

Impact of oxygen-containing carbonyl and ether groups on dielectric properties of poly(oxa)norbornene cyclic olefins

Chao Wu*, Ajinkya A. Deshmukh*, Lihua Chen†, Rampi Ramprasad†,
Gregory A. Sotzing* and Yang Cao*^{‡,§}

**Institute of Materials Science, University of Connecticut
Storrs, CT 06269, USA*

†*School of Materials Science and Engineering, Georgia Institute of Technology
Atlanta, GA 30332, USA*

‡*Department of Electrical and Computer Engineering, University of Connecticut
Storrs, CT 06269, USA*

§yang.cao@uconn.edu

Received 26 September 2022; Revised 30 January 2023; Accepted 10 April 2023; Published 31 May 2023

Flexible dielectric polymers that can withstand high electric field and simultaneously have high dielectric constant are desired for high-density energy storage. Here, we systematically investigated the impact of oxygen-containing ether and carbonyl groups in the backbone structure on dielectric properties of a series of cyclic olefin. In comparison to the influence of the $-\text{CF}_3$ pendant groups that had more impact on the dielectric constant rather than the band gap, the change of the backbone structure affected both the dielectric constant and band gaps. The one polymer with ether and carbonyl groups in the backbone has the largest band gap and highest discharge efficiency, while it has the lowest dielectric constant. The polymer without any ether groups in the backbone has the smallest band gap and lowest discharge efficiency, but it has the highest dielectric constant. Polymers that have no dipolar relaxation exhibit an inversely correlated dielectric constant and band gap. Enhancing the dipolar relaxation through rational molecular structure design can be a novel way to break through the exclusive constraint of dielectric constant and band gap for high-density energy storage.

Keywords: Polymer dielectric; band gap; glass transition; conduction; energy density; DFT.

1. Introduction

Dielectric energy storage with an ultra-fast charging–discharging rate is the key to advanced electrical and electronic systems that require high power density.^{1–6} High-density dielectric energy storage materials are highly desired to meet the demands of ever-increased payload efficiency and miniaturization of the system.^{7–10} The energy density of linear dielectric materials is proportional to the dielectric constant and quadratically dependent on the operational electric field.^{1,11} Therefore, high breakdown strength is the foremost parameter for dielectrics not only for better reliability for high electric field operation but also for higher energy density.² The dielectric constant is also important to further improve the energy density of a dielectric material.

Breakdown of dielectric polymers is a complicated process that is affected by multiple factors, including electronic, thermal and mechanical parameters.¹² For polymers, the morphological disorder originated from the weak inter-chain interactions and long chain arrangement also affected the breakdown strength.¹³ In addition, the interface between

dielectrics and metal electrodes is also a key factor that influenced the breakdown strength.^{14,15} Among the factors that have been investigated, the band gap dominated the breakdown strength of dielectrics.^{16,17} Large band gaps give rise to higher breakdown strength and lower conduction loss.¹⁸ However, the band gap of polymers exhibited an inverse relationship with the dielectric constant attributed to the exclusive constraint between the electronic dielectric constant and band gap.^{2,19,20} To explore polymers with well-balanced dielectric constant and band gap for higher energy density, it is of significance to systematically study the impact of polymer structure on dielectric constant, band gap and high field properties.

Based on rational molecular design, we previously synthesized a series of cyclic olefins dielectrics with a large band gap, high-glass transition temperature and varied dielectric constant by changing the pendant group.^{18,19,21,22} In this work, we further study the impact of the backbone structure on dielectric properties by introducing different oxygen-containing groups.

§Corresponding author.

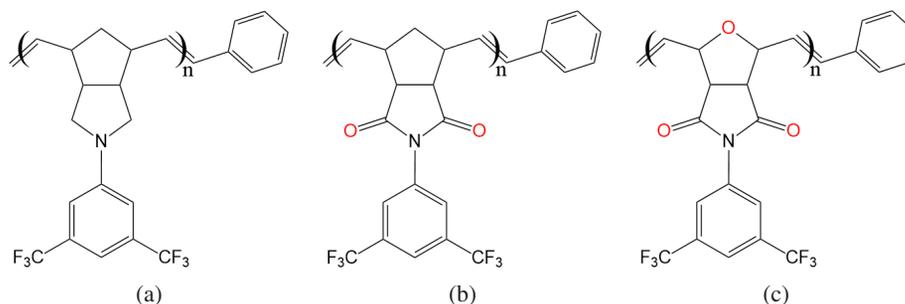


Fig. 1. Chemical structure of (a) PRFNB (P1), (b) PFNB (P2) and (c) POFNB (P3).

