A Novel Lattice-Hardening Process To Achieve Highly Efficient and Thermally Stable Nonlinear Optical Polymers

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Organic second-order nonlinear optical (NLO) polymers have received increasing interest because of their potential application in high-speed electrooptic (E−O) devices with very broad bandwidth.[1,2] Recently, very large E−O coefficients and low drive voltages have been demonstrated in several prototype E−O modulators using guest/host poled polymers.[1,2] Although these progresses are very encouraging, there is still a strong need to further improve thermal stability and mechanical properties of these materials in order to fulfill the requirements for multilayer fabrication process and long-term device operation.[1a,c−e] To reach this goal, the most commonly employed method is to covalently attach chromophores onto a polymer backbone and then harden the resulting material with a subsequent cross-linking reaction.[1d,e,2,3]

While there are many lattice-hardening approaches that have been reported in the literature, most of these possess certain deficiencies. For example, the commonly observed “nonlinearity−stability tradeoff” often prevents the realization of the full potential of high optical nonlinearity in these materials. Usually, a significant reduction (20−40%) of E−O activity is often observed in these hardened polymers.[2,3] This is because that lattice-hardening and poling processes are often proceeded together in conventional NLO thermosets. The steadily increased glass-transition temperature (T_g) and interchain entanglements of polymer chains during the lattice-hardening process significantly increase the difficulty in aligning dipolar chromophores. As a result, it lowers E−O activity of these poled materials. Recently, a series of efficient and thermally stable chromophores based on the chromone-derived acceptors have been reported by our group that possess good optical transparency for backplane interconnect applications at 830 nm.[4] Even though these chromophores possess quite promising poroperties, the E−O coefficient (r_{33}) obtained from a perfluorocyclobutane (PFCB) thermoset using this type of chromophore is much lower than that was previously obtained from a guest−host system (10 vs 23 pm/V at 830 nm).[3c]

To overcome this nonlinearity−stability tradeoff, a new poling process is required to increase rotational freedom of NLO chromophores. Ideally, this process should be prior to and be separated from the cross-linking process. Moreover, to maintain the achieved polar order of the resulting poled polymer, the reaction for subsequent cross-linking should be triggered only by a very mild condition preferably without further temperature elevation. By taking into account of all these requirements, we have developed a novel lattice-hardening approach using the Diels−Alder [4 + 2] cycloaddition reaction.[5] This novel methodology completely reverses the thermal processing sequence of cross-linking reactions previously used and provides significant advantages over the conventional NLO thermosets. Here we report the synthesis, processing, and E−O properties of several highly efficient NLO polymers using the Diels−Alder cycloaddition reaction that exhibit combined large optical nonlinearity, tunable processability, and high thermal stability.

Following the similar synthetic route developed by our group earlier,[6] three different functional moieties, including the derivatives of a chromone-type chromophore **2**, a furan-capped maleimide **3** (dienophile), and diene-containing rings **4a−c**, were sequentially attached onto the poly(vinylphenol) backbone as side chains to afford the cross-linkable NLO polymers **5a−c** (Scheme 1). Polymers **5a−c** were fully characterized by ^{1}H NMR, UV−vis spectroscopy, GPC, and thermal analysis. The chromophore content of these polymers is all normalized to the same loading level of 25 wt %. This was confirmed by both relative integration comparison of the characteristic peaks in ^{1}H NMR spectrum and the thickness-dependent quantitative analysis of the UV−vis spectra of their solid films.

