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Highly Efficient and Thermally Stable Nonlinear Optical Dendrimer for Electrooptics

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For the fabrication of practical E−O devices, critical material requirements, such as large E−O coefficients, high stability (thermal, chemical, photochemical, and mechanical), and low optical loss, need to be simultaneously optimized.[1] In the past decade, a large number of highly active nonlinear optical (NLO) chromophores have been synthesized, and some of these exhibit very large macroscopic optical nonlinearities in high electric field poled guest/host polymers.[2] To maintain a stable dipole alignment, it is a common practice to utilize either high glass-transition temperature (T_g) polymers with NLO chromophores as side chains or cross-linkable polymers with NLO chromophores that could be locked in the polymer network.[3] However, it is difficult to achieve both large macroscopic nonlinearities and good dipole alignment stability in the same system. This is due to strong intermolecular electrostatic interactions among high dipole moment chromophores and high-temperature aromatic-containing polymers, such as polyimides and polyquinolines that tend to form aggregates. The large void-containing dendritic structures[4−8] may provide an attractive solution to this critical issue because the dendrons can effectively decrease the interactions among chromophores due to the steric effect. Furthermore, these materials are monodisperse, well-defined, and easily purifiable compared to polymers that are made by the conventional synthetic approaches.

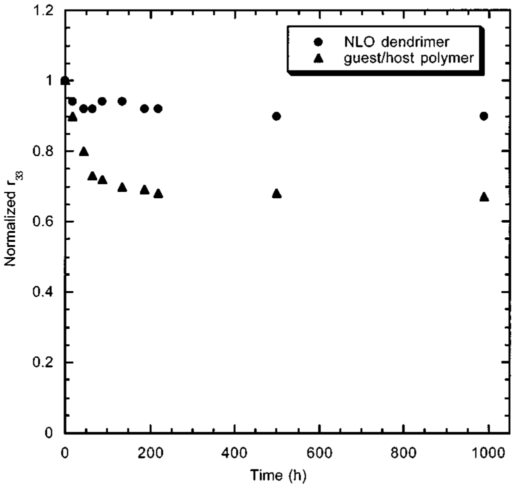

Figure 1. Temporal stability of the poled/cross-linked NLO dendrimer and guest/host polymer system at 85 °C in nitrogen. Normalized r_{33} as a function of baking time.

Table 1. Electrooptic Coefficients and Temporal Stability of Three NLO Material Systems

material system	electrooptic coefficient (r_{33}, pm/V, at 1.55 μm)	temporal stability (%, after 1000 h at 85 °C)
1. cross-linkable dendrimer	60	>90
2. guest/host polymer	<30	<65
3. non-cross-linkable dendrimer	<10	fast decay

In this paper, we report the synthesis and characterization of a cross-linkable NLO dendrimer **3** exhibiting very large optical nonlinearity and excellent thermal stability. This NLO dendrimer was constructed through a double-end functionalization of a 3-D shape phenyl-tetracyanobutadienyl (Ph-TCBD) thiophene−stilbene-based NLO chromophore[9] as the center core and the cross-linkable trifluorovinyl ether-containing dendrons[10,11] as the exterior moieties (Scheme 1). Spatial isolation from the dendrimer shell decreases chromophore−chromophore electrostatic interactions, and thus enhances macroscopic optical nonlinearity because electrostatic interactions among chromophores play a critical role in defining the maximum macroscopic optical nonlinearity that can be achieved for a given chromophore.[12] In addition, the NLO dendrimer can be directly spin-coated without the usual prepolymerization process needed to build up viscosity, since it already possesses a fairly high molecular weight (4664 Da). The chromophore loading density of the dendrimer is 33 w/w %, which is confirmed by elemental analysis. There are also several other advantages derived from this approach, such as excellent alignment stability and mechanical properties, which are obtained through the sequential hardening/cross-linking reactions during the high-temperature electric-field poling process. Very large E−O coefficient ($r_{33} = 60$ pm/V at 1.55 μm), and long-term alignment stability (retaining >90% of its original r_{33} value at 85 °C for more than 1000 h) were achieved for the poled dendrimer.

