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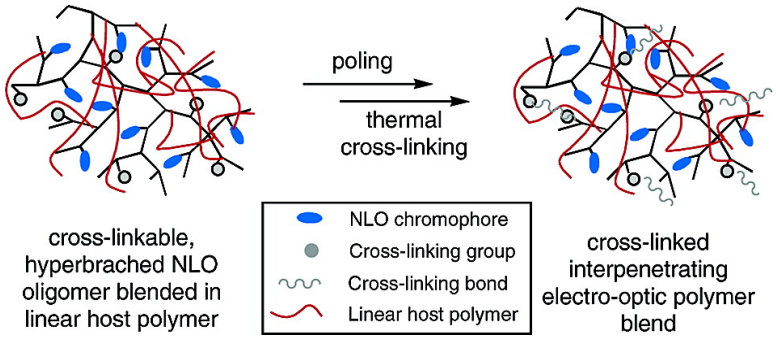

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A New Approach to Highly Electrooptically Active Materials Using Cross-Linkable, Hyperbranched Chromophore-Containing Oligomers as a Macromolecular Dopant

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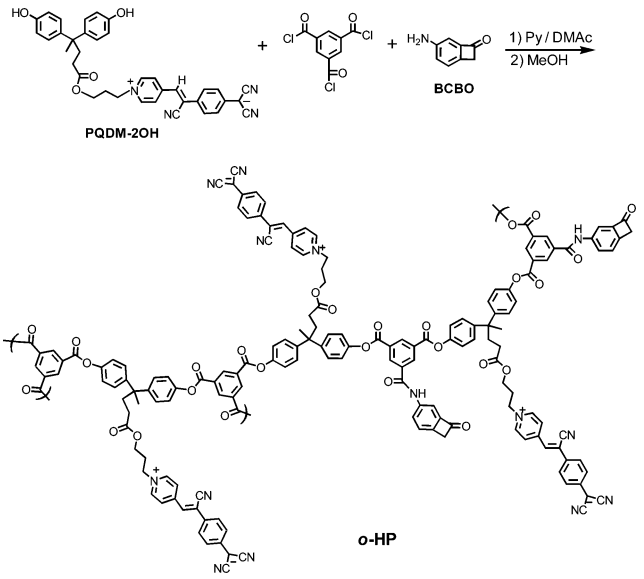
Second-order nonlinear optical (NLO) polymers are being actively pursued for applications in high-speed electrooptic (EO) modulators and other devices.[1] To be practically useful for device applications, NLO polymers must possess some basic properties, such as large and stable EO response and good thermal and photochemical stability. Equally importantly, suitable NLO materials must be able to be formulated and standardized to fulfill the processing requirement for device development. For most developmental work on EO devices,[2] the guest−host type of NLO materials is routinely employed, mainly because of wide selection and easy control of the material compositions through doping molecular chromophores in host polymers. However, phase separation over time and poor temporal stability of the poled NLO materials limit this process for studying various EO devices. Linking the chromophores via covalent bonds onto polymer chains can effectively increase the chromophore loading, prevent phase separation, and stabilize the dipole orientation.[1,3] However, this process lacks flexibility in material formulation, since each host polymer must be selected and each polymer with a given loading of chromophores should be made in a batch-to-batch production. It is difficult to precisely control the compositions and properties (e.g., molecular weight) of NLO materials from batch to batch, and it is also tedious to screen potential host polymers and vary the polymer/chromophore compositions for various device applications. Thus, for device development, it is highly desirable if NLO materials in various compositions can be quickly obtained by simple formulation of a given chromophore.

Herein we propose a new approach to highly efficient NLO materials, which involves the use of cross-linkable, hyperbranched chromophore-containing oligomers as a macromolecular dopant to formulate NLO materials suitable for device development. This unique approach is designed with the following considerations and unique features. (1) A hyperbranched oligomer should have better chain mobility in host polymers than a high molecular weight linear polymer, which should facilitate the chromophore orientation during the poling process. Evidently, dendritic and dendronized NLO polymers have been shown to have very high poling efficiency (e.g., 80%).[4] (2) The cross-linking of hyperbranched oligomers within a host polymer should result in the formation of the host polymer-reinforced, quasi-interpenetrating networks, which can effectively prevent the chromophore relaxation. (3) The chromophore-containing oligomer is readily available in larger quantities than well-defined dendrimers and is easier to isolate and purify than the chromophore itself. (4) A wide range of NLO homogeneous polymer materials can be readily formulated for device development by simply blending a given chromophore-containing oligomer with many host polymers.

