Simple Spacer-Free Dye-Polyelectrolyte Ionic Complex: Side-Chain Liquid Crystal Order with High and Stable Photoinduced Birefringence

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Azo-containing polymer materials are of immense interest for their potential in various optical and optoelectronic applications, and a host of them have been synthesized and investigated.[1] One of the simplest and least expensive means to obtain such materials is by mixing available azo dyes in common polymers.[1,2] To achieve high loading of the dye molecules without phase separation, as is essential for many applications, recourse is made to strong noncovalent[1,3] or synthetically more onerous covalent[1–3] bonding of the dye to the polymer. The former has the advantage that the materials are relatively easily assembled from readily available components;[3,4] e.g., the ionic complex formed from poly(styrene sulfonic acid) and disperse red 1 (DR1) via proton transfer.[3a] This dye, like many others, is rod-shaped. Thus, such motifs are also used as calamitic rigid cores in thermotropic side-chain liquid crystal polymers (SCLCPs).[1,2] Here, we will show that a similar dye/polyelectrolyte ionic complex (1) has liquid crystal (LC) smectic A (SmA) order, despite the absence of flexible spacer and tail; and (2) exhibits high photoinduced birefringence (PIB) that is both temporally and thermally stable.

A side-chain flexible spacer is commonly present in thermotropic SCLCPs, following its pioneering introduction by Finkelmann and coll.[5] It serves to decouple antagonistic tendencies of the polymer backbone and the mesogenic moiety sufficiently to allow LC order to appear.[5,6] However, the first SCLCPs reported in the literature, and occasional later ones, incorporated neither a flexible spacer nor a flexible tail.[7–11] A notable example is poly(4-biphenyl acrylate) (PBA),[9] the first SCLCP with an equilibrium mesophase to have been discovered; the structural model proposed corresponds to what we now identify as a bilayer SmA mesophase. Thermotropic LCs of low molar mass also generally possess one or more flexible moieties in addition to a rigid core. But recent work,[12] including revival of very old work,[12c,13] has emphasized that rigid molecules free of flexible chains can be liquid crystalline. The present contribution will show that ionically complexed side-chain polymers free of flexible spacer and tail can likewise generate liquid crystal order.

Such complexes are part of a large class of supramolecular SCLCPs investigated over the past decade and more, based mainly on hydrogen or ionic bonding of small-molecule amphiphiles or "side chains" (including with azo moieties) to polymers.[14] Almost all such materials to date incorporate a flexible spacer between the polymer backbone and mesogenic core, or otherwise only a flexible side chain (as in polyelectrolyte−surfactant complexes[15]). One exception is

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(2) See for example: (a) Bosshard, Ch.; Sutter, K.; Prêtre, Ph.; Hulliger, J.; Flörsheimer, M.; Kaatz, P.; Günter, P. , Eds.; *Organic Nonlinear Optical Materials*; Gordon and Breach: New York, 1995. (b) Marks, T. J.; Ratner, M. A. *Angew. Chem., Int. Ed.* **1995**, *34*, 155. (c) Todorov, T.; Nikolova, L.; Tomova, N. *Appl. Opt.* **1984**, *23*, 4309.

(3) See for example: (a) Priimagi, A.; Cattaneo, S.; Ras, R. H. A.; Valkama, S.; Ikkala, O.; Kauranen, M. *Chem. Mater.* **2005**, *17*, 5798, (b) Vishalakshi, B. *J. Polym. Sci., Part A: Polym. Chem.* **1995**, *33*, 365. (c) Buruiana, T.; Buruiana, E. C.; Airinei, A.; Greco, I. *Eur. Polym. J.* **2001**, *37*, 343. (d) Stumpe, J.; Goldenberg, L.; Kulikovska, O. E.C. Patent Appl. EP20040020997, 2006.

(4) In terms of ease of synthesis, mention may be made as well of the ionic self-assembly of charged azo-dyes with oppositely charged small molecules (generally with flexible alkyl chains present), some of which also show LC behavior along with high dichroic ratios: (a) Zakrevskyy, Y.; Stumpe, J.; Faul, C. F. J. *Adv. Mater.* **2006**, *18*, 2133. (b) Zakrevskyy, Y.; Stumpe, J.; Smarsly, B.; Faul, C. F. J. *Phys. Rev. E* **2007**, *75*, 031703.

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(11) It has long been known that a sufficiently long flexible tail in the side chain can also allow LC order to appear, as observed for comb polymers having simple alkyl side chains. Platé, N. A.;Shibaev, V. P. *J. Polym. Sci., Macromol. Rev.* **1974**, *8*, 117. Furthermore, many early SCLCPs consist of directly attached side-chain rigid groups with long alkyl chains (see, for example, refs 7–10).

