Reinforced Site Isolation Leading to Remarkable Thermal Stability and High Electrooptic Activities in Cross-Linked Nonlinear Optical Dendrimers

Zhengwei Shi,[†] Jingdong Luo,[†] Su Huang,[†] Xing-Hua Zhou,[†] Tae-Dong Kim,[†]
Yen-Ju Cheng,[†] Brent M. Polishak,[‡] Todd R. Younkin,[§] Bruce A. Block,[§] and
Alex K.-Y. Jen*[,†,‡]

Department of Materials Science and Engineering and Department of Chemistry, University of Washington, Seattle, Washington 98195, and Intel Corporation, Components Research, Hillsboro, Oregon 97124

Received July 5, 2008. Revised Manuscript Received August 23, 2008

A series of cross-linkable electro-optic (E-O) dendrimers have been developed with anthracene- and acrylate-containing dendrons functionalized on the periphery of chromophores that can form thermally stable Diels−Alder adducts. These new E-O dendrimers with a high density of standardized **AJL8**-type chromophore are originally prone to thermo-decomposition in their thermoplastic form but can be converted into thermally stable networks to provide excellent site isolation for these chromophores. After poling, large E-O coefficients (up to 84 pm/V at 1310 nm) can be obtained in these dendrimers. These poled E-O dendrimers can maintain their alignment stability at 200 °C for 30 min and also possess impressive long-term stability at 150 °C for more than 200 h. This result provides a very effective molecular engineering approach to systematically increase the thermal stability of highly polarizable dipolar chromophores for high temperature on-chip applications.

Introduction

Extensive research to produce oriented nonlinear optical (NLO) chromophores exhibiting large electro-optic (E-O) activity and good thermal stability has been pursued for years.[1,2] Recent studies showed that effective site isolation and molecular assembly are very critical for improving the performance of such materials.[3,4] In newly reported dendritic molecular glasses, chromophores with large hyperpolarizability ($\beta\mu$) have been selectively functionalized and self-assembled into well-defined architectures, leading to materials with high poling-induced acentric order and large E-O coefficients (r_{33} values of up to 100−300 pm/V at 1310 nm wavelength).[3] These materials provide a powerful platform to build innovative optical devices, such as low-V_π Mach−Zehnder interferometers,[5] E-O ring resonators,[6] polymer−silicon slotted waveguide modulators,[7] and so forth. Although these advances are very encouraging, it is believed that more impact could be accomplished for high-speed information processing if the well-established semiconductor processes of microelectronics can be applied to photonics. This would provide a tremendous boost to the development of devices for urgently needed high bandwidth information processing.[8] In order to fulfill this goal, materials need to meet numerous stringent requirements in manufacturing, assembly, storage, and end-use environments of devices. Therefore, the search for organic E-O materials with sufficient r_{33} values and excellent thermal stability is a great challenge. The poling induced polar order of large $\beta\mu$ chromophores in any organic spin-on materials must withstand prolonged operation temperatures of up to 100 °C and brief temperature excursions during processing that may exceed 250 °C.[9] To date, many studies have been performed on improving one or some of

---

* Corresponding author. E-mail: ajen@u.washington.edu.

[†] Department of Materials Science and Engineering, University of Washington.

[‡] Department of Chemistry, University of Washington.

[§] Intel Corporation.

(1) (a) Lee, M.; Katz, H. E.; Erben, C. D.; Gill, M.; Gopalan, P.; Heber, J. D.; McGee, D. J. *Science* **2002**, *298*, 1401. (b) Enami, Y.; DeRose, C. T.; Mathine, D.; Loychik, C.; Greenlee, C.; Norwood, R. A.; Kim, T. D.; Luo, J.; Tian, Y.; Jen, A. K.-Y.; Peyghambarian, N. *Nature Photonics* **2007**, *1*, 183.

(2) (a) Hochberg, M.; Baehr-Jones, T.; Wang, G.; Shearn, M.; Harvard, K.; Luo, J.; Chen, B.; Shi, Z.; Lawson, R.; Sullivan, P.; Jen, A. K.-Y.; Dalton, L.; Scherer, A. *Nat. Mater.* **2006**, *5*, 703. (b) Facchetti, A.; Annoni, E.; Beverina, L.; Morone, M.; Zhu, P.; Marks, T. J.; Pagani, G. A. *Nat. Mater.* **2004**, *3*, 910. (c) Marder, S. R.; Cheng, L. T.; Tiemann, B. G.; Friedli, A. C.; Blanchard-Desce, M.; Perry, J. W.; Skindhoej, J. *Science* **1994**, *263*, 511.

