

performed on other conjugated polymers have shown complex dependence of the signal intensity on electrode potential sweep rates. Future work will describe the magnetic properties of poly-I and the dependence of its ESR signal on temperature.

### Conclusions

Poly(*N*-3-thenylphthalimide), poly-I, was electrochemically synthesized, and the resulting polymeric films exhibited electrochemical and electrochromic reversibility and enhanced porosity. The bulky electron-withdrawing substituent at the 3-position widens the bandgap and favors the presence of localized charges, which, in turn,

negatively affects the conductivity of the resulting polymer.

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**Registry No.** Poly I (homopolymer), 124605-41-0; I(3-methylthiophene) (copolymer), 124605-40-9.

## Second Harmonic Generation by Merocyanine in Mesomorphic Films. An Anomalous Electrostatic Field Effect

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Poled thin films of merocyanine obtained by photo- or thermochromic conversion of spiropyran incorporated in various mesogenic molecules, including liquid-crystal polymers, quasi-liquid crystals, and blends, exhibit strong second harmonic generation (SHG). As well as the "conventional" SHG deriving from the  $\chi^{(2)}_{xxx}$  component, where  $x$  is the poling direction (in the plane of the film), the films exhibit an even stronger anomalous "perpendicular" SHG via  $\chi^{(2)}_{zzz}$  hyperpolarizability when an electric field in the  $x$  direction is reapplied to the samples at room temperature. It is believed that this anomalous SHG arises from merocyanine aggregates stacked in the  $z$  direction being rotated by the field.

Poling a polymeric film containing dopant chromophore molecules or side-chain groups with high molecular hyperpolarizabilities ( $\beta$ ) has become a widely used strategy for preparation of films with large second-order optical nonlinearity exhibiting properties such as second harmonic generation (SHG) and electrooptic modulation (see refs 1-10 and references therein). The usual method of film preparation involves applying a strong external electrostatic field (up to  $10^6$  V/cm) to a doped film heated to above its glass transition temperature ( $T_g$ ), leading to a preferential alignment of dipolar chromophore groups along the field direction. Cooling to room temperature (below  $T_g$ ) prior to removal of the field enables a "freezing in" of the net polar alignment. In practice, some residual molecular mobility is often retained, leading to a loss of the polar alignment over a period of time (ranging from minutes to months) that depends on both polymer matrix

and chromophore properties.

Second-order nonlinear optical processes such as SHG are described quantitatively by the second-order susceptibility tensor,  $\tilde{\chi}^{(2)}$ . Under the electric dipole approximation, a second-order polarization,  $P^{2\omega}$ , is induced by the incident (optical) electric field  $E^\omega$  according to

$$P^{2\omega}_i = \chi^{(2)}_{ijk} E^\omega_j E^\omega_k \quad (1)$$

The observed second harmonic generation efficiency is proportional to the square of  $P^{2\omega}$ . From symmetry considerations, it is readily apparent from eq 1 that in a centrosymmetric medium all components  $\chi^{(2)}_{ijk} = 0$ . Furthermore, in media symmetric about a plane  $i = 0$  all  $\chi^{(2)}$  components containing the index  $i$  either one or three times must similarly be zero. Thus for the case of a polymer poled in the  $x$  direction as discussed above, the only nonzero components are  $\chi^{(2)}_{xxx}$ ,  $\chi^{(2)}_{xyy} = \chi^{(2)}_{zzz}$ , and  $\chi^{(2)}_{yxy} = \chi^{(2)}_{zzz}$ .

A further property of the  $\tilde{\chi}^{(2)}$  tensor of poled films relates to the dependence of the magnitude of components to the strength of the poling field. In the limit of independent interactions of each molecular species with the poling field, a dipolar chromophore is stabilized by an interaction energy of  $\mu \cdot E = \mu E \cos \theta$ , where  $\theta$  is the angle between the molecular dipole direction and the external field. The equilibrium distribution of  $\theta$  values in the sample is determined by the appropriate Boltzmann factors, noting that usually  $\mu E \ll kT$ . In the most commonly studied case of an optically nonlinear chromophore dominated by a single molecular hyperpolarizability component along the same axis as the dipole moment, it is readily shown that the above nonzero  $\tilde{\chi}^{(2)}$  components of a poled film scale

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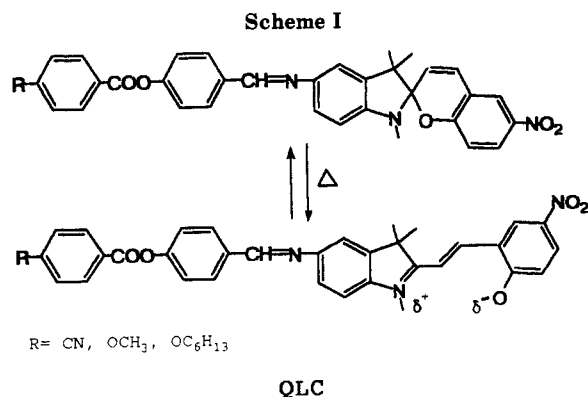
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linearly with the poling field strength, in agreement with experimental results.<sup>2,10</sup>

While nonlinear optical materials based on poled amorphous glassy<sup>1-10</sup> and ferroelectric<sup>11</sup> polymers have been extensively studied and even examined in devices,<sup>12</sup> there have been much fewer publications regarding SHG in poled *liquid-crystal* polymers doped with high- $\beta$  chromophores. The relevant difference between doping an amorphous or LC polymer is the microscopic polymeric host environment felt by the dopant molecule or group. In an amorphous polymer matrix the dopant is found in an isotropic host environment, which is negligibly perturbed by the poling field. Thus simple considerations of isolated dopant dipoles interacting with the poling field have adequately explained experimental observations. On the other hand, a polymeric LC provides a microscopically anisotropic environment even without a poling field and the possibility that applying an electric field causes macroscopic alignment of LC domains.