To synthesize a hyperbranched NLO oligomer (*o*-HP), an A_2-type monomer (PQDM-2OH, Scheme 1) and a B_3-type monomer (1,3,5-benzenetricarbonyl chloride) were selected. The chromophore [pyridinium tricyanoquinonedimethane (PQDM)] in *o*-HP is zwitterionic[5] and has an extremely large β value of 1930×10^{-30} esu at 1.07 μm in DMF (or β_0 value of -590×10^{-30} esu) from the Hyper−Rayleigh scattering measurement.[6] Recently, EO coefficients up to 45 pm/V at 1550 nm have been demonstrated with the linear polyimides containing PQDM.[7] To form the interpenetrating networks during the poling process at elevated temperatures, 5-aminobenzocyclobutenone (BCBO) was introduced as a new cross-linker into *o*-HP during the polymerization. It has been demonstrated that the BCBO group, by itself or in a variety of polymers, can undergo a ring-opening reaction above 200 °C to form a reactive vinylketene intermediate.[8] The subsequent dimerization and polymerization of the vinylketene groups lead to the polymer cross-linking.

Scheme 1. Preparation of Hyperbranched NLO Oligomers



The monomer concentration, reaction temperature, and time were carefully optimized to avoid gel formation and to control the molecular weight of the products (see Supporting Information). *o*-HP could be prepared in gram quality in laboratory scale and could be scaled up readily. It was characterized by NMR, IR, and GPC ($M_n = 3300$). The inherent viscosity was determined in *N*,*N*-dimethylforamide (DMF) at 30 °C, typically being 0.18 dL/g. The chromophore content in *o*-HP was determined to be 65 wt % by UV−vis spectroscopic analysis, which is close to the feed ratio of 67 wt % by calculation.

o-HP is soluble in polar aprotic solvents such as DMF and *N*-methylpyrrolidinone (NMP) and has a strong intramolecular, charge-transfer (CT) absorption at 659 nm, similar to that of PQDM-2OH in DMF solution. Large negative solvatochromism (60 nm) was observed from acetone ($\epsilon = 20.7$) to methanol ($\epsilon = 32.7$). The glass transition temperature ($T_g = 122$ °C) and thermal stability

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Table 1. Properties of Guest−Host Polymers Containing *o*-HP, PQDM-2OH, and LP in PES

guest in PES (wt %)	ND[a] cm^{-3}	λ_{max}[b] nm	n[c]	T_g[d] °C	r_{33}[e] pm/V
o-HP(5)	4×10^{19}	724	1.6286	202	25
o-HP (10)	7×10^{19}	717	1.6291	192	44
o-HP (15)	10×10^{19}	707	1.6304	175	65
o-HP (20)	13×10^{19}	699/486	1.6317	154	22
PQDM-2OH (5)	7×10^{19}	704	1.6187	116	23
LP (5)	4×10^{19}	712	1.6302	212	18

[a] Number density of PQDM. [b] Absorption of guest−host polymer films. [c] Refractive index at 1.55 μm. [d] Measured by DSC in nitrogen with a heating rate of 10 °C/min. [e] At 1550 nm.

(T_d = 276 °C for 5% weight loss in nitrogen) were characterized by differential scanning calorimetry (DSC) and thermogravimetry, respectively. An exothermic peak starting around 195 °C was observed from the first DSC heating scan, because of the cross-linking reaction of BCBO groups, and was absent in the second scan. After being treated above 200 °C, *o*-HP became insoluble and its blends in poly(ether sulfone) (PES) were partially soluble or swelled in organic solvents (e.g., DMF), indicating the formation of cross-linked, interpenetrating networks.

