nection drawn[21] between the hydrodynamic renormalization group fixed point and the smallest eigenvalue from the Kirkwood–Riseman theory ($h^* \approx 0.25$). The veracity of the conformational distribution function may strongly affect the universality of the physics underlying polymer hydrodynamics.

The next challenge before eliminating variable h^* values will be to consider other polymer–solvent systems with intermediate chain expansion. Such experiments are presently under way in this laboratory. Success here will require choosing, and justifying from theory or experiment, appropriate values for the local and global excluded-volume parameters.

Acknowledgment. We are grateful for helpful discussions with Dr. Robert L. Sammler, Dr. Jack F. Douglas, Dr. Shi-Qing Wang, and Professor Karl F. Freed. We are indebted to Dr. Sammler and Professor John L. Schrag for making available computer programs which were used extensively. This work was supported by the National Science Foundation, Polymers Program (Grant DMR-8715567).

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Registry No. Polystyrene, 9003-53-6; toluene, 108-88-3.

Communications to the Editor

Polyphenylene Ether Based Thin-Film Nonlinear Optical Materials Having High Chromophore Densities and Alignment Stability

Challenges confronting the rational construction of poled polymeric nonlinear optical (NLO) materials[1] include maximizing chromophore number densities as well as achieving and preserving maximum electric field induced acentricity of the microstructure. Chromophore-functionalized glassy polymers represent an advance in this respect,[2] and we recently reported improved second-haromonic generation (SHG) efficiencies and temporal stabilities vis-à-vis guest–host "doped" systems.[3a] Nevertheless, current generation polystyrene-,[2,3] polyacrylate-,[4] and polyethylene-based[5] materials are intrinsically limited in a designed functionalization level to a maximum of one chromophore molecule per repeat unit (in most cases, considerably less has been achieved) and to architectures having undesired residual chain mobility, as suggested by T_g data.[2–6] This paper addresses several of these issues and describes the synthesis and characterization of a new class of highly functionalized SHG polymers derived from the robust, high-T_g (205–210 °C) thermoplastic poly(2,6-dimethyl-1,4-phenylene oxide) (PPO).[7] Although we illustrate with a well-characterized model chromophore, the synthetic approach should be general. To better define the transparency characteristics of the subject films, we also report the fabrication of a waveguide.

PPO was prepared by oxidative coupling of 2,6-dimethylphenol and was purified as described elsewhere[8] (Scheme I; $\bar{M}_n = 27\,000$).[9] Bromination[10] in refluxing tetrachloroethane afforded materials (PPO–Br$_x$) with functionalization levels on the order of 1.6–1.8 Br/repeat unit (predominantly methyl bromination) as ascertained by elemental analysis and ^{1}H NMR.[11] *N*-(4-Nitrophenyl)-*S*-prolinoxy- (NPPO-) was chosen as a model chromophore substituent since the optical properties of NPPOH have been extensively characterized[12] and since it is readily amenable to $\lambda = 1.064$ μm NLO experimentation. Reaction of PPO–Br$_x$ with NPPO$^-$ (from NPPOH + NaH) in dry *N*-methylpyrrolidone (NMP; 4 days at 60 °C) afforded the chromophore-functionalized polymer (PPO–(NPP)$_x$; Scheme I; 1.43–1.63 NPPO/repeat unit;[13] $T_g \approx 173$ °C) after precipitation with acetone, washing with H_2O, Soxhlet extraction with MeOH, and vacuum drying for 24 h at 60–70 °C. Polymer films were cast onto ITO-coated conductive glass from triply filtered NMP solutions in a class 100 laminar-flow clean hood. The solvent was slowly evaporated at 80 °C, and the resulting films were dried in vacuo at 150–170 °C for 24 h. These PPO–NPP films have excellent transparency characteristics (vide infra; $\lambda_{max} = 405 \pm 2$ nm; 405 ± 2 nm as a solution in NMP), adhere tenaciously to glass, and are impervious to most organic solvents. Film thickness were 1–4 μm by profilometry.