Meredith et al.<sup>13</sup> measured SHG from nematic liquid-crystal polymer films doped with 4-(dimethylamino)-4'-nitrostilbene aligned in a 6 kV/cm electrostatic field. Poling of the dopant was achieved, as observed via the SHG signals. However, after removal of the poling field, the low  $T_g$  of the polymer led to rather rapid loss of the alignment that could be induced either thermally or by the laser used to perform the SHG measurements.

Another nonlinear optical glassy mesophase containing merocyanine groups of very high hyperpolarizability<sup>14-16</sup> was prepared from spiropyran molecules containing mesogenic groups.<sup>17</sup> These molecules exhibit thermochromic properties associated with the reversible reaction shown in Scheme I.

These compounds form a metastable nematiclike mesophase, known as quasi-liquid crystals (QLCs), upon heating of amorphous films prepared by fast evaporation of benzene solution. Although the equilibrium concentration of merocyanine is low ( $\approx 5\%$ ), the presence of these highly polarizable units plays a major role in stabilizing the QLC state against crystallization. The mesophase occurs well below the melting point of the crystalline spiropyran. QLC films aligned in an electrostatic field ( $>5$

kV/cm) showed enhanced stability, and in glassy supercooled conditions at room temperature their molecular ordering is preserved practically indefinitely.

Detailed studies have indicated that the QLCs represent an intrinsic two-component spiropyran-merocyanine mesophase with properties that are substantially determined by strong interactions between these components, which are in thermal equilibrium with each other.<sup>18</sup>

QLCs that have been aligned in an electrostatic field exhibit optical nonlinearity and SHG in the glassy state due to polar orientation and high hyperpolarizability of merocyanine units. The polar ordering can be enhanced in the glassy state by reapplying the electric field, as manifested by  $\chi^{(2)}$  increasing linearly with the applied field.<sup>19</sup>

The merocyanine content in a QLC film is determined by the thermochromic spiropyran-merocyanine conversion, because unlike many other indolinespiroprans QLCs do not possess photochromic properties.

Recently<sup>20,21</sup> we reported side-chain liquid-crystal polyacrylic copolymers containing spiropyran side groups. These copolymers exhibit both thermo- and photochromic properties (Scheme II). Above  $T_g$  the polymers can be aligned in an electrostatic field, forming an oriented nematic glass on cooling below  $T_g$ . In this article we demonstrate that this provides a means of inducing SHG by photochromic spiropyran-merocyanine conversion and that this effect can be enhanced by blending the polymer with QLCs. We also show here that when an external electrostatic field is applied to the glassy films parallel to the aligning direction, the SHG signal increases not only via the "usual"  $\chi^{(2)}_{xxx}$  component (parallel to the field) but also via a very strong term  $\chi^{(2)}_{zzz}$  perpendicular to the film plane. Investigations of this anomalous effect are also described.

## Experimental Section

**Materials.** Photochromic liquid-crystal polyacrylate depicted in Scheme II with  $n = 5$  (denoted below by PLCP) containing  $\approx 20\%$  of spiropyran comonomer ( $x:y = 1:4$ ) was prepared by free-radical copolymerization in 3:1 toluene-THF solution,<sup>21</sup>  $\bar{M}_w \approx 2.5 \times 10^4$ . Polyacrylonitrile, containing  $\approx 20\%$  of the same spiropyran monomer (Sp-PAN) was prepared by a similar procedure. Quasi-liquid crystals with R = C<sub>6</sub>H<sub>13</sub>O- and CH<sub>3</sub>O- (denoted by QLC(1) and QLC(2)) were synthesized as described elsewhere.<sup>22</sup> A conventional low molecular weight liquid crystal, 4-(cyanophenyl) 4-heptylbenzoate (denoted by ILC), was purchased from Aldrich.

**Film Preparation.** Preparation of polymer and QLC films and their alignment in an electric field have been described previously.<sup>20,22</sup> Films of PLCP and QLC blends for SHG measurements were prepared by casting from benzene-THF solution (2:1) onto a hot ( $\approx 80^\circ\text{C}$ ) glass slide, onto which parallel thin-film aluminum electrodes had been deposited 2 mm apart. The films were dried in vacuum at  $45^\circ\text{C}$  for 2 h. After alignment in an electrostatic field of  $\approx 10$  kV/cm at a temperature above  $T_g$  but below the clearing point ( $T_c$ ) the films were cooled to room temperature in the field with simultaneous UV irradiation. This procedure gave aligned films of 1-2- $\mu\text{m}$  thickness and a deep red color. This color slowly faded over 1-2 weeks. Films more than 2 weeks old were thus designated as "old".

The spiropyran-acrylonitrile copolymer (Sp-PAN) films were prepared in a similar way, although no matrix alignment in the field was observed.

