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A Triptycene-Containing Chromophore for Improved Temporal Stability of Highly Efficient Guest−Host Electrooptic Polymers

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Supporting Information

Guest−host electrooptic (EO) polymers are composite materials consisting of nonlinear optical (NLO) chromophores dispersed in a polymer host. Because of the relatively simple sample preparation, guest−host EO polymers serve as ideal model systems to study the structure−property relationships of materials and to prototype proof-of-concept EO devices. However, for practical applications, guest−host EO polymers are limited by the phase separation between large dipole moment chromophores and the polymeric matrix as well as the thermal relaxation of poling-induced polar order. These problems are associated with the plasticization of the polymeric matrix by the introduction of the chromophoric dopant. In general, the chromophoric dopants increase the free volume of polymer composites; as a result, they lower the glass transition temperature (T_g) and compromise the temporal stability of poled EO films. Over the past two decades, extensive research efforts have been conducted to resolve these problems. Several major approaches include the covalent incorporation of NLO chromophores into the structures of main-chain polymers[1] and side-chain polymers,[2] the self-assembly or the layer-by-layer deposition processes,[3] and a variety of cross-linkable EO polymers.[4] Many of these systems have effectively addressed the stability issues of EO polymers and provided additional advantages including high chromophore loading and good temporal stability.[5] Nevertheless, compared to simple guest−host polymers, these material systems are often more complex requiring extra synthetic efforts to build multifunctional NLO chromophores and delicate processing protocols taking into account considerable chemical sensitivities.

Given the mixed success of previous systems, new design principles are needed to develop highly efficient and thermally stable EO polymers for a broader scale of photonic applications. In this report, we focus our efforts on how to effectively improve the material performance of guest−host EO systems in poly(bisphenol A carbonate) (BPAPC). BPAPC possesses an excellent combination of desirable properties with price/performance balance and is a premier choice of engineering plastics for a variety of applications.[6] Together with its analogues such as amorphous co-polycarbonates (APC) containing a bisphenol from the hydrogenated isophorone, these technically valuable polymers have relatively high T_gs ranging from 150 to 230 °C but display extensive solid-state motion even at sufficiently low temperatures around −100 °C.[6,7] Theoretical calculations and solid-state NMR studies showed that complete 180° flips of phenyl ring on the backbone of BPAPC could occur in the glassy state of the polymer hundreds of degrees below its macroscopic T_g.[7] It has also been suggested that such free rotation occurs possibly at both the ring−carbonate and ring−isopropylidine connections with very low intramolecular activation barriers. These analyses dictate the molecular relaxation mechanism for the exceptional ductility and impact strength of polycarbonates and are probably responsible for the good poling efficiency of guest−host EO materials. The major challenge in the development of polycarbonate-based guest−host EO polymers is how to effectively stabilize the poling-induced polar order and enhance the maximal loading density of large hyperpolarizability (β) chromophores in the matrices without compromising other desirable properties of polycarbonates. In this regard, we identified that triptycene moieties could introduce favorable intermolecular interactions to create new guest−host EO polymers with unique advantages over the previous systems.[5,8]

Iptycene moieties are rigid molecules with the aromatic rings attached to a [2.2.2]bicyclooctatriene bridgehead system. The simplest member of this family is triptycene, in which three phenyl rings are joined together through two bridgehead carbons. Recently, a growing number of research efforts have been reported using the rigid three-dimensional structure of the triptycene structures to introduce new supramolecular interactions and achieve new material properties.[9] Swager et al. led pioneering efforts in this subject, and they have discovered that the internal molecular free volume (IMFV) of triptycene was capable of directing the organization of polymer chains.[10] In particular, they suggested a molecular "threading" mechanism, where the section of flexible polymer chains prefers to thread through the cavities of triptycene units, minimizing the IMFV and improving the mechanical properties of polymers.[11] Such "threading" interactions can also improve the shearing and compressive properties of polymers through the interlocking interactions of the triptycene structure with adjacent polymer backbones. Furthermore, Long and Swager previously found the IMFV of triptycene could be used to guide the alignment of liquid crystalline molecules and even affect the alignment rate of such phases under applied electric fields.[12] Inspired by these key findings, we have developed a new type of guest−host EO polymer that is formulated by doping a triptycene-modified