Contact poling of the PPO–NPP films was carried out at 160–170 °C (40 min) with 1.2 MV/cm fields using tech-

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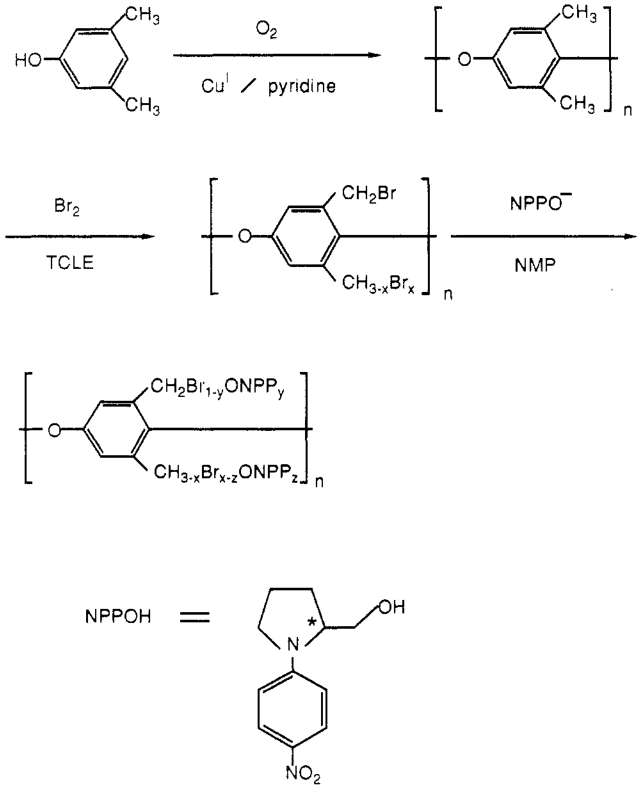
Scheme I



niques described previously.[2,3] After cooling the film to room temperature, the field was maintained for an additional 90 min. Corona poling[14] was carried out at 180–190 °C (30 min) using a needle-to-film distance of 1.0 cm and a +4-kV potential. After the film had cooled to room temperature, the field was maintained for an additional 90 min. Second-harmonic data were measured at 1.064 μm in the p-polarized geometry using the instrumentation and calibration techniques described previously.[2,3] Second-harmonic coefficients were calculated from the angular dependence of the second-harmonic intensity and the equations of Jerphagnon and Kurtz for uniaxial materials, assuming furthermore that $d_{31} = d_{24} = d_{15} = d_{33}/3$.[15,16] This latter assumption has been verified for other poled, chromophore-functionalized polymers.[2a]

Table I presents compositional and NLO data for representative PPO–NPP films. Assuming approximate additivity of PPO[7] and NPPOH[12a] densities, it can be seen that the present chromophore number densities are substantial compared to guest–host NLO materials ($\lesssim 2 \times 10^{20}/\mathrm{cm}^3$) and to typical chromophore-functionalized polymers (ca. $8\text{–}15 \times 10^{20}/\mathrm{cm}^3$).[3c,4] As a point of reference, the corresponding number density for crystalline NPPOH is $37 \times 10^{20}/\mathrm{cm}^3$.[12a] In regard to SHG efficiency, the present d_{33} values are also substantial with the corona-poled datum of 65×10^{-9} esu comparing favorably with the largest values yet reported for any poled functionalized polymer system[17] (cf. $d_{36} = 1.1 \times 10^{-9}$ esu for KDP[15a] and $d_{31} = 14.2 \times 10^{-9}$ esu for $LiNbO_3$[1f]). A slight but reproducible decline in d_{33} on increasing the chromophore functionalization level from 1.43 to 1.63 is also noted. Although it may reflect unfavorable chromophore aggregation effects,[4] these are not obvious in optical spectra of the variously functionalized materials. In viewing the present d_{33} data it should also be noted that $\mu_z\beta_{zzz}$ for NPPOH, 300×10^{-30} cm^5·D/esu at $\lambda = 1.064$ μm,[12b] is relatively small. Hence, considerably larger d_{33} values may be achievable with other chromophore substituents (cf. $\mu_z\beta_{zzz} = 1090 \times 10^{-30}$ cm^5·D/esu for Disperse Red-1 at $\lambda = 1.356$ μm[18]).

