Notes

Head-to-Tail Dipolar Chromophore Assemblies: Synthesis and Enhanced Electric Field Induced Orientation of Oligomers Larger Than Dimer

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Received April 11, 1990;
Revised Manuscript Received July 19, 1990

Introduction

Amorphous polymers containing electric field oriented dipolar chromophores embedded in a glassy matrix constitute a leading class of second-order nonlinear optical materials.[1] Structure–activity relationships have been elucidated for relevant molecular quantities of the chromophores, including the second-order susceptibility β and the $\beta \times \mu$ product,[2] and means have been developed for achieving the thermodynamically allowed orientation of the chromophores as solutes in polymer matrices by application of high electric fields.[3] Current research is focused on ensuring the long-term stability of the orientation in these materials[4] and increasing the effective dipole moments of the active components through molecular assembly.[5]

Incorporating the chromophores in the matrices as head-to-tail oligomers may lead to increases in both the stability and magnitude of the polar directionality. It has been suggested that even a 10–20% increase in length of the molecule containing the chromophore may decrease the randomization rate of the solute molecule severalfold after poling.[6] Oligomerization would result in an increase in molecular length which might lead to far greater orientational stability, without diluting the chromophores with large, optically inactive substituents. Head-to-tail assembly would also increase orientability because of the cumulative dipole moment on which the electric field would operate. The enhancement in bulk $\chi^{(2)}$ due to this effect is approximately a factor of $n\langle\cos\theta\rangle^2$, where n is the degree of oligomerization and $\langle\cos\theta\rangle$ is the average cosine of the angles of the chromophore moments with the overall oligomer chain direction, assuming equilibrium is reached with the field.[7]

We have already reported[8] the synthesis of dimers and of oligomeric mixtures ($M_w \approx 2000$) of chromophores of general structures **1a** and **1b**. The piperazine linking groups in these compounds provide an electron-donating amino substituent as well as a means of enforcing a 110° segment-to-segment angle, as demonstrated by molecular models and X-ray structure determination of a representative fragment. It was also shown that the dipole moments of the dimers are predicted by the geometrical relationship between the segments. The maximum projected enhancement of $\chi^{(2)}$ in a polymer doped with these dimers relative to equivalent monomeric chromophores is a factor of 1.4. If the relative geometry of the overall chain and the individual segments remains constant in larger oligomers, the enhancements will rise in proportion to the lengths of the oligomers; for example, the enhancement for a tetramer would be a factor of 2.8. However, it could not be assumed a priori that oligomers of structure **1a** would necessarily meet this geometric criterion, since multiple rotations about the single bonds flanking the vinyl groups can bring about doubled-back or nonextended conformations which need not be considered in the case of dimers. It was not possible to check the higher oligomers discussed previously for dipole moment additivity because of their insolubility in sufficiently nonpolar solvents.

Herein we describe the synthesis and isolation of oligomers **1a** with narrow length distributions intermediate between the dimers and dodecamers previously prepared. A solution-phase dielectric characterization and a poling experiment on a tetrameric fraction were performed. Determinations of $\beta \times \mu$ for the monomeric unit and electroptic coefficients and birefringences of the tetramer poled in poly(methyl methacrylate) are also reported and compared with data from azo dye–methacrylate mixtures.

Results

We previously demonstrated the preparation of head-to-tail-linked dipolar oligomers from bifunctional chromophores.[8] However, these oligomers are somewhat intractable and could not be properly characterized. We therefore prepared smaller oligomers in order to evaluate the conformational changes and dipole moment additivities in this system as a function of length.

As a first step toward the preparation of the oligomers, the bifunctional chromophore **6** was synthesized. The diphenylazo analogue had previously been prepared,[8b] but the simple phenyl derivatives lent themselves better to characterization. The synthesis required several steps (Scheme I), but **6** could be prepared in large quantities with an overall yield of 46% from **2**.