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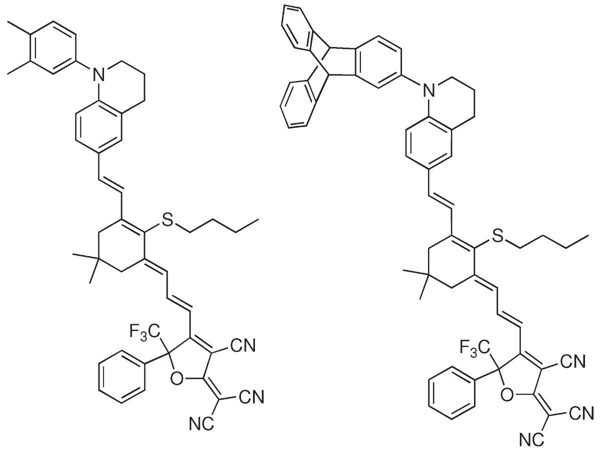
push−pull phenyltetraene chromophore into BPAPC. The study reveals that the incorporation of the triptycene moiety remarkably improved the relevant physicochemical properties of guest−host EO polymers in a manner that has not been previously achieved in conventional systems.

The triptycene moiety was attached to the aniline donor of a push−pull phenyltetraene chromophore to form the chromophore AJPL172 (Figure 1). The chromophore AJPL170 was synthesized as a comparison model compound. The synthesis of the two chromophores follows the scheme we have reported previously.[13] Structurally, these two chromophores have the same conjugated backbone of push−pull structure, yet differ in molecular weight by the triptycene modification at the donor end of AJPL172. The differences in the physical and optical properties of the two chromophores are shown in Table 1. In solutions and thin films, AJPL172 consistently displays a hypsochromic shift of absorption maxima ($\lambda_{\max}$s) in comparison to AJPL170. We attribute such differences to the introduction of the triptycene moiety in AJPL172, in which the triptycene moiety provides a relatively nonpolar nanoenvironment surrounding the donor of the chromophore. As shown in Figure 2, when doped into BPAPC, the thin film absorption spectrum of AJPL172 shows reduced absorption inhomogeneous line-broadening. This result can be also attributed to the "spacer" effect in the solid state from the triptycene modification. Previous studies by Obata[14] and Barto[15] have shown correlations concerning van der Waals interactions between spacer groups of conjugated molecules and host polymer matrices, respectively. Both studies found weak van der Waals interactions between the spacer groups and the host polymer can reduce the absorption inhomogeneous line-broadening of tetraphenylporphine and high-β nonlinear optical chromophores in polymer matrices.

Thermal analyses by differential scanning calorimetry (DSC) were performed to investigate the possible impact of the triptycene moiety on the phase transition behavior of the chromophore and its guest−host polymers. In monolithic form, both AJPL170 and AJPL172 have very similar glass transition temperatures around 110 °C, and no melting points with the chromophores decomposition temperatures at around 200 °C. However, when doped into BPAPC, dramatic differences were observed (Figure 3). For these doped polymer films, number density was used to quantify the loading level of chromophores in BPAPC for parallel comparison. Therefore, 17 and 34 wt % of AJPL170 were doped into BPAPC (AJPL170/BPAPC hereafter), which correspond to a number density of 1.5×10^{20} and 3.1×10^{20} cm^{-3}, respectively. To retain such equivalent number densities, the formulation by doping 20 and 40 wt % of AJPL172 into BPAPC (AJPL172/BPAPC hereafter) were used. DSC showed that AJPL170/BPAPC exhibits relatively broad and featureless glass transition, and its T_g (onset) is around 132 °C for 17 wt % of chromophore loading, which drops to 125 °C at 34 wt %. This result follows the general trend of guest−host EO polymers, in which their T_gs decrease with higher chromophore


AJPL170

AJPL172

Figure 1. Structures of the chromophores AJPL170 and AJPL172.

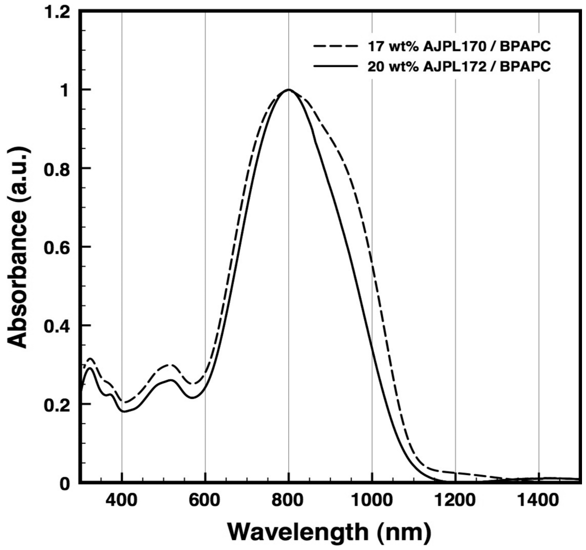


Figure 2. Normalized UV−vis absorption spectra of AJPL170/PC and AJPL172/PC with equal chromophore number density.

