Enhanced Thermal Stability of Electrooptic Polymer Modulators Using the Diels–Alder Crosslinkable Polymer

Y.-H. Kuo, Jingdong Luo, W. H. Steier, *Life Fellow, IEEE*, and Alex K.-Y. Jen

***Abstract*—A thermally stable modulator using a novel Diels–Alder crosslinkable electrooptic (EO) polymer was fabricated. This new material system presents a smartly controlled process to overcome the EO coefficient–thermal stability tradeoff of conventional thermosetting EO polymers and obtains poling efficiency and thermal stability simultaneously. The modulator showed long-term stability at 85 °C, which shows potential for industrial applications.**

***Index Terms*—Electrooptic (EO) modulator, electrooptic polymer, polymeric devices, thermal stability.**

I. Introduction

POLYMER electrooptical (EO) devices have been studied for several years because of their high EO coefficients, relatively low dielectric constant, and potential for integration with other materials [1]. One obstacle to commercialization has been the long-term thermal stability of the devices related to the relaxation of the EO molecules from their polar alignment. This alignment is created during processing by electric field poling of the material. In guest–host systems, the guest EO chromophore is dispersed in a host polymer, which allows relatively free rotation of the chromophores during poling to achieve high poling efficiency and large EO coefficients [2]. Since the chromophores are not attached to the polymer matrix, the alignment relaxes over time and it is difficult to meet the industrial standard of 85 °C long-term stability. To harden the polymer lattice and improve the thermal stability, a number of approaches have been investigated including thermosetting and covalent attachment of the chromophore to the polymer with or with out crosslinking. In thermoset materials, the chromophore is attached to the prepolymer component and a three-dimensional polymer is formed during the high-temperature poling process. In the crosslinking approach, the chromophore is covalently attached to the polymer either as a side pendant or as part of the main chain, and crosslinking is possible either between the polymer backbone or between the free end of the attached chromophore. The crosslinking is initiated during the high-temperature poling. Both of these approaches end with a hardened polymer with an effective high glass-transition temperature (T_g) in which the thermal relaxation is impeded [4], [5]. The drawback of these approaches is that the competing processes of poling and lattice hardening occur simultaneously, which reduces the poling efficiency and the EO coefficient. The steadily increased Tg and entanglement between polymer chains significantly hinder the dipole alignment [6]. A third approach has the chromophore side chain attached as a pendant to a high Tg polymer system without crosslinking [7], [8]. Thus, a high T_g backbone polymer, such as polyimide, is required to reach high thermal stability. Since the poling is done near this high Tg, the chromophores must be designed to withstand the high temperature. In this letter, a novel polymer PSDA-AJL4 using the Diels–Alder (DA) reaction to harden the polymer lattice was employed to achieve high thermal stability [9]. PSDA-AJL4 takes advantage of both the poling efficiency of a guest–host system and the high thermal stability of a crosslinked system by smartly controlling the crosslinking process.

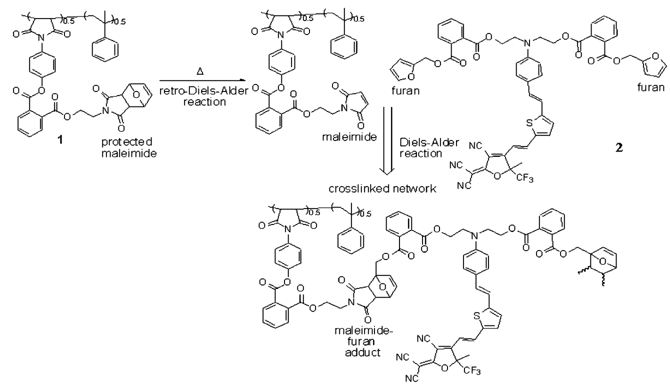

Fig. 1. Structures of PSDA-AJL4 and schematic representation of DA reaction.

