

A Side-Chain Dendronized Nonlinear Optical Polyimide with Large and Thermally Stable Electrooptic Activity

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Organic second-order nonlinear optical (NLO) materials have received increasing interests due to their potential applications in high-speed electrooptic (E–O) devices with very broad bandwidth (up to 150 GHz) and low driving voltages (<1 V).¹ In the pursuit of a new generation of highly efficient NLO polymers for device fabrications, we have recently developed a series of dendritic chromophores and chromophore-containing dendrimers that possess very interesting nanostructures and E–O activities. By controlling their size, shape, and molecular architecture, we have achieved dramatically enhanced poling efficiency in these materials.^{2–6} These encouraging results motivate us to extend the similar site-isolation principle to several commercially available linear polymers. We have incorporated chromophores that contain fluorinated dendrons onto a hydroxylstyrene photoresist polymer to afford side-chain dendronized NLO polymers.⁷ This new approach allows us to achieve both high poling efficiency and reduced synthetic time for E–O materials simultaneously. An exceptionally large E–O coefficient (97 pm/V at 1.3 μ m) has also been demonstrated. This value is almost twice higher than those obtained in the guest–host systems. Even though these results are very impressive, these materials do not possess the thermal stability that is needed for practical applications. The poling-induced polar order will decay quite rapidly upon heating due to low glass-transition temperature (T_g) of the polystyrene backbone.

To improve this deficiency, we try to apply the site-isolation concept to high-temperature polyimides. In the past decade, thermally stable and high- T_g polyimides were vigorously pursued for fabricating E–O devices.^{1c–e,8} However, most of the NLO polyimides suffer from low poling efficiency due to the intrinsic chain rigidity and π – π stacking of the aromatic backbone. Usually, a high-temperature poling process is needed for orienting chromophore dipoles. As a result, only a very small number of chromophores can tolerate these stringent conditions and afford moderate optical nonlinearity. It remains a very challenging task to achieve large nonlinearity and good thermal stability simultaneously. This is also the main reason that significantly hinders the rapid deployment of E–O devices.⁸

Here, we report the synthesis and characterization of a high- T_g aromatic polyimide with pendant den-

dronized NLO chromophores functionalized on a cardo-bisphenol linkage of a rigid aromatic polyimide backbone. Polyimides with this kind of cardo structure usually possess very high T_g , excellent thermal stability, and good solubility.⁹

Scheme 1 outlines the synthetic route for the preparation of this cardo-type polyimide **PI-OH** with pendant phenol groups. After the base hydrolysis of **1**, it was further reacted with excess aniline in the presence of aniline hydrochloride to afford 9,9-bis(4-aminophenyl)-2,7-dihydroxyfluorene (**3**). The polymerization of diamine monomer **3** with 4,4'-(hexafluoroisopropylidene)diphthalic anhydride was carried out in *m*-cresol using isoquinoline as catalyst. The resulting polyimide, **PI-OH**, is readily soluble in common organic solvents, such as THF, DMF, and DMSO. It was fully characterized by ¹H NMR, ¹³C NMR, GPC, and thermal analysis. The weight-average molecular weight (M_w) of **PI-OH** is approximately 7.3×10^4 with a polydispersity index of 1.9. A distinct T_g was observed at 345 °C by differential scanning calorimetry (DSC). The high T_g value of **PI-OH** can be attributed to its rigid cardo structure along with the presence of polar hydroxy pendant groups, which in turn produce significant interchain interactions. As revealed by thermogravimetric analysis (TGA), this polymer also exhibits outstanding thermal stability with less than 5% weight loss occurring at 514 °C.

The postfunctionalization process was conducted by condensing this precursor polymer with **R₁OH**, the carboxylic derivatives of a dendron-capped polyene-type CLD chromophore, and a smaller pentafluorobenzoic acid, sequentially. These steps proceeded in one pot under a very mild condition using 1,3-dicyclohexylcarbodiimide (DCC) and 4-(dimethylamino)pyridinium 4-toluenesulfonate (DPTS) as the condensation reagents. The resultant NLO polyimide (**PI-CLD**) was fully characterized by ¹H NMR, ¹⁹F NMR, and UV–vis spectroscopy, GPC, and thermal analysis. It shows excellent solubility in common organic solvents, such as chloroform, tetrahydrofuran (THF), and cyclopentanone. By comparing the relative integration of aromatic and aliphatic characteristic peaks in the ¹H NMR spectrum, it was found that 50 mol % of the phenol groups were consumed by **R₁OH**. It can be converted to a ~25 wt % loading level of the core chromophore (donor–conjugation bridge–acceptor moiety excluding the dendritic part) in **PI-CLD**. This was further proved by quantitative analysis of the UV–vis spectra of its solution in 1,4-dioxane.