(3) Kim, T.-D.; Kang, J.-W.; Luo, J.; Jang, S.-H.; Ka, J.-W.; Tucker, N.; Benedict, J. B.; Dalton, L.; Gray, T.; Overney, R.; Park, D. H.; Herman, W. N.; Jen, A. K.-Y. *J. Am. Chem. Soc.* **2007**, *129*, 488.

(4) Sullivan, P. A.; Rommel, H.; Liao, Y.; Olbricht, B. C.; Akelaitis, A. J. P.; Firestone, K. A.; Kang, J.-W.; Luo, J.; Davies, J. A.; Choi, D. H.; Eichinger, B. E.; Reid, P. J.; Chen, A.; Jen, A. K-Y.; Robinson, B. H.; Dalton, L. R. *J. Am. Chem. Soc.* **2007**, *129*, 7523.

(5) Baehr-Jones, T.; Penkov, B.; Huang, J.; Sullivan, P.; Davies, J.; Takayesu, J.; Luo, J.; Kim, T.-D.; Dalton, L.; Jen, A.; Hochberg, M.; Scherer, A. *Appl. Phy. Lett.* **2008**, *92*, 163303/1.

(6) Sun, H.; Pyajt, A.; Luo, J.; Shi, Z.; Hau, S.; Jen, A. K.-Y.; Dalton, L.; Chen, A. *IEEE Sens. J.* **2007**, *7*, 515.

(7) Wang, G.; Baehr-Jones, T.; Hochberg, M.; Scherer, A. *Appl. Phys. Lett.* **2007**, *91*, 143109.

(8) Baehr-Jones, T. W.; Hochberg, M. J. *J. Phys. Chem. C* **2008**, *112*, 8085.

(9) Miller, R. D.; Burland, D. M.; Jurich, M.; Lee, V. Y.; Moylan, C. R.; Thackara, J. I.; Twieg, R. J.; Verbiest, T.; Volksen, W. *Macromolecules* **1995**, *28*, 4970.

10.1021/cm801828w CCC: $40.75

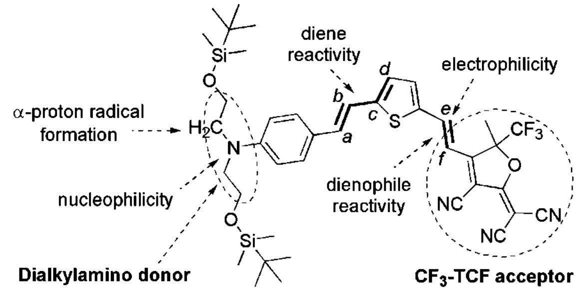


Figure 1. Speculative analysis of the chemical instability of the **AJL8** chromophore at high temperatures.

these required properties.[10−12] However, none of the materials developed so far can meet all of the above criteria. Furthermore, the thermal stability and decomposition mechanisms of present generation highly polarizable chromophores are not well understood.

Here we report a new strategy to tackle this very challenging problem and gain greatly improved stability in organic E-O dendrimers through reinforced site isolation. The intrinsic stability of typical high-r_{33} E-O dendrimers and binary polymers under high temperature (up to 200 °C) was also investigated. These materials often contain high concentrations of chemically sensitive chromophores, which are spaced apart by either physical $\pi-\pi$ interactions or "loosely" cross-linked polymeric networks containing flexible tether groups.[3,13] Most of these materials have relatively low to moderate glass transition temperatures (T_g) and are only thermally stable enough (85−150 °C) to satisfy the basic fabrication and operation of conventional optical modulators.

However, rapid decomposition of chromophores is often observed for these materials under higher temperatures.[3,13] From both thermal and spectroscopic analyses of a standardized dipolar chromophore, 2-[4-(2-{5-[2-(4-{Bis-[2-(tert-butyl-dimethyl-silanyloxy)-ethyl]-amino}-phenyl)-vinyl]-thiophen-2-yl}-vinyl)-3-cyano-5-methyl-5-trifluoromethyl-5H-furan-2-ylidene] malononitrile (**AJL8**, Figure 1) under heating, it was found that a bimolecular reaction mechanism is responsible for the initial decomposition of the chromophore. Since the detailed mechanism for site-specific reactivity of NLO chromophores has not been well understood in the past, this provides a very useful baseline study for further optimization of organic E-O materials for high temperature applications.[14,15] One possible solution to this quandary is to create reinforced site isolation via controlled lattice hardening in E-O dendrimers and polymers. In pursuit of this, we have synthesized a new type of cross-linkable dendritic molecular glass, in which the anthracene−acrylate-based Diels−Alder (DA) cycloaddition was employed as a new protocol for high-temperature lattice hardening. Due to the high chromophore density, these dendrimers are initially vulnerable to thermal decomposition in their individual soft forms, which can be sequentially converted into thermally stable networks via DA cross-linking. More importantly, such a dynamic lattice hardening is compatible with the poling process. After poling, large E-O coefficients (up to 84 pm/V) of these materials are stable up to 200 °C for 30 min of thermal excursion. They also showed impressive long-term stability at 150 °C for more than 200 h. This exceptional result indicates a very effective route to improve thermal stability of highly efficient chromophores via reinforced site isolation.

