

Perspective

Rational design of all-organic flexible high-temperature polymer dielectrics

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SUMMARY

Advanced polymer dielectrics are desired for high-temperature, high-density, and high-efficiency energy storage. The paradox of mutually exclusive constraints between high field endurance, dielectric polarization, and thermal stability amounts to a huge obstacle in the design of all-organic polymer dielectrics for safe operation under harsh conditions. Although there are a plethora of functional group class polymers that have been investigated and reported, there remains a large unexplored design space. A perspective of the magnitude of the grand challenge, accelerated and targeted exploration of polymer dielectrics with the rational molecular design assisted by informatics-based approaches, is presented here for the generative design and further development of polymers with superior thermal stability, high electric field endurance, and strong dielectric polarization.

INTRODUCTION

Dielectrics are a unique class of materials that can rapidly store and release electric energy based on polarization and depolarization processes that occur via charge and discharge cycles with ultra-high power densities of gigawatts (GW) per cubic meter. Dielectrics can assist regulating the electric power to arbitrary desired forms, with widespread applications in, e.g., all-electric aircraft, ship and vehicle propulsion, pulsed-electromagnetic-energy-propelled accelerators in nuclear power, radiation medicine, radiochemistry, radiobiology and lasers, etc.^{1–6} In comparison to inorganic dielectric materials, polymer dielectrics are known to exhibit graceful failure mode at higher breakdown fields. With inherent benefits of flexibility, ease of processing, and low density, polymers exhibit enormous potential for a broad range of applications.^{2,4,7,8} An ever-increasing demand of device miniaturization and payload efficiency in nearly all electrical and electronic systems calls for dielectrics with higher energy density and ability to withstand higher electric fields.⁹ The rapid maturing of cutting-edge wide-bandgap (WBG) semiconductors allows for full system functionality of electrical and electronic systems at temperatures well above 150°C. With outer space exploration and downhole oil and gas drilling and lifting, electrical and electronic device operating temperatures can exceed 150°C, thereby pushing demand limits on future high-temperature, processable polymers capable of withstanding high electric fields.

The current state-of-the-art polymer for capacitive energy storage is biaxially oriented polypropylene (BOPP), having continuous operating temperatures of up to 85°C. Varieties of polymers have been demonstrated for high-temperature applications, e.g., poly(ether ketone) (PEEK), polyetherimide (PEI), and polyimide (PI), but

PROGRESS AND POTENTIAL

Polymer dielectrics that can withstand electric field and temperature extremes are of considerable significance for electrical and electronic applications in harsh environments. Polymers represent a class of organic materials with intriguing inter-correlated properties. The constraints among key parameters coupled with the demands of flexibility and processability give rise to grand challenges for the design and development of polymers. This perspective article presents an overview of a sophisticated systematic approach for the exploration of desired polymer dielectrics.



only at moderate electric fields, far less than those for BOPP; this is due to the soaring conduction loss at high electric fields for these aromatic dielectric polymers, leading to poor energy storage performance, especially at elevated temperatures.^{3,4,7}

One of the strategies reported is to improve the thermal stability of polymers that could essentially endure high electric fields.^{7,10} Crosslinking has been demonstrated as an effective way to improve the thermal stability of polymers.¹¹ Another alternative is to suppress the high field conduction in commodity high-temperature polymers by incorporating large-bandgap inorganic or organic components.^{3,12–20} Although encouraging, the design space of crosslinking and composites is limited by the intrinsic properties of these commodity all-organic polymers. Flexible all-organic polymer dielectrics are desired for concurrent electric field and temperature extremes.

For linear dielectrics, the energy density U_e can be expressed by $U_e = 1/2\epsilon_r\epsilon_0E^2$, where ϵ_r is the relative permittivity, i.e., dielectric constant; ϵ_0 is the vacuum permittivity; and E is the applied electric field.²¹ Energy density of capacitive energy storage is quadratically dependent on the applied electric field, making it the most important variable for optimization. The dielectric constant plays an important role as well with a linear dependency on its effect with energy density. Discharge efficiency is another key parameter for capacitive energy storage,²² and therefore, increasing the energy density should not be at the cost of discharge efficiency. This perspective article provides an overview of the strategies and approaches to break the mutual constraints between thermal stability, high field endurance, and dielectric polarization of polymer dielectrics for high-temperature and high-density energy storage. Viewpoints of utilizing high-throughput computation and data-driven, machine-learning-assisted screening of polymer candidates are also provided, considering the complicated interactions between these parameters and the vast design space of polymers.