Table 1. Summary of the Physical Properties of AJPL170, AJPL172, and Their Guest−Host Polymers

	$\lambda_{\max}$ in solution (nm)				guest−host polymers in BPAPC			
entries	1,4-dioxane	CH_3CN	$CHCl_3$	T_g (°C) of monolithic glasses[a]	$\lambda_{\max}$ (nm)[b]	T_g (°C) (loading)[a]	r_{33} (pm/V)[c]	temporal stability (%)[d]
AJPL170	718	763	803	111	807	132 (17 wt %)		
						125 (34 wt %)	166	81
AJPL172	716	754	799	109	801	137 (20 wt %)		
						151 (40 wt %)	172	93

[a] Glass transition temperatures of monolithic chromophores and guest−host polymers measured by DSC under nitrogen at the heating rate of 10 °C/min. [b] Thin films of AJPL170/BPAPC-17 wt % and AJPL172/BPAPC-20 wt %. [c] EO coefficient measured at 1310 nm by a simple reflection technique. [d] Temporal alignment stability of poled films: the percentage of the initial r_{33} values after isothermal annealing at 85 °C for 130 h.

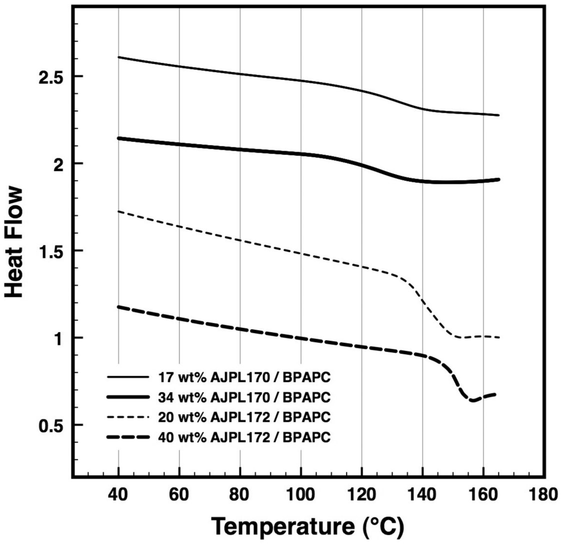


Figure 3. Thermal analysis of AJPL170 and AJPL172 at different concentrations in BPAPC by differential scanning calorimetry (DSC) at 10 °C min^{-1} under nitrogen.

loading due to the plasticization effect. In contrast, the T_g of AJPL172/BPAPC is increased significantly by 16 °C, from 137 °C at the loading of 20 wt % to 151 °C at 40 wt %. The glass transition peaks of AJPL172/BPAPC are much more distinct and steeper than those of AJPL170/BPAPC. Furthermore, the T_g of AJPL172/BPAPC with the chromophore loading of 40 wt % stays constantly at 151 °C after multiple annealing cycles, which is higher than the individual T_gs of AJPL172 (110 °C) and BPAPC (147 °C). These results cannot be simply interpreted by the Fox equation for the analysis of miscible polymer blends.[16] The Fox equation gives the T_g of blended polymer by $1/T_g = \phi_1/T_{g1} + \phi_2/T_{g2}$, where ϕ_i is the mass fraction and T_{gi} is the glass transition for the ith component. The T_gs of AJPL170/BPAPC composite from DSC are slightly lower (by 5 °C) than the estimated values by the Fox equation. However, the experimental T_g of AJPL172/BPAPC with 40 wt % of chromophore is much higher than expected. This variation could suggest a stronger noncovalent guest—host interaction through the triptycene modification in AJPL172/BPAPC. After multiple annealing cycles, the distinct and unchanged glass transition peaks of AJPL172/BPAPC preliminarily support this hypothesis by illustrating the improved compatibility and morphological stability of polymer composites. Another indirect indicator is the reduced absorption inhomogeneous line broadening in thin film spectra of AJPL172/BPAPC aforementioned, since favorable guest—host interaction would provide a mechanism to reduce the formation of chromophoric aggregates.