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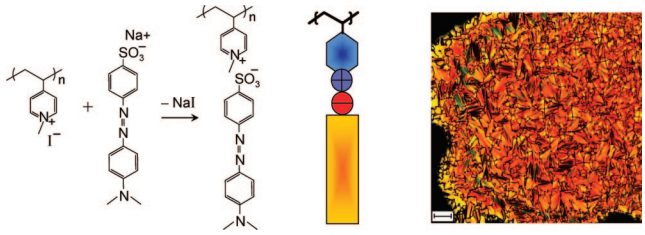

Figure 1. Left, "synthesis" of the supramolecular ionic complex of methylated P4VP (P4VPMe) and methyl orange (MO). Center, schematic representation of the complex. Right, polarizing optical micrograph of a solution-cast film of the MO/P4VPMe complex (scale bar: 2 μm).

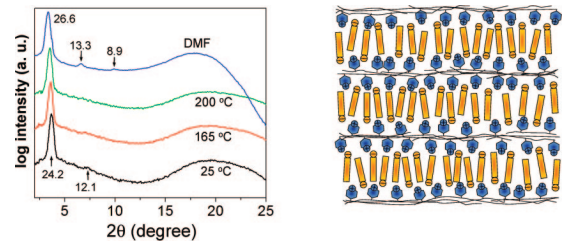

Figure 2. Left, X-ray diffractograms of the MO/P4VPMe complex at the temperatures indicated, and at room temperature in concentrated DMF solution (ca. 60 wt %), with Bragg spacings given in angstroms. Right, possible molecular packing model for the MO/P4VPMe complex.

an H-bonded complex of phenol derivatives (e.g., 4′-methoxy-4-hydroxyazobenzene) with a random copolymer of 4-vinyl pyridine and butyl acrylate, reported to be nematic.[16] However, the use of a copolymer with a flexible counit and the thermal lability of the H-bond make this system less rigid than what can be expected from equimolar ionic complexation to a homopolymer.[17]

Specifically, we study the ionic complex, obtained by ion-exchange procedures,[18] of methyl orange (MO) to methylated poly(4-vinylpyridine) (P4VPMe) (Figure 1). MO is a commercially available azo-containing rod-shaped dye possessing a terminal anionic group, no flexible spacer, and a short bulky tail, while commercially available P4VP is easily quaternized. Energy-dispersive analysis of the complex indicated the absence of Na and I ions; NMR in DMSO-d_6 and elemental analysis indicated 100% complexation.[18]

The dried MO/P4VPMe complex is essentially intractable up to high temperature, becoming liquidlike with almost simultaneous onset of degradation at ca. 240 °C according to thermogravimetric analysis and differential scanning calorimetry (DSC).[18] In polarized optical microscopy (POM), the initially opaque powder momentarily shows strong birefringence as it liquefies, suggesting anisotropy before degradation (after which it is permanently isotropic). These properties resemble what was described for PBA, except that the latter has a reversible SmA−isotropic transition near 270 °C.[9] To obtain an identifiable POM texture, we prepared a thin film by solvent-casting from DMF.[18] As shown in Figure 1, this provides a well-defined focal-conic and fan-shaped texture, stable up to degradation, that is typical for LC order like SmA.

X-ray diffraction (XRD) provides direct information on the molecular packing structure (Figure 2). The ambient-temperature diffractogram of the complex shows, at wide angles, a broad halo and, at low angles, a sharp first-order reflection, for a Bragg spacing of 24.2 Å, accompanied by a much weaker reflection corresponding to 12.1 Å. The 2:1 ratio suggests lamellar order. Its periodicity is comparable to a single molecular length of the MO/4VPMe repeat unit. This data is consistent with a single-layer or a fully interdigitated bilayer SmA structure. The XRD pattern, and hence molecular packing, is invariant up to degradation.

The SmA structure is indirectly confirmed by the XRD of a DMF solution of the complex (ca. 60 wt %), where a third diffraction order is visible (Figure 2). The somewhat larger lamellar thickness (26.6 Å) compared to the dried sample is consistent with swelling by DMF. It may be argued that the LC structure in the dried film is nonequilibrium, frozen in from the lyotropic state. Because of quasi-simultaneous isotropization and degradation, this cannot be ruled out; however, the similarity in molecular architecture and properties to PBA, which is a thermotropic LC, argues for the present complex having an equilibrium LC structure. Surfactant/polyelectrolyte complexes involving sulfonate groups also typically exhibit LC order up to degradation.[15]

A structural packing model for the complex mesophase is illustrated in Figure 2. The fully interdigitated bilayer structure, with laterally alternating oppositely charged ionic groups, permits efficient packing of the MO molecules while accommodating the complexed polymer backbones that tend to meander two-dimensionally between the MO subplanes. Because MO itself is crystalline up to degradation, the disordered LC state of the complex mesophase must be attributed to the constraints on the MO packing imposed by the 4VPMe counterions combined with their (atactic) polymer chain connectivity.