Results and Discussion

Thermal Analysis of AJL8 **Chromophore. AJL8** was selected as the model compound for studying the thermal decomposition pathway of dipolar chromophores. **AJL8** exhibits a relatively large molecular hyperpolarizability (β values around 4000 × 10^{-30} esu).[16] By doping 25 wt % of **AJL8** into an amorphous polycarbonate (**APC**), the guest−host polymer can be poled at ~ 150 °C, leading to a moderate r_{33} value of ~50 pm/V at 1310 nm wavelength with good temporal stability at 85 °C. Because of the reasonable nonlinearity and stability in **AJL8/APC** system, this material can be used in conventional E-O devices. However, the thermal stability of **AJL8**-type chromophores has never been thoroughly studied for temperatures greater than 200 °C.

The chemical structure of **AJL8** contains a strong dialkylamino donor and CF_3-TCF acceptor.[16] Because of its strong charge transfer nature, this type of molecule is susceptible to reactions with nucleophilic/electrophilic moieties and diene/dienophile (Figure 1). Previously, it was found that the dialkylamino donor tends to decompose under high temperatures[17] due to its nucleophilicity and the α-hydrogens adjacent to the nitrogen.[18] The chemical sensitivity of this chromophore could be further located along its π-conjugated bridge, owing to the reactivity of the electron-rich vinylthiophene-based butadiene from C_a to C_d, the electrophilicity of C_e, and the reactivity of electron-deficient double bonds at the acceptor end. These considerations indicate the potential complexity of chromophore decomposition pathways at high temperatures.

Thermal stability of **AJL8** has been studied earlier by differential scanning calorimetry (DSC). At a heating rate

---

(10) (a) Kang, H.; Facchetti, A.; Jiang, H.; Cariati, E.; Righetto, S.; Ugo, R.; Zuccaccia, C.; Macchioni, A.; Stern, C. L.; Liu, Z.; Ho, S.-T.; Brown, E. C.; Ratner, M. A.; Marks, T. J. *J. Am. Chem. Soc.* **2007**, *129*, 3267. (b) Faccini, M.; Balakrishnan, M.; Diemeer, M.; Hu, Z.-P.; Clays, K.; Asselberghs, I.; Leinse, A.; Driessen, A.; Reinhoudt, D.; Verboom, W. *J. Mater. Chem.* **2008**, *18*, 2141.

(11) Ma, H.; Chen, B.; Sassa, T.; Dalton, L. R.; Jen, A.K.-Y. *J. Am. Chem. Soc.* **2001**, *123*, 986.

(12) (a) Shi, Z.; Hau, S.; Luo, J.; Kim, T.-D.; Tucker, N.; Ka, J.-W.; Sun, H.; Pyajt, A.; Chen, A.; Dalton, L.; Jen, A. K-Y. *Adv. Funct. Mater.* **2007**, *17*, 2557. (b) Kim, T.-D.; Luo, J.; Cheng, Y,-J.; Shi, Z.; Hau, S.; Jang, S.-H.; Zhou, X.-H.; Tian, Y.; Polishak, B.; Huang, S.; Ma, H.; Dalton, L.; Jen, A. K-Y *J. Phys. Chem. C* **2008**, *112*, 8091.

(13) Luo, J.; Huang, S.; Cheng, Y.-J.; Kim, T.-D.; Shi, Z.; Zhou, X.-H.; Jen, A. K.-Y. *Org. Lett.* **2007**, *9*, 4471.

(14) (a) Furuta, P.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **2003**, *125*, 13173. (b) Gorman, C. B.; Smith, J. C. *Acc. Chem. Res.* **2001**, *34*, 60. (c) Kawa, M.; Fréchet, J. M. J. *Chem. Mater.* **1998**, *10*, 286. (d) Muller, C.; Ackerman, L. J.; Reek, J. N. H.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *J. Am. Chem. Soc.* **2004**, *126*, 14960.

(15) (a) Li, Q.; Li, Z.; Ye, C.; Qin, J. *J. Phys. Chem. B* **2008**, *112*, 4928. (b) Harth, E. M.; Hecht, S.; Helms, B.; Malmstrom, E. E.; Fréchet, J. M. J.; Hawker, C. J. *J. Am. Chem. Soc.* **2002**, *124*, 3926.