It has been observed that highly polarizable push–pull compounds like CLD-type chromophores are highly solvatochromic in polar solvents and solid-state environments. For example, a CLD-type chromophore without the protection of dendritic moieties shows significant different λ_{max} s in various polymer matrices: 657 nm in poly(methyl methacrylate) (PMMA), 667 nm in amorphous polycarbonate (APC), and 698 nm in a polar polyquinoline (PQ-100).¹⁰ Since **PI-CLD** is a side-chain dendronized NLO polymer with a quite polar and rigid polyimide backbone, it should possess a quite different microenvironment to the NLO chromophores compared to that of the flexible polystyrene backbone reported earlier (Figure 1 inset).⁷ However, even such a different macromolecular environment, **PI-CLD** shows a very similar chromophoric charge-transfer absorption peak

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Scheme 1. Synthesis of Cardo-Type NLO Polyimide (PI-CLD) with Dendronized Chromophore

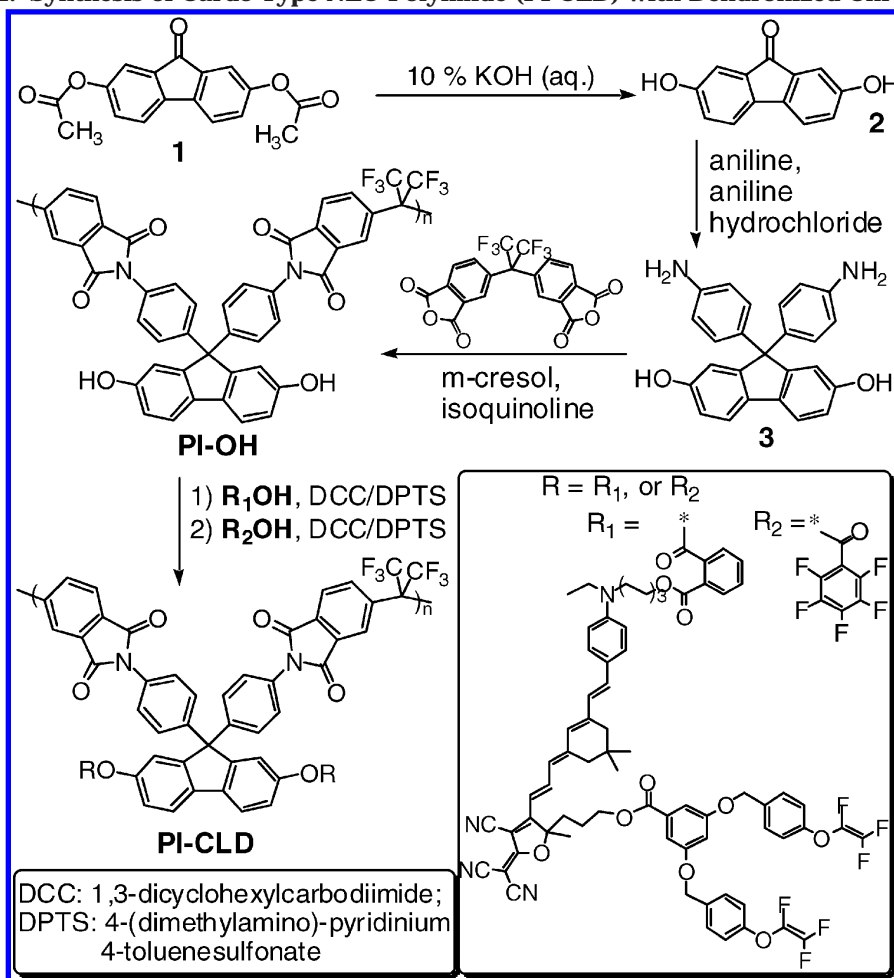


Table 1. Physical Property Comparison between Two Side-Chain Dendronized NLO Polymers PI-CLD and PS-CLD

	λ_{\max} (nm)	n_{1300}^a (n_{TE}/n_{TM})	n_{1550}^b (n_{TE}/n_{TM})	T_g (°C)	dye content (wt %)	poling field (V/ μm)	r_{33}^c (pm/V)	poling efficiency (%) ^d ($r_{\text{actual}}/r_{\text{theo}}$)
PI-CLD	711	1.7104/1.6864	1.6875/1.6660	155	25	85	71	81
PS-CLD	708	1.5851/1.5776	1.5813/1.5738	90	20	142	97	78

^a The refractive indexes at 1.3 μm . ^b The refractive indexes at 1.55 μm . ^c The experimental EO coefficient at 1.3 μm . ^d The ratio of experimental r_{33} value (r_{actual}) to theoretically predicted r_{33} value (r_{theo}) using the two-level model.