In these new polymer products, two types of diene moieties were incorporated. One is the pristine furan molecule that was capped onto the maleimide. This precapping prevents the cross-linking reaction from occurring before the lattice-hardening step. As a result, all of these polymers show excellent solubility in common organic solvents, such as methylene dichloride, THF, and cyclopentanone. By simply heating the polymer to a higher temperature around 110 °C, the low boiling point furan was cleaved by the retro-Diels−Alder reaction and easily evaporated from the bulk material (Figure 1). This thermal deprotecting step has been confirmed by thermal analysis of these polymers. Thermal gravimetric analysis (TGA) of these polymers showed a steep weight loss of ∼4.5 wt % within the temperature range between 110 and 150 °C, which corresponds to the endothermic peaks that were observed at the similar temperature range using differential scanning calorimetry (DSC). The isothermal heating of each polymer sample at 110 °C for 30 min also resumed the weight loss of ∼4.5 wt %, a value that is in good agreement with the furan content used for protection. After isothermal heating, the sample became completely insoluble even though it was rapidly quenched to room temperature. This indicates the ease of the Diels−Alder cross-linking reaction between the side chains of imido group and the corresponding second diene moiety of the polymers. To obtain thermally stable adducts for cross-linking, three diene moieties with electronically fine-tuned structures were selected. By adding an electron-withdrawing ester group onto the 3-position of furan,[7] the temperature for the retro-DA reaction of the cross-linking polymer **5a** can be increased much higher to 145 °C. By using a more deactivated furan diester in polymer **5b**, it even creates a thermally irreversible cross-linked adduct. The same phenomenon can also be found in polymer **5c** by using imido and

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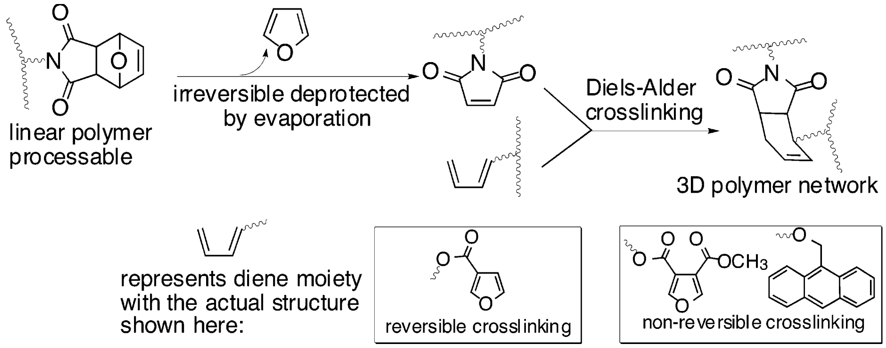


Figure 1. Representation of the Diels–Alder reactions.

Scheme 1. Synthesis of the Chromone-Containing NLO Polymers 5a–c Cross-Linkable by Diels–Alder Reactions (DCC = 1,3-Dicyclohexylcarbodiimide; DPTS = 4-(Dimethylamino)pyridinium 4-Toluenesulfonate)

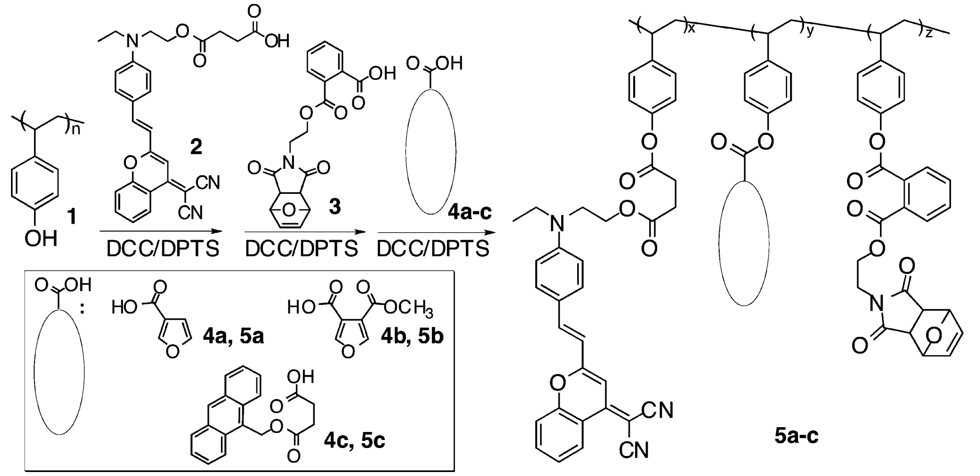
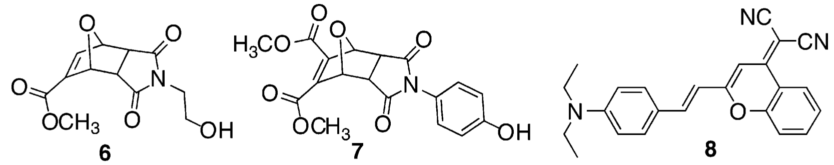


Chart 1. Model Compounds 6 and 7 for Diels–Alder Cross-Linking Study and Chromone-Type Chromophore 8 for E–O Performance Evaluation



anthryl groups as the cross-linking moieties. All these thermal characteristics have been verified by performing thermal analysis on cross-linked polymers and their similar model compounds (**6** and **7** in Chart 1).