Table I
Second-Harmonic Coefficients and Temporal Stability Data for NPP-Functionalized Poly(2,6-dimethyl-1,4-phenylene oxide)

functionalizn level[a]	NPPO no. density, $10^{20}/\mathrm{cm}^3$	poling method	d_{33},[b] 10^{-9} esu	τ_1,[c] days	τ_2,[d] days
1.43	~22	contact (1.2 MV/cm)	13	0.9	412
1.43	~22	corona	65	0.3	39
1.63	~26	corona	55		

[a] NPPO groups per PPO repeat unit. [b] At $\lambda = 1.064$ μm; measured within 0.5 h of poling at 25 °C. [c] Short-term SHG decay constant from a least-squares fit to eq 1. Data taken at 25 °C. [d] Long-term SHG decay constant from a least-squares fit to eq 1. Data taken at 25 °C.

Temporal characteristics of contact-poled and corona-poled PPO–$(NPP)_x$ NLO properties are illustrated in parts A and B of Figure 1, respectively. Time-dependent decay of SHG efficiency is a ubiquitous, undesired, but highly informative characteristic of present generation poled chromophore–polymer NLO films, with the rapidity reflectng the facility of internal motions, which restore preferential chromophore orientations to (random) thermodynamic equilibrium and the microstructure to minimum free volume.[2,3,19,20] As has been noted previously for other functionalized polymers,[2,3] the present $d_{33}(t)$ data cannot be fit to a single exponential, suggesting that greater than one rate process is operative (e.g., disparate reorientation rates in matrix regions having free volumes greater than or less than a certain threshold value[20a]). More satisfactory fits of the present data are obtained to a presently phenomenological biexponential expression (eq 1),

$$d_{33} = Ae^{-t/\tau_1} + Be^{-t/\tau_2} \tag{1}$$

and derived τ_1 and τ_2 values, obtained by a least-squares fit, are given in Table I. The τ_2 for the contact-poled PPO–$(NPP)_x$ film appears to be the largest value reported to date and corresponds to a degradation in d_{33}, after the initial, rapid decay, of less than 10% in 50 days (Figure 1A). Such processes are expected to be additionally moderated in systems with hydrogen bonding,[3c] cross-linking,[21] and more massive chromophores.[19] We have reported elsewhere that poled (PS)O–NPP film τ_1 and τ_2 values are significantly reduced as contact poling fields are increased;[2a] i.e., the system is driven further from thermodynamic equilibrium. The present results for the corona-poled film are in accord with this trend (Figure 1B) in that both τ_1 and τ_2 are significantly diminished when higher poling fields are employed.[22]

In situ SHG monitoring of the poling process[3b,5,21,23] provides invaluable information on polymer microstructural mobility as a function of temperature and various processing parameters.[3b,21] As can be seen in Figure 2, chromophore orientational response to the corona poling field, as indicated by the evolution of a large SHG signal, occurs *far below* T_g. This observation is in accord with evidence in the parent polymer of some hindered phenylene backbone rotation persisting to low temperatures.[24] It can also be seen in Figure 2 that d_{33} increases more rapidly as T_g is approached (not unexpectedly) and reaches a maximum as the temperature falls. This latter behavior is in accord with a simple isolated molecule model[15] for chromophore response to an electric field (eqs