(16) Jen, A.; Luo, J.; Kim, T. D.; Chen, B.; Jang, S. H.; Kang, J. W.; Tucker, N.; Hau, S.; Tian, Y.; Ka, J. W.; Haller, M.; Liao, Y.; Robinson, B.; Dalton, L.; Herman, W. *Proc. SPIE-Int. Soc. Opt. Eng.* **2005**, *5935* (Linear and Nonlinear Optics of Organicmaterials), 49.

(17) Moylan, C. R.; Twieg, R. J.; Lee, V. Y.; Swanson, S. A.; Betterton, K. M.; Miller, R. D *J. Am. Chem. Soc.* **1993**, *115*, 12599.

(18) Staub, K.; Levina, G. A.; Barlow, S.; Knowalczyk, T. C.; Lackritz, H.; Barzoukas, M.; Fort, A.; Marder, S. R. *J. Mater. Chem.* **2003**, *13*, 825.

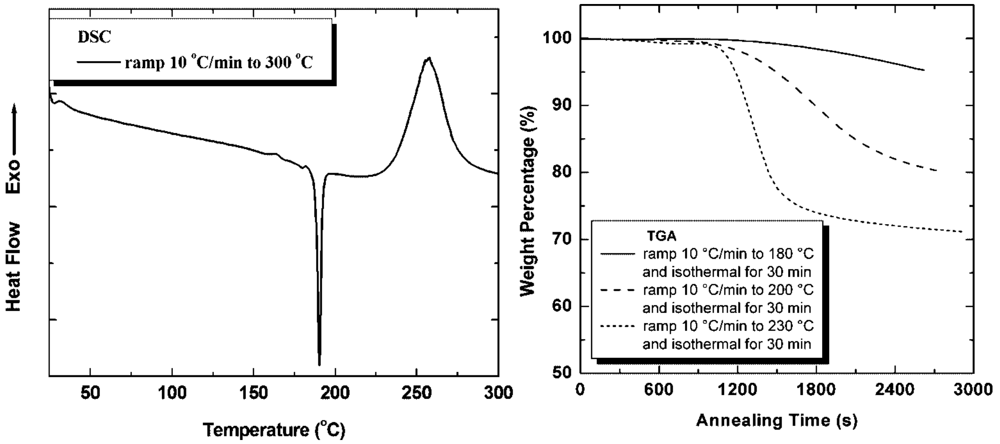


Figure 2. Thermal analysis of **AJL8** chromophore.

of 10 °C/min under nitrogen atmosphere, **AJL8** was found to start to decompose at temperature above its melting point (192 °C) (Figure 2). This thermally induced decomposition can be quantified by programmed thermal gravimetric analysis (TGA). The weight loss of the compound was very minimal (<1 wt %) during the first 15−20 min of temperature ramp up and then started to increase nonlinearly with the time of isothermal annealing. The relative rate of weight loss is highly temperature dependent, and the decomposition of compound is much faster at higher annealing temperatures. Surprisingly, even at a temperature of 180 °C which is lower than its melting point, a ~5 wt % weight loss has been observed after 30 min of isothermal annealing. This level of weight loss indicates non-negligible chromophore decomposition, which has been verified by thin layer chromatography (TLC).

Study of Thermal Decomposition Pathway for AJL8 **Chromophore.** The crystalline **AJL8** sample was first isothermally heated at 200 °C for 5 min. After cooling under N_2 to room temperature, the residual sample still has good solubility in common organic solvents, allowing the decomposed products to be analyzed by TLC, UV−vis−NIR, ^{1}H NMR, and mass spectrometry. Harsher curing conditions, such as higher temperature or longer curing time, often gave insoluble solids, which may be the polymerized byproducts after thermolysis. These tests provide useful information about the critical pathway for **AJL8** thermal decomposition.

The absorption spectrum of the cured samples measured in THF is quite different from that of the pristine **AJL8**. The absorption maximum (λ_{max}) has blue-shifted by ~80 nm, which coincides with the absorption of a much shorter chromophore **1** (Figure 3). Indeed, the cured product contains **1** as the major component (~60%), which was verified by the combined analysis of TLC, ^{1}H NMR, and mass spectrometry. (Figure 4)

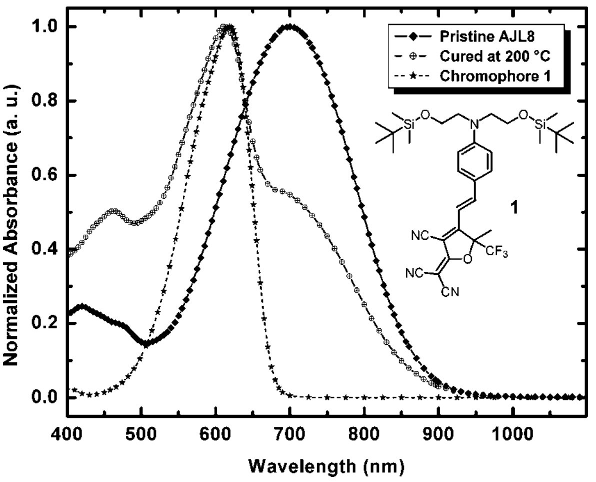


Figure 3. Comparing the solution absorption spectra of **AJL8**, its sample after thermal curing (ramp to 200 °C at the rate of 10 °C/min and kept at this temperature for 5 min under nitrogen), and a short chromophore **1** (structure inserted) in THF. The concentration has been normalized to be 0.67 mg/mL.

