negative layer spacing temperature coefficient of the polyester disappears and the positive coefficient of the polyimide seems to dominate. The thermal behavior of the 30 wt % blend is similar. In fact, the transition to an apparently isotropic melt seen with the pure polyester disappears and a layered mesophase is seen to about 350 °C, where thermal decomposition becomes a serious problem. One explanation for this might be a "stiffening" of the polyester backbone by the very rigid polyimide component. This behavior is currently being investigated in detail.

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Registry No. PI16 (copolymer), 115563-56-9; PI16 (SRU), 112231-33-1; PE16 (copolymer), 115563-54-7; PE16 (SRU), 115563-57-0.

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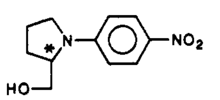
Persistent, Efficient Frequency Doubling by Poled Annealed Films of a Chromophore-Functionalized Poly(*p*-hydroxystyrene)

All synthetic strategies for polymeric second-harmonic generation (SHG) materials[1] must address the crucial issues of maximizing chromophore densities while achieving maximum, persistent noncentrosymmetry. An attractive alternative to poling glassy polymers simply doped with nonlinear optical (NLO) chromophores[2-4] are materials in which NLO chromophores are covalently linked to the polymer backbone,[5,6] thus offering potential impediment both to phase separation at high chromophore densities and to deleterious relaxation[4a] of poling-induced chromophore alignment. We report here an embodiment[7] of this strategy which employs structure-enforcing hydrogen-bond networks,[8] achieves high chromophore densities, and affords polymer films with persistent (on a timescale of months) second-harmonic coefficients d_{33} ($^1/_2\chi^{(2)}_{333}(-2\omega;\omega,\omega)$) equal to or in excess of the corresponding value for $LiNbO_3$. General observations relevant to NLO film processing and the applicability of current theoretical models[3] are also reported.

Poly(*p*-hydroxystyrene)[9] ($\bar{M}_W \approx 6000$; $T_g \approx 155$ °C) was functionalized[10] to varying levels (15–60% of phenol rings) with the tosylate[11] of *N*-(4-nitrophenyl)-L-prolinol (NPPOH,[12] eq 1) and was purified by washing with acetone

$$\text{(PS)OH} + \text{NPPOTs} \xrightarrow{H_2O,\ OH^-} \text{(PS)O-NPP} + \text{HOTs} \qquad (1)$$

NPPOH =


and repeated precipitation from THF with methanol. Products were characterized by 400-MHz ^{1}H NMR, FT-IR, elemental analysis, DSC, and optical spectrophotometry.[13] In a class 100 laminar-flow clean hood, 1–5-μm films of (PS)O-NPP were cast onto ITO-coated conductive glass from multiply filtered THF solutions. The films were then annealed at 100 °C for 2 h prior to dc poling. The effect of annealing is to enhance the ultimate poling fields which can be achieved and the temporal stability of the SHG capacity (vide infra). The reason appears to be removal of traces of THF and other volatiles (verified by FT-IR) which plasticize the material and enhance macromolecule mobility (supported by DSC[14]), independent or concurrent changes in the hydrogen-bonding network[15] (verified by FT-IR[16]) which may also affect mobility and changes in film morphology (suggested by SEM) which may seal imperfections leading to dielectric breakdown during poling.[17] The annealed films were covered with an aluminum electrode, heated to 80 °C, and poled by incrementally increasing the field with online current monitoring (to detect the onset of dielectric breakdown processes). The film was held at the maximum field for 0.5 h and then cooled in the presence of the field. Careful film fabrication and annealing allowed poling at dc fields as high as 1.8 MV/cm, which appears to be near the limit of what is practicable for typical polymer thin films.[17] In contrast, experiments with *doped* NPPOH/PS or (PS)OH films indicated phase separation (and opacity) at chromophore concentrations as low as 5 mol %, frequent breakdown at low poling fields (presumably reflecting greater mobility), and weak, shorter lived SHG performance (presumably reflecting greater chromophore mobility).

Table I
Second-Harmonic Coefficients for Chromophore-Functionalized Polystyrenes[a]

material	functionalization level % phenyl rings	poling field, MV/cm	d_{33},[b] 10^{-9} esu
$(PS)CH_2$-DR	12.5	0.3	2.7[c]
$(PS)CH_2$-DASP	4.5	0.3	0.12[c]
(PS)O-NPP	15.0	0.7	5.1 (5.7)
(PS)O-NPP	25.0	0.3	3.0 (3.6)
(PS)O-NPP	48.0	0.6	11.6 (10.9)
(PS)O-NPP	48.0	1.6	18.0 (29)

[a] Measured within 0.5 h of poling; λ = 1.064 μm. [b] Experimental SHG coefficients. Quantities in parentheses are theoretical values of d_{33} estimated from eq 2 and 3. [c] From ref 5. DR = 2-[4-[(4-nitrophenyl)azo]-*N*-ethylanilino]ethoxy; DASP = 4-(4-(dimethylamino)styryl)pyridinium iodide.

