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Polymers and Blends Exhibiting Two-Dimensional Asymmetry and Optical Nonlinearity upon Poling by an Electric Field

Electric field poling of polymeric films containing a dipolar chromophore of high hyperpolarizability (β) is a common method for achieving noncentrosymmetric structures, which may be exploited for applications such as second harmonic generation (SHG) and electrooptic modulation.[1-5] Nematic side-chain liquid-crystal polymers (LCP) doped with a high β dye molecule also reveal SHG after poling.[6] If the high β chromophore is not very miscible with the LCP, it could be incorporated by copolymerization of a monomer containing the chromophore with monomers containing the mesogenic group.[7] However, these chromophores generally inhibit the polymerization and cause cross-linking of the macromolecules. A convenient way to obtain high concentrations of the high β group in mesomorphic glasses is the synthesis of photochromic liquid-crystal polymers (PLCP) containing spiropyran units, which do not markedly inhibit polymerization. When UV irradiated or heated, the spiropyran units are converted to a high β-merocyanine dye;[8-10] see Figure 1. In addition, low molecular weight mesogenic molecules containing thermochromic spiropyran units can also form glassy mesomorphic films,[11-13] known as quasi liquid crystals (QLCs), containing marked concentrations of merocyanine groups.

Recently, second harmonic generation of 1064-nm laser light was studied on poled films of QLC and PLCP.[14-16] Homogeneously aligned films on glass substrates were poled by electrostatic fields of 10 kV/cm at elevated temperature (above T_g) followed by cooling and removal of the field. Photochromic films were also UV irradiated simultaneously with the poling.

Poled films whose SHG was examined several days after poling exhibited SHG characteristic of films asymmetric along the poling direction (designated x); i.e., the largest coefficient of second harmonic generation is $\chi^{(2)}_{xxx}$. However, when an electric field of similar strength to that employed during poling was reapplied (at *room temperature*) in the x-direction, these samples showed in addition an asymmetry along the z-direction, such that SHG via the $\chi^{(2)}_{zzz}$ component was the strongest SHG. After the electric field was removed the $\chi^{(2)}_{zzz}$ SHG decayed over about 1 h.

Further detailed studies[15,16] indicated that the "anomalous" asymmetry and SHG in the z-direction could be attributed to aggregates of merocyanine and that their interactions with the nematic matrix and the glass surface are of great importance. In particular, this effect is retained when the glass surface is coated with a homogeneously aligning polymeric layer, such as polyimide, but lost when the surface is coated with poly(methyl methacrylate).[16]

The aggregated molecules constitute molecular stacks, called H-aggregates, with antiparallel molecular dipole arrangements. Due to interactions with the mesogenic units and the substrate, it is believed that individual merocyanine molecules in the stacks are more or less parallel to the mesophase direction, with the stacking axis normal to the substrate surface. Application of the poling field seems to cause some reorientation of individual dipoles within a merocyanine aggregate, resulting in a noncentrosymmetric structure. In order to achieve $\chi^{(2)}_{zzz}$ nonlinearity from these aggregates, we must also postulate[16] charge-transfer asymmetry in the stacking direction (z) brought about by the interaction with the glass substrate.

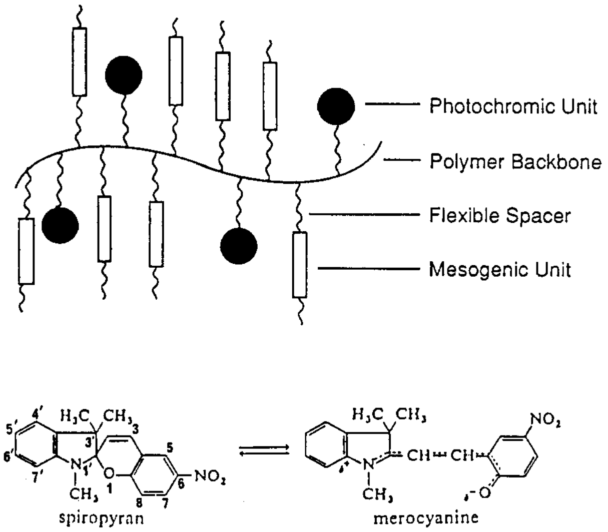

Figure 1. Schematic structure of a photochromic liquid-crystal polymer (PLCP) and spiropyran–merocyanine conversion.

