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High thermal stability 40 GHz electro-optic polymer modulators

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Abstract: As a consequence of the urgent demand for an electro-optic (EO) polymer modulator with an elevated temperature stability, we have prepared a selection of EO polymers having glass transition temperatures of up to 194°C. The measured half-wave voltage characteristics of the fabricated Mach-Zehnder interference modulators revealed an excellent thermal resistance at 105°C for approximately 2,000 hours. By utilizing traveling-wave electrodes on the modulator, the high-frequency response at 10-40 GHz was evaluated under ascending temperatures. The advantage of such high-temperature stability EO polymer modulators was clearly demonstrated by the continuous frequency response up to 130°C.

OCIS codes: (250.7360) Waveguide modulators; (250.2080) Polymer active devices; (230.2090) Electro-optical device.

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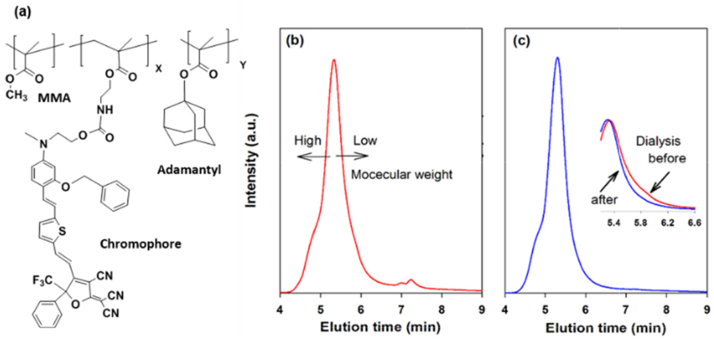
1. Introduction

Electro-optic (EO) polymers are a new class of materials, which have been widely researched over the last few years for utilization in high-speed waveguide modulators. The straightforward advantages include; high EO coefficients, ultrafast response times, low dielectric losses and compatibility with other materials and devices [1,2]. These unique material properties are essential to meet the demands of current telecommunications devices with a lower-power consumption, higher-frequency modulation, and a smaller device footprint. In fact, the recent development of the polymer modulator opens up the possibility of signal transmission over 100 Gbps [3,4]. Achieving higher baud rates is an important objective towards optical interconnection at short-reach applications, so that polymer modulators with serial 100 Gbps might be a cost effective solution [5,6]. To date, a number of polymer modulators have demonstrated an improvement in the bandwidth properties of over 40-70 GHz by utilizing the traveling-wave electrode configurations [7–9].

Based on the material development in previous studies, host-guest polymers and chromophores with high molecular hyperpolarizabilities are key to provide high performance waveguide modulators [10]. It is conceivable that there will continue to be further exploration of polymer-based EO devices for future optoelectronic applications. On the other hand, the environmental stabilities of the polymer modulators are another important issue to be investigated urgently. Clearly EO polymers with enhanced thermo-physical properties in terms of high glass transition temperatures (T_g) and decomposition temperatures (T_d) are preferable to assure the temporal stability against elevated temperatures. We have previously demonstrated that side-chain EO polymers created by chemically attaching the chromophores to the polymers are alternatives to the commonly used host-guest polymers [11–13]. The EO properties in phase modulators, MZI modulators, and ring modulators showed EO coefficients (r_{33}) higher than 100 pm/V and frequency responses of up to 40 GHz [14]. The thermal and temporal stability tests of the EO polymer films and waveguides demonstrated excellent thermal resistance at 85°C [11,15]. Such a thermal resistance meets the materials requirements for industrial optoelectronic applications including Telecordia GR468-CORE used for the thermal stability test. Extra efforts are needed to improve the temperature resistance to reach greater than 100°C. Therefore, we have prepared side-chain EO polymers having an enhanced T_g of 194°C in this study, and evaluated the modulation at 105°C for 2,000 hours. We also measured the 10-40 GHz response of the modulator under elevated temperatures. The results confirmed the high-temperature EO polymer modulator performed well with little degradation of the modulation index up to 130°C.