The enhanced T_g of AJPL172/BPAPC-40% also motivated us to test the temporal stability of its poled films. This test, once being performed in parallel with AJPL170/BPAPC, should provide direct evidence to the presence of strong guest—host interaction and highlight the role of triptycene moiety in affecting the temporal stability and molecular relaxation of poled films. Therefore, the formulated solutions of AJPL170/BPAPC and AJPL172/BPAPC in dibromomethane (6.0 wt % solid content) were spin-coated onto ITO glass substrates and then baked overnight at 80 °C under vacuum, yielding optical quality thin films with thickness of around 1—2 μm. The ITO substrates from thin film devices were selected to have suitable conductivity, low reflectivity, and good transparency to minimize errors in EO measurements. A thin layer (>100 nm) of gold was then sputtered on top of the polymer films to serve as the top electrode and mirror. The sample is poled using a field of 100 V/μm at an initial temperature of 50 °C, while increasing the temperature at a rate of 10 °C/min until the glass transition temperature was reached. The poled sample was then cooled to ambient room temperature, and the applied field was removed. The r_{33} values of poled films were measured by using the modified Teng—Man reflection technique at a wavelength of 1310 nm (Table 1).[17]

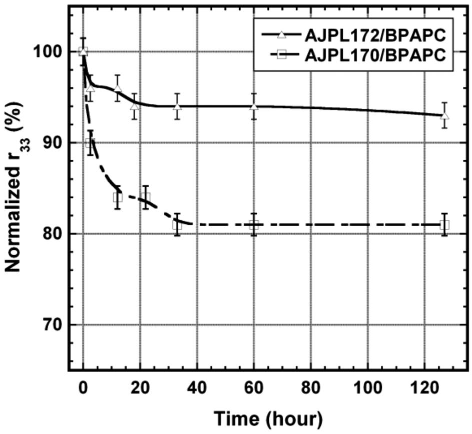


Figure 4. Temporal alignment stability of AJPL170 (34 wt %) and AJPL172 (40 wt %) in BP-APC at 85 °C under a nitrogen atmosphere.

Both AJPL170/BPAPC and AJPL172/BPAPC exhibited large r_{33} values of around 170 pm/V, suggesting the negligible effect of the triptycene moiety on the achievable polar order of poled films. A significant difference arises in the temporal alignment stability of two EO polymers. As shown in Figure 4, after being annealed at 85 °C for 130 h, the poled films of AJPL172/BPAPC can retain more than 90% of its initial r_{33} value, and this percentage is considerably higher than those of AJPL170/BPAPC and other higher T_g guest—host EO polymers such as CLD1/APC.[18] This much improved temporal stability of AJPL172/BPAPC provides a direct measure that the molecular relaxation in the poled films has been restricted through the addition of the triptycene moiety on the chromophore structure.

To further quantify the effect of the triptycene moiety on the dipole relaxation of guest—host polymers, a series of thermally stimulated discharge (TSD) studies were performed.[19] In this study, poled films of AJPL170/BPAPC-34 wt % and AJPL172/BPAPC-40 wt % were connected to a Keithley 617 electrometer in a short circuit configuration and put into a programmable heater. The temperature was first held at 50 °C for 10 min and then heated up to 180 °C at a ramping rate of 1 °C/min. The current was recorded and plotted as shown in Figure 5. In the TSD spectrum, a notable α peak and a large rising slope after the glass transition can be observed. Previous studies have shown the α peak of an EO polymer is a direct indication of the dipole relaxation process.[19] The sharp rise after the T_g is attributed to the ρ peak, which is related to the release of trapped charges for poled films. Integration in the time domain of both curves yielded total charge releases at the magnitude of 57 nC, which confirms the peaks correspond to the dipole relaxation behavior at the same magnitude. In the spectra, the α peak of the AJPL172/BPAPC system appears at 137 °C, which is 16 °C