KEY REQUIREMENTS FOR POLYMER EXPLORATION AND DESIGN

Thermal stability

Pertaining to constraints in design, polymer dielectrics for high-temperature energy storage must have superior thermal stability. The thermal stability of polymers can be characterized by the glass transition temperature (T_g) for amorphous polymers or the combination of T_g and melting temperature (T_m) for semi-crystalline polymers. Some semi-crystalline polymers, such as BOPP, have a very low T_g , and the melting of the crystalline regions will define the temperature limit for its operation as a dielectric film. However, if a semi-crystalline polymer were to go through a T_g during capacitor operation, the large-scale segmental movement of polymer chains leads to a reduction of mechanical strength and the polymer dielectric can experience a decrease of the breakdown strength. Further, above T_g , the orientation of dipoles with increased polymer chain movement results in α relaxation and gives rise to the increased polarization loss.²³ Therefore, high T_g is a significant property for high-temperature capacitive energy storage for polymer dielectrics, whether it be an amorphous polymer or semi-crystalline, as shown in Figure 1. The thermal properties of polymers can be improved by increasing the rigidity of polymer chains, whether it be in the backbone with rigid aromatics or alicyclics or whether it be larger pendant groups derivatized from the same polymer main chain.^{24–26}

High-electric-field endurance

As the foremost property of polymer dielectrics, the high field endurance represents two aspects: (1) high breakdown strength and (2) low conduction loss at high electric

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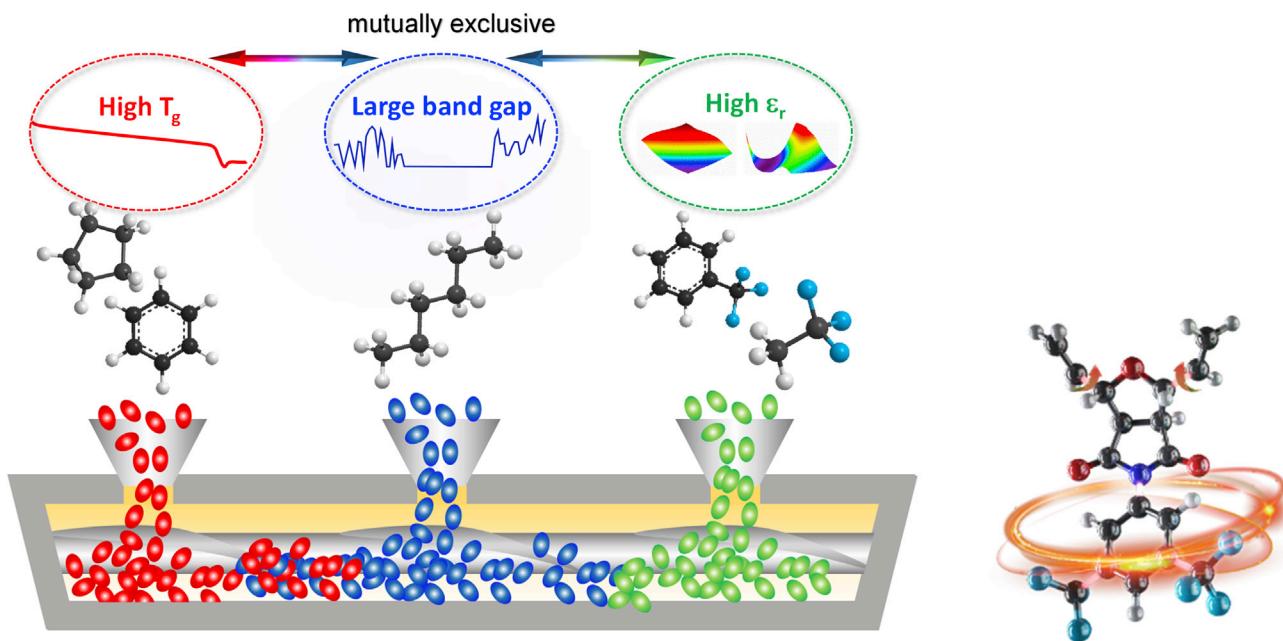


Figure 1. Key parameters of polymer dielectrics for high-density and high-temperature capacitive energy storage

fields. Under extremely high electric fields, carrier transport becomes inevitable in polymer dielectrics, with the presence of defects due to the topological disorder. Such topological disorders are inherent properties of long-chain polymers. Carrier with high mobility could then gain sufficiently high kinetic energies to cause impact ionization, cumulating to aging, further defects generation, and breakdown. The breakdown strength represents the upper limit of the electric field a dielectric material can withstand. Therefore, the conduction-related loss shall be kept extremely low in dielectrics, because a large amount of energy loss can produce joule heat, leading to accelerated degradation and premature breakdown. At high electric fields, electrical conduction dominates the energy loss of polymer dielectrics due to the soaring injection of charges from electrodes and transport in the bulk of polymers, especially at elevated temperatures.^{4,27,28} Hence, high breakdown strength and suppressed electrical conduction are desired for polymer dielectrics.