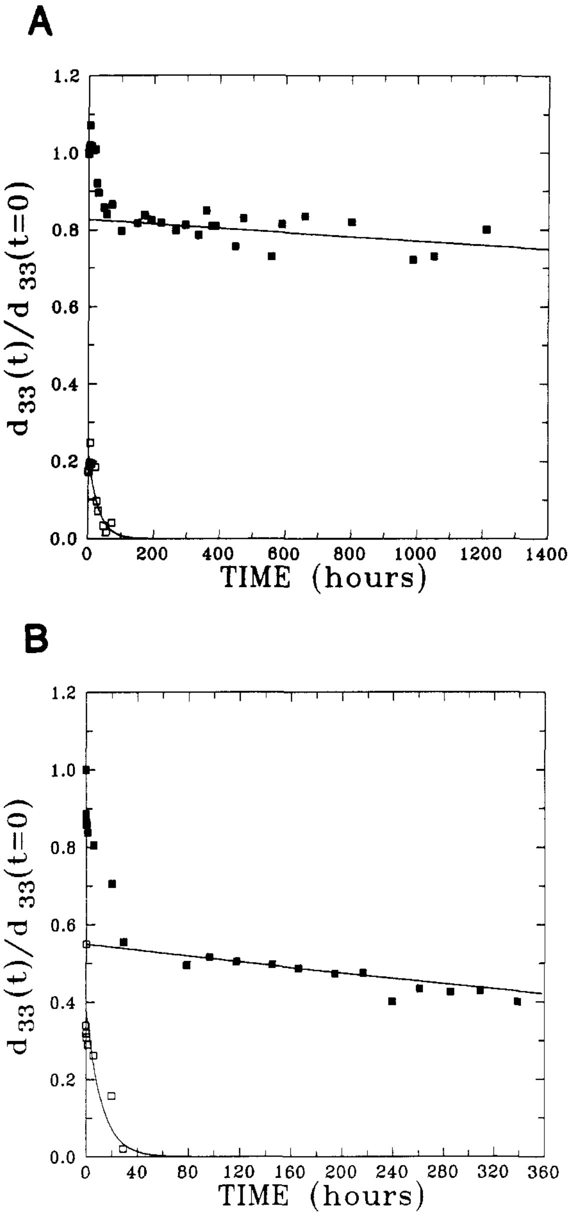


Figure 1. (A) Temporal characteristics of the second-harmonic coefficient of a PPO-(NPP)$_x$ film (1.43 NPP moieties per repeat unit) contact-poled at 1.2 MV/cm. Decay data taken at 25 °C. The solid lines show the two exponential components of the least-squares fit to eq 1. (B) Temporal characteristics of the second-harmonic coefficient of a corona-poled PPO-(NPP)$_x$ film (1.43 NPP moieties per repeat unit). Decay data taken at 25 °C. The solid lines show the two exponential components of the least-squares fit to eq 1.

2 and 3), which predicts, in cases of significant residual

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

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

mobility, increasing d_{33} with falling temperature. Here μ is the chromophore dipole moment, E_p is the poling field, the f's are local field factors, and L_3 is the third-order Langevin function.

Preliminary waveguiding experiments were performed on several PPO-NPP films to better define their optical characteristics. A planar waveguide structure consisting of air/film/glass layers was used. The waveguide modes were excited with a He-Ne laser (0.633 μm) using prism-coupling techniques with SF6 glass (n = 1.797)

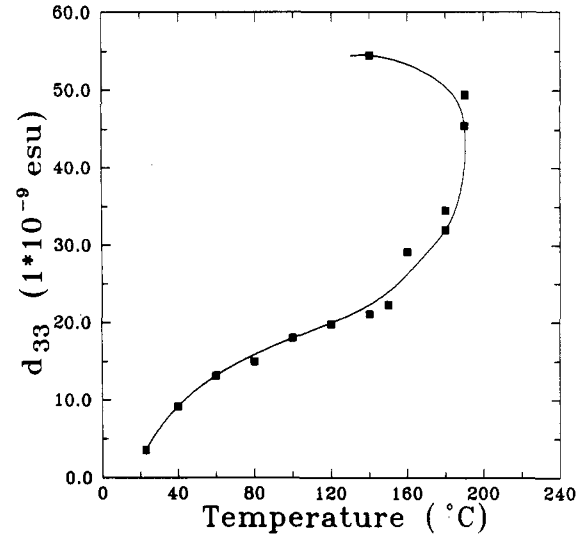


Figure 2. Response (measured in situ) of the second-harmonic coefficient of a PPO-(NPP)$_x$ film to a corona-poling field as a function of temperature. Heating rates: 25 → 150 °C, ~+4.3°/min; 150 → 180 °C, ~+0.9°/min; 180 → 130 °C, ~-2.0°/min. The line is drawn as a guide to the eye.