The dendrimer **3** was synthesized by the Mitsunobu condensation between the carboxyl groups on the three branches of the desirable core molecule **2** and the hydroxy-containing chromophore precursor **1** that has cross-linkable trifluorovinyl ether on the dendrons. Then, the intermediate was reacted with tetracyanoethylene (TCNE) to activate the Ph-TCBD electron acceptor (Scheme 1). The purity and structure of the dendrimer **3** were fully characterized by gel permeation chromatography

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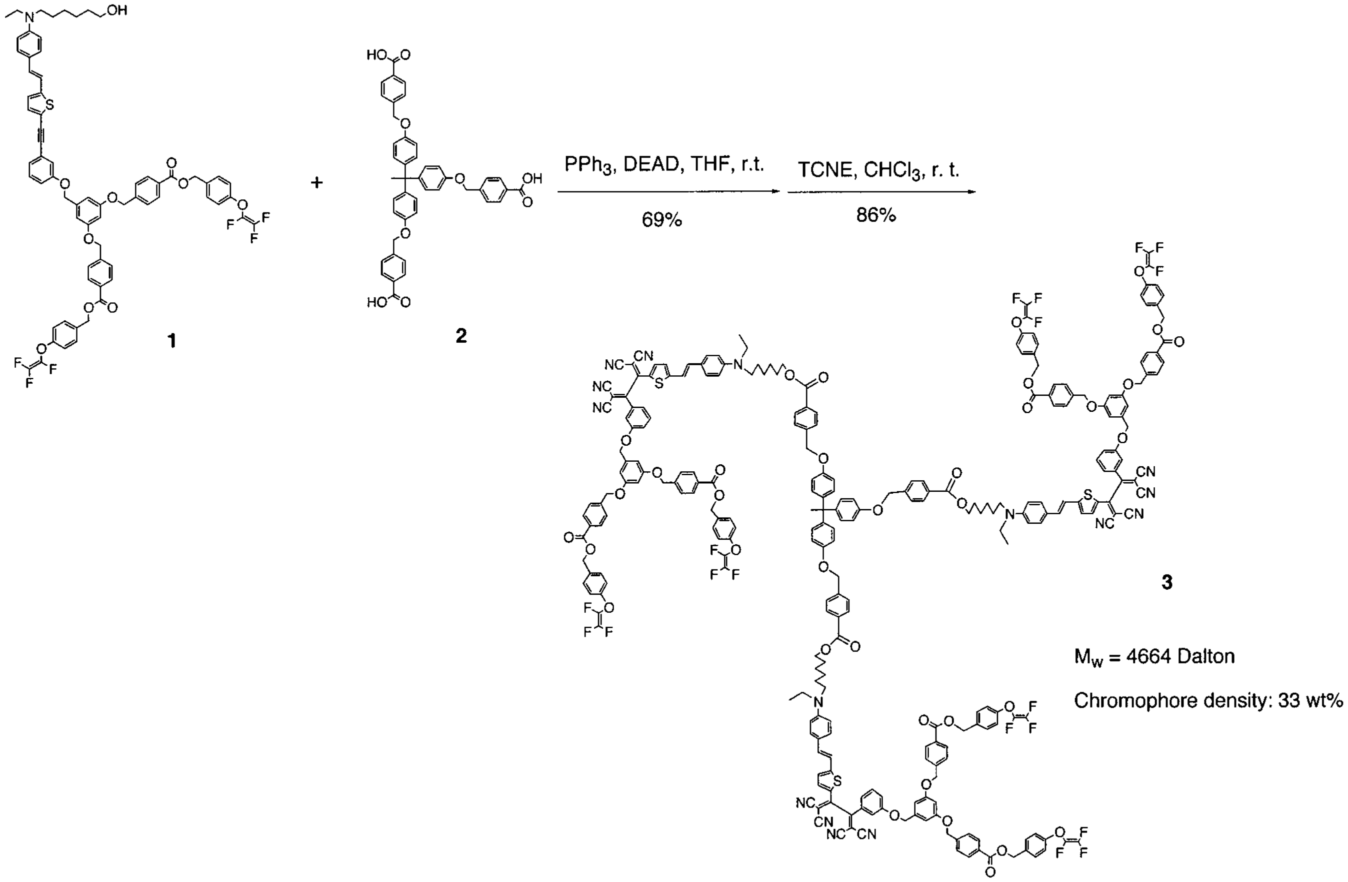
Scheme 1. Synthesis of the Cross-Linkable NLO Dendrimer