PSDA-AJL4 initially exists as a two-component guest–host system as shown in Fig. 1. Here, component 1 acts as polymer host with furan-protected maleimide "dienophile" crosslinking group, and component 2 is an EO chromophore bearing the furan "diene" crosslinking group. Components 1 and 2 can be mixed together using cyclopentanone as the solvent, and the resultant solution has reasonable shelf life without any gelation prior to deprotection. No attachment of the chromophore to the polymer host occurs because of the furan protection groups. The furan protection group in component 1 can be thermally cleaved by a retro DA reaction at a temperature above 110 °C. At this

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Y.-H. Kuo and W. H. Steier are with the Department of Electrical Engineering, University of Southern California, Los Angeles, CA 90089-0483 USA (e-mail: ykuo@usc.edu).
J. Luo and A. K.-Y. Jen are with the Department of Material Science and Engineering, University of Washington, Seattle, WA 98195-2120 USA.
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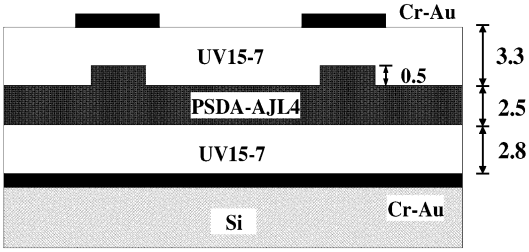

Fig. 2. Cross section of waveguide structure.

elevated temperature, the material behaves as typical guest–host polymers since the attachment of the chromophore can only be triggered afterwards by a DA reaction at a lower temperature of 90 °C. The material is therefore efficiently poled at 125 °C while in the guest–host state, and the temperature is then dropped to 90 °C with the poling field still applied. The aligned chromophores then attach to the thermally stable polymer backbone.

Therefore, in this material system there is no competition between the poling and the crosslinking processes that limits the poling efficiency in thermoset and conventional crosslinked materials. The retro DA reaction can achieve both a high EO coefficient and high thermal stability simultaneously. This technique can also apply to various chain polymers and chromophores by attaching maleimide and furan function groups separately to the two compounds [9], [10].

II. Device Fabrication

The Mach–Zehnder (MZ) interferometer modulator was fabricated using PSDA-AJL4 as the core layer and UV15-7 as the cladding material. UV15-7 is a commercial UV curable epoxy from Masterbond.[1] It has refractive index of 1.535 at 1.55 μm. Cured PSDA-AJL4 has a refractive index of 1.63 at 1.55 μm and 1.65 at 1.31 μm. Propagation losses of 2.7 dB/cm at 1.55 μm of PSDA-AJL4 thin film was measured using a liquid immersion technique [11]. An EO coefficient (r_{33}) of 88 pm/V at 1.31 μm was measured in single-layer films of PSDA-AJL4 with 100-V/μm poling and measured using a simple reflection ellipsometry method [12].

The cross section of the ridge-type waveguide is shown in Fig. 2. Gold (Au) with a chromium (Cr) adhesion layer was used as both driving and ground electrodes. A solution of 1:1 cyclopentanone-diluted UV15-7 was used to spin coat the lower cladding. The UV15-7 film becomes hard and chemically resistant after UV curing and 125 °C baking for 1 h. PSDA-AJL4 in cyclopentanone was spin coated on top of UV15-7 to form the guiding layer. After 85 °C baking in a vacuum oven overnight, the PSDA-AJL4 is free of solvent residue and resistant to photoresist. Normal photolithography methods and reactive ion etching (RIE) were used to fabricate the ridge structure. The width of the waveguide is 5 μm and ridge height is 0.5 μm. Diluted UV15-7 was again spin coated as the upper cladding. An overnight baking temperature of 85 °C was used after UV curing of the upper cladding to prevent crosslinking of PSDA-AJL4. Cr and Au were then coated using e-beam evaporation and patterned by photolithography and wet etching.

[1]Master Bond Inc., Hackensack, NJ. [Online] Available: http://www.masterbond.com/.

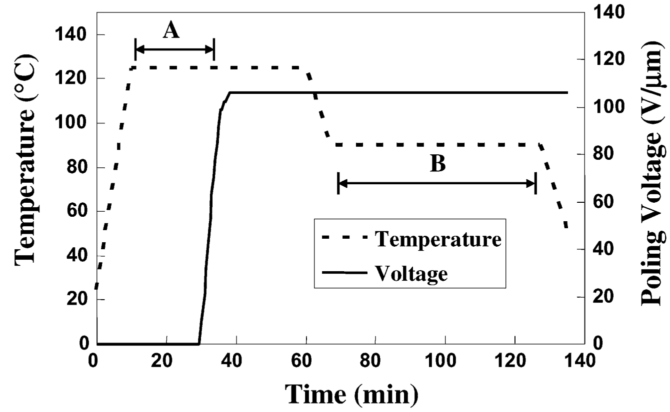

Fig. 3. Poling profile for PSDA-AJL4 MZ modulator. Period A: evaporation of furan protection group. Period B: lattice hardening by DA reaction.