prisms as the couplers. The refractive index of the films was determined from the coupling angles of various waveguide modes.[25] For a 1.4-μm-thick, unpoled PPO-NPP film (1.43 functionalization level), two TE modes were observed. The coupling angles for these modes (TE$_0$ and TE$_1$) were measured to be 29.6° and 25.1°, respectively. From these angles, a refractive index of 1.584 ± 0.001 is calculated. The refractive index of a neat PPO film was similarly determined to be 1.580 ± 0.001 at 0.633 μm. Preliminary measurements of scattering loss were carried out with an output coupling prism. By measuring the output intensity as a function of the separation between the input and output coupling prisms, we estimate a loss coefficient of $\alpha < 1$ dB/cm for both the PPO-NPP and neat PPO films.

Acknowledgment. This research was supported by the NSF-MRL program through the Materials Research Center of Northwestern University (Grant DMR8821571) and by the Air Force Office of Scientific Research (Contract AFOSR-86-0105).

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Received November 20, 1989
Revised Manuscript Received January 26, 1990

Desilylation and Michael Addition Reactions of (Trimethylsilyl)ethynyl Ketones: A Novel One-Pot Synthesis of Enamine Ketones, Bis(enamine ketones), and Poly(enamine ketones)

The conventional synthesis of enamine ketones involves the Michael-type addition of amines to hydrogen-terminated ethynyl ketones at room temperature and requires a long reaction period.[1-3] Hydrogen-terminated ethynyl ketones are traditionally prepared by desilylation of (trimethylsilyl)ethynyl ketones using aqueous borax or basic buffer solutions.[4,5] The classical synthesis of (trimethylsilyl)ethynyl ketones involves the Friedel–Crafts reaction of acyl chloride/$AlCl_3$ complexes with bis(trimethylsilyl)acetylene.[4,6] Aliphatic bis(enamine ketones) and aliphatic poly(enamine ketones) have been prepared similarly from aliphatic bis(hydrogen-terminated ethynyl ketones).[7,8] Aromatic bis(hydrogen-terminated ethynyl ketones) have been used to prepare aromatic bis(enamine ketones) and aromatic poly(enamine ketones).[9,10]

Other previously reported methods for the preparation of poly(enamine ketones) include the reaction of diamines with 1,6-diethoxy-1,5-hexadiene-3,4-dione[11] and 2,2′-disubstituted bis(4-ethoxymethylene-5-oxazolone)[12] and the trifluoroacetic acid catalyzed reaction of diamines with aromatic bis(1,3-diketones).[13] Our goal was to develop a more direct synthesis of enamine ketones and poly(enamine ketones) using readily available starting materials.

Herein we report the first example of a one-pot synthesis of enamine ketones and bis(enamine ketones) by the direct reaction of primary (1°) and secondary (2°) amines with (trimethylsilyl)ethynyl ketones and bis[(trimethylsilyl)ethynyl ketones], respectively, in the presence of methanol or ethanol and solvents such as benzene, dimethylformamide, *N*,*N*-dimethylacetamide, and *m*-cresol at temperatures of 90–110 °C. Under these conditions, enamine ketones and bis(enamine ketones) are formed rapidly (2–4 h) in high yield. Also, the one-pot synthesis of poly(enamine ketones) by the reaction of diamines with bis[(trimethylsilyl)ethynyl ketones] under similar conditions is reported for the first time.

Studies of the reaction of a model (trimethylsilyl)ethynyl ketone, 3-(trimethylsilyl)-1-phenyl-2-propyn-1-one[4] (**1**), with aniline in the presence and absence of methanol (Scheme I) show that desilylation occurs only in the presence of both aniline and methanol. The product, *cis*-1-benzoyl-2-(*N*-phenylamino)ethene (**6**), was formed in

0024-9297/90/2223-1894$02.50/0