In the present work we expand the systems exhibiting $\chi^{(2)}_{zzz}$ SHG following poling in the x-direction. The systems examined were, according to the above hypothesis, comprised of a nematic host matrix and various high β species, which form dimers or aggregates. We compare this effect for various PLCPs and QLCs alone with the effect observed in the same materials and LCPs doped with additional dichroic dyes. Three main goals were pursued: (i) to demonstrate the generality of this effect for high β dyes, which are prone to form aggregates; (ii) to find systems showing the strongest $\chi^{(2)}_{zzz}$ coefficient; (iii) to find systems in which the $\chi^{(2)}_{zzz}$ SHG signal is not lost rapidly after removal of the electrostatic field.

We have used as our nematic matrix the LCPs, PLCPs, and QLCs shown in Figure 2. Two substituted stilbene derivatives, DANS = 4-(dimethylamino)-4′-nitrostilbene and MBANS = 4-[(4-methoxybenzoyl)oxy]benzylideneamino(p-nitrostilbene), were used as the high β dyes doped in these matrices (see Figure 2). For DANS, $\beta = 4.5 \times 10^{-28}$ esu.[17] DANS was used earlier[6] as a high β guest dopant for SHG in a LCP matrix. This study, as well as new data on DANS fluorescence,[10,18] has suggested that DANS, and therefore MBANS, can aggregate in LCP matrices and will thus represent a good test of our hypothesis that dye aggregates can give rise to SHG via $\chi^{(2)}_{zzz}$.

Syntheses of the QLCs, LCPs, PLCP(1), and PLCP(2) were described earlier.[8,10,12] The acrylic monomer with the 6,8-dinitrospiropyran group, required for the preparation of PLCP(3), was synthesized according to ref 8 by using 2,6-dinitrosalicylaldehyde instead of 6-nitrosalicylaldehyde.

The spiropyran comonomer content in the PLCP(1) and PLCP(2) was 15%. The thermal equilibrium between the spiropyran and merocyanine forms for the dinitrospiropyran in PLCP(3) is shifted toward the merocyanine. In ethanol solution, about 70% of the molecules are converted to the merocyanine.[19] A high proportion of merocyanine in a PLCP leads to very strong aggregation and even phase separation of merocyanine aggregates. This problem was overcome by taking a spiropyran comonomer content of only 5 mol % for PLCP(3), as well as by using a relatively low molecular weight fraction of the polymer.

A commercial sample (Kodak) of DANS was used without further purification. MBANS was synthesized by con-

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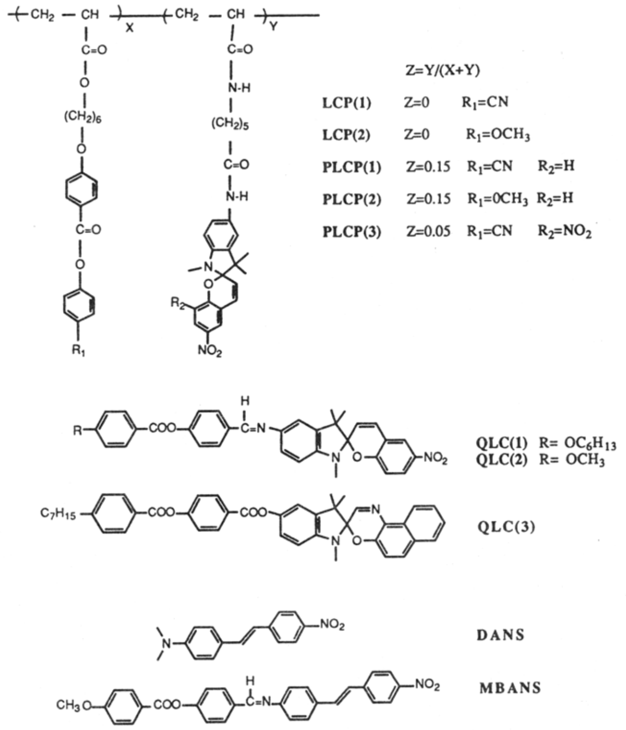

Figure 2. Liquid-crystal polymers (LCP), photochromic liquid-crystal polymers (PLCP), quasi liquid crystals (QLC), and high β dopants (DANS, MBANS) used in this study.

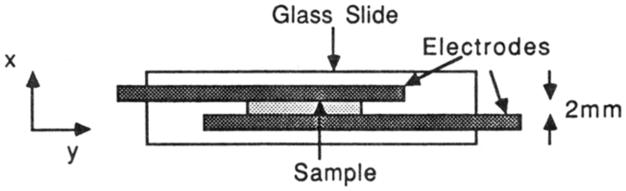

Figure 3. Geometry of samples.

densation of 4-[(4-methoxybenzoyl)oxy]benzaldehyde with 4-amino-4′-nitrostilbene according to ref 12.