Preparation of oligomer fractions with narrow molecular weight distributions involved reaction of the monofunctional chromophores **7** and **8** with varying amounts of **6** in refluxing ethanol with piperidine as catalyst. The oligomers were characterized by GPC on a μ-Spherogel column (500 Å), referenced to polystyrene and to dimers of similar chemical structure and known molecular weights. Although they were not completely resolved, individual peaks were observed for each oligomer of chain length 2–8. All batches contained a substantial fraction of dimer, identified as predominantly **9** by NMR. The GPC traces for the batches prepared with 1 and 2 equiv of **6** were similar, with dimer, trimer, and tetramer fractions in each. Material prepared with 6 equiv showed peaks for each possible chain length up to 8. By means of differential solubilities in EtOH and CH_2Cl_2, we were able to separate the dimeric materials and fractionate the higher molecular weight materials (see Experimental Section). In this manner, trimer–tetramer, pentamer–hexamer, and heptamer–octamer fractions were obtained. The 3–4 unit length material was subjected to additional fractionation to give a product substantially enriched in tetrameric chromophores, with only 5% by weight consisting of molecules less than 3 or more than 5 units long. The NMR spectrum of this material showed proton signals for nitro- and aldehyde-terminated oligomers in a 1:1 mole

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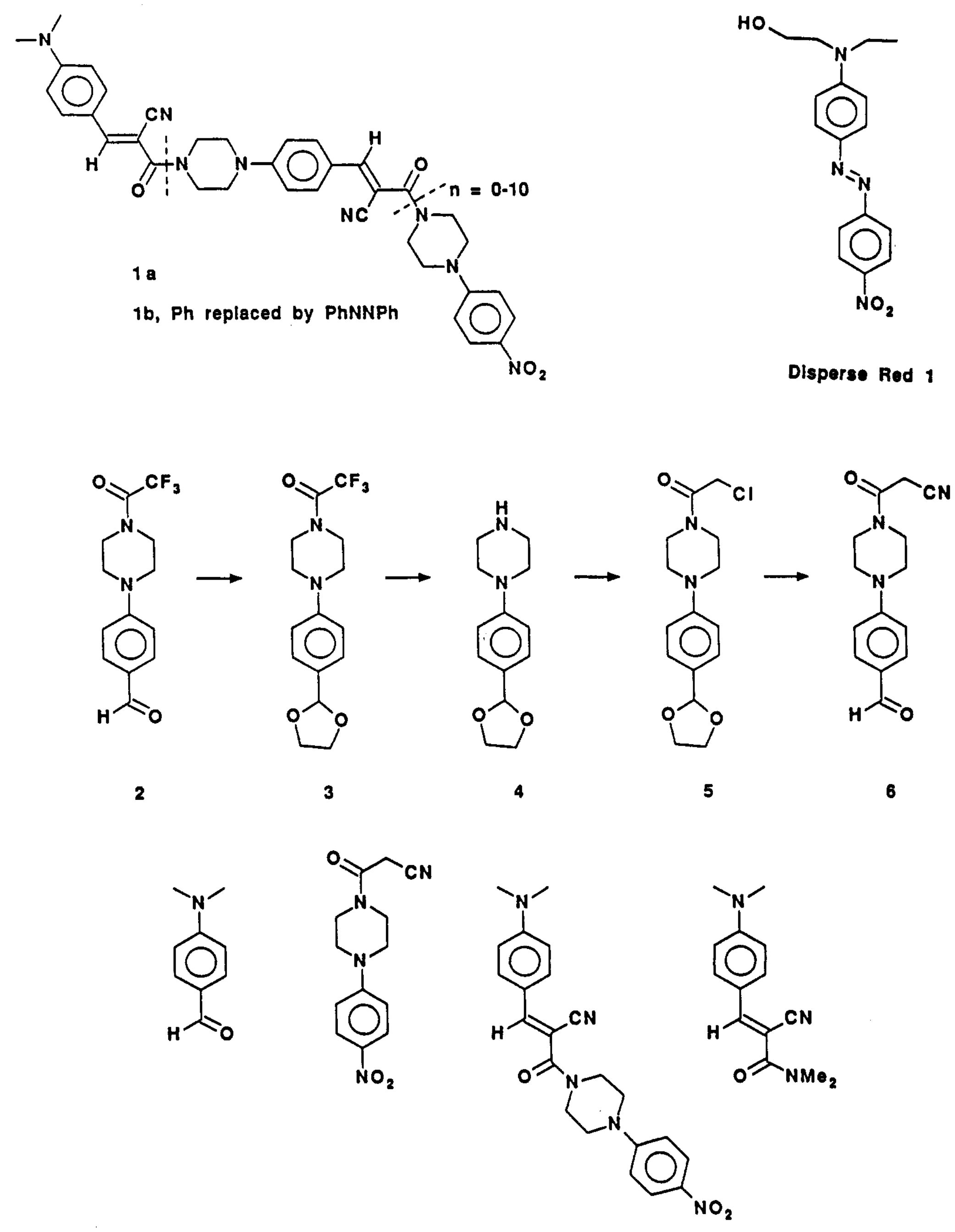
Scheme I