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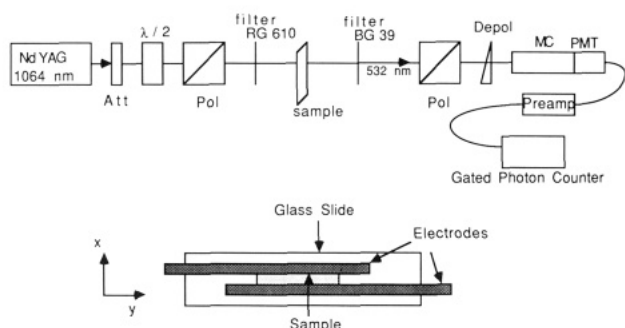
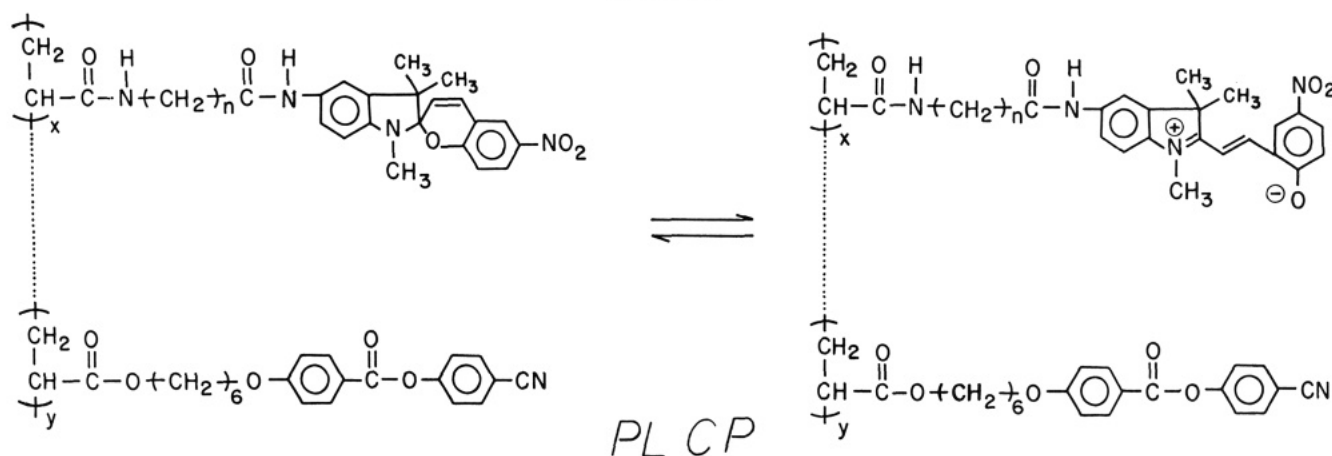
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Scheme II

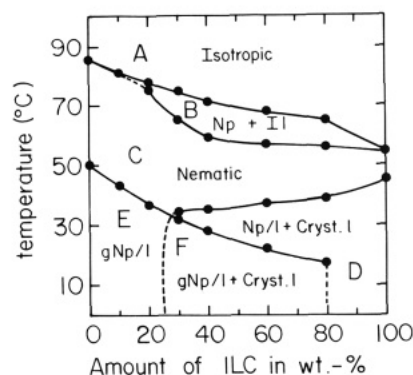


**Figure 1.** Experimental system for SHG measurements, and thin-film sample geometry.

In addition, some other samples were prepared for comparison of SHG signals. One PLCP film was prepared in which the electric field alignment was omitted; another film was prepared omitting the UV irradiation. Finally, one PLCP sample was prepared in the usual way, except that a poly(methyl methacrylate) (PMMA) film was used as the substrate instead of glass.

**Measurements.** Methods of material characterization and film examination, including gel permeation chromatography, differential scanning calorimetry (DSC), polarization microscopy, and optical absorption, were described earlier.<sup>17-22</sup>

The experimental system for second harmonic generation is depicted in Figure 1. A neodymium-YAG laser (Spectra-Physics DCR-11) provides 8-ns pulses of 1064-nm radiation at a repetition rate of up to 10 Hz. Only a small amount (usually 0.1–6 mJ/pulse) of the available laser pulse energy is utilized, and the laser beam is weakly focused to a diameter of 1–2 mm at the sample. The laser polarization can be varied by using a  $\lambda/2$  plate and a polarizer. The input cutoff filter (Schott RG-610) eliminates any harmonic radiation that may have been produced by the laser or optical components. After passing through the sample, the fundamental beam is blocked by the output filter (Schott BG-39), which transmits any generated 532-nm radiation through a polarizer, a medium-resolution monochromator (Jobin Yvon H20-UV), and a high-gain photomultiplier (RCA 8575). A quartz wedge depolarizer is employed to eliminate any dependence of detection efficiency on polarization. The PMT output is amplified 25-fold and analyzed by a gated photon counter (Stanford Research SR400) gating synchronously with the laser pulse. Where necessary, the signals were reduced in a controlled manner (by further attenuation on either the input or output side) so that the photon counter registered an average count rate of  $\leq 0.4$  photons/pulse. Typically, signals were averaged over  $\approx 1000$  pulses. It was verified that the detector response arose from genuine SHG by checking that signals scaled with the square of the input laser intensity and that the signals vanished when the detection monochromator



**Figure 2.** Phase diagram of PLCP (P) and ILC (I) blends (gN = glassy nematic; N = nematic; I = isotropic).

was detuned from 532 nm, when the detector gating was not synchronous with the laser pulse, or when the sample was removed.

In all experiments reported here, SHG was measured at room temperature in transmission with the electric field alignment direction (designated the  $x$  axis) vertical, and sample  $xy$  plane at either  $45^\circ$  or normal to the input laser (see Figure 1). Thus the latter geometry, which was employed in an earlier publication,<sup>19</sup> can probe only the in-plane  $\chi^{(2)}$  components (i.e., those with only  $x$  and  $y$  indexes). In the  $45^\circ$  geometry a horizontal fundamental or harmonic field therefore contains a component in both the  $y$  and  $z$  directions, thus also accessing  $\chi^{(2)}$  components with  $z$  indexes.

During some SHG measurements an electric field was simultaneously reapplied across the electrodes (the sample was kept at room temperature). The electric field applied during SHG measurements did not exceed that applied during sample preparation.