2. EO polymer and modulator fabrication

Figure 1(a) shows the synthesized EO polymers, which consist of an adamantyl unit to enhance the thermal property and a phenyl vinylene thiophene chromophore to impart the EO activity. The EO polymers were synthesized according to a modified literature procedure [11]. Because of the simple acrylate chemistry of the radical polymerization, loadings of the chromophore and adamantyl were variable as desired. Generally, loading of adamantly into an acrylate polymer enhances the T_g, so that three types of the EO polymers were synthesized with 34-54 wt% adamantyl as listed in Fig. 1. As expected, the Tg increased up to 194°C by increasing the loading of the adamantly into the polymer backbone. The obtained high-T_g properties are the key to enhance the thermal stabilities of the polymer modulators. The concentration of incorporated chromophore was between 24 and 37 wt%, which depended on the construction of the polymer backbones. Purification of the EO polymers is important to enhance the temporal stability. Figure 1(b) shows the GPC trace of the precipitated EO polymer after reaction, highlighting the main polymer peak and a small side peak. The side peak was attributed to the residual chromophore after the post-polymerization functionalization [11]. In order to exclude residual chromophore, dialysis was carried out and the resulting GPC trace showed only one polymer peak as shown in Fig. 1(c). The dialysis tube had the molecular weight cut off (MWCO) of 2,000 g/mol, so that the purification also extracted the lower-molecular weight oligomers from the polymerization. Evidence of this can be found by a slight narrowing of the molecular weight distribution of the polymer.



Polymer	Tg (°C)	Chromophore (wt%)	Adamantyl (wt%)	Vπ•L (V•cm)
EO172	172	37	34	1.6
EO182	182	35	46	2.0
EO194	194	24	54	2.2

Fig. 1. (a) The EO polymers used in this study and the physical properties are summarized in the table. The π-voltage-length products (V_π•L) were measured for the modulators with 1.0 cm-long electrodes, (b) the GPC trace of the precipitated EO polymer, and (d) the GPC trace after dialysis. The insert shows the magnified molecular weight distribution before and after dialysis.

The waveguide MZI modulator was fabricated with a standard inverted-rib structure, consisting of SiO_2 cladding layers, EO polymer core, and electrodes as shown in Figs. 2(a) and 2(b). The bottom electrode was deposited onto the silicon wafer by the vacuum deposition. We used a sol-gel SiO_2 solution to make films of the cladding [14]. The 4 µm-thick SiO_2 film was prepared from an ethanol solution of the sol-gel trimethoxysilyl derivative by spin-coating technique and heating. The inverted-rib structure was patterned as the MZI by conventional photolithography followed by the RIE etching with CHF_3 gas. By choosing a 5.0 µm-wide and 1.0 µm-depth of the trench, a single TM mode optical transmission was obtained at the wavelength of 1550 nm. The EO polymer was spin-coated by using cyclopentanone as the solvent, and dried at 105°C for 24 hours under vacuum to form a 1.5 µm-thick film. Then, a sol-gel SiO_2 layer was spin-coated as the top cladding. The MZI consists of the moderate Y-junction and two-arm interferometer. The junction is 5 mm-long which was sufficient to minimize the optical loss, and the distance between the arms was 300 µm. Finally, the traveling-wave electrodes were patterned onto the modulator to test the high-frequency response. The 3 µm-thick, 20 µm-wide, and 1.0 cm-long gold electrodes were patterned by an electroplating technique using the photolithography process. In order to induce the EO activity, the EO polymer waveguides were polled by applying 400-500 V through the top and bottom electrodes. The poling temperatures were set to around the T_g of the EO polymers.

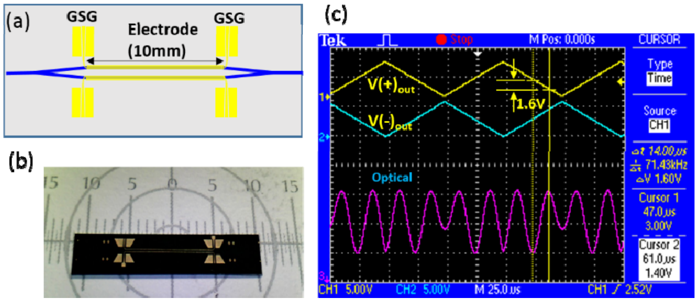


Fig. 2. (a) The schematic top view of the EO polymer MZI with the traveling-wave electrode, (b) the fabricated modulator chip, and (c) the measured transfer function of the modulator at 10 kHz.