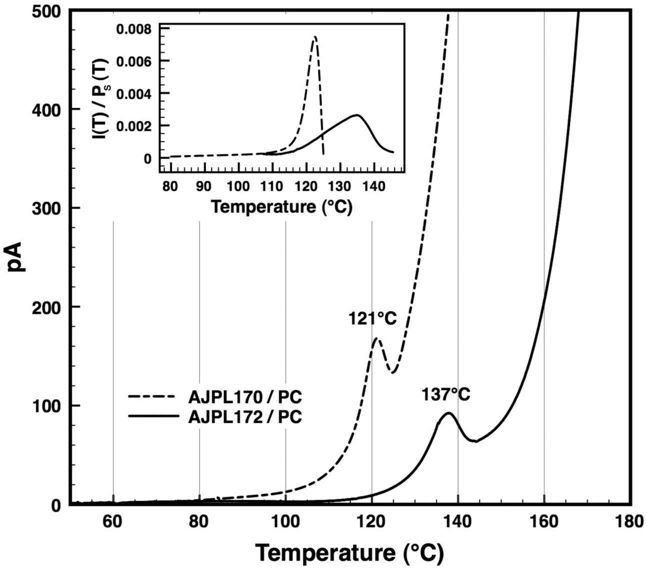


Figure 5. TSD spectra of poled AJPL170/PC (34 wt %) and AJPL172/PC (40 wt %) taken at 1 °C/min from 50 to 180 °C. Inset: depolarization rate measurements of 34 wt % AJPL170/PC and 40 wt % AJPL172/PC.

higher than that of the α peak of the AJPL170/BPAPC system at 121 °C. Additionally, significant differences are further observed in the rates of depolarization for the AJPL170/BPAPC and AJPL172/BPAPC (see the inset of Figure 5). In this regard, the slope for the depolarization rate of AJPL172/BPAPC clearly displays a marked difference. The sum of these TSD results indicates that incorporation of the triptycene moiety in AJPL172/BPAPC shifts the dipole relaxation to a higher temperature range and decreases the depolarization rate of poled films. This analysis clearly explains the enhanced temporal stability of AJPL172/BPAPC.

The above experimental studies strongly support the hypothesis of stronger guest—host interaction as the underlying mechanism accounting for exceptional properties of AJPL172/BPAPC. The higher activation energy barrier for depolarization is attributable to the stronger noncovalent interactions or the preexisting entanglement between the triptycene moiety on the AJPL172 chromophore and the polycarbonate backbone. During the poling, two intertwined processes are expected: (i) the orientational rotation of the chromophores in response to the electric field and (ii) the local reorganization of segments in response to the enhanced macroscopic polar order of materials. After the poling, the polar order of chromophores is frozen in the polymer matrix due to the decreased molecular rotational freedom of the polymer at the ambient temperature. This process can reorganize the polymer composite into a more stabilized state by minimizing the IMFV. More specifically, the polycarbonate chains can be packed into the IMFV of the triptycene moiety, thereby inducing the entanglement of the chromophore with the polymer matrix.

This molecular behavior is also consistent with previous studies of triptycene-containing materials.[11,12] In a study conducted by Swager, the triptycene moieties were appended to the mesogen guest molecules and physically hindered the switching times of the liquid crystalline host, especially when the triptycene moieties were appended at either end of the guest molecules. For triptycene-containing polyesters and polycarbonates, Thomas also revealed unconventional thermal behavior due to the incorporation of triptycene moiety in the copolymer backbone.[11c] The polycarbonate copolymer with 25% of triptycene-based unit expressed improved mechanical properties and a T_g of 176 °C, which is 24 °C higher than that of BPAPC. At this loading ratio, they proposed that incorporation of triptycene moieties could increase interchain interactions introduced by molecular threading. Their data suggested that the triptycene units interact with the phenyl units and interfere with cooperative motions of the carbonate units, where the relaxation process of BPAPC typically involves 6—9 connected repeating units.[11] Our DSC studies also revealed the similar T_g enhancement and improved morphological stability against phase separation for the guest—host polymer, which was doped with a high concentration (40 wt %) of triptycene-functionalized AJPL172. The loading percentage of this composition corresponds to the ratio of triptycene groups to the unit of bisphenol A carbonate groups (BPA) at 1:5.5, which is close to that of main-chain copolymers in Thomas' study. Therefore, we speculate that a strong guest—host interaction is present in AJPL172/BPAPC-40 wt % and conserve the similar structural motif, where the triptycene moiety of AJPL172 interacts with the phenyl ring and/or carbonate unit of BPAPC through a molecularly threaded interaction. This analysis is in accordance with all the experimental results of this study and complies with previous relevant literature. In comparison, such guest—host interaction is absent in AJPL170/BPAPC without the triptycene modification or is less significant in AJPL172/BPAPC-20 wt % due to a much smaller ratio of the triptycene groups to the BPA unit at 1:11.

