

Remarks on the Design of Flexible High-Temperature Polymer Dielectrics for Emerging Grand Electrification – Exemplified by Poly(oxa)norbornenes

Chao Wu¹, Ajinkya A. Deshmukh², Zongze Li^{1,3}, Lihua Chen⁴, Abdullah Alamri², Yifei Wang¹, Jierui Zhou^{1,3}, Omer Yassin², Rampi Ramprasad⁴, Gregory A. Sotzing², and Yang Cao^{1,3}

¹Electrical Insulation Research Center, Institute of Materials Science

²Polymer Program and Department of Chemistry

³Department of Electrical and Computer Engineering
University of Connecticut, Storrs, CT, United States

⁴School of Materials Science and Engineering
Georgia Institute of Technology, Atlanta, GA, United States

ABSTRACT

Polymer dielectrics essentially revolutionized the electrical power system, pervasively used in nearly all the key electronic and electrical devices, due mainly to their suitably large bandgaps. However, insufficient attention has been paid to the bandgap in the design of new polymer dielectrics for high temperatures. In this paper, we present a unified principle for the design of flexible, high temperature polymer dielectrics. As exemplified by our recently discovered poly(oxa)norbornenes (POFNB), saturated bicyclics with varying carbonyl and ether groups in the bicyclic repeat units, connected by unconjugated alkenes and freely rotatable single bonds in conjunction with freely rotating fluorinated benzene ring side-groups, can impart flexibility yet retain thermal stability while providing large bandgaps to olefinic polymers. The results indicate that POFNB has stably low conduction current under concurrent high electric field and elevated temperatures beneficial from its large band gap of ~5 eV and high glass transition temperature of 186 °C.

Index Terms — polymer dielectric, band gap, high electric field, elevated temperature, conduction

1 INTRODUCTION

POLYMER dielectrics are widely used insulators due to their high breakdown strength, great scalability, facile processability, light weight and high mechanical strength. While the conduction and breakdown of dielectric materials are intrinsically dominated by the bandgaps [1–3], insufficient attention has been paid thus far to bandgaps in the selection and design of polymer dielectrics. This is in part due to the fact that most polymers are deemed good dielectrics with bandgaps sufficient for operation under moderate fields. It shall be noted that commodity dielectrics, such as polyolefins, possess intrinsically large bandgaps due to their fully saturated σ -bonding main chains [4]. Good examples are the (crosslinked) polyethylene (PE) used widely for power cables [5, 6] and (biaxially stretched) polypropylene (PP) for film capacitors [7], both having bandgaps >6 eV. Conventional high-temperature

polymers like poly(ether ether ketone) (PEEK), polyetherimide (PEI) and polyimide (PI) have been used in numerous applications requiring high temperatures (>100 °C), but lower fields than applications using PP and PE. This orthogonal treatment of operating field and temperature can no longer meet the stringent requirements of emerging grand electrification. For instance, modernization of power grid with rapid expansions in scale, voltage, power towards Super- and Smart-Grids, with largely enhanced flexibility, resiliency, demand-response and sustainability, as well as continued miniaturization of electronics, all call for flexible polymer dielectric materials that can withstand higher voltage/field while delivering lower loss under extreme electric field and temperature [4, 5, 7, 8]. Furthermore, with future developmental needs for harsh operation temperatures exceeding 150 °C for hybrid propulsion for commercial passenger airplanes and downhole oil and gas exploration and production, new polymer dielectrics will not only entail excellent insulating properties, but also high-temperature resistance [8].

Manuscript received on 2 March 2021, in final form 20 May 2021, accepted 10 June 2021. Corresponding author: Y. Cao.