Films of 1–2-μm thickness were cast onto glass substrates (containing aluminum electrodes), which had been previously cleaned by boiling in 1:1 THF/hexane. The sample geometry is shown in Figure 3. In the SHG measurements we use a pulsed Nd-YAG laser (1064 nm) as our source.[15,16] The $\chi^{(2)}_{xxx}$ susceptibility component is found by using the input laser polarized parallel to the sample x axis and detecting SHG output of similar polarization. Due to the sample thin-film geometry, excitation by purely z-polarized light is not possible. Thus $\chi^{(2)}_{zzz}$ is measured by using light polarized at 45° in the yz plane, which we achieve by using p-polarized light, and placing the sample xy plane at 45° to the laser beam. It has been verified that the $\chi^{(2)}_{zzz}$ term is responsible for the SHG measured under such conditions by sample rotation, thus changing the components of the polarization along the y and z axes by factors of $\cos\theta$ and $\sin\theta$, respectively. The observed SHG field closely matched the exponentially "damped" $\sin^3\theta$ dependence expected for $\chi^{(2)}_{zzz}$ susceptibility; the damping is caused by increased absorption, scattering, and phase mismatch as the optical path length through the sample increases with θ.[20]

SHG measurements were performed 4 days after the samples were prepared and poled at elevated temperature. We first checked for "permanent" SHG by measuring the SHG in the absence of any DC field (zero-field measurements) and then reapplying a DC field for 10 min at *room temperature*. Results are summarized in Table I.

Table I
Second-Order Susceptibility Coefficients (±20%) of Glassy Mesomorphic Poled Films Measured 4 Days after Preparation and When an Electric Field is Reapplied at Room Temperature

sample, composn	electric field, kV/cm	$\chi^{(2)}_{xxx}$, 10^{-9} esu/cm^3	$\chi^{(2)}_{zzz}$, 10^{-9} esu/cm^3
1. PLCP(1)[a]	10	0.1	0.6
2. PLCP(2)	0	0.07	0.4
	12	0.07	0.7
3. QLC(1)[a]	10	0.3	1.1
4. QLC(3)[a]	12	0.06	0.1
5. QLC(1)–QLC(2), 1:3[a]	10	0.2	2.0
6. QLC(1)–PLCP(1), 1:4[a]	10	0.2	2.0
7. QLC(1)–PLCP(2), 1:4[a]	10	0.2	5.2
	50	2.2	44
8. QLC(1)–PLCP(3), 1:4	0	0.08	4.4
	10	0.3	5.2
9. QLC(3)–PLCP(1), 1:4	0	0.07	0.3
	12	0.08	1.3
10. 2% DANS in QLC(1)–QLC(2), 1:3	0	0.2	0.4
	10	0.4	4.4
11. 2% DANS in QLC(3)[a]	10	1.3	5.2
12. 2% DANS in LCP(1)[a]	10	0.3	2.6
	50	2.3	23
13. 2% DANS in LCP(2)[a]	10	2.9	2.2
14. 2% DANS in PLCP(1)[a]	10	0.2	2.6
15. 2% DANS in PLCP(2)	0	0.2	0.1
	12	0.3	2.5
16. 2% DANS in QLC(1)–PLCP(1), 1:4	0	<0.01	0.2
	10	0.4	6.4
	50	5.8	60
17. 2% DANS in QLC(1)–PLCP(2), 1:4	0	0.2	0.1
	12	1.8	8.0
18. 10% MBANS in QLC(1)	0	0.03	1.5
	10	0.2	2.6
19. 10% MBANS in QLC(3)[a]	10	0.2	2.6

[a] For zero applied field, 4 days after preparation, $\chi^{(2)}_{xxx}$ and $\chi^{(2)}_{zzz} < 5 \times 10^{-11}$ esu. [b] The measurement using a field of 50 kV/cm was performed with the sample immersed in mineral oil.

It is seen from zero-field measurements in Table I that most samples had relatively small "permanent" $\chi^{(2)}$ coefficients. Where they were measurable ($\geq 5 \times 10^{-11}$ esu), we usually found $\chi^{(2)}_{xxx} > \chi^{(2)}_{zzz}$. Two important exceptions (samples 8 and 18 of Table I) showed much larger "permanent" $\chi^{(2)}$ coefficients, with $\chi^{(2)}_{zzz} \gg \chi^{(2)}_{xxx}$.

