

Thermal stability control of electro-optic (EO) polymer based norbornene for hybrid EO modulator

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Abstract: Electro-optic (EO) polymers have been considered as promising materials using in several EO applications including telecommunication. This is due to the urgent demand of EO modulators providing both high EO coefficient as well as high thermal stability. In this work, derivatives of norbornene were polymerised into EO polymer consisting of both EO active and thermal control units. These EO polymers based norbornene were conveniently prepared under mild condition with less procedures that was suitable for large scale production. Moreover, they showed several physical advantages over traditional PMMA, such as higher thermal stability as well as well-control molecular weight. The EO polymers were then fabricated into hybrid EO modulator with silicon and were poled at evaluated temperature. The main characteristic of EO modulator, half-wave voltage (V_{π}), will be further discussed.

Keywords: EO polymer, norbornene, norbornene-dicarboximide, optoelectronics, EO modulator.

1. INTRODUCTION

Electro-optic (EO) polymers have been extensively considered as promising materials in wide range of optoelectronics applications including telecommunication. This is because organic EO polymers have shown several advantages over traditional inorganic lithium niobate, such as adjustable EO coefficient as well as compatibility with other optical elements. Since then, development of EO polymers, containing EO chromophore, has been intensively investigated to meet *Telecordia* standard tests for commercial optical materials.

Variety of poly(methyl metacrylate) (PMMA)s has been one of the most widely used polymers using as a host in EO polymers. However, synthesis of PMMAs has to be performed using radical polymerisation using radical initiator which decompose electron-rich EO chromophore. Therefore, EO chromophore is generally connected to PMMA backbone after polymerisation. This two-step synthesis additionally requires dialysis as a removal of unreacted chromophore [2].

Thus, in this work, we have purposed derivatives of norbornene as main polymer backbone due to its ease of synthesis, high glass transition temperature (T_g), and excellent optical transparency which are critical needs for EO polymer-based modulators.

2. EXPERIMENTAL

Experimental consists of polymerisation of several norbornene derivatives and their thermos-physical properties, as well as the evaluation designs for thermal stability control. In addition, the preliminary experiment of EO polymer-based modulator was also studied.

2.1 Polymerisation of norbornene derivatives and evaluation of thermal stability

Fig. 1 showed synthesis of norbornene-based EO polymers *via* ring opening metathesis polymerisation (ROMP) using Grubbs 3rd generation catalyst (G3) as an initiator under inert atmosphere. **R** refers to pendant

groups which are cyclohexyl (R1) and hexyl (R2). Phenyl vinyl thiophene or FTC chromophore (highlighted in green) was originally prepared by our research group, exhibiting high hyperpolarizability and thermal stability [3].

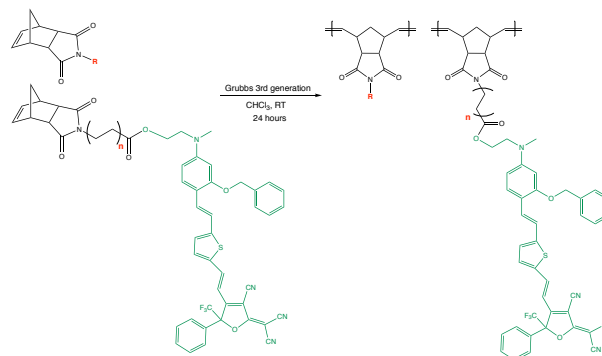


Fig. 1. Polymerisation of norbornene derivatives *via* ROMP.

The evaluation of thermal stability was investigated not only by pendant R, but also length of hydrocarbon chain linking between norbornene-dicarboximide (NDI) backbone and FTC chromophore. Loading density of the active chromophore was varied from 30 wt% to 60 wt%.

2.2 Fabrication of EO polymer-based modulator

Fabrication process of EO modulator was performed on silicon wafer with Al and Au as bottom and top electrodes, respectively. The cladding layers to prevent polymer breakdown under evaluated temperature is sol-gel. After that, the complete modulator was poled under high temperature close to T_g and strong electric field at 400V. This was to orient the alignment of EO chromophore to be in non-centrometric symmetry resulting in EO effect under applied electric field. The half-wave voltage (V_{π}), the important characteristic of fabricated EO modulator, was then measured using input polarised light at 1550 nm. The output light was then collected at the other fiber and channeled to a photodetector.