2. Experimental Methods

2.1. Materials

Ether group is introduced to the backbone and symmetric carbonyl groups are within the fused five-membered ring in the form of imide groups. Repeat units of the investigated polymers are illustrated in Fig. 1. These three polymers P1, P2 and P3 were synthesized using a ring-opening metathesis polymerization with Grubbs generation 2 catalyst and made into free-standing films by solution casting method. Details of the synthesis and film fabrication could be found in the supporting information (Schemes S1–S4, Figs. S1–S6). Compared to PRFNB (P1), in PFNB (P2), we introduce carbonyl in the second 5-membered ring fused to the backbone, forming imide groups. In POFNB (P3), we further introduce the ether group in the saturated 5-membered ring in the backbone, forming a heterocyclic structure. Relative to PRFNB (P1), the effect of the carbonyl in imide groups on high electric field conduction would be identified. The contribution of the ether group is verified based on the comparison of POFNB (P3) and PFNB (P2).

2.2. DFT computation

The density of states of the designed polymers was estimated using density functional theory (DFT), as implemented in the Vienna Ab-Initio Simulation Package (VASP). Given the expensive computational cost, two repeat units with H terminal atoms were used to construct the physical models, as shown in Fig. 2.

2.3. Electrical measurement

The band gap was measured through UV Visible Spectroscopy using Agilent's 5000 UV/VIS/NIR spectrometer.¹⁸ The

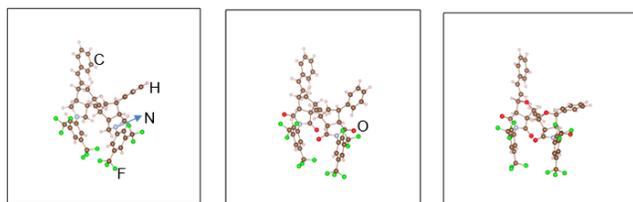


Fig. 2. DFT models for PRFNB, PFNB and POFNB.

dielectric constant was measured using a Solartron 1296 dielectric interface and Solartron SI 1260 frequency response analyzer and the value at 100 Hz is utilized as the dielectric constant. Displacement-Electric (DE) field loops were measured under a unipolar positive half sinusoidal wave of 100 Hz.

3. Results and Discussion

The computed and experimentally measured band gap of these three polymers are shown in Fig. 3, exhibiting the order of POFNB (P3) > PFNB (P2) > PRFNB (P1). The dielectric constant of these three polymers is also investigated and shown in Figs. 3 and S7. POFNB (P3) that concurrently has carbonyl and ether groups in the backbone structure exhibits the largest band gap and lowest dielectric constant. In contrast, PRFNB has the smallest band gap and highest dielectric constant.

Combining the band gaps and dielectric constants of well-established commercial polymer dielectrics (see Fig. 4), band gaps are inversely related to dielectric constants. *m*-POFNB, *p*-POFNB and *o*-POFNB are three previously reported polymers that have the same backbone structure with POFNB (P3) and a single $-CF_3$ at the pendant benzene ring. Out of them, *m*-POFNB has enhanced dipolar relaxation due

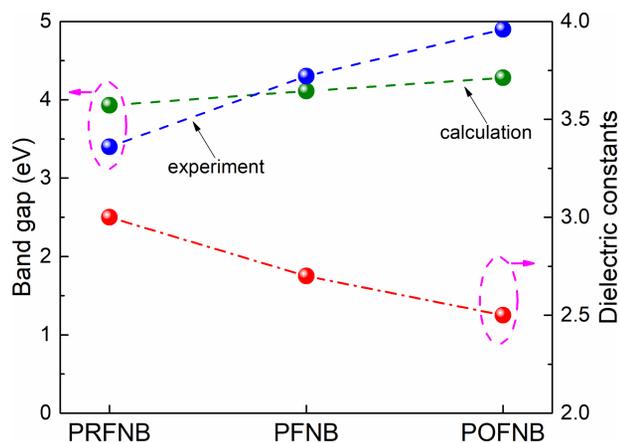


Fig. 3. Band gaps and dielectric constants for PRFNB (P1), PFNB (P2) and POFNB (P3).