Photoinduced birefringence (PIB) curves of a spin-coated MO/P4VPMe film in N_2 atmosphere[18] are shown in Figure 3. Application of a 488 nm Ar writing laser (1 W/cm^2 power) for 10 s at room temperature gives a PIB value of about 0.18.[18,19] The saturation value was determined to be 0.31.[18] After removal of the 10 s excitation, there is very little thermal relaxation (about 5%, mainly within the first 10 s). The curves obtained at 70 (not shown) and 100 °C are

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(18) See the Supporting Information for details.

(19) A thermal cis−trans relaxation rate of 0.4 s^{-1} was determined for this system, orders of magnitude faster than typical rates for other MO-based azo dyes: Barrett, C.; Natansohn, A.; Rochon, P. *Chem. Mater.* **1995**, *7*, 899 and ref 3c. This suggests that the ionic interactions alter the electronic structure of the chromophore significantly.

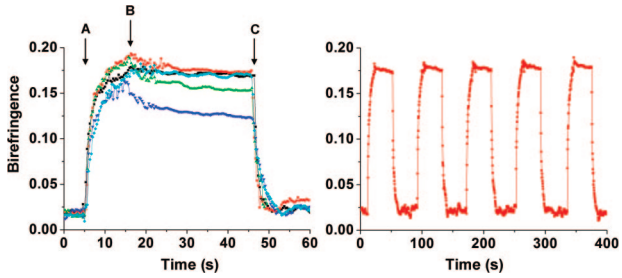

Figure 3. Photoinduced birefringence (PIB) in a spin-coated film (200 nm thick) of the MO/P4VPMe complex. Left, PIB curves (A, write ON 10 s; B, write OFF 30 s; C, erasure ON) taken at the same spot in the order: black, freshly prepared film at 20 °C; red, 100 °C; green, 150 °C; blue, 180 °C; cyan, cooled back to 30 °C. Right, multiple write-erase cycles (25 °C; write ON 10 s, write OFF 30 s, erase ON 30 s, erase OFF 10 s); only the first five of eight identical cycles are shown.

essentially identical, giving enhanced PIB values that approach 0.20 after 10 s of writing; relaxation after cessation of writing reaches the same plateau value of 0.17 as at room temperature. At 150 °C, the 10 s PIB still approaches 0.20, but after removal of the laser there is noticeably more relaxation that, however, stabilizes at above 0.15. It is only at 180 °C that a decrease in the 10 s PIB is observed, followed by relaxation over the entire 30 s off period; nevertheless, the end PIB value remains quite high at 0.12. These observations are reversible on cooling, as illustrated in Figure 3 by the curve obtained at 30 °C. In addition, at all temperatures the PIB can be completely removed by optical erasure within a few seconds. The sequence of write−erase cycles shown in Figure 3 indicates excellent reproducibility with no degradation of signal. The above performance may be attributed to the absence of flexible components combined with the ionic character of the complex, giving a quite rigid (and therefore high Tg) material, as well as to the high dye content and possibly the LC order.[1a] It is also worth mentioning that it is possible to inscribe a surface relief grating (SRG) on a film of this complex.[18]

At comparable exposure doses,[20] previously studied amorphous azo polymers generally give much lower PIB values than the present complex.[21,22] However, higher values, similar to ours or less, are obtained when the azo group is attached to the polymer backbone via a rigid moiety (attributed to a high T_g)[23] or when the polymer is semicrystalline.[21b] SCLCPs using highly anisotropic azotolane moieties can also provide high PIBs.[24,25] However, none of these polymers have the advantage of relatively easy synthesis and preparation. In some cases, little or no relaxation occurs after cessation of excitation,[21b,26] but good performance is not maintained at the high temperatures observed for the MO/P4VPMe complex (in the cases where this was investigated). Just recently, Priimagi et al. showed that H-bonding of DR1 to polymers also enhances PIB values and stability, but again much less than in the present ionic complex.[27]

In summary, we have shown that ionic complexation of crystalline MO to amorphous P4VPMe generates a solid material with smectic A order stable to degradation. This is the first published example, to our knowledge, of an ionically complexed side-chain polymer free of flexible spacer and tail that shows LC order.[28] It provides exceptionally high and reversibly erasable PIB with excellent temporal and thermal stability, competitive with if not superior to those of the best (all-covalent) azo polymers reported to date, yet much simpler to synthesize.[3,4] The properties can be easily tailored and optimized, in particular through choice and ratio of chromophore(s) and (co)polymer.

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Supporting Information Available: Synthetic, complexation, and preparation procedures; instrumentation used; characterization data (elemental analysis, NMR, UV−vis, TGA, DSC); saturation PIB curve; SRG image; additional comments (pdf). This material is available free of charge via the Internet at http://pubs.acs.org.

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(20) The PIB depends on the exposure dose (power of writing laser multiplied by writing time) and the intrinsic response of the chromophore at the writing wavelength used (photoisomerization quantum yield, cis−trans isomerization rate, etc.). Thus, comparisons possible depend on the information available and, in some cases, are extrapolated. A high exposure dose may also cause irreversible changes in the exposed region that affect potential relaxation processes.

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