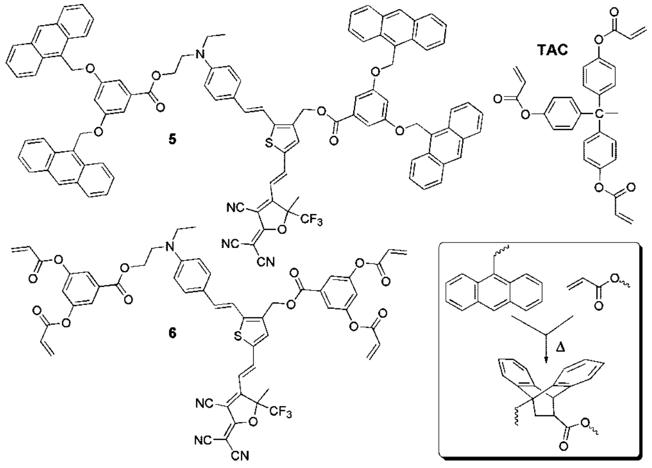
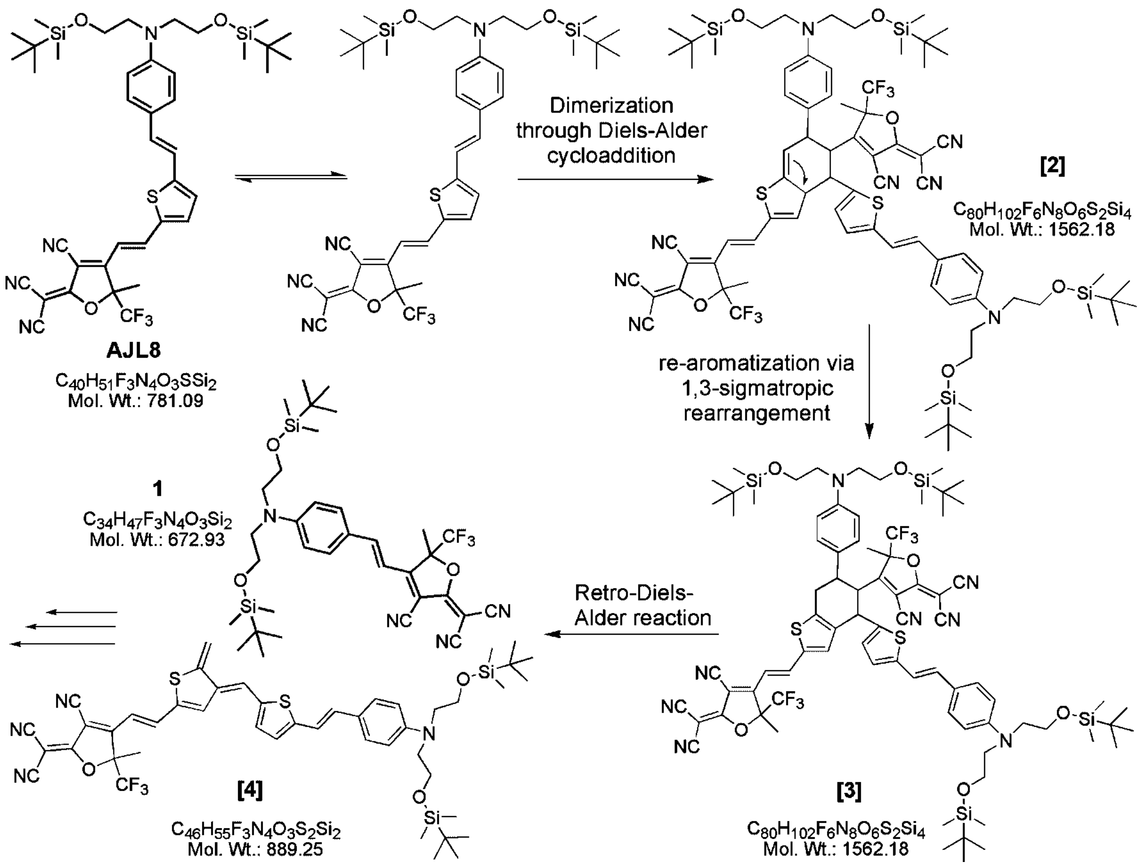


Figure 4. Structures of DA cross-linkable E-O dendrimer **5** and **6** and a dienophile cross-linker TAC.