3. RESULTS AND DISCUSSION

3.1 Thermos-physical properties of EO polymers and thermal stability control

Fig. 1 showed physical properties of series of EO polymers. Actual loading density was ranging from 20 to 57 wt% as the amount of chromophore-NDI monomer increased. All polydispersity (PDI) were under 2.00 indicating well-control molecular weight of polymers which will be significant issue in device fabrication. Nevertheless, glass transition temperatures needed to be lower than decomposition temperature of FTC chromophore (210 °C) to prevent EO breakdown of polymers during poling process. Thus, connecting carbon chain connecting between NDI backbone and FTC chromophore were extended to 4 and 6, in order to increase mobility of polymers. However, with exact polymerisation condition with **3a**, **3e** (n=4) and **3f** (n=6) did not show significant change in thermal stability.

Table 1. Physical properties of polymers **3a-d** (R1, n=2) and **3e-f** (R1, n=4 and 6)

Polymers	n	%Cr	M _n (g/mol)	PDI	T _g (°C)
3a	2	22	15200	1.19	219
3b	2	33	21600	1.27	243
3c	2	42	30200	1.44	245
3d	2	57	36800	2.00	238
3e	4	21	16100	1.28	216
3f	6	24	16600	1.26	211

The attempt to control thermal stability was further optimized by replacing pendant group R1 to R2 which is hexyl chain. As shown in Table 2, polymer **4a** remained showing relatively high T_g, this is probably because of intermolecular interaction between π -rich FTC chromophore among each polymer chains. However, by lengthening hydrocarbon linking segment clearly showed that T_g of polymers notably decreased.

Table 2. Physical properties of polymers **4a-c** (R2)

Polymers	n	%Cr	M _n (g/mol)	PDI	T _g (°C)
4a	2	38	17400	1.72	235
4b	3	32	22600	1.55	*
4c	4	35	28600	3.64	154
4d	5	35	22500	1.54	157
4e	6	28	28900	2.50	*

* DSC results did not show clear T_g due to their amorphous property.

Although the control of thermal stability of EO polymers remains needed to be improved, EO polymers based norbornene showed several potentials to be used in EO applications, including ease of preparation in large volume. Moreover, in comparison with traditional PMMA, polymers based norbornene showed well control molecular weight which will be advantage in fabrication process.

3.2 Preliminary result of EO polymer-based modulator

As a preliminary study of performance of EO polymer based norbornene, polymer **4c** having T_g 154 °C was fabricated into modulator in the silicon hybrid waveguide.

Poling temperature was varied from 140, 150, 160 and 170°C to examine the most applicable poling efficiency. Unfortunately, the devices cracked as poling at 160 and 170 °C. This is probably due to higher poling temperature than that of glass transition temperature of polymer. Poled modulator at 140 °C showed V _{π} at 8.80 V (Fig. 2) which is relatively high confirming that poling efficiency was inadequate to align chromophore molecules to be in noncentrosymmetry. However, V _{π} of poled device at 150 °C will be measured and further to be discussed.

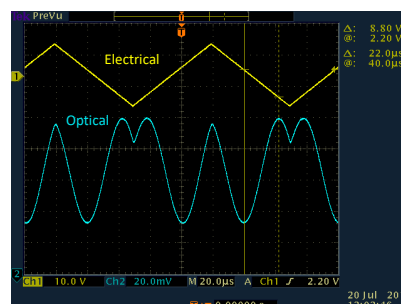


Fig. 2. The measured transferred function of the EO modulator

4. CONCLUSION

EO polymers based norbornene derivatives were efficiently prepared *via* ROMP which is mild condition for active FTC chromophore. This could be considered as potential preparation for short period of time as well as large volume production. Moreover, even though the evaluation of thermal control of EO polymers remains to be studied, EO polymers based norbornene derivatives showed advantages, such as molecular weight control and higher thermal stability, over PMMA. These parameters are critical in fabrication process as they could noticeably effect film quality of EO polymer. As hybrid modulator made of EO polymer and silicon, the device was poled at evaluated temperature to examine best poling efficiency. This is the ongoing experiment and will be discussed later.

5. REFERENCES

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