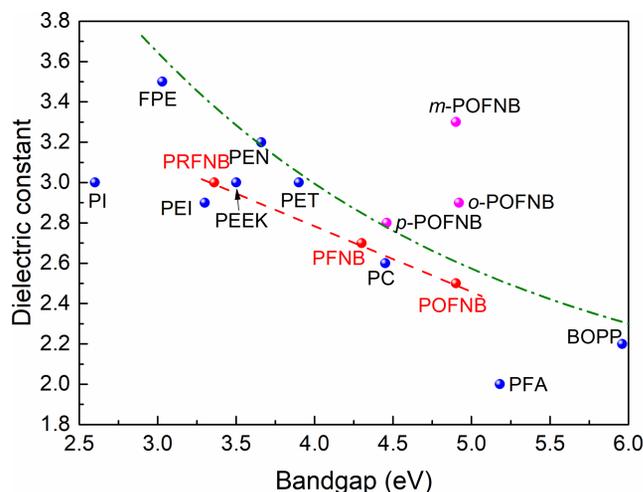


Fig. 4. The relationship between experimentally measured dielectric constant and band gap for synthesized and commercial dielectric polymers.

to the asymmetrically fluorinated pendant group, appearing as an outlier in the inverse relationship. Dipolar relaxation could be an option to break through the inverse relationship between dielectric constants and band gaps dominated by the exclusive constraint of band gap and electronic dielectric constant. Comparing the structure of the seven polynorbornenes, it is found that the position of the pendant $-\text{CF}_3$ groups slightly impacts the band gap while it had a more significant influence on the dielectric constant. In contrast, the oxygen-containing carbonyl and ether groups in the backbone structure play an important role in determining both the band gap and dielectric constant.

To further elucidate the influence of the dielectric constant and band gap on the energy storage performance of the three polymers investigated, DE loops were used to experimentally measure the discharged energy density and charge–discharge efficiency as a function of the electric field, as shown in Fig. 5. The thickness of films for the DE loops measurement is around $10\ \mu\text{m}$. The area within the loops denotes the loss in a charging–discharging cycle. From PRFNB (P1), PFNB (P2) to POFNB (P3), the loss decreases from a side-by-side comparison under the same electric field. The slope of the loops represents the dielectric constant, decreasing from PRFNB (P1), PFNB (P2) to POFNB (P3). The discharged energy density is therefore the highest for PRFNB (P1) at the same electric field. The quantitative charge–discharge efficiency could be obtained from the DE loops. The efficiency decreases with an increase of the electric field, attributing to the nonlinearly increased conduction loss. With the largest band gap, the efficiency is the highest for POFNB (P3) among the three polymers ($>95\%$ even at $700\ \text{MV/m}$). While the efficiency of PRFNB (P1) is the lowest compared to POFNB (P3) and PFNB (P2) owing to the lowest band gap. Under an extremely high electric field, the electrical conduction increases dramatically because of the fierce charge

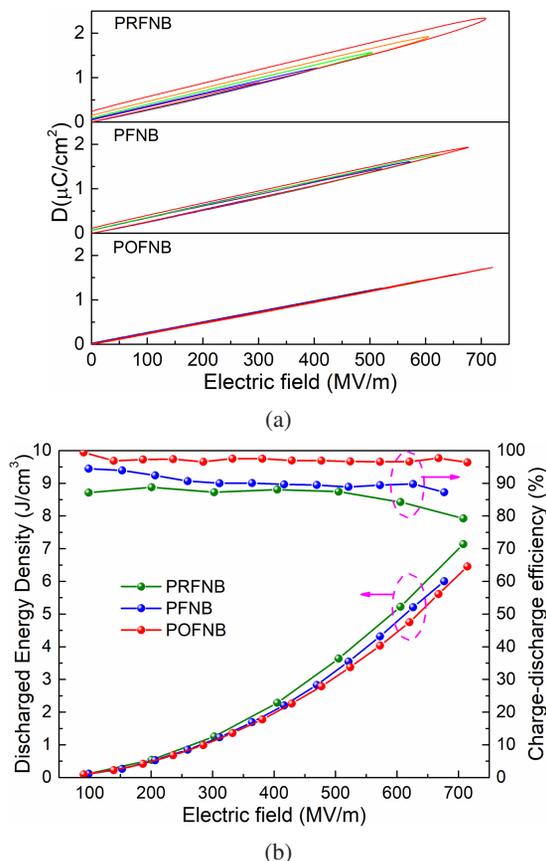


Fig. 5. Capacitive energy storage properties. (a) Electric DE field loops. (b) Discharged energy density and efficiency.

injection from the electrodes and charge transport in the bulk of polymer dielectrics. The large amount of Joule heat produced by the conduction current leads to thermal breakdown under electric field far below the intrinsic breakdown strength of polymer dielectrics. Therefore, more attention should also be paid to efficiency. All these findings indicate that a rational design to balance the trade-off between dielectric constant and band gap for high energy density and high efficiency is desired to explore novel polymer dielectrics.