The scheme of tandem DA and retro-DA reactions was proposed as the primary decomposition pathway for **AJL8** chromophore. In this scheme, two **AJL8** molecules dimerize to form a DA adduct **2**. The metastable compound **2** undergoes 1,3-sigmatropic rearrangement to give **3** with the regenerated thiophene ring. Under elevated temperatures, compound **3** is subject to retro-DA reaction to afford the shorter chromophore **1**. This proposed scheme is based on following experimental evidence: (1) The analysis of the mass spectrum of decomposed products by electrospray ionization showed three distinct peaks with the charge/mass ratio (*m*/*z*) values corresponding to species **1** (100), **AJL8** (55), **4** (10) or its isomers and **2** or **3** (trace), respectively, and the numbers in the parentheses are the relatively

Scheme 1. Proposed Tandem Diels-Alder and Retro-Diels-Alder Decomposition Pathway of AJL8 Chromophore



intensities of peaks; (2) large dipole moment chromophores like **AJL8** tend to pack antiparallel[19] which facilitates intermolecular DA cycloaddition reaction; (3) the s-cis conformer, with respect to C_b—C_c, could be formed through σ-bond rotation at elevated temperatures to induce some reactivities of **AJL8** at the butadiene structure from C_a to C_d;[13] (4) compound **1** is unlikely to be the homolysis product of **AJL8**, due to the fact that nearly no weight loss has been observed during sample preparation and the thermal activation energy at the curing temperature of 200 °C is far below the bond dissociation energy of the molecule; and (5) more rapid chromophore decomposition is expected once such a pathway is initiated and generates unstable species such as **2**, **3**, and **4** causing avanlanche-like chromophore decomposition. (Scheme 1)

New Anthracene—Acrylate-Based Diels—Alder Lattice Hardening for Reinforced Site-Isolation in Cross-Linkable Dendrimers. Good site isolation of chromophores provided by NLO dendrimers and dendronized polymers has been adopted for years to overcome their strong electrostatic interactions and achieve good poling efficiency. DA lattice hardening is by far one of the most adaptable schemes for cross-linking these materials to enhance temporal stability.[12,20] Our approach here is to enhance the site isolation effect via high temperature DA lattice hardening to sustain over 200 °C or beyond heating and to suppress the possible bimolecular reaction pathway of chromophore decomposition.

A DA cross-linkable E-O dendrimer[12a] **5** was chosen for the model study. This dendrimer was functionalized with four anthryl groups at the periphery. A new triacrylate monomer (**TAC**) was used as the dienophile cross-linker. This compound has excellent compatibility with **5**, and the 1:1 binary mixture of **5** and **TAC** (hereafter **5/TAC**, Figure 5) is highly amorphous. The formulated solution of **5/TAC** was spin-coated onto glass and indium tin oxide (ITO) substrates to form high optical quality films with micron thickness. The onset temperature (T_x) of the anthracene—acrylate-based DA cross-linking reaction is around 120 °C, which is close to its glass transition temperature (T_g). In comparison, the composite of **5/TMI**, in which **TMI** is a previously used

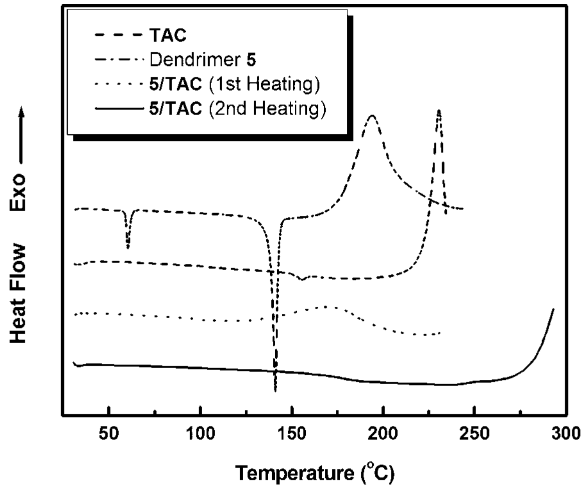


Figure 5. Thermal analysis of **TAC**, **5**, and **5/TAC** before and after curing by differential scanning calorimetry (DSC) at 10 °C/min under nitrogen.

---

(19) Kinnibrugh, T. L.; Timofeeva, T. V.; Clot, O.; Akelaitis, A.; Dalton, L. R. *Acta Crystallogr.* **2006**, *E62*, o4804.

(20) Luo, J.; Haller, M.; Li, H.; Kim, T. D.; Jen, A. K.-Y. *Adv. Mater.* **2003**, *15*, 1635.