DOI: 10.1109/TDEI.2021.009620

A recent study disclosed an inverse relationship between the bandgaps of common high temperature polymers with their glass transition temperatures (T_g) [4]. Intrinsically, these established high-temperature polymers cannot be operated at the same high electric fields as PE or PP as required in the aforementioned emerging applications for high density and high payload efficiency due to dramatically increased conduction current. In this letter, we use the newly discovered polynorbornenes to elucidate a unified design approach for flexible, high-temperature polymer dielectrics, operable under high field. Saturated bicyclics with varying carbonyl and ether groups in the bi-cyclic repeat units, connected by unconjugated alkenes and freely rotatable single bonds in conjunction with freely rotating fluorinated benzene ring side-groups, can impart flexibility yet retain thermal stability while providing large bandgaps to olefinic polymers. Furthermore, we report the high-electric-field conduction of POFNB in comparison with the best insulating materials available, i.e., high-density PE (HDPE), biaxially oriented PP (BOPP), Kapton® Polyimide (PI), at ambient and elevated temperatures to demonstrate its superior performance, well suited for concurrent harsh conditions of electrical and thermal extremes.

2 EXPERIMENTAL DETAILS

Following the ring-opening metathesis polymerization (ROMP) of poly-(oxa)fluoronorbornene using the Grubbs generation 2 catalyst [4], two more types of poly-fluoronorbornenes were synthesized, as summarized in Table 1, along with 3 other state-of-the-art dielectric films.

Table 1. Information of polymer film dielectrics.

Abbre.	Polymer	Thickness (μm)	Vender
PRFNB	Polyfluoronorbornene reduced	~ 10	This work
PFNB	Polyfluoronorbornene	~ 10	
POFNB	Poly(oxa)fluoronorbornene	~ 10	
BOPP	Biaxially oriented polypropylene	7.8	Bolloré
HDPE	High density polyethylene	9	Goodfellow
Kapton® PI	Kapton® polyimide	8.5	DuPont

Electronic density of states for poly-fluoronorbornenes and poly-(oxa)fluoronorbornene are computed using first-principles density functional theory (DFT) to provide further insights into the band structure of the synthesized polymers, whereas the band gaps of these polymers in this work are experimentally investigated using ultraviolet-visible spectroscopy (UVS) [4].

Due to rapid aging under high field, conventional quasi-steady state conduction measurements can only reach a field of about two thirds of the breakdown strength. In this letter, the high field conduction was measured using a specially designed system, which can dynamically cancel the capacitive component to probe conduction current as low as 10 ppm during voltage ramp up to breakdown [9].

3 RESULTS AND DISCUSSION

The chemical structures of PRFNB, PFNB and POFNB are illustrated in Figure 1. All designed with nonconjugated bicyclic structure of the backbone for high thermal stability without sacrificing the bandgap, PRFNB, PFNB and POFNB are introduced with varying carbonyl and ether groups in the bicyclics to reveal the effects of oxygen-containing functional groups in modifying their T_g and band structure. The T_g for PRFNB is 160 °C, while much higher T_g of 212 and 186 °C are achieved for PFNB and POFNB, respectively, due possibly to largely enhanced hinderance of backbone movement with the addition of two carbonyl groups in the bicyclics.

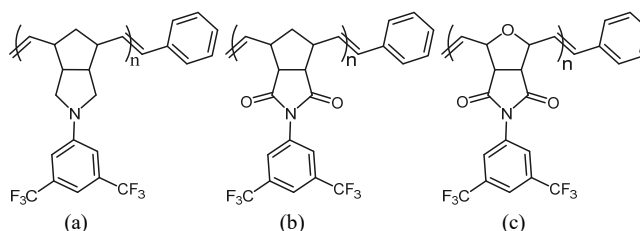


Figure 1. Repeat unit of (a) PRFNB, (b) PFNB and (c) POFNB

The DFT electronic density of states for PRFNB, PFNB and POFNB are shown in Figure 2, in good agreement with their experimentally determined optical bandgaps of 3.4, 4.3 and 4.9 eV, respectively. It appears that the presence of two carbonyl groups to the bicyclics enhances not only the T_g , but also the bandgap of polynorbornenes. In addition, the electron withdrawing ether leads apparently to the largest band gap among the polynorbornenes synthesized.