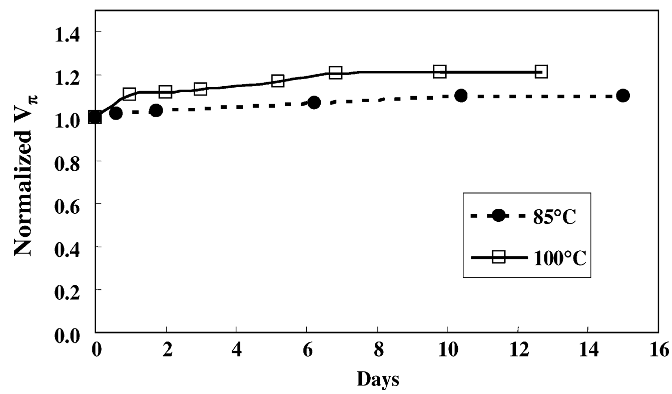

Fig. 4. Degradation of V_π under elevated temperatures. No further change of V_π was observed after 10 days of baking.

A two-step poling process, as shown in Fig. 3, was employed to align the chromophore and crosslink the polymer matrices. After ramping up the temperature to 125 °C, a 20-min, baking without applying poling voltage was intended to thermally cleave and evaporate the furan protection group. If the furan is not completely evaporated, it can lead to increased conductivity. The poling voltage was raised up slowly to prevent current breakdown. Finally, a poling voltage of 105 V/μm was applied throughout the following poling process. After 20-min poling, the temperature was reduced to 90 °C and held for 1 h to trigger the DA reaction for lattice hardening.

III. Device Performace

The finished device has a total length of 34 mm and electrode length of 20 mm. The resulting MZ modulator has V_π of 7.3 V at 1.55 μm and 5.0 V at 1.31 μm, corresponding to r_{33} of 21 and 25 pm/V. The modulator was not push–pull poled. The combined fiber-chip-lens insertion loss is 10 dB at 1.55 μm, which shows no significant poling-induced loss compared to the thin-film measurement.

To test the thermal stability, modulators were kept in a vacuum oven at elevated temperature, then removed, and V_π was measured periodically. The degradation of performance is shown in Fig. 4. For the device kept in an 85 °C oven for more than 10 days, it shows only a 10% increase of V_π. Even under 100 °C baking, V_π only increased up to 20%, and the EO polymer maintains more than 80% of original nonlinearity.

Compared to the EO coefficient measured in poled single film, we obtained ∼30% of this value in our devices. This is due to the high conductivity of PSDA-AJL4 and the use of a more resistive cladding material [13], [14]. The maximum poling current density for our modulators was two orders of magnitude smaller than the current density in a single film. This indicates lower voltage across the core layer and reduced poling efficiency. There are less resistive materials for cladding, such as UV15LV from Masterbond. However, PSDA-AJL4 is relatively brittle and requires good surface and material compatibility with cladding layers. The attempt to use UV15LV as lower cladding was not successful because of cracking of the PSDA-AJL4.

IV. Conclusion

We have fabricated a thermally stable EO polymer modulator using a novel crosslinkable polymer, PSDA-AJL4. This new polymer system employs a smartly controlled crosslinking process to overcome the traditional tradeoff between the EO coefficient and the thermal stability by using a DA reaction. This approach allows the polymer to behave as a guest–host material during poling while the crosslinking occurs at a lower temperature after the chromophore alignment.

The experimental results show a 10% reduction of the EO coefficient at 85 °C and less than 20% at 100 °C. The poling efficiency can be improved by reducing the core material conductivity, perhaps by removing ionic impurities produced in polymer synthesis, and by the use of a more suitable cladding material.

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