M_w = 4664 Dalton

Chromophore density: 33 wt%

(GPC), matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry, and ^{1}H and ^{19}F NMR spectroscopy. The GPC trace shows a single, sharp, and symmetrical peak that indicates a single component in the material. This result was confirmed by the MALDI-TOF mass spectrometry that a peak corresponding to the mass unit of the NLO dendrimer with the formula of $C_{269}H_{207}F_{18}N_{15}O_{36}S_3$ was obtained. All of the resonance peaks in the ^{1}H NMR spectrum can be assigned to the protons of different moieties on the NLO dendrimer.

The NLO dendrimer is soluble in chloroform, cyclopentanone, and THF. Pinhole free thin films can be processed directly from the dendrimer solution using cyclopentanone/mesitylene as the co-solvents. The UV/vis spectrum of the dendrimer film exhibits a strong absorption maximum at 655 nm ascribed to the $\pi-\pi^*$ charge-transfer band of the NLO chromophore. The NLO dendrimer also possesses very low birefringence ($n_{TE} = 1.6419$, $n_{TM} = 1.6408$) at 1.55 μm due to its 3-D isotropic structure.

Thermal analysis of **3** by differential scanning calorimetry showed an endothermic melting peak at 73 °C and an exothermic transition above 140 °C, at which temperature the peripheral trifluorovinyl ether groups were polymerized and cross-linked. For E−O measurements, the solution of **3** in mesitylene/cyclopentanone (22 w/w % solution, filtered through a 0.2 μm syringe filter) was spin-coated onto an indium tin oxide (ITO) glass substrate. The film was heated under vacuum at 85 °C overnight to remove residual solvent. The dipole alignment was achieved by corona poling, and the r_{33} value was measured using a simple reflection technique[13] at 1.55 μm. After sequential heating (at 130 °C for 4 min, 150 °C for 5 min, 165 °C for 15 min, and 175 °C for 8 min) and poling (with 3.0 kV at 175 °C for 6 min and 3.2 kV at 190 °C for 10 min), a very large E−O coefficient ($r_{33} = 60$ pm/V) was achieved. The resulting poled dendrimer also possessed excellent temporal stability that retained >90% of its original r_{33} value at 85 °C for more than 1000 h (Figure 1). In comparison, E−O studies of a guest/host system in which a nondendron-modified similar structure chromophore (optimized loading level: 30 wt %) was formulated into a high-temperature polyquinoline (PQ-100). The T_g of the resulting system is plasticized to approximately 165 °C. After the same sequential heating and corona poling as that for the dendrimer, the guest/host system showed a much smaller E−O coefficient (less than 30 pm/V) and worse temporal stability (only retained <65% of its original r_{33} value at 85 °C after 1000 h). In addition, the attempt to corona pole a non-trifluorovinyl ether functionalized dendrimer only showed a very fast decay of E−O signal (<10 pm/V) after the sample being poled and measured at room temperature. This is due to the intrinsic low T_g (<50 °C) and very large free volume of the dendrimer (Table 1). On the basis of these results, the large r_{33} of the poled dendrimer is largely due to the dendritic effect which allows the NLO dendrimer to be efficiently aligned. On the other hand, the high temporal stability of the poled dendrimer mainly results from the efficient sequential cross-linking/poling process.

In conclusion, we have developed a highly efficient and thermally stable NLO dendrimer consisting of a 3-D shape Ph-TCBD-containing chromophore that was double-end functionalized with the dendritic envelope and thermally cross-linkable trifluorovinyl ether periphery. The resulting dendrimer exhibits a combination of large r_{33} value of 60 pm/V at 1.55 μm and good temporal stability at 85 °C. Various structural parameters can be further fine-tuned to provide E−O materials with optimal physical properties.

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