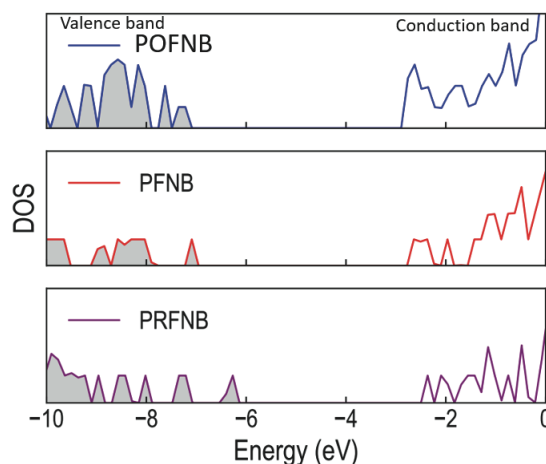


Figure 2. The electronic density of states (DOS) for PRFNB, PFNB and POFNB.

As POFNB has the largest band gap and relatively high glass transition temperature among synthesized poly-fluoronorbornenes and poly-(oxa)fluoronorbornene, the high field conduction of POFNB was investigated in comparison with the state-of-the-art polymer dielectrics. The integral conduction current (ICC) of POFNB, HDPE, BOPP and PI measured directly by the designed system together with the calculated conduction current density are shown in Figure 3.

The ratio of the conduction current at 100 °C and RT at ~500 MV/m (P_{500}) for POFNB is 2.2, while it is 24.3 for BOPP. For HDPE at 200 MV/m, the ratio of the conduction current at 100 °C versus that at RT, P_{200} , is 238. In a side-by-side comparison, P_{200} is ~1 for POFNB and 5.8 for BOPP. That is, below 200 MV/m, the conduction of POFNB is nearly independent of the temperature. The temperature dependence of the conductivity for POFNB is an order of magnitude smaller than that of BOPP and two orders of magnitude lower than that of HDPE.

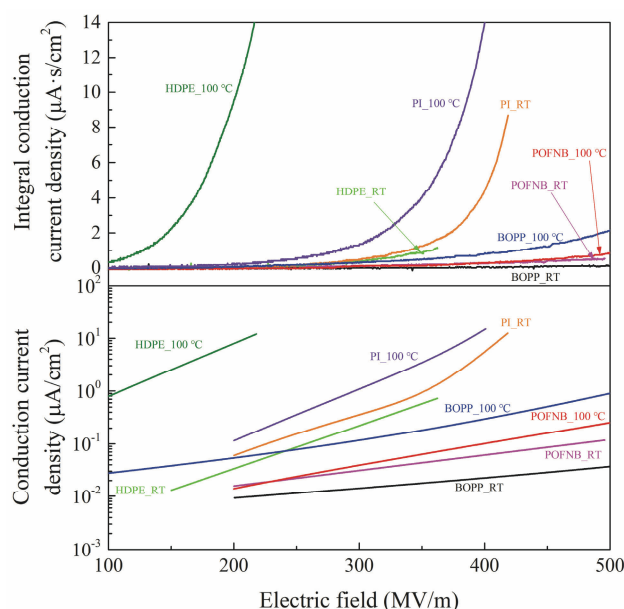


Figure 3. Integral conduction current density and conduction current density of POFNB, BOPP, HDPE and PI at room temperature and 100 °C.

The overall low conduction of POFNB and its small temperature dependence indicate tremendous application space for high electric field, and, more importantly, for concurrent high temperature use. For instance, high voltage direct current (HVDC) power cable operates with a large current density and ultra-high voltage. The resultant temperature gradient in power cable insulation can lead inevitably to a non-uniform conduction and thus distorted electric field thereby increasing the risk of space charge accumulation related aging and breakdown [10, 11]. The excellent thermal stability and small temperature dependence of the conduction for POFNB are beneficial to the insulation subjected to a large temperature gradient as in the case of HVDC cabling. With the rapid development and maturing of wide-band-semiconductor switches, power electronic converters and electric propulsion drives can be designed with unprecedentedly high power density and payload efficiency if new power dense passives, such as capacitors and insulators, can be made available for high temperature and high voltage operations. With low conduction loss and high breakdown strength attributed to its large bandgap, together with also a superior thermal stability, POFNB could potentially fill such an urgent development gap. In addition, monomers are prepared from tremendously cheap chemicals, such as furan and maleimide, undergoing high yielding Diels-

Alder chemistry, and the polymers are synthesized using versatile ring-opening metathesis polymerization, imparting POFNB with enormous potential for mass production.