For E–O measurements, the filtered solutions (12 wt % of solid content, filtered through a 0.2 μm PTFE filter) of **5a**–**c** in cyclopentanone were spin-coated onto indium tin oxide (ITO) glass substrates. The films were baked under vacuum at 80–85 °C overnight to ensure removal of the residual solvent. Thin layer of gold was then sputtered onto the films as the top electrode for poling experiments. At 110 °C under nitrogen, all these films were poled using an applied electric field of 1.50 MV/cm. The E–O coefficient (r_{33}) values were measured using the reflection technique at 0.83 μm.[8] All these poled films showed very encouraging E–O coefficients: 33 pm/V for **5a**, 37 pm/V for **5b**, and 26 pm/V for **5c**.

To evaluate the efficiency of chromophore alignment in these cross-linkable polymers, polymer **5a** was compared with a typical guest–host system. In this case, a similar chromone-derived chromophore **8** was doped into a poly(methyl methacrylate) (PMMA) host at the same 25 wt % loading level. The sample was then poled at 75 °C (close to its T_g) with an electric field of 1.0 MV/cm for 5 min under nitrogen to afford an optimized r_{33} value (30 pm/V at 0.83 μm) in this guest–host system. Then, polymer **5a** was also poled under the same electric field, resulting in an exactly the same E–O coefficient of 30 pm/V. This proves that similar high poling efficiency can be reached in hardened polymers **5a**,**b** as those exhibited in thermoplastic polymers. The relatively low E–O activity from the polymer **5c** is probably due to the large temperature difference between the poling temperature and its intrinsic T_g (110 vs 75 °C) that causes too much thermal fluctuation during poling.

Because of efficient lattice-hardening of the DA reaction, these materials also exhibited very good temporal alignment stability. After the initial relaxation, the poled films **5a**,**b** retained ~80% of their original r_{33} values even after baking at 85 °C for 500 h (Figure 2).

High E–O activities and good thermal stability of these NLO polymers demonstrate the advantages of using Diels–Alder cross-linking reaction to overcome the nonlinearity–stability tradeoff. When the poling field was applied, the deprotection step significantly delayed the cross-linking reactions, since it can only be triggered after sufficient deprotection. This “additional” deprotection step separates the poling process from the lattice-hardening very well without disturbing the cross-linking reaction. As a result, dense cross-linking can be

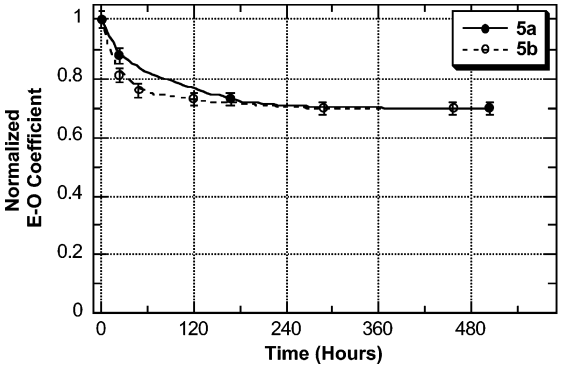


Figure 2. Temporal stability of the poled polymers **5a** and **5b** with normalized E−O coefficient vs time.

achieved even at a constant temperature of 110 °C. This mild condition, which was reflected by the steady poling currents, can maintain the obtained alignment of chromophores very well. To the best of our knowledge, these advantages have not been explored before in most of the conventional thermosets.[1,2,5]

In conclusion, through the novel Diels−Alder lattice-hardening process we can achieve high poling efficiency of a thermoplastic while maintain thermal stability of a densely cross-linked polymer. The resultant materials exhibit large r_{33} values (up to 37 pm/V at 0.83 μm) and good temporal stability at 85 °C. Furthermore, by modifying the electronic properties of the cross-linking reagents, it allows us to fine-tune processing temperature and reversibility of these Diels−Alder reactions to optimize thermal stability and processability.

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