1a

2 3 4 5 6

7 8 9 10

ratio and otherwise was consistent with the postulated structure **1a**, with peaks like those for analogues previously reported[8] and indicating no significant impurities. This material was used for dipole moment determinations.

Dielectric measurements in chloroform, assuming a tetrameric structure (MW = 880) over a concentration range from 1.6×10^{-3} to 7.3×10^{-4} M, gave a dipole moment of 16.6 ± 1 D. A 10 wt % sample of the tetramer in poly(methyl methacrylate) (PMMA) with an isotropic refractive index of 1.495 was poled[9] as a 2-μm film on aluminized silicon with either a gold or aluminum top electrode at 120 °C in a field of 1 MV/cm. The poled film had an electrooptic coefficient of 0.6 pm/V and a birefringence of 0.006. Both of these values decayed to 45% of their original magnitudes after 9 weeks at ambient temperature. The molecular hyperpolarizability β of a model for the repeating unit of the oligomers, **10**, was determined by electric field induced second-harmonic generation[2] to be $(13 \pm 4) \times 10^{-30}$ cm^5/esu at 1.356 μm in dioxane.

Discussion

The solution dipole moment of the tetramer may be evaluated in light of the orientational dielectric polarization expected from the same four chromophores as an ensemble of unconnected monomers. The effective dipole moment calculated from the polarization of this ensemble equals the square root of the sum of the squares of the four individual dipole moments[10] (μ of **10** = 5.1 D, μ of the nitroaniline group $\approx$ 7 D), in this case ca. 11 D. Thus, the value measured for the tetramer, 16.6 D, represents a significant enhancement, which could only be observed if the desired extended conformation of the chromophores that is enforced in the dimer is maintained in the longer oligomer as well. The tetramer dipole moment corresponds to the four chromophores adding their moments as vectors with an average segment-to-segment angle of 100°, only slightly less than the enforced angle in the dimer. Therefore, undesired doubled-back conformations in the tetramer, which would be resistant to electric field alignment, are disfavored relative to the useful, extended conformers in $CHCl_3$ solution.

The electrooptic coefficient may be compared to that of a 10% Disperse Red 1 film treated similarly, in which a coefficient of 3 pm/V was obtained.[11] Assuming r is proportional to $\beta \times \mu$ and to concentration, with $\beta \times \mu$ taken to be 1100×10^{-30} cm^5 D/esu for the azo dye[2] at 1.356 μm and correcting for dispersion and refractive index dependencies,[12] an approximate $\beta \times \mu$ of 500×10^{-30} cm^5 D/esu may be calculated for the tetramer. If the sum of the $\beta \times \mu$ values for the four segments of the tetramer is ca. 300×10^{-30} cm^5 D/esu ($5.1 \times 13 \approx 70$ for each amidic chromophore and 140 for the nitroaniline, half the tetramers being nitro terminated), then r is enhanced in the tetramer film by a factor of 1.6 versus a hypothetical film of analogous monomers at the same total chromophore concentration. The birefringence of the Disperse Red 1 film was 0.003, half that of the tetramer film, even though the linear polarizabilities[2] of the single-ring chromophores used here are comparable to or less than those of azo dyes on a weight basis.