Second-harmonic coefficients of the (PS)O-NPP samples were measured at 1.064 μm in the p-polarized geometry by using the instrumentation and calibration techniques described previously.[5] Second-harmonic coefficients were calculated from the angular dependence of the second-harmonic intensity and the formalism of Jerphagnon and Kurtz for uniaxial materials, assuming also that $d_{31} = d_{24} = d_{15} = {}^1/_3 d_{33}$.[3,10,18] Film thicknesses were measured after SHG experiments by using a Tencore Alpha-Step 200 profiler. Representative data are set out in Table I. It can be seen that the (PS)O-NPP second-harmonic coefficients are rather large, exceeding the corresponding d_{36}

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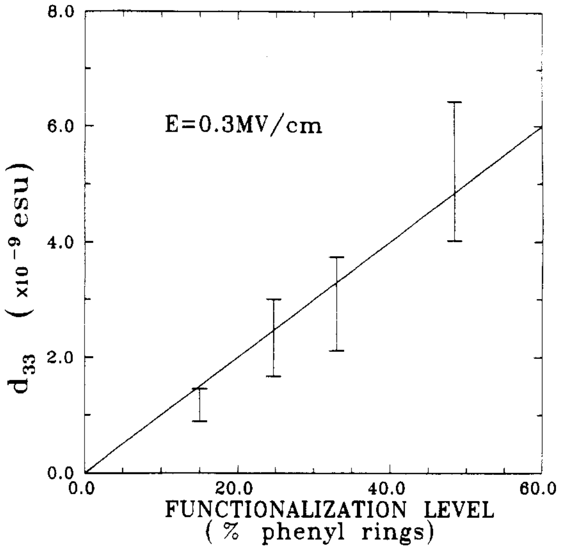

Figure 1. Second-harmonic coefficients of (PS)O-NPP films poled at 0.3 MV/cm as a function of chromophore functionalization level.

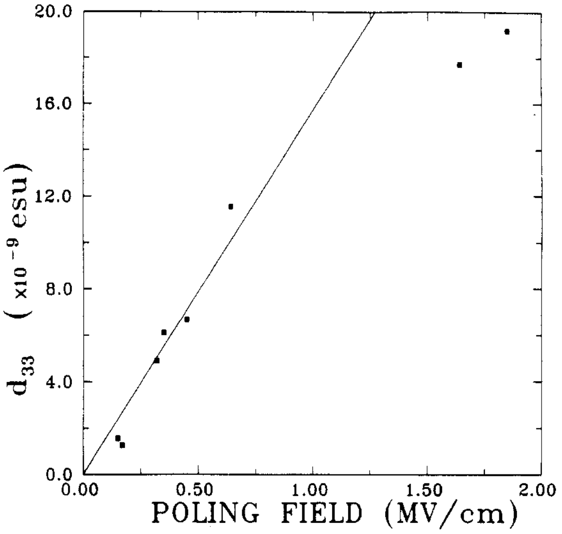

Figure 2. Second-harmonic coefficient of (PS)O-NPP films (48% chromophore functionalization level) as a function of dc poling field.

of KDP (1.1×10^{-9} esu)[3a] and equaling or exceeding d_{31} of $LiNbO_3$ (14.2×10^{-9} esu).[1e] An isolated chromophore, Langevin function description of the chromophore response to the poling field[3] yields the functional dependence given by eq 2 and 3. Here N is the chromophore number

$$d_{33} = \tfrac{1}{2}Nf^{2\omega}f^{\omega}f^{\omega}\beta_{zzz}L_3(p) \qquad (2)$$

$$p = \frac{f^{0}\mu E_{p}}{kT} \qquad (3)$$

density, μ is the chromophore molecular dipole moment, β_{zzz} is the appropriate molecular hyperpolarizability tensor, E_p is the poling field, L_3 is the third-order Langevin function, and the f's are the corresponding local field factors. The degree to which this model is valid (especially at high values of N and E_p) is of considerable interest. As can be seen in Figure 1, there is a fairly linear dependence of d_{33} on NPP functionalization level (which should approximately scale as the chromophore density at low functionalization levels) up to the highest chromophore densities. The dependence of d_{33} on dc poling field is shown in Figure 2. It can be seen that there is a departure from linear dependence at highest fields. Saturation effects are predicted[1c,3] at poling fields sufficiently high that $f^{0}\mu E_p \approx kT$ (i.e., $E_p \gtrsim 1.3$ MV/cm in the present case). Table I also shows generally good agreement between experimental d_{33} values and those estimated from eq 2 and 3, using the published $\mu\beta_{zzz}$ value for NPPOH[19] and optical constants for polystyrene.[20]