Although the harmonic signal generated at 532 nm could be reabsorbed via the absorption of the merocyanines, the small thickness of the samples ( $\approx 1\text{--}2\ \mu\text{m}$ ) ensured that the optical density at this wavelength remained below 0.2 and thus was not a significant problem. Furthermore, since such thicknesses are less than typical coherence lengths,<sup>7,13</sup> destructive interference effects (Maker fringes) should be avoided.

## Results and Discussion

**A. Material Characterization.** Phase behavior and spectral and kinetic properties of individual QLCs and PLCPs were described in previous papers.<sup>17-22</sup> Here we characterize mainly the blends of PLCP with QLCs and ILC (4-(cyanophenyl) 4-heptylbenzoate).

**Phase Diagrams.** The phase diagram of PLCP and ILC blends (Figure 2) is very similar to that of the liquid-crystal homopolymer, which does not contain the

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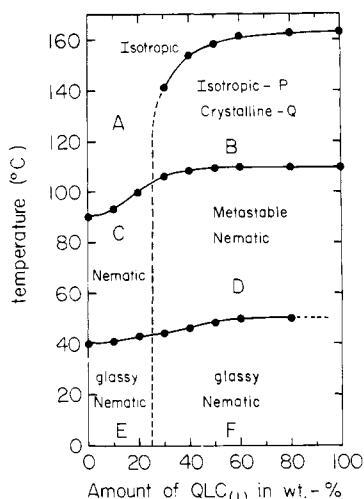


Figure 3. Phase diagram of PLCP (P) and QLC(1) (Q) blends.

photochromic units with the same ILC reported by Ringsdorf et al.<sup>23</sup> PLCP is plasticized ( $T_g$  goes down) by ILC, while crystallization of the latter is markedly depressed at high copolymer content. Full miscibility of the components was observed in the nematic phase, while it is restricted to  $\approx 25\%$  of ILC in the glassy state.

The phase diagram of PLCP-QLC(1) blends depicted in Figure 3 shows full miscibility of these two mesomorphic compounds below the clearing temperature. Metastability of the nematic blends in the region D is determined mainly by the inherent metastability of the QLC mesophase itself.<sup>17,18</sup> Fast preparation and cooling of the blend to below  $T_g$  prevented phase separation and gave a uniform glassy film (region F). Conversely, annealing of the mesophase above  $T_g$  accelerated phase segregation, apparently due to merocyanine aggregation. In fact, the boundary between regions C and D and between E and F should be considered as only approximate because we cannot exclude that on longer annealing further aggregation and crystallization of QLC might occur.

According to the conclusion inferred from a previous study<sup>21</sup> PLCP consists of both mesomorphic and amorphous domains. The photochromic groups are predominantly located in amorphous sites due to the strong structural incompatibility of spiropyran and mesogenic units. The close similarity of the phase diagram of PLCP (Figure 2) and that obtained from the homopolymer in ref 23 shows that spiropyran groups do not markedly affect the compatibility of ILC with PLCP.

Unlike ILC, which plasticizes the polymer, blending PLCP with QLC increased  $T_g$ . Apparently the free volume of the blend is lower, and its structure is more rigid than that of the polymer because QLCs are more compatible both with mesogenic and photochromic groups. This also explains why these two components are miscible in all proportions.

**Absorption Spectra.** The photochromic properties of the blends were not very different from those of PLCP alone.<sup>21</sup> UV irradiation of a glassy blend film led to the appearance of a visible absorption band with  $\lambda_{\max} \approx 590\text{--}595$  nm, which is slightly red shifted with respect to the  $\lambda_{\max} \approx 580\text{--}585$  nm of UV-irradiated PLCP (Figure 4). This can be explained by a contribution from QLC absorption for which  $\lambda_{\max} \approx 600$  nm.<sup>18,22</sup> Blend films that were UV irradiated during cooling (such films were used for SHG) have an absorption band shifted to the blue,

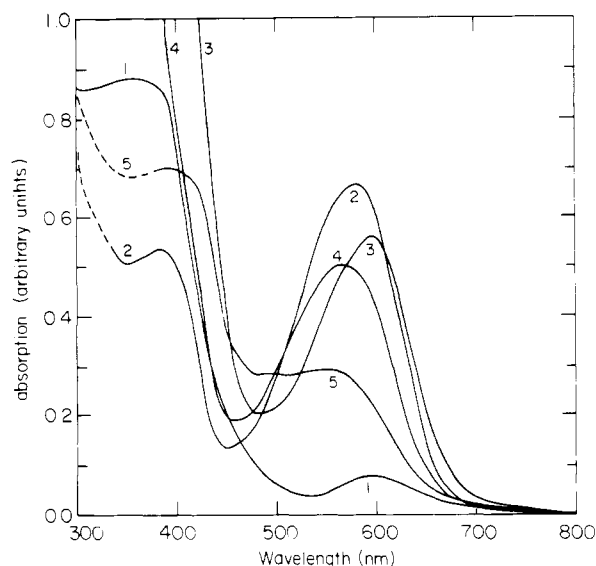


Figure 4. Absorption spectra of (1) QLC(1)-QLC(2) blend 1:3; (2) PLCP after UV irradiation; (3) PLCP-QLC(1) blend 4:1 after UV irradiation; (4) PLCP-QLC(1) blend 1:4 after UV irradiation; (5) PLCP-QLC(1) blend 4:1 after annealing for 2 h at 50 °C.