From these data, it may be concluded that the tetramer is in a somewhat extended, polable conformation in the polymer film, though not as extended as in $CHCl_3$ solution. However, the errors inherent in the electrooptic measurement and in converting from r-derived β's to β's obtained from second-harmonic measurements do not allow for a rigorous evaluation of the enhancement due to oligomerization. Poling-induced conformational extension could have increased the effective dipole moment in the polymer above what was measured in solution, and intramolecular wraparound or aggregation caused by phase incompatibility might have lowered that quantity. The lowering of the effective $\beta \times \mu$ product in the oligomers due to the negative contribution of the amide moments and the possible lack of coincidence of the principal β vector with μ are also omitted from the present approximation.

The decay in orientational order in the tetramer-polymer sample was less than in what is generally observed for smaller azo dyes, which lose 70–80% of their alignment in 1–2 months.[3] Thus, even in an oligomer of modest length, a stability advantage is observed, without diluting the chromophores with inactive lengthening groups.

Conclusion

It is possible to synthesize and manipulate size-selected fractions of oligomeric mixtures of rigid, dipolar chromophores. These oligomers display significant dipole moment additivity in solution and in polymer films, as evidenced by enhanced electric field induced orientation. While the specific compounds discussed here are insufficiently hyperpolarizable for direct use in nonlinear optical devices, the general strategy of increasing the stability and orientational order of poled materials by incorporating head-to-tail-linked dipolar moieties might still be considered when fabricating thin films of chromophores with higher β values or in cases where birefringence is the quantity to be optimized.

Experimental Section

1-(4-(2-Dioxolanyl)phenyl)piperazine (4). Compound **2**[8a] (5 g, 0.0175 mol) was heated in 200 mL of benzene with ethylene glycol (1.6 g, 0.026 mol) and pyridinium hydrochloride (0.8 g) with very slow distillation of solvents into a Dean–Stark trap. After 30 h, the solution was washed with 50 mL of concentrated aqueous $NaHCO_3$ and concentrated to yield 5.5 g (95%) of **3**, indistinguishable from **2** by TLC. ^1H NMR ($CDCl_3$) δ 3.25 (m, 4 H, CH_2N), 3.78 (m, 2 H, CH_2N), 3.83 (m, 2 H, CH_2N), 4.00 (t, 2 H, CH_2O), 4.10 (t, 2 H, CH_2O), 5.74 (s, 1 H, CH), 6.91 (d, 2 H, ArH), 7.42 (d, 2 H, ArH).

This was heated at reflux with stirring in 100 mL of EtOH, 50 mL of 2% NaOH in H_2O, and 5 mL of toluene. The solution was concentrated to give a white solid, which was washed successively with 50 mL each of H_2O and Et_2O. Yield: 2.6 g (67%) of **4**; ^1H NMR ($CDCl_3$) δ 3.08 (m, 4 H, CH_2N), 3.25 (m, 4 H, CH_2N), 4.09 (t, 2 H, CH_2O), 4.68 (t, 2 H, CH_2O), 5.83 (s, 1 H, CHO), 6.97 (d, 2 H, ArH), 7.41 (d, 2 H, ArH); mass spectrum (relative intensity) 234 (65, M^+), 192 (100). The analytical sample was further triturated with H_2O and extracted into CH_2Cl_2. Anal. Calcd for $C_{13}H_{18}N_2O_2$: C, 66.64; H, 7.74; N, 11.96. Found: C, 65.29; H, 7.14; N, 11.88. Despite the slightly low C and H values, no contamination was apparent by NMR or MS.

1-(4-(2-Dioxolanyl)phenyl)-4-(2-chloroacetyl)piperazine (5). Chloroacetyl chloride (Aldrich, 4.86 g, 0.043 mol) in CH_2Cl_2 (50 mL) was added dropwise over 30 min to a solution of **4** (10 g, 0.043 mol) and triethylamine (4.34 g, 0.043 mol) in 200 mL of CH_2Cl_2 cooled to 0 °C. After stirring for an additional 2 h, the reaction mixture was washed with aqueous sodium bicarbonate and with H_2O, and the organic layer was dried over Na_2SO_4, filtered, and evaporated to give **5** (yield: 13 g, 98%). ^1H NMR ($CDCl_3$) δ 3.22 (m, 2 H, CH_2N), 4.04 (t, 2 H, CH_2O), 4.12 (s, 2 H, CH_2Cl; t, 2 H, CH_2O), 5.78 (s, 1 H, CHO), 6.90 (d, 2 H, ArH), 7.39 (d, 2 H, ArH).