4. Conclusions

In summary, three cyclic olefin polymer dielectrics were designed and synthesized to study the impact of the backbone structures on band gap which is the key proxy of breakdown, dielectric constant and energy storage properties. Oxygen-containing ether group and carbonyl groups were incorporated into the bicyclic backbone structure. The band gap and dielectric constant are inversely related due to the exclusive constraint between band gap and electronic dielectric constant. Compared to the effect of the $-\text{CF}_3$ pendant groups majorly on dielectric constant, the change of the backbone had an obvious impact on both dielectric constant and band gap. The polymer PRFNB (P1) without any oxygen-containing

groups in the backbone possesses the highest dielectric constant of 3 and the smallest band gap of 3.4 eV. The polymer POFNB (P3) with both ether group and carbonyl group has the smallest dielectric constant of 2.5 and largest band gap of 4.9 eV. Therefore POFNB (P3) has the highest charge-discharge efficiency due to the largest band gap. This work demonstrates that a rational design of the molecular structure to enhance the dipolar relaxation could be a powerful way to develop outperforming polymer dielectrics for high-density energy storage applications.

Acknowledgments

This work is supported by the Office of Naval Research through a multidisciplinary university research initiative (MURI) grant (N00014-17-1-2656) and a capacitor program grant (N00014-19-1-2340). Chao Wu and Ajinkya A. Deshmukh contributed equally to this work.

Supplementary Material

The Supplementary Material is available at: <https://www.worldscientific.com/doi/suppl/10.1142/S2010135X23410059>