In conclusion, we have demonstrated a new type of triptycene-functionalized dipolar chromophore (such as AJPL172) with improved temporal stability and compatibility in a guest—host polymer. A large EO coefficient of 172 pm/V at 1310 nm and excellent temporal stability at 85 °C have been achieved in poled films of AJPL172/BPAPC with a high chromophore loading density of 3.1×10^{20} cm^{-3}. This new design offers an elegant approach for improving the temporal stability and compatibility of guest—host EO polymers for device applications. It has been elucidated that a strong guest—host interaction accounts for the excellent properties of AJPL172/BPAPC through the molecular threading effect of the triptycene moiety. The EO polymer is a unique functional material platform, which can record the possible IMFV effects of triptycene modification through multiple electrooptic characterization tools, such as achievable polar order, temporal stability of poled films, and thermally stimulated depolarization spectrum. These studies have provided unique and ample insight toward a deeper understanding of the relaxation mechanism in triptycene-containing molecular and polymeric materials for further understanding the poling/annealing processes required for photonic applications.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Experimental details and additional characterization. This material is available free of charge via the Internet at http://pubs.acs.org.

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REFERENCES

(1) (a) Carter, K. R.; Hedrick, J. L.; Twieg, R. J.; Matray, T. J.; Walsh, C. A. *Macromolecules* **1994**, *27*, 4851–4852. (b) Xu, C.; Wu, B.; Becker, M. W.; Dalton, L. R.; Ranon, P. M.; Shi, Y.; Steier, W. H. *Chem. Mater.* **1993**, *5*, 1439–1444. (c) Li, Z.; Wu, W.; Ye, C.; Qin, J.; Li, Z. *J. Phys. Chem. B* **2009**, *113*, 14943–14949. (d) Li, Q.; Li, Z.; Ye, C.; Qin, J. *J. Phys. Chem. B* **2008**, *112*, 4928–4933. (e) Weder, C.; Neuenschwnder, P.; Suter, U. W.; Prêtre, P.; Kaatz, P.; Günter, P. *Macromolecules* **1994**, *27*, 2181–2186. (f) Kang, C.-S.; Heldmann, C.; Winkelhahn, H.-J.; Schulze, M.; Neher, D.; Wegner, G.; Wortmann, R.; Glania, C.; Krämer, P. *Macromolecules* **1994**, *27*, 6156–6162. (g) Hayden, L. M.; Kim, W.-K.; Chafin, A. P.; Lindsay, G. A. *Macromolecules* **2001**, *34*, 1493–1495. (h) Döbler, M.; Weder, C.; Ahumada, O.; Neuenschwander, P.; Suter, U. W.; Follonier, S.; Bosshard, C.; Günter, P. *Macromolecules* **1998**, *31*, 7676–7681.

(2) (a) 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*, 4970–4974. (b) Walsh, C. A.; Burland, D. M.; Lee, V. Y.; Miller, R. D.; Smith, B. A.; Twieg, R. J.; Volksen, W. *Macromolecules* **1993**, *26*, 3720–3722. (c) Teng, C. C. High-speed electro-optic modulators from nonlinear optical polymers. In *Nonlinear Optics of Organic Molecules and Polymers*; Nalwa, H. S., Ed.; CRC Press: Boca Raton, FL, 1996; pp 441−464.