4 CONCLUSIONS

In this letter, we elucidate a holistic principle for the design of high temperature polymer dielectrics via simultaneously tuning the band gap and the glass transition temperature. A high temperature polyolefin, POFNB, designed by a new strategy, is composed of saturated fused bicyclics in the polymer backbone rather than conventional aromatic structure for better thermal stability without compromising the bandgap. Oxygen-containing carbonyl and ether functional groups are introduced in the backbone to further modify the band structure. POFNB thus has a large bandgap (4.9 eV) and simultaneously a high glass transition temperature (186 °C). At 100 °C, POFNB revealed much lower conduction current relative to BOPP and HDPE, the best reported insulating materials, and PI, one of the best reported high-temperature polymers. At 200 MV/m, the conduction of POFNB is nearly independent of the temperature over the temperature range investigated. The temperature coefficient of POFNB is one order of magnitude lower than that of BOPP, and two orders of magnitude lower than HDPE. The greatly suppressed conduction under ambient and elevated temperatures coupled with its extremely low temperature coefficient make POFNB a promising candidate for a broad range of applications, particularly under concurrent high electric field and high temperature.

ACKNOWLEDGMENT

This work is supported through a multidisciplinary university research initiative (MURI) grant (N00014-17-1-2656) and a capacitor program grant (N0014-19-1-2340), both from ONR.

REFERENCES

- [1] R. Coelho, *Physics of Dielectrics for the Engineer*, Elsevier, 1974.
- [2] M. Ieda, "Electrical conduction and carrier traps in polymeric materials," *IEEE Trans. Dielectr. Electr. Insul.*, vol. EI-19, no. 3, pp. 162–178, 1984.
- [3] C. Wu et al., "Targeted co-designs of dielectric polymers tolerant to enormous electric field and temperature via material-informatic discovery acceleration," *J. Mater. Chem. A*, 2021 (submitted).
- [4] C. Wu et al., "Flexible temperature-invariant polymer dielectrics with large bandgap," *Adv. Mater.*, vol. 32, 2000499, 2020.
- [5] A. M. Pourrahimi et al., "The Role of Interfaces in Polyethylene/Metal-Oxide Nanocomposites for Ultrahigh-Voltage Insulating Materials," *Adv. Mater.*, vol. 30, 1703624, 2018.
- [6] M. Fu et al., "Space charge formation and its modified electric field under applied voltage reversal and temperature gradient in XLPE cable," *IEEE Trans. Dielectr. Electr. Insul.*, vol. 15, no. 3, pp. 851–860, 2008.
- [7] A. Mannodi-Kanakithodi et al., "Rational Co-Design of Polymer Dielectrics for Energy Storage," *Adv. Mater.*, vol. 28, pp. 6277–6291, 2016.
- [8] J. Watson and G. Castro, "A review of high-temperature electronics technology and applications," *J. Mater. Sci.: Mater. Electron.*, vol. 26, pp. 9226–9235, 2015.
- [9] Z. Li et al., "Transient characterization of extreme field conduction in dielectrics," *AIP Advances*, vol. 6, 115025, 2016.
- [10] M. Tefferi et al., "Novel EPR-insulated DC cables for future multi-terminal MVDC integration," *IEEE Electr. Insul. Mag.*, vol. 35, no. 5, pp. 20–27, 2019.
- [11] G. Marzanti and M. Marzotto, *Extruded Cables for High Voltage Direct Current Transmission: Advance in Research and Development*, Pwr. Engineering Series, Wiley-IEEE Press, 2013.