For electric poling and EO studies, *o*-HP was doped into a high T_g (220 °C) PES (Ultrason E3010). Other polymers such as poly(bisphenol A carbonate) (PC), poly(vinyl pyrrolidinone) (PVP), and polyetherimide (PEI) also appeared as a good matrix for *o*-HP. The T_g and refractive indices (n_{TE}) of *o*-HP/PES blends were in a range of 154−202 °C and 1.628−1.632 (at 1550 nm), as determined by DSC and prism coupling method, respectively (Table 1). No phase separation in films was noticed by examination under optical microscope (50×) until the *o*-HP loading reached up to 20 wt %, which is equivalent to the number density of PQDM of 13×10^{19} cm^{-3}. At this point, a sharp blue-shifted absorption band appeared at 486 nm in the UV−vis spectrum of the *o*-HP/PES film.

The *o*-HP/PES films with thickness of 2−3 μm were prepared by casting a solution in DMF (3 wt %/v) onto ITO glass substrates. The films were vacuum-dried at 100 °C overnight to remove residual solvent before sputtering a thin layer of gold (∼150 nm) onto the films as the top electrode for parallel electrode poling. The poling was done at temperatures near the T_g (i.e., 170−190 °C) for 30−40 min, followed by further heating at 200−210 °C for 5 min. The poling voltages applied across the films were 0.7−0.9 MV/cm. EO coefficients (r_{33}) of the poled *o*-HP/PES films were measured using the Teng−Man setup.[9] A continuous increase of r_{33} values can be seen with the increase of *o*-HP content in PES (Table 1). The highest r_{33} value of 65 pm/V was obtained for the sample containing 15 wt % of *o*-HP (ND = 10×10^{19} cm^{-3}), which is significantly larger than that (45 pm/V) of side-chain NLO polyimides containing a similar amount of PQDM.[7] Further increase of the *o*-HP content (e.g., 20 wt %) led to a sharp decrease in EO coefficients, due to severe aggregation of chromophores. The temporal stability of EO response was founded to be excellent, as the r_{33} value of the poled *o*-HP/PES sample (15 wt %) maintained more than 90% of its original value after holding at 85 °C in nitrogen over 1200 h (Figure 1).

For comparison, a linear analogue (LP) derived from PQDM-2OH and isophthaloyl chloride (see Supporting Information) and PQDM-2OH were blended in PES, respectively. Phase separation was observed when the number density of PQDM in both blends was higher than 7×10^{19} cm^{-3}. The obtained EO coefficients were much lower, being 18 pm/V for LP/PES and 23 pm/V for PQDM-2OH/PES, than those obtained from *o*-HP/PES (65 pm/V with ND = 10×10^{19} cm^{-3} and 44 pm/V with ND = 7×10^{19} cm^{-3}). The observed enhancement in EO coefficients with the *o*-HP/PES system indicates a higher poling efficiency, presumably due to higher chain mobility and less chromophore interaction.

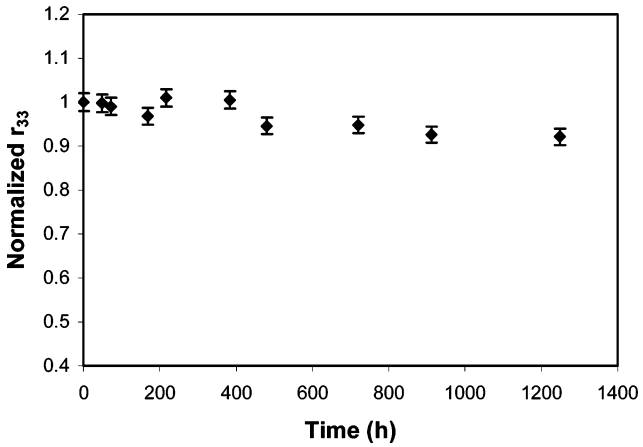

Figure 1. Temporal stability of the poled and cross-linked *o*-HP/PES (15 wt %) blend at 85 °C in nitrogen. Normalized r_{33} as a function of time.

In conclusion, we demonstrated a new approach toward highly efficient NLO materials by using a cross-linkable, hyperbranched NLO oligomer as a macromolecular guest and a commercially available polymer as a host. This approach offers advantages over other known routes involving the use of side-chain NLO polymers and molecular chromophore-doped polymer systems, such as larger EO coefficients, excellent temporal stability, and versatility and flexibility in material preparation and formulation.

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Supporting Information Available: Syntheses and characterizations of PQDM-2OH, *o*-HP, and LP. This material is available free of charge via the Internet at http://pubs.acs.org.

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