3. Measurements

In Fig. 2(c), the 10 kHz-frequency modulation was performed on the MZI modulator (EO172) to evaluate the half-wave voltage (V_π) property. The input light from a 1550 nm laser was coupled into the modulator by a polarized maintaining fiber in TM polarization. The output light was collected by another fiber and channeled to a photodetector. The differential voltages with a triangular waveform from the function generator were applied into the two electrodes of the modulator. All modulators (EO172, 182, and 194) showed π-voltage-length products (V_π•L) of around 1.6-2.2 V•cm, which depended on the loading of chromophore and the poling condition at different temperatures.

Thermal and temporal stability tests were performed by heating the EO polymer modulators at 85°C or 105°C in air, and re-measuring the V_π at strategic time intervals. Testing at 85°C is relevant to industrial generic reliability as it is required for optoelectronic devices. Testing at 105°C is a severe evaluation to meet the strict quality to improve the reliability. Figure 3(a) shows the change of V_π at 85°C for the modulator of EO172. The result showed excellent thermal stability after very small increase in V_π value within initial hundreds hours, then keeping the same V_π values for 2,000 hours. In the experiment it is interesting to note that the dialysis purification was very effective to improve the temporal reliability of the EO polymer modulator. When we used EO172 (un-dialyzed) for the MZI modulator, we found a significant degradation of the EO activity during the initial period of 300 hours, after which a gradual degradation continued for a long period. We considered that the observed degradation of the EO activity was attributed to the thermal disordering of the low-molecular weight residuals in the crude polymer. In order to evaluate the higher temperature resistance, 105°C tests were performed for EO172 and EO194, and the results were compared in Figs. 3(a) and (b). Clearly, EO194 revealed an enhanced thermal and temporal stability, while EO172 showed continuous graduation at 105°C. It is also noted that variations of the measured V_π are diminished after suitable period of the thermal annealing. The recorded change of the V_π for the EO194 modulator was only 0.1-0.2 V.

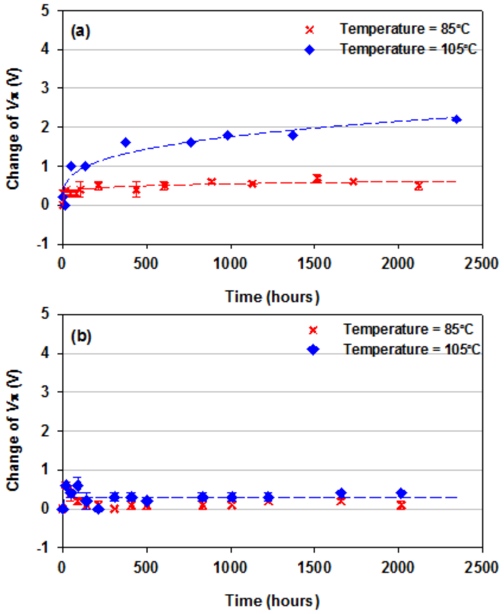


Fig. 3. The temperature dependence (85°C and 105°C) of the change of V_π for the EO polymer modulators using (a) EO172 and (b) EO194.

The polymer modulator has one obvious advantage for a high frequency response due to the relatively small velocity mismatch between RF and optical waves [16–18]. The RF response of the EO polymer modulator and its temperature dependence are characterized by using sideband spectroscopy. In the measurement, the output light from the modulator was directly connected to an optical spectrum analyzer, and the transmission spectra were measured by applying RF signals to the electrodes. Figures 4(a)-4(c) show the measured spectra for the modulator EO194, which were taken at 25°C with the high-frequency signals of 10, 20, and 40 GHz. The clear sidebands were observed with equal spacing corresponding to the RF frequencies. Generally, the power ratio (ΔP) of the main peak (J_0) and sideband (J_1) is proportional to the square of zero-order and first-order Bessel function of the first kind, where the modulation index (η) can be expressed as $\Delta P = J_0/\mathrm{J}_1 = [J_0(\eta)/J_1(\eta)]^2$ [18,19]. When the modulator was heated at 90°C under the same optical condition in Figs. 4(d)-4(f), the measured spectra exhibited a negligible change showing clear sideband peaks at every frequency similar to the spectra at 25°C. For such a large temperature difference, we should consider the changes of the EO coefficient, materials refractive indices, optical and RF loss. In our experiments, the measured V_π of E194 was almost independent to temperatures of up to 90°C, so that the waveguide figure of merit defined by $\mathrm{n}^3 r_{33}$ should not contribute to the high-frequency response.