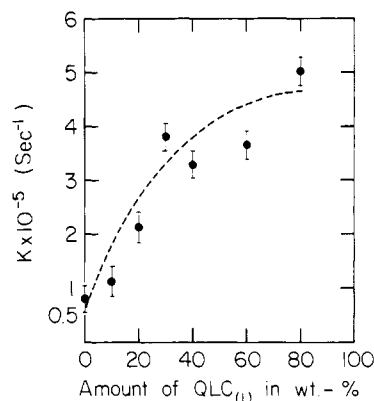


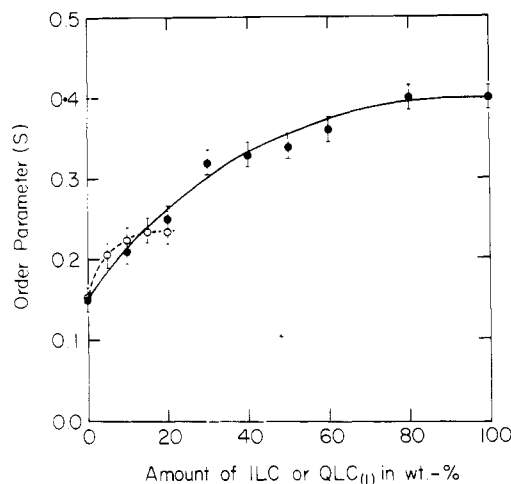
Figure 5. Thermal decay rate constant of merocyanines in PLCP-QLC(1) blends.

which indicates a stronger contribution of merocyanine dimers and probably higher aggregates to the film absorption.<sup>20,21</sup> Annealing of blends above  $T_g$  without irradiation resulted in a broad absorption plateau in the range 480–570 nm. A very similar spectrum was obtained earlier for PLCP itself<sup>20</sup> which was ascribed to merocyanine aggregates (mostly dimers) formed via thermochromic reaction.

**Thermal Decay of Photoinduced Color.** Glassy PLCP-QLC blends that had been UV irradiated exhibited thermal decoloration. The initial stage of this reaction (up to  $\approx 6\%$  decrease in initial absorption) obeyed first-order kinetics. The decoloration proceeds faster with increased QLC content (see Figure 5). Earlier, we have shown<sup>21</sup> that a solvatochromic effect of CN-substituted mesogenic groups in the copolymer strongly stabilizes the merocyanine form of the photochrome. Decoloration was markedly faster in copolymers with methoxy-substituted mesogenic groups.<sup>21</sup> Apparently, in blends we observe a similar effect: increasing the QLC content, which does not contain CN groups, accelerates the thermal decoloration even though the blend matrix seems to be more rigid than the polymeric matrix.

**Electric Field Alignment.** Earlier we reported alignment of QLCs<sup>17-19,22</sup> and PLCP<sup>20,21</sup> in an electrostatic field and the order parameters of different dyes, including

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**Figure 6.** Order parameter of PLCP with ILC (○) and QLC(1) (●) blends.

merocyanine, as estimated from the linear dichroism of the dye in the aligned film. The order parameter ( $S$ ) of the dye can be calculated from the absorption of polarized light by a homogeneously aligned film as

$$S = (D_{\parallel} - D_{\perp}) / (2D_{\perp} + D_{\parallel}) \quad (2)$$

where  $D_{\parallel}$  and  $D_{\perp}$  are the absorption of light polarized parallel and perpendicular to the liquid crystal director.

The order parameter of merocyanine formed on irradiation of PLCP-QLC(1) blends, as a function of blend composition, is presented in Figure 6. The merocyanine groups belong mainly to the copolymer because the QLC component is not photochromic and contributes substantially less to the color formation. The fact that blending with QLC substantially improved the merocyanine alignment is consistent with our assumption about the compatibility of QLCs with both mesogenic and photochromic groups. An improvement of the alignment was also observed for PLCP-ILC blends (Figure 6) for ILC concentrations up to 25%, above which phase separation occurs.

**B. Second Harmonic Generation.** A summary of relative SHG signal strengths obtained from the various PLCP and QLC samples and blends, both with and without applying an external electric field, is given in Table I. Some scatter of signal strengths is observed from different samples of nominally identical composition; this may be attributed to small differences in thickness and alignment.

**Measurements in the Absence of an Electric Field.** Freshly prepared samples showed SHG where the dominant contribution was  $\chi^{(2)}_{xxx}$ , where  $x$  is the direction of electric field alignment: i.e., a strong  $I_{v-v}$  signal where both the input fundamental and generated harmonic are vertically polarized. The intensity of the various samples increased in the sequence Sp-PAN < QLCs < PLCP < PLCP-QLC blends. By comparison with the signal from a "standard" of crystalline quartz<sup>13</sup> we estimate that the strongest signal, observed from a PLCP-QLC blend, had  $\chi^{(2)}_{xxx} \approx 1 \times 10^{-10}$  esu/cm<sup>3</sup>. No significant signal was observed in the horizontal output direction with horizontally polarized input when the sample was either normal or at 45° to the beam; thus  $\chi^{(2)}_{yyy} = \chi^{(2)}_{zzz} = \chi^{(2)}_{yyz} = \chi^{(2)}_{yzz} = \chi^{(2)}_{zyy} = \chi^{(2)}_{zyz} = 0$ . This result was expected since, as discussed in the Introduction, no asymmetry is expected in either the  $y$  direction (in the plane of the sample, but perpendicular to the aligning direction) or in the  $z$  direction, normal to the surface. We also note that these results agree with earlier work on QLC.<sup>19</sup>