(3) (a) Lenahan, K. M.; Wang, Y.-X.; Liu, Y.; Claus, R. O.; Heflin, J. R.; Marciu, D.; Figura, C. *Adv. Mater.* **1998**, *10*, 853–855. (b) Fischer, P.; Koetse, M.; Laschewsky, A.; Wischerhoff, E.; Jullien, L.; Persoons, A.; Verbiest, T. *Macromolecules* **2000**, *33*, 9471–9473. (c) Rashid, A. N.; Erny, C.; Gunter, P. *Adv. Mater.* **2003**, *15*, 2024–2027. (d) Garg, A.; Davis, R. M.; Durak, C.; Heflin, J. R.; Gibson, H. W. *J. Appl. Phys.* **2008**, *104*, 053116. (e) Heflin, J. R.; Guzy, M. T.; Neyman, P. J.; Gaskins, K. J.; Brands, C.; Wang, Z.; Gibson, H. W.; Davis, R. M.; Van Cott, K. E. *Langmuir* **2006**, *22*, 5723–5727. (f) Frattarelli, D.; Schiavo, M.; Facchetti, A.; Ratner, M. A.; Marks, T. J. *J. Am. Chem. Soc.* **2009**, *131*, 12595–12612. (g) Kang, H.; Evmenenko, G.; Dutta, P.; Clays, K.; Song, K.; Marks, T. J. *J. Am. Chem. Soc.* **2006**, *128*, 6194–6205. (h) Facchetti, A.; Beverina, L.; van der Boom, M. E.; Dutta, P.; Evmenenko, G.; Shukla, A. D.; Stern, C. E.; Pagani, G. A.; Marks, T. J. *J. Am. Chem. Soc.* **2006**, *128*, 2142–2153. (i) Yitzchaik, S.; Marks, T. J. *Acc. Chem. Res.* **1996**, *29*, 197–202. (j) Marks, T. J.; Ratner, M. A. *Angew. Chem., Int. Ed. Engl.* **1995**, *14*, 155–173. (k) Halter, M.; Plocinik, R. M.; Coffey, D. C.; Bhattacharjee, S.; Mazur, U.; Simpson, G. J.; Robinson, B. H.; Keller, S. L. *Chem. Mater.* **2008**, *20*, 1778–1787.

(4) (a) Oviatt, H. W.; Shea, K. J., Jr.; Kalluri, S.; Shi, Y.; Steier, W. H.; Dalton, L. *Chem. Mater.* **1998**, *10*, 146–155. (b) Hubbard, M. A.; Marks, T. J.; Yang, J.; Wong, G. K. *Chem. Mater.* **1989**, *1*, 167–169. (c) Park, J.; Marks, T. J.; Yang, J.; Wong, G. K. *Chem. Mater.* **1990**, *2*, 229–231. (d) Jin, Y.; Carr, S. H.; Marks, T. J.; Lin, W.; Wong, G. K. *Chem. Mater.* **1992**, *4*, 963–965. (e) Hubbard, M. A.; Marks, T. J.; Lin, W.; Wong, G. K. *Chem. Mater.* **1992**, *4*, 965–968. (f) Mao, S. S. H.; Ra, Y.; Guo, L.; Zhang, C.; Dalton, L. R.; Chen, A.; Garner, S. M.; Steier, W. H. *Chem. Mater.* **1998**, *10*, 146–155. (g) Bai, Y.; Song, N.; Gao, J. P.; Sun, X.; Wang, X.; Yu, G.; Wang, Z. Y. *J. Am. Chem. Soc.* **2007**, *127*, 2060–2061. (h) Luo, J.; Haller, M.; Li, H.; Kim, T.-D.; Jen, A. K.-Y. *Adv. Mater.* **2003**, *15*, 1635–1638. (i) Shi, Z.; Luo, J.; Huang, S.; Cheng, Y.-J.; Kim, T.-D.; Polishak, B. M.; Zhou, X.-H.; Tian, Y.; Jang, S. H.; Knorr, D.; Overney, R.; Younkin, T.; Jen, A. K.-Y. *Macromolecules* **2009**, *42*, 2438–2445. (j) Scarpaci, A.; Blart, E.; Montembault, V.; Fontaine, L.; Rodriguez, V.; Odobel, F. *Chem. Commun.* **2009**, 1825–1827.

(5) (a) Delaire, J. A.; Nakatani, K. *Chem. Rev.* **2000**, *100*, 1817–1846. (b) Yesodha, S. K.; Pillai, C. K. S.; Tsutsumi, N. *Prog. Polym. Sci.* **2003**, *29*, 45–74. (c) Cho, M. J.; Choi, D. H.; Sullivan, P. A.; Akelaitis, A. J. P.; Dalton, L. R. *Prog. Polym. Sci.* **2008**, *33*, 1013–1058. (d) Dalton, L. *Adv. Polym. Sci.* **2002**, *158*, 1–86. (e) Kajzar, F.; Lee, K.-S.; Jen, A. K.-Y. *Adv. Polym. Sci.* **2003**, *161*, 1–85. (f) Dalton, L. R. *J. Phys.: Condens. Matter* **2003**, R897–R934. (g) Marder, S. R. *Chem. Commun.* **2006**, *2*, 131–134. (h) Marder, S. R.; Kippelen, B.; Jen, A. K.-Y.; Peyghambarian, N. *Nature* **1997**, *388*, 845–851.

(6) Freitag, D.; Fengler, G.; Morbitzer, L. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1598–1610.