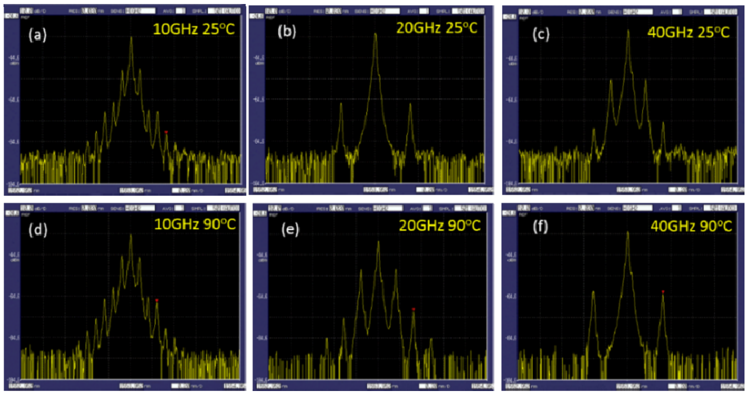


Fig. 4. The measured optical transmission spectra of the EO polymer modulator (EO194) at (a, b, and c) 10-40 GHz at 25°C and (d, e, and f) 10-40 GHz at 90°C.

In order to clarify the details of the temperature dependence, we measured the change of the modulation index as shown in Fig. 5 at various temperatures. Though high-temperature drift during the experiments is problematic to apply the DC bias to set the phase-balance of the modulator, the measured spectra demonstrate rather small changes of the modulation indices. It is interesting to note that the modulator slightly increased the modulation indices around 80-90°C, while abrupt degradation cannot be found up to 130°C. Furthermore, the EO property was completely recovered to its original activity when the device was cooled down at room temperature. The observed thermal resistance of EO194 is attributed to the high glass transition temperature and materials purity. The viability of using such high-temperature EO polymers has been demonstrated for the EO modulators, which provided excellent thermal reliabilities for a long period.

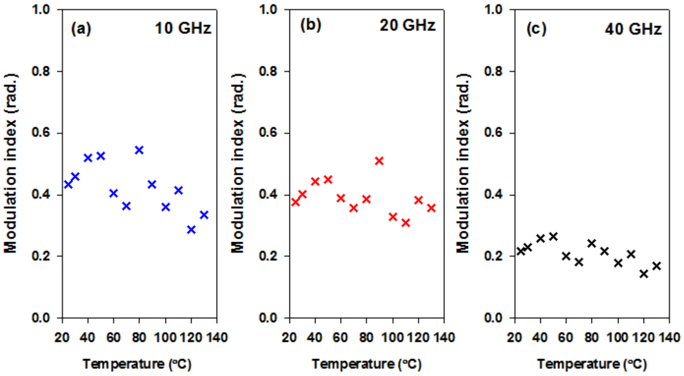


Fig. 5. The temperature dependence of the modulation indices at (a) 10 GHz, (b) 20 GHz, and (c) 40 GHz for the EO polymer MZI.

4. Summary

We prepared a series of EO polymers with a high T_g of between 172 and 194°C for application in waveguide modulators. Both the high-T_g and purified EO polymers delivered an enhanced resistance against the elevated temperatures. The measured thermal and temporal stability of the MZI modulator, especially prepared by using EO194, showed excellent results maintaining the EO activity at 105°C for 2,000 hours. Such a strong thermal stability is clearly an enhancement over commonly used organic EO materials based on the guest-host system. We also demonstrated the high frequency response of the EO polymer modulator. The 10-40 GHz test showed little change in the modulation indices, furthermore significant degradation of the EO property could not be found during the examinations. Based on these promising experimental results, we expect that our highly stable EO material could be utilized in a wider range of polymer modulator applications.

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