**Table I. Relative SHG Signals Measured in Transmission<sup>a</sup>**

	no field <sup>b</sup>	in dc electric field, <sup>c</sup> 10 <sup>4</sup> V/cm		
		$I_{v-v}$	$I_{h-h}$	$I_{v-h}$
PLCP-QLC(1)	3-10	(6 ± 2) × 10 <sup>2</sup>	20-30	1 × 10 <sup>2</sup>
blend 4:1, fresh				
PLCP-QLC(1)	<0.1	1 × 10 <sup>2</sup>	5	6
blend 4:1, old				
QLC(1)-QLC(2)	0.4-1.0	(6 ± 3) × 10 <sup>2</sup>	20 ± 10	(1-2) × 10 <sup>2</sup>
blend 1:3, fresh				
QLC(1)-QLC(2)	<0.1	4 × 10 <sup>2</sup>	5	40
blend 1:3, old				
QLC(1)	0.3	(1-2) × 10 <sup>2</sup>	50	40
PLCP	1-2	40-60	5-10	
PLCP, not aligned	<0.1	(2 ± 1) × 10 <sup>2</sup>	3-5	15
PLCP, aligned	<0.1	30-40	2	
without irradiation				
PLCP on PMMA	0.3	<0.1	0.3	
Sp-PAN	0.5	2-4	2-4	
10% ILC-PLCP		40	1-2	5

<sup>a</sup> The plane of the sample was at 45° to propagation of the input laser beam. The  $x$  direction of the sample, i.e., the direction of the alignment by the dc electric field, was always vertical.  $I_{v-v}$  = signal for vertically polarized input, vertically polarized SHG output;  $I_{v-h}$  = vertically polarized input, horizontally polarized SHG output, etc. <sup>b</sup> In all samples, the other signal components, viz.  $I_{h-h}$ ,  $I_{v-h}$ , and  $I_{h-v}$ , were not observed. <sup>c</sup> In all samples no significant  $I_{h-v}$  signal was observed.

**Table II. Comparison of Relative SHG Signal Intensities for a PLCP-QLC(1) Blend (4:1) Film at 45° and Normal Incidence<sup>a</sup>**

	no field	in dc electric field, 10 <sup>4</sup> V/cm		
		$I_{v-v}$	$I_{h-h}$	$I_{v-h}$
45° to beam	3	5 × 10 <sup>2</sup>	20	100
normal to beam	3	0.4	20	0.1

<sup>a</sup> Experimental conditions as in Table I.

It was also seen that in these samples the SHG via the  $\chi^{(2)}_{xxx}$  component decreased over a time scale of several weeks, which can be attributed to both orientational relaxation and the spontaneous merocyanine fading to the spiropyran form (which has a much smaller  $\beta$ ) described above. The signals could readily be reactivated by repeating the preparation treatment.

**Measurements under an Applied Electric Field.** When SHG signals were measured while a dc electric field of  $\approx 10^4$  V/cm was applied across the electrodes at room temperature a very significant change was observed in the SHG behavior of some samples (see Table I). In mesomorphic samples a very strong  $I_{h-h}$  signal (i.e., horizontally polarized input and output) appeared when samples were at 45° to the beam, as did an  $I_{v-h}$  signal (i.e., vertical input, horizontal output). The  $I_{h-v}$  signal, however, remained very weak. The  $I_{v-v}$  signal, the only significant signal in the absence of the dc field, increased much less dramatically when the field was applied (see below). In the field the signal strengths were usually  $I_{v-v} < I_{v-h} < I_{h-h}$ ; the strongest  $I_{h-h}$  signals corresponded to  $\chi^{(2)} \approx 2 \times 10^{-9}$  esu/cm<sup>3</sup>.

When the sample was normal to the input laser beam,  $I_{h-h}$  and  $I_{v-h}$  signals were not observed either with or without the applied dc field. The  $I_{v-v}$  signal was again observed in the absence of the dc field, and it increased when the field was applied. Typical results for a fresh 4:1 PLCP-QLC blend with the sample at 45° and normal incidence to the laser are compared in Table II.

We note that for 45° incidence, the  $I_{h-h}$  and  $I_{v-h}$  signals were observed from both freshly prepared and "deactivated" samples several weeks old. As discussed above, the latter samples show a very much weaker  $I_{v-v}$

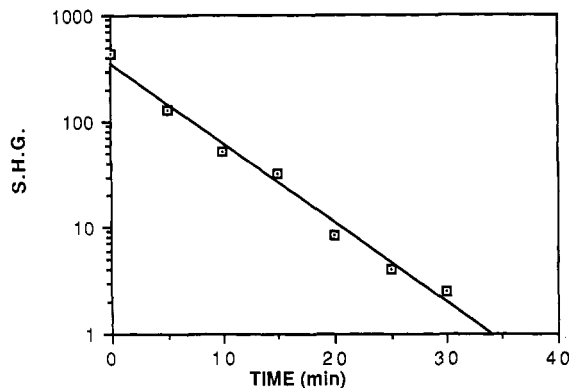


Figure 7. Decay of  $I_{h-h}$  SHG signal of a QLC(1)-QLC(2) blend (1:3) following the removal of the electric field.

signal in the absence of the dc field.

The appearance of the strong  $I_{h-h}$  and  $I_{v-h}$  signals in the electric field was unexpected, since the electric field is applied in the vertical direction only and thus is not expected to induce asymmetry in either of the horizontal directions  $y$  or  $z$ . We thus checked whether these signals may be due to  $\chi^{(3)}$  process originating in either the sample or substrate, mixing the optical field twice and the dc field. However, these signals did not vanish when the dc field was shut off, eliminating this possibility and confirming that the signals are from a  $\chi^{(2)}$  process and that a horizontal asymmetry is induced. Nevertheless, these signals did eventually disappear after the dc field was removed, decaying in a first-order manner over about an hour (see Figure 7). Since similar dc fields are applied in the preparation procedure, the fact that strong  $I_{h-h}$  and  $I_{v-h}$  signals were never observed when SHG was measured without the dc field already implied that these signals would not be permanent.