(7) (a) Jones, A. A. *Macromolecules* **1985**, *18*, 902–906. (b) Hutnikt, M.; Argon, A. S.; Suter, U. W. *Macromolecules* **1993**, *26*, 1097–1108. (c) Hutnikt, M.; Argon, A. S.; Suter, U. W. *Macromolecules* **1991**, *24*, 5970–5979.

(8) (a) Luo, J.; Zhou, X.-H.; Jen, A. K.-Y. *J. Mater. Chem.* **2009**, *19*, 7410–7424. (b) Dalton, L. R.; Sullivan, P. A.; Bale, D. H. *Chem. Rev.* **2010**, *110*, 25–55. (c) Verbiest, T.; Houbrechts, S.; Kauranen, M.; Clays, K.; Persoons, A. *J. Mater. Chem.* **1997**, *7*, 2175–2189. (d) Burland, D. M.; Miller, R. D.; Walsh, C. A. *Chem. Rev.* **1994**, *94*, 31–75. (e) Marks, T. J.; Ratner, M. A. *Angew. Chem., Int. Ed.* **1995**, *34*, 155–173.

(9) Chong, J. H.; MacLachlan, M. J. *Chem. Soc. Rev.* **2009**, *38*, 3301–3315.

(10) Swager, T. M. *Acc. Chem. Res.* **2008**, *41*, 1181–1189.

(11) (a) Tsui, N. T.; Paraskos, A. J.; Torun, L.; Swager, T. M.; Thomas, E. L. *Macromolecules* **2006**, *39*, 3350–3358. (b) Tsui, N. T.; Torun, L.; Pate, B. D.; Paraskos, A.; Swager, T. M.; Thomas, E. L. *Adv. Funct. Mater.* **2007**, *17*, 1595–1602. (c) Tsui, N. T.; Yang, Y.; Mulliken, A. D.; Torun, L.; Boyce, M. C.; Swager, T. M.; Thomas, E. L. *Polymer* **2008**, *49*, 4703–4712.

(12) (a) Long, T. M.; Swager, T. M. *Adv. Mater.* **2001**, *13*, 601–604. (b) Long, T. M.; Swager, T. M. *J. Am. Chem. Soc.* **2002**, *14*, 3826–3927. (c) Long, T. M.; Swager, T. M. *J. Mater. Chem.* **2002**, *12*, 3407–3412.

(13) (a) Cheng, Y.-J.; Luo, J.; Huang, S.; Zhou, X. H.; Shi, Z.; Kim, T.-D.; Bale, D. H.; Takahashi, S.; Yick, A.; Polishak, B. M.; Jang, S.-H.; Dalton, L. R.; Reid, P. J.; Steier, W. H.; Jen, A. K.-Y. *Chem. Mater.* **2008**, *20*, 5047–5054. (b) Cheng, Y.-J.; Luo, J.; Hau, S.; Bale, D. H.; Kim, T.-D.; Shi, Z.; Lao, D. B.; Tucker, N. M.; Tian, Y.; Reid, P. J.; Dalton, L. R.; Jen, A. K.-Y. *Chem. Mater.* **2007**, *19*, 1154–1163.

(14) Obata, M.; Machida, S.; Horie, K. *J. Polym. Sci., Part B: Polym. Phys.* **1999**, *37*, 2173–2181.

(15) Barto, R. R.; Frank, C. W.; Bedworth, P. V.; Ermer, S.; Taylor, R. E. *J. Chem. Phys.* **2005**, *122*, 234907.

(16) Fox, T. C. *Bull. Am. Phys. Soc.* **1956**, *1*, 123.

(17) (a) Teng, C. C.; Man, H. T. *Appl. Phys. Lett.* **1990**, *56*, 1734–1736. (b) Park, D. H.; Lee, C. H.; Herman, W. N. *Opt. Express* **2006**, *14*, 8866–8884.

(18) Zhang, C.; Dalton, L. R.; Oh, M.-C.; Zhang, H.; Steier, W. H. *Chem. Mater.* **2001**, *13*, 3043–3050.

(19) (a) Köhler, W.; Robello, D. R.; Dao, P. T.; Willard, C. S.; Williams, D. J. *J. Chem. Phys.* **1990**, *93*, 9157–9166. (b) Neagu, E. R.; Marat-Mendes, J. N.; Das-Gupta, D. K.; Neagu, R. M.; Igreja, R. *J. Appl. Phys.* **1997**, *82*, 2488–2496.