(4-(Cyanoacetyl)piperazinyl)benzaldehyde (6). Acetal **5** (13 g, 0.042 mol) was dissolved in 200 mL of CH_2Cl_2, and the solution was cooled to 0 °C. Tetrabutylammonium cyanide (22.5 g, 0.084 mol) in 50 mL of CH_2Cl_2 was added dropwise over 30 min, and the mixture was stirred at room temperature an additional 3 h. Water was added and the mixture was washed with aqueous HCl until the H_2O layer was at pH 6, thereby deprotecting the aldehyde functional group. The layers were separated, and the organic phase was dried over Na_2SO_4 and evaporated. After column chromatography on silica gel (CH_2Cl_2 eluant), **6** was isolated in 74% yield (8.0 g). ^1H NMR δ 3.50 (m, 2 H, CH_2N), 3.57 (m, 2 H, CH_2N), 3.60 (s, 2 H, CH_2CN), 3.69 (m, 2 H, CH_2N), 3.85 (m, 2 H, CH_2N), 6.94 (d, 2 H, ArH), 7.78 (d, 2 H, ArH), 9.82 (s, 1 H, CHO). A sample of **6** was converted to its dinitrophenylhydrazone in ethanolic HCl and recrystallized from that solvent., Anal. Calcd for $C_{19}H_{19}N_7O_4$: C, 55.75; H, 4.68. Found: C, 55.50; H, 4.41.

Oligomers 1a. One equivalent (0.002 mol) each of **7** and **8** and n (n = 1, 2, 6) equiv of **6** were dissolved in EtOH (25–50 mL), and a drop of piperidine was added. The reaction mixture was stirred at reflux for 2 h, and a yellow precipitate formed either during the heating or after cooling to room temperature, depending on the chain lengths.

The various batches were characterized by GPC on a 500-Å μ-Spherogel column with CH_2Cl_2 as eluant, with molecular weights referenced to polystyrene standards as well as to molecules of similar chemical structure and known molecular weight, such as dimer **9**.

The dimeric fraction was removed from the other oligomers by trituration of the solids with EtOH. Separation of the higher oligomers by chain length was accomplished by repeated dissolution in CH_2Cl_2 followed by precipitation with EtOH. The 1- and 2-equiv batches were combined, and after two purification cycles a material was obtained that was essentially free of dimeric species and was shown by GPC to be "mostly" tetramer. This material was used without further purification for dipole moment measurements.

After removal of the dimer material by EtOH trituration, the "6-equiv" batch was further fractionated by dissolving the solid in hot CH_2Cl_2. Upon cooling to room temperature, a yellow-brown glassy solid separated from the solution. GPC showed this fraction to be mostly octamer, with a small amount heptamer. Addition of $\approx$5% EtOH to the remaining CH_2Cl_2 solution caused precipitation of a yellow solid which GPC showed to be essentially 5- and 6-unit oligomers. Evaporation of the solvents gave a trimer–tetramer fraction.

Dipole moments were obtained by measuring the capacitance of serially diluted chloroform solutions in a cell that has been previously described.[8a] The capacitance measurements for the tetramer were obtained between 1.6×10^{-3} and 7.3×10^{-4} M, and the plot of $d\epsilon$ vs dw (w = solute weight fraction) gave a straight line of slope 83.22 with a correlation coefficient of 0.9891. Birefringence and electrooptic coefficients were obtained from refractive indices measured with a prism coupler in t_m and t_e modes in the presence and absence of applied voltage.

Acknowledgment. We are grateful to M. G. Kuzyk, K. D. Singer, and C. W. Dirk for helpful discussions. We also thank A. M. Mujsce for obtaining the mass spectra and L. Shepherd for the use of a refractometer.

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Registry No. **2**, 122648-76-4; **3**, 131237-07-5; **4**, 131237-08-6; **5**, 131237-09-7; **6**, 131237-10-0; PMMA (homopolymer), 9011-14-7; disperse red 1, 2872-52-8; ethylene glycol, 107-21-1; chloroacetyl chloride, 79-04-9.