Thus the dc electric field clearly induces a *transient* asymmetry in either the  $y$  or  $z$  direction. Since the strong  $I_{h-h}$  and  $I_{v-h}$  signals do not appear when the sample is normal to the beam (i.e., the horizontal polarization direction parallel to  $y$ ), we verify that no asymmetry is induced in the  $y$  direction. Thus these strong signals can arise only from an induced asymmetry in the  $z$  direction (normal to the plane of the sample) meaning that the  $I_{v-h}$  signal arises from the  $\chi_{zzx}^{(2)}$  component and the  $I_{h-h}$  signal must arise from among the  $\chi_{zzz}^{(2)}$ ,  $\chi_{zyy}^{(2)}$ , and  $\chi_{yzy}^{(2)}$  components. By carrying out analogous measurements at  $45^\circ$  incidence, but with the  $y$  axis vertical, we were able to conclude that the dominant contribution to this SHG signal comes via  $\chi_{zzz}^{(2)}$ .

Finally, we note the dependence of the  $I_{h-h}$  and  $I_{v-v}$  signals on the electric field is different (see Figure 8).  $I_{v-v}^{1/2}$  ( $\sim \chi_{zzx}^{(2)}$ ) increases relatively slowly and linearly with the electric field, in agreement with earlier work<sup>19</sup> and the expected behavior for interaction between isolated dipole moments in a nematic environment and a dc electric field.<sup>13,19,24</sup> The  $\chi_{zzz}^{(2)}$  component clearly shows a different behavior, which in the range studied can be fitted well by  $I_{h-h}^{1/2}$  proportional to the square of the electric field (see Figure 8).

**Nature of the Anomalous  $I_{h-h}$  SHG Signals.** The results presented above confirm that poled photochromic liquid-crystal polymers containing merocyanine groups can exhibit strong SHG. However, the data presented here differ from earlier work on poled polymers and QLCs in that SHG arises not only via the usual  $\chi_{zzx}^{(2)}$  term (asym-

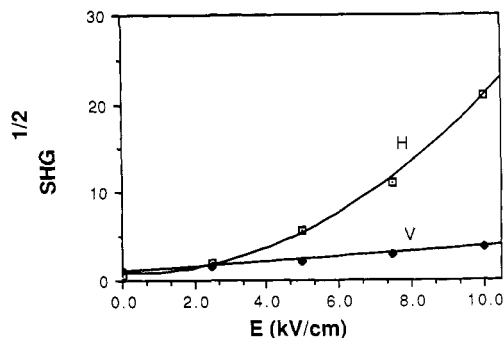


Figure 8. Dependence of  $I_{v-v}^{1/2}$  (V) and  $I_{h-h}^{1/2}$  (H) signals of a QLC(1)-QLC(2) blend (1:3) on the applied electric field. The  $I_{v-v}^{1/2}$  data are fitted by a linear dependence on the field;  $I_{h-h}^{1/2}$  is fitted by a quadratic dependence.

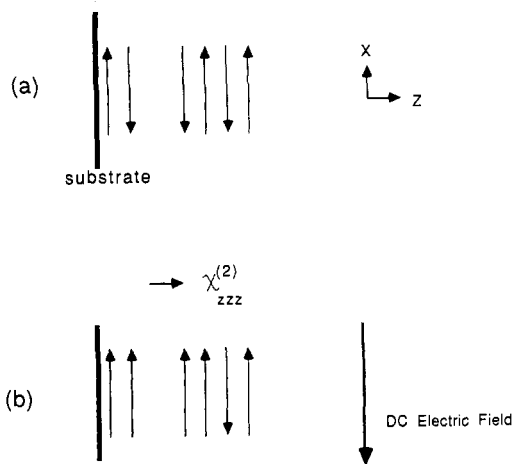


Figure 9. Proposed structure of merocyanine aggregates in the absence (a) and presence (b) of an electric field. The arrows represent the dipole moments of individual molecules.

metry parallel to the poling field) but also via components derived from the nominally isotropic  $z$  direction. Indeed, the  $\chi_{zzz}^{(2)}$  term appears to be the strongest  $\bar{\chi}^{(2)}$  component in these systems.

Elucidation of the process responsible for the  $I_{h-h}$  signal when dc electric fields are applied may be assisted by a consideration of which systems strongly exhibit this signal and which do not (see Table I). Since strong  $I_{h-h}$  signals are observed in the "old" samples of QLC and PLCP-QLC blends, as well as for the PLCP samples prepared without UV irradiation, we conclude that the  $I_{h-h}$  signal can come only from merocyanine dimers or higher aggregates. According to the results described above (see sections on characterization and SHG in absence of dc field) the nonaggregated merocyanine units (i.e., isolated dipolar groups) have either decayed (the "old" samples) or were not formed at all (PLCP sample prepared without irradiation). The merocyanine groups in such samples are preserved only in the aggregated form. The second fact shown in Table I and supporting our hypothesis is that the prealignment of a PLCP film in the field, which is crucial for the zero-field  $I_{v-v}$  signal generated by aligned individual merocyanine units, is not required for the field induced  $I_{h-h}$  signal.