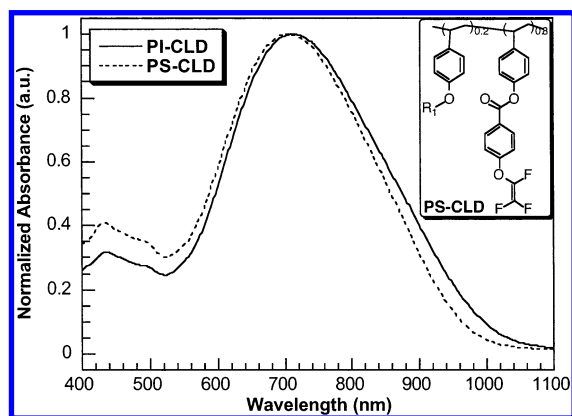


Figure 1. UV-vis spectrum comparison of two side-chain dendronized NLO polymers in different polymer matrixes: PI-CLD, polyimide; PS-CLD, polystyrene.

compared to that of **PS-CLD** (Figure 1). The UV-vis spectra of the thin film **PI-CLD** and **PS-CLD** on glass slides exhibit similar main absorption bands with absorption maxima (λ_{\max} s) at 711 and 708 nm, respectively, both of which are ascribed to the π - π^* charge-

transfer band of the CLD chromophore (Table 1). This comparison demonstrates that the environment around the chromophores is dictated by the site-isolation effect provided by the surrounding dendrons and is independent of the polymer matrix that we selected. This finding is also in good agreement with the similar solvatochromism study of the 3-D shape dendritic chromophore that we previously reported.³

The E-O measurements for **PI-CLD**, and the detailed comparisons of its poling parameters with those of **PS-CLD**, are critical for evaluating the role of the dendrons in affecting the poling efficiency of **PI-CLD**. The solution of **PI-CLD** in cyclopentanone (11 wt %, filtered through a 0.2 μm syringe filter) was spin-coated onto indium tin oxide (ITO) glass substrates. The films were baked under vacuum at 100 °C overnight to ensure the removal of the residual solvent. Then a thin layer of gold was sputtered onto the films as the top electrode for performing the high-electric field poling. The optimum poling condition of the film was achieved at 155 °C with a DC electric field of 0.85 MV/cm. The r_{33} value was measured using the thin-film reflection technique at 1.3 μm ¹¹ and showed a very large E-O coefficient of

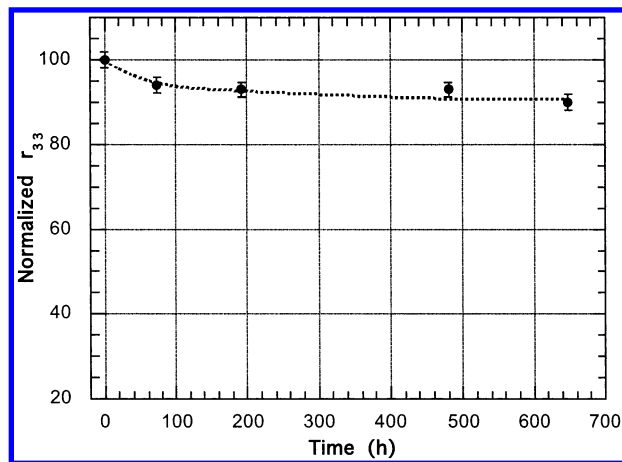


Figure 2. Temporal stability of E–O activity of PI-CLD at 85 °C.

71 pm/V. This high r_{33} value represents $\sim 81\%$ of the highest achievable r_{33} value (88 pm/V) that is predicted by using the two-level model.¹² Most importantly, when compared to the flexible polymer **PS-CLD**, the similar high poling efficiency ($\sim 80\%$ of the theoretically achievable E–O activity) has been reproduced in high T_g and rigid polymer **PI-CLD**.

Moreover, this high- T_g **PI-CLD** exhibits a much improved alignment stability compared to that of **PS-CLD**. The poled **PI-CLD** retains higher than 90% of its original r_{33} value after more than 600 h at 85 °C (Figure 2). For comparison, the flexible polymer **PS-CLD** with a much lower T_g (90 °C) shows only 37% of its original r_{33} value after heating at 70 °C for 144 h.

The structural features of **PI-CLD** can explain very well for its high poling efficiency and excellent thermal stability. This cardo-type polyimide has a rigid and 3-D extended main chain, and along the V-bended repeating units, the dendronized chromophores are attached on the fluorene ring that is perpendicular to the imido backbone. This kind of spatial arrangement can suppress strong interchain interactions of polyimide and reduce potential phase separation between the highly aromatic, rigid polyimide backbone and chromophores. In addition, the cardo-type linkage of the dendronized chromophores may also facilitate the self-assembly of these NLO molecules to form potentially ordered cylindrical rigid rods which will facilitate the dipole alignment during the poling process because less steric hindrance caused by chromophore/polymer chain entanglements.

In conclusion, we have successfully applied the site-isolation principle to a rigid 3-D cardo-type polyimide with very high T_g . High poling efficiency has been achieved to afford a very large E–O coefficient (71 pm/V at 1.3 μm). More than 90% of this value can be retained at 85 °C for more than 650 h. Comprehensive studies to optimize the properties of these high- T_g materials for E–O device fabrication are in progress.

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Supporting Information Available: Text giving detailed experimental information for material preparation and structural characterization. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (12) Katz, H. E.; Dirk, C. W.; Schilling, M. L.; Singer, K. D.; Sohn, J. E. *Mater. Res. Soc. Symp. Proc.* **1987**, *109*, 127. The r_{33} value at 1.55 μm is 58 pm/V estimated from the same two-level model using the experimental value of 71 pm/V at 1300 nm.

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