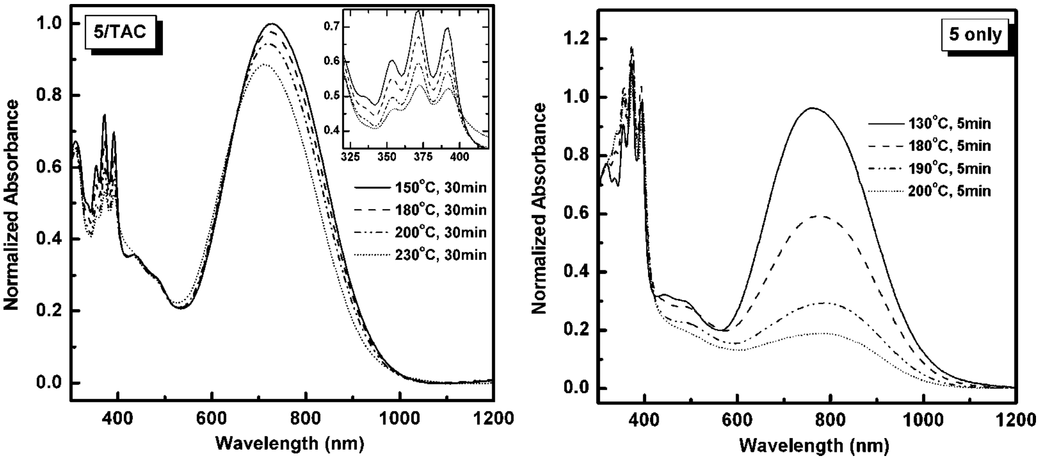


Figure 6. UV−vis−NIR absorption spectra of thin films **5/TAC** (right) and **5** only (left) upon thermal curings. Note that these spectra are normalized to initial absorption peak.

trismaleimide cross-linker (**TMI**), tends to form gel in a fairly low temperature range (from ambient temperature to 65 °C) within a few hours due to high reactivity of anthracene−maleimide-based DA cycloaddition.[12a] Since **TAC** is a deactivated dienophile compared to **TMI**, it reduces the temperature gap between T_x and T_g to facilitate processing. This provides significant advantages for using the **5/TAC** system, such as an easier controlled poling process, higher poling efficiency, and longer storage time for unpoled films.

More importantly, the results from DSC showed that the onset decomposition temperature (T_{dec} in second heating) of **5/TAC** is ~60 °C higher than that of **5**, indicating improved thermal stability of materials after cross-linking. Thermal stabilities of **5/TAC** and **5** were compared at different temperatures by measuring the absorption spectra of thin films after isothermal heating, to quantitatively follow the possible chromophore decomposition. **5/TAC** exhibited excellent thermal stability. The thin films of **5/TAC** showed <10% of decrease in absorbance after being cured at 200−230 °C for 30 min as opposed to ~75% of absorbance decrease when **5** was cured at 200 °C for 5 min (Figure 6). The curing time for **5** has to be reduced to only 5 min at each specified temperature interval to detect a sensible absorbance change of the chromophore prior to its complete disappearance. All cured films of **5/TAC** possess very good solvent resistance toward THF, 1,1,2-trichloroethane (TCE), and acetone. Upon curing, the intensity of typical anthryl absorption bands located at 350, 370, and 390 nm also decreased considerably, suggesting good efficiency of DA lattice hardening via this new anthracene−acrylate protocol.

Furthermore, **TAC** was replaced by dendrimer **6** to formulate the equivalent binary mixture of **5/6**, which contains a much higher chromophore loading level (39 wt %) than that of **5/TAC** (23 wt %). The results from DSC showed that the onset decomposition temperature of **6** is ~175 °C, which is not surprising due to thermal-induced radical polymerization of the periphery acrylates. However, by the same analysis of DSC and isothermal heating shown above, the cross-linked **5/6** showed much better thermal stability at high temperatures up to 230 °C, which is as good as that of **5/TAC**. All these studies systematically proved that reinforced site isolation via DA lattice hardening dramatically improves the thermal stability of E-O dendrimers that contain high concentrations of **AJL8**-type chromophores.