References

- ¹Y. Shen, X. Zhang, M. Li, Y. Lin and C. Nan, Polymer nanocomposite dielectrics for electrical energy storage, *Natl. Sci. Rev.* **4**, 23 (2017).
- ²A. Mannodi-Kanakithodi, G. M. Treich, T. D. Huan, R. Ma, M. Tefferi, Y. Cao, G. A. Sotzing and R. Ramprasad, Rational co-design of polymer dielectrics for energy storage, *Adv. Mater.* **28**, 6277 (2016).
- ³Y. Wang, J. Cui, Q. Yuan, Y. Niu, Y. Bai and H. Wang, Significantly enhanced breakdown strength and energy density in sandwich-structured barium titanate/poly(vinylidene fluoride) nanocomposites, *Adv. Mater.* **27**, 6658 (2015).
- ⁴Q. Feng, S. Zhong, J. Pei, Y. Zhao, D. Zhang, D. Liu, Y. Zhang and Z. Dang, Recent progress and future prospects on all-organic polymer dielectrics for energy storage capacitors, *Chem. Rev.* **122**, 3820 (2022).
- ⁵Y. Zhou, Q. Li, B. Dang, Y. Yang, T. Shao, H. Li, J. Hu, R. Zeng, J. He and Q. A. Wang, A scalable, high-throughput, and environmentally benign approach to polymer dielectrics exhibiting significantly improved capacitive performance at high temperatures, *Adv. Mater.* **30**, 1805672 (2018).
- ⁶X. Liu, M. Zheng, G. Chen, Z. Dang and J. Zha, High-temperature polyimide dielectric materials for energy storage: Theory, design, preparation and properties, *Energy Environ. Sci.* **15**, 56 (2022).
- ⁷H. Pan, F. Li, Y. Liu, Q. Zhang, M. Wang, S. Lan, Y. Zheng, J. Ma, L. Gu, Y. Shen, P. Yu, S. Zhang, L. Chen, Y. Lin and C. Nan, Ultrahigh-energy density lead-free dielectric films via polymorphic nanodomain design, *Science* **365**, 578 (2019).
- ⁸Z. Shen, J. Wang, Y. Lin, C. Nan, L. Chen and Y. Shen, High-throughput phase-field design of high-energy-density polymer nanocomposites, *Adv. Mater.* **30**, 1704380 (2018).
- ⁹M. Feng, C. Zhang, G. Zhou, T. Zhang, Y. Feng, Q. Chi and Q. Lei, Enhanced energy storage characteristics in PVDF-based nanodielectrics with core-shell structured and optimized shape fillers, *IEEE Access* **8**, 81542 (2020).
- ¹⁰X. Huang, B. Sun, Y. Zhu, S. Li and P. Jiang, High-k polymer nanocomposites with 1D filler for dielectric and energy storage applications, *Prog. Mater. Sci.* **100**, 187 (2019).
- ¹¹C. Wu, Z. Li, G. M. Treich, M. Tefferi, R. Casalini, R. Ramprasad, G. A. Sotzing and Y. Cao, Dipole-relaxation dynamics in a modified polythiourea with high dielectric constant for energy storage applications, *Appl. Phys. Lett.* **115**, 163901 (2019).
- ¹²L. A. Dissado and J. C. Fothergill, *Electrical Degradation and Breakdown in Polymers* (Peter Peregrinus, London, 1992).
- ¹³H. Ishii, K. Sugiyama, E. Ito and K. Seki, Energy level alignment and interfacial electronic structures at organic/metal and organic/organic interfaces, *Adv. Mater.* **11**, 606 (1999).
- ¹⁴B. Zhang, J. Liu, M. Ren, C. Wu, T. J. Moran, S. Zeng, S. E. Chavez, Z. Hou, Z. Li, A. M. LaChance, T. R. Jow, B. D. Huey, Y. Cao and L. Sun, Reviving the “Schottky” barrier for flexible polymer dielectrics with a superior 2D nanoassembly coating, *Adv. Mater.* **33**, 2101374 (2021).
- ¹⁵D. Kamal, Y. Wang, H. D. Tran, L. Chen, Z. Li, C. Wu, S. Nasreen, Y. Cao and R. Ramprasad, Computable bulk and interfacial electronic structure features as proxies for dielectric breakdown of polymers, *ACS Appl. Mater. Interfaces* **12**, 37182 (2020).
- ¹⁶C. Wu, L. Chen, A. Deshmukh, D. Kamal, Z. Li, P. Shetty, J. Zhou, H. Sahu, H. Tran, G. Sotzing, R. Ramprasad and Y. Cao, Dielectric polymers tolerant to electric field and temperature extremes: Integration of phenomenology, informatics, and experimental validation, *ACS Appl. Mater. Interf.* **13**, 53416 (2021).
- ¹⁷J. McPherson, J. Kim, A. Shanware, H. Mogul and J. Rodriguez, Proposed universal relationship between dielectric breakdown and dielectric constant, *Technical Digest — International Electron Devices Meeting*, San Francisco, CA, USA, 2002, pp. 633–636, doi: 10.1109/IEDM.2002.1175919
- ¹⁸C. Wu, A. A. Deshmukh, Z. Li, L. Chen, A. Alamri, Y. Wang, R. Ramprasad, G. A. Sotzing and Y. Cao, Flexible temperature-invariant polymer dielectrics with large bandgap, *Adv. Mater.* **32**, 2000499 (2020).
- ¹⁹C. Wu, A. A. Deshmukh, O. Yassin, J. Zhou, A. Alamri, J. Vellek, S. Shukla, M. Sotzing, R. Casalini, G. A. Sotzing and Y. Cao, Flexible cyclic-olefin with enhanced dipolar relaxation for harsh condition electrification, *Proc. Natl. Acad. Sci.* **118**, e2115367118 (2021).
- ²⁰V. Sharma, C. Wang, R. G. Lorenzini, R. Ma, Q. Zhu, D. W. Sinkovits, G. Pilania, A. R. Oganov, S. Kumar, G. A. Sotzing, S. A. Boggs and R. Ramprasad, Rational design of all organic polymer dielectrics, *Nat. Commun.* **5**, 4845 (2014). <https://doi.org/10.1038/ncomms5845>
- ²¹C. Wu, A. A. Deshmukh, Z. Li, L. Chen, A. Alamri, Y. Wang, J. Zhou, O. Yassin, R. Ramprasad, G. A. Sotzing and Y. Cao, Remarks on the design of flexible high-temperature polymer dielectrics for emerging grand electrification — exemplified by poly(oxa)norbornenes, *IEEE Trans. Dielectr. Electr. Insul.* **28**, 1468 (2021).
- ²²A. A. Deshmukh, C. Wu, O. Yassin, A. Mishra, L. Chen, A. Alamri, Z. Li, J. Zhou, Z. Mutlu, M. Sotzing, P. Rajak, S. Shukla, J. Vellek, M. A. Baferani, M. Cakmak, P. Vashishta, R. Ramprasad, Y. Cao and G. Sotzing, Flexible polyolefin dielectric by strategic design of organic modules for harsh condition electrification, *Energy Environ. Sci.* **15**, 1307 (2022).