When the electrostatic field was reapplied, samples exhibited a sharp increase in the "perpendicular" $\chi^{(2)}_{zzz}$ component and a much smaller increase in $\chi^{(2)}_{xxx}$. One sample, 2% DANS in LCP(2), did, however, exhibit $\chi^{(2)}_{xxx} \approx \chi^{(2)}_{zzz}$ when the field was reapplied. We note that LCP(2) forms a *smectic* glass[10] and that our previous study[15] showed that significant differences in nonlinearity can occur between nematic and smectic host matrices presumably because in the latter the mesogenic units tend to acquire homeotropic (perpendicular to the glass surface) alignment.

Comparison of the data measured when a field of 10 kV/cm is reapplied shows that $\chi^{(2)}_{zzz}$ of PLCPs and QLCs alone can be greatly enhanced by blending them together or by doping with DANS or MBANS molecules. The relatively low $\chi^{(2)}_{zzz}$ of PLCPs alone is believed to be due to the fact that the photochromic side groups and the mesogenic domains in PLCPs are partially space separated, resulting in a diminished polar ordering of the merocyanine units in these films. In PLCP–QLC blends, the order parameter of merocyanine is higher than that of PLCP alone,[10,16] which is in accord with our hypothesis of $\chi^{(2)}_{zzz}$ arising from aggregates aligned by the mesogenic domains. Better penetration into the mesogenic domains is also achieved by DANS in PLCPs and QLCs as is also borne out by the order parameters[10,18] and increased $\chi^{(2)}_{zzz}$. We also note the possibility that, in these latter samples, intermolecular DANS–merocyanine interactions could be contributing to the observed nonlinearity, as has been found for Langmuir–Blodgett films of closely related molecules.[21]

Two compositions (samples 8 and 18 in Table I) containing the MBANS molecule or the PLCP with dinitrospiropyran groups showed long-term stability of the $\chi^{(2)}_{zzz}$ SHG. In both of these cases the concentration of the high β moiety was large, which may be an important factor in the long-term stabilization of the nonlinearity.

The nonlinearity increases with the strength of the poling field. We showed earlier that for fields of up to 10 kV/cm the $\chi^{(2)}_{zzz}$ term increased approximately quadratically with the field, while the dependence of $\chi^{(2)}_{xxx}$ was linear. Three samples (7, 12, and 16 in Table I) were poled at both 10 and 50 kV/cm. This 5-fold increase in the field caused a further increase of both $\chi^{(2)}_{zzz}$ and $\chi^{(2)}_{xxx}$ by about a factor of 10 in all three cases.

In conclusion, we have clearly demonstrated that asymmetric ordering both parallel and perpendicular to the poling field is a widespread phenomenon for dye aggregates in nematic matrices. These films therefore exhibit numerous independent nonzero $\chi^{(2)}$ coefficients, which can be an advantage in applications such as phase-matched SHG in thicker films or electrooptic modulation.[16] Blend compositions that further enhance the perpendicular ordering and its stability have also been found, leading to very large $\chi^{(2)}$ coefficients, close to 10^{-7} esu/cm^3.

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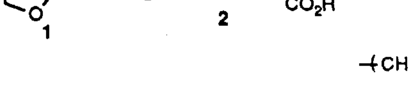
Ring-Opening-Closing Alternating Copolymerization of 2-Phenyl-1,3,2-dioxaphospholane with Muconic Acid

Ring-opening polymerization constitutes an important area in polymerization chemistry, in which various cyclic monomers polymerize via ring opening to produce linear polymers.[1] On the other hand, cyclopolymerization, or ring-forming polymerization, has long been known, in which monomers of a linear structure give polymers of a ring-closed structure.[2] On the basis of a new concept to combine these two modes of polymerization, the present paper reports a novel copolymerization of 2-phenyl-1,3,2-dioxaphospholane (**1**) with *cis,trans*-muconic acid (**2**), where monomers **1** and **2** provide a ring-opened and ring-closed structural unit, respectively, of product copolymer **3** in an alternating arrangement (*ring-opening-closing alternating copolymerization*). During the copolymerization, the phosphorus atom of monomer **1** is oxidized from P(III) to P(V) in **3**, whereas monomer **2** is reduced from unsaturated carbons to saturated carbons in **3** ("oxidation–reduction alternating copolymerization").[3,4]



The reaction of the 1:1 monomer feed ratio proceeded without any added initiator to give an alternating copolymer **3**. A mixture of monomers **1** (0.168 g, 1.0 mmol)

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