Poling and E-O Properties of Cross-Linkable Dendrimers. To study poling and E-O properties of these dendrimers, the TCE solutions of **5/TAC** and **5/6** (with 9 wt % solid content) were filtered through a 0.2 μm syringe filter and spin-coated onto ITO-coated glass substrates to afford micrometer-thick films with good optical quality. The selected ITO substrate has suitable conductivity, low reflectivity, and good transparency for poling and E-O measurement of these thin film samples.[21] The films were baked at 60 °C under vacuum overnight, then a thin layer of gold was sputtered onto the films as the top electrode for contact poling. The sequential curing and poling processes were applied to the samples following the similar procedures reported previously.[12a] Typically, the samples were annealed at temperatures ~100−120 °C to initiate partial cross-linking of the binary mixture **5/TAC** or **5/6**. This is needed to enhance the dielectric strength of materials prior to the sequential curing/poling process at elevated temperatures. During annealing, only low voltages ~10−20 V/μm were applied. Then the temperatures were ramped to 180−200 °C at a rate of 5 °C/min, while the significantly improved dielectric properties of films allow much higher voltages of up to 150−170 V/μm to be applied sequentially. Finally, the samples were cooled to room temperature, and the poling field was removed. The r_{33} values of poled films were measured by using the modified Teng−Man reflection technique at the wavelength of 1310 nm (Table 1).[22]

Relatively large r_{33} values of 44 pm/V and 84 pm/V were obtained for **5/TAC** and **5/6**, respectively, which are almost linearly proportional to their chromophore contents. This level of E-O activities is about 10−20% lower than those of the lower T_g cross-linkable dendrimers. According to the oriented gas model, the orientational factor of $\mu E/(5k_BT)$ decreases at much higher poling temperatures, where E represents the poling field, k_B is the Boltzmann constant, and T is the poling temperature. Both poled samples showed

---

(21) Park, D. H.; Lee, C. H.; Herman, W. N. *Opt. Express* **2006**, *14*, 8866.
(22) Teng, C. C.; Man, H. T. *Appl. Phys. Lett.* **1990**, *56*, 1734.

Table 1. Physical and Optical Properties of 5, 6, 5/TAC, and 5/6

material entries	dye[a] content (wt %)	λ_{max}[b] (nm)	T_g[c] (°C)	T_x[c] (°C)	T_{dec}[c] (°C)	thermal stability[d] (%)	poling temp. (°C)	poling field (MV/cm)	r_{33}[e] (pm/V) at 1310 nm
5	32.0	776	155		212	<10			
6	49.0	700	85		175	<10			
5/TAC	23.0	709		127	268	89	120−182	1.0	44
5/6	39.0	708		112	270	89	130−200	0.9	84

[a] Net weight percentage of chromophore within dendrimer. [b] The wavelengths of the absorption maxima on thin films after curing. [c] Analytic results of differential scanning calorimetry (DSC) at a heating rate of 10 °C/min on thermo-equilibrate samples: T_g, glass transition temperature; T_x, onset cross-linking temperature; T_{dec}, onset decomposition temperature. [d] Residual percentage of chromophore after the thin films were isothermally cured. The chromophore content was quantified by the absorbance of the film at λ_{max}. Temperature/duration of curing: 230 °C/30 min for **5/TAC** and **5/6**; 200 °C/5 min for **5** and **6**. [e] Electro-optic coefficients measured at 1310 nm by simple-reflection technique.

outstanding temporal stability at high temperatures. For example, after the poled samples of **5/6** were exposed to thermal excursion at either 200 °C for 30 min or 150 °C for 200 h, around 75% of the initial poling-induced r_{33} values were still retained.

Conclusion

In summary, we have thoroughly analyzed the potential decomposition pathway for a standardized highly polarizable chromophore under heating and provided new insights for the development of high performance organic E-O materials: (1) The initial thermo-induced decomposition pathway of **AJL8** chromophore has been proposed as a bimolecular tandem DA and retro-DA reaction, which triggers rapid decomposition of the chromophore at elevated temperatures. (2) A new lattice hardening protocol based on anthracene−acrylate DA cycloaddition has been explored to enhance the site isolation effect in E-O dendrimers. The resultant dendrimers with high chromophore concentrations could be converted into densely cross-linked networks, which are isothermally stable up to 230 °C. This chemistry of lattice hardening is compatible with the poling process, leading to relatively large and thermally stable E-O activities of up to 84 pm/V at the wavelength of 1310 nm. (3) This study provides very encouraging evidence that thermal stability of highly polarizable donor−acceptor chromophores could be prolonged via reinforced site isolation. The stability of **5/TAC** and **5/6** is tentatively limited to 230 °C. This is most likely due to the fact that the relatively high content of the flexible tether moieties limits the highest achievable T_g values in the current materials. The improvement of organic E-O materials at high temperatures is critically dependent on enhancing the intrinsic thermal and chemical stability of dipolar chromophores, tailoring the nanostructures in high T_g polymers, and exploring new lattice hardening protocols. With recent advances in these aspects, it should now be possible to achieve exceptional thermal stability (>250 °C) from organic E-O materials exhibiting large r_{33} values of up to 200 pm/V. These further research efforts are being pursued and will be reported in due course.

Acknowledgment. Financial support from Intel Corporation, National Science Foundation (NSF-STC Program under Agreement Number DMR-0120967), and Boeing-Johnson Foundation are acknowledged.

CM801828W