electroluminescent devices. Electron microscopy and electron diffraction of **1b,c** are currently being investigated and should give a more precise picture of the exact nature and structure of these sanidic phases.^{11c}

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