Aggregates composed of several molecules, each possessing a large dipole moment, are expected to have an equilibrium zero-field structure in which the neighboring individual dipole moments are antiparallel, so as to minimize the energy from dipole-dipole interactions (see Figure 9a). Our earlier measurements proved that not only individual merocyanine groups but also aggregated

(24) van der Vorst, C. P. J. M.; Picken, S. J. *SPIE Conf. Proc.* 1987, 866, 99.

ones are aligned along the mesophase director.<sup>20</sup> Application of the dc field may bring about some reorientation of individual dipoles within a stack, resulting in a non-centrosymmetric structure (see Figure 9b). Such a mechanism of electric-field-induced SHG was demonstrated earlier for another type of merocyanine aggregates, called merocyanine quasi-crystals.<sup>16,25</sup>

We thus postulate that aggregates such as depicted in Figure 9b may be responsible for the strong SHG signal arising mainly via  $\chi^{(2)}_{zzz}$ . To have an electric-dipole-allowed SHG signal along the  $z$  axis, electronic excitation would have to result in a (vectorial) difference between the ground- and excited-state dipole moments<sup>2</sup> along  $z$ . This would be achieved by *intermolecular* charge transfer in the stacks, as is suggested by the blue shift in the absorption spectra of aggregates.<sup>26,27</sup>

A further constraint of this model is that these aggregates must have asymmetry in the  $z$  direction. We believe that this is induced by the strong interactions between the glass substrate and the mesophase. A corollary of this, therefore, is that in the absence of such interactions the  $I_{h-h}$  signal should be absent. Consequently, further support for our model comes from two other observations: (i) The fact that no  $I_{h-h}$  signal was observed from the PLCP film cast on poly(methyl methacrylate) is explained by the different substrate-mesophase interactions in the two cases (PLCP on glass and PLCP on PMMA), where only the former provides the interaction necessary to achieve an  $I_{h-h}$  signal. (ii) The amorphous film of polyacrylonitrile containing merocyanine groups also did not produce a very significant  $I_{h-h}$  signal.

Although the evidence for the above model is not overwhelming, it appears to be the most plausible model consistent with our experimental observations. We now show that several more "conventional" models based on SHG by individual dipolar units cannot be reconciled with these observations.

(a) *The preferred direction of the merocyanines is not parallel to the field.* Since the electric field also aligns the mesogenic units, the NLO chromophore, which is connected through chemical bonds to the mesogenic unit, may be constrained to a different alignment. However, this explanation does not appear to be applicable here, as the molecular structure of individual units, as well as the order parameters reported here (Figure 6) and earlier<sup>20,21</sup> suggests that the mesogenic and merocyanine chromophores should be parallel, or nearly so.

(b) *The anomalous signal arises from an interface rather than the bulk.* Since the symmetry in the  $z$  direction of any medium is broken at an interface, we consider

whether the anomalous SHG signals could come from one or more aligned molecular layers at the air/mesophase or glass/mesophase interface. A strong  $\chi^{(2)}_{zzz}$  signal is expected for high- $\beta$  chromophores aligned normal to an interface.<sup>28</sup> The magnitude of  $\chi^{(2)}_{zzz}$  ( $10^{-9}$  esu/cm<sup>3</sup>) multiplied by the thickness ( $2 \times 10^{-4}$  cm) would require a surface susceptibility of  $2 \times 10^{-13}$  esu/cm<sup>2</sup>. This does not seem feasible since for merocyanine,  $\beta \approx 10^{-28}$  esu/molecule,<sup>2,14,19</sup> and a surface layer has only  $\approx 10^{14}$  molecules/cm<sup>2</sup>, of which at most only a few percent are merocyanine.

(c) *The poling field has a component in the  $z$  direction.* Since our samples are thicker than the electrodes, the field lines passing through some of the sample will have a component along the  $z$  axis. However, this effect should be vanishingly small, considering the ratio of film thickness (1–2  $\mu$ m) to the electrode separation (2 mm), and thus could not produce  $\chi^{(2)}_{zzz} > \chi^{(2)}_{xxx}$ .

(d) *SHG via a quadrupolar mechanism.* In principle, the  $I_{h-h}$  SHG signal could arise via a quadrupolar process, where

$$P_z^{2\omega} = (\chi^{(2)}_{zzz})^{\text{eff}} E_z E_z = \Gamma_{zzzz} E_z \partial / \partial z E_z \quad (3)$$

which is nonzero even if there is no asymmetry in the  $z$  direction. Since quadrupolar SHG signals are usually quite small,<sup>29,30</sup> it is highly unlikely that a quadrupolar mechanism is responsible for these signals.

In conclusion, we have observed a new effect in the SHG of poled nematic phases containing high- $\beta$  groups, in which the strongest SHG arises via the  $\chi^{(2)}_{zzz}$  component, where  $z$  is normal to the poling direction. Under a poling field of  $10^4$  V/cm this coefficient is  $10^{-9}$  esu/cm<sup>3</sup>, which is comparable to the best results obtained from polymers poled at these field strengths. We believe that this effect is caused by aggregates stacked normal to the glass substrate surface. Further study of these materials is clearly warranted, both to elucidate theoretically whether the postulated aggregate structure can account for the strong  $\chi^{(2)}_{zzz}$  component and to understand its electric field dependence. If the approximately quadratic dependence continues under stronger fields, an extremely large  $\chi^{(2)}$  coefficient may be achieved. In addition, we note that these samples offer the very attractive quality of three quite large  $\chi^{(2)}$  components in an electric field— $\chi^{(2)}_{zzz}$ ,  $\chi^{(2)}_{xxx}$ , and  $\chi^{(2)}_{zzx}$ . Also, the preparation procedure of these poled films enables some control of sample birefringence, meaning it should be possible to achieve phase matching for some combination of the fundamental and harmonic field in the  $x$  and  $z$  directions. Thus thicker samples of these materials could be efficient harmonic generators, most useful for wavelengths above 1200 nm, where reabsorption of the harmonic would not occur.

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