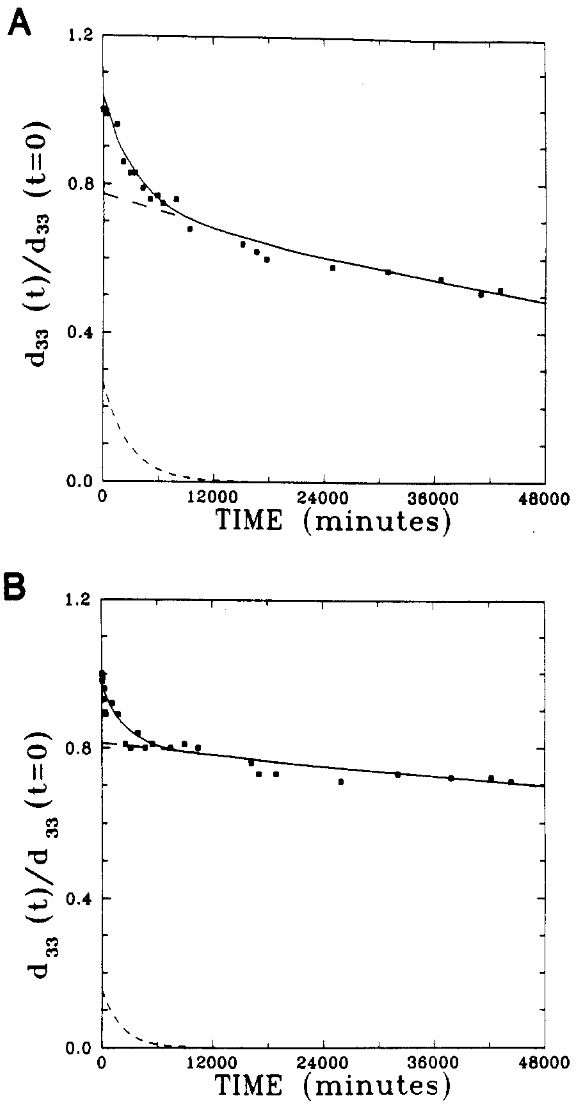

Figure 3. (A) Temporal behavior of the second harmonic coefficient of an unannealed (PS)O-NPP film (25% functionalization level) at room temperature. The solid line shows a two-exponential fit (eq 4) to the data points while the two dashed lines represent the component functions. (B) Temporal behavior of the second-harmonic coefficient of an annealed (PS)O-NPP film (25% functionalization level) at room temperature. The solid line shows a two-exponential fit (eq 4) to the data points while the dashed lines represent the component functions.

The temporal stability of SHG efficiency reflects complex reorientational processes by which chromophore orientations relax to thermodynamic equilibrium/minimum free volume. Unlike the doped chromophore/polymer systems studied to date, the persistence of (PS)O-NPP SHG is long-lived. The restricted chromophore mobility imparted by covalent linkage to the polymer backbone as well as by hydrogen-bonding networks[15] is doubtless an important factor. Typical d_{33} decay data at room temperature (25 ± 3 °C) are shown in Figure 3. The effects of film annealing are clearly evident and are in accord with the other changes in film properties noted above. The exact form of the decay function, which cannot be fit to a single exponential, suggests several relaxation processes. Fits to a two-exponential model (eq 4) are

$$d_{33} = Ae^{-t/\tau_1} + Be^{-t/\tau_2} \tag{4}$$

shown in Figure 3. For the annealed sample, approximate half-lives for short-term and long-term decay are 1.5 and 195 days, respectively. We find that the amplitude of the short-term process is more sensitive to the presence of THF and can be greatly diminished by annealing. This argues that the short-term process involves facile chromophore reorientation in THF-rich (high local free volume) microenvironments. Preliminary experiments also indicate that the long-term decay rate of d_{33} is increased by higher chromophore densities and by higher poling fields. That effective poling can be carried out more than 20 °C below T_g underscores the importance of secondary relaxation processes[21] in achieving/dissipating preferential chromophore alignment.

The present results considerably expand what is known about the properties of NLO chromophore-functionalized polystyrenes. Equally important, they suggest future synthetic and processing strategies for materials with even more efficient frequency-doubling properties.

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New Entanglement Model of Condensed Linear Polymers: Localized Gauss Integral Model

Entanglement of polymers is usually discussed in terms of the tube model.[1] This model has succeeded in explaining numerous viscoelastic properties of entangled polymers very well, but its physical foundation has not yet been fully established. A more fundamental approach to this problem is to introduce topological invariants such as the Gauss integral (GI) explicitly into the statistical mechanics of polymers.[2] This approach has been used to calculate the modulus of network polymers and the second virial coefficients of ring polymers in the Θ state, A_2^{Θ}.[3] Although the two theories have so far been studied inde-