While the complexity of interplays among electronic, thermal, mechanical, and chemical processes in polymer under high electric fields makes the study of engineering breakdown mechanism far from fully understood,^{27,29} past studies revealed the dominant role of the bandgap in determining the electrical conduction and intrinsic breakdown strength of dielectric materials.^{30–32} The bandgap is the energy gap between the valence band and conduction band, which, along with the optical phonon cutoff frequency, intrinsically determines the breakdown strength of dielectric materials.³³ The relationship between the breakdown strength and bandgap of inorganic dielectric materials has been statistically studied,^{30,31} and large bandgaps give rise to higher inter-band ionization energy and higher breakdown strength. In addition, the study of the temperature-dependent breakdown strength of a dozen dielectric polymers^{32,34} suggests that the breakdown strength exhibits a high Pearson correlation coefficient with the bandgap. While the actual breakdown in polymer remains a complex phenomenon in the presence of complicated chemical and physical disorders, a large bandgap is considered crucial for polymers to withstand high electric fields, as shown in Figure 1.

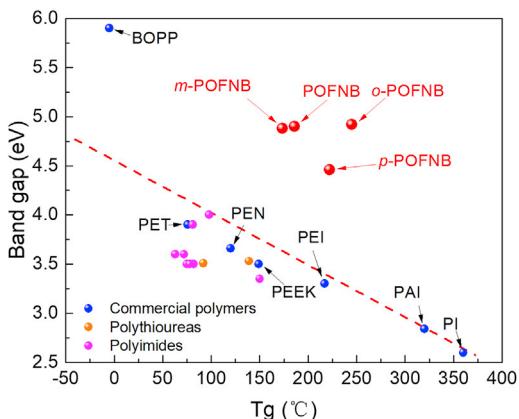


Figure 2. The inverse relationship between T_g and large bandgap for conventional high-temperature polymers with conjugated aromatic backbones and a strategically designed flexible polymer with concurrent high T_g and large bandgap breaking such constraint

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Dielectric polarization

The energy density is proportional to the dielectric constant for linear dielectric materials. In addition to high field endurance, dielectric constant is another key factor for further improving the energy density of dielectric materials, as shown in Figure 1. Dielectric constant is an indicator of the polarizability of dielectric materials, arising from different types of relaxation processes. Three types of polarization can be utilized in capacitive energy storage. Electronic polarization and atomic polarization are caused by the relative shift of electrons and ions, which happen at very high frequencies ($>10^{11}$ Hz). Dipolar relaxation is attributed to the orientation of dipoles, which occurs in relatively lower frequency ranges compared with electronic and atomic polarization. Therefore, the relaxation of electronic polarization and atomic polarization would not give rise to a significant polarization loss in the operational frequency range of the capacitive energy storage, while dipolar relaxation might introduce high polarization loss if interactions of adjacent dipoles cannot be effectively decoupled. Close attention should be paid to the molecular design of a new polymer to ensure a low loss when utilizing the dipolar relaxation for capacitive energy storage.

DESIGN STRATEGY FOR POLYMERS WITH LARGE BAND GAP AND HIGH T_g

Challenges of improving the bandgap

Bandgap should be kept in mind when improving the thermal stability of polymer dielectrics. Our recent study suggests, however, that commodity high-temperature polymers generally have conjugated backbones, which will diminish the bandgap and give rise to high conduction loss at high electric fields.^{4,34} A conjugated structure with delocalized electrons shared by multiple nuclei lowers the energy of the system and thus enhances the thermal stability in polymer chemistry, while the overlapped orbitals also allow delocalized electrons to transfer more easily with lower energy. The bandgap of conventional aromatic polymers reveals an inverse relationship with the T_g , as shown in Figure 2. For example, one of the best commodity high-temperature polymers, Kapton polyimide (PI), has the lowest bandgap of 2.6 eV among the dielectric polymers investigated. Therefore, care must be taken, as improving the thermal stability by simply increasing the rigidity and restricting the chain movement may not apply to polymer dielectrics for capacitive energy storage at high temperatures. Furthermore, these conjugations could lead to compromised flexibility and hence limited processability, which are important for capacitors as well as for most electronic applications. For instance, the reported aromatic conjugated poly(arylene ether urea) (PEEU)^{22,35} and poly(2,6-dimethyl-1,4-phenylene oxide) (SO₂-PPO)^{36,37} cannot be made into flexible free-standing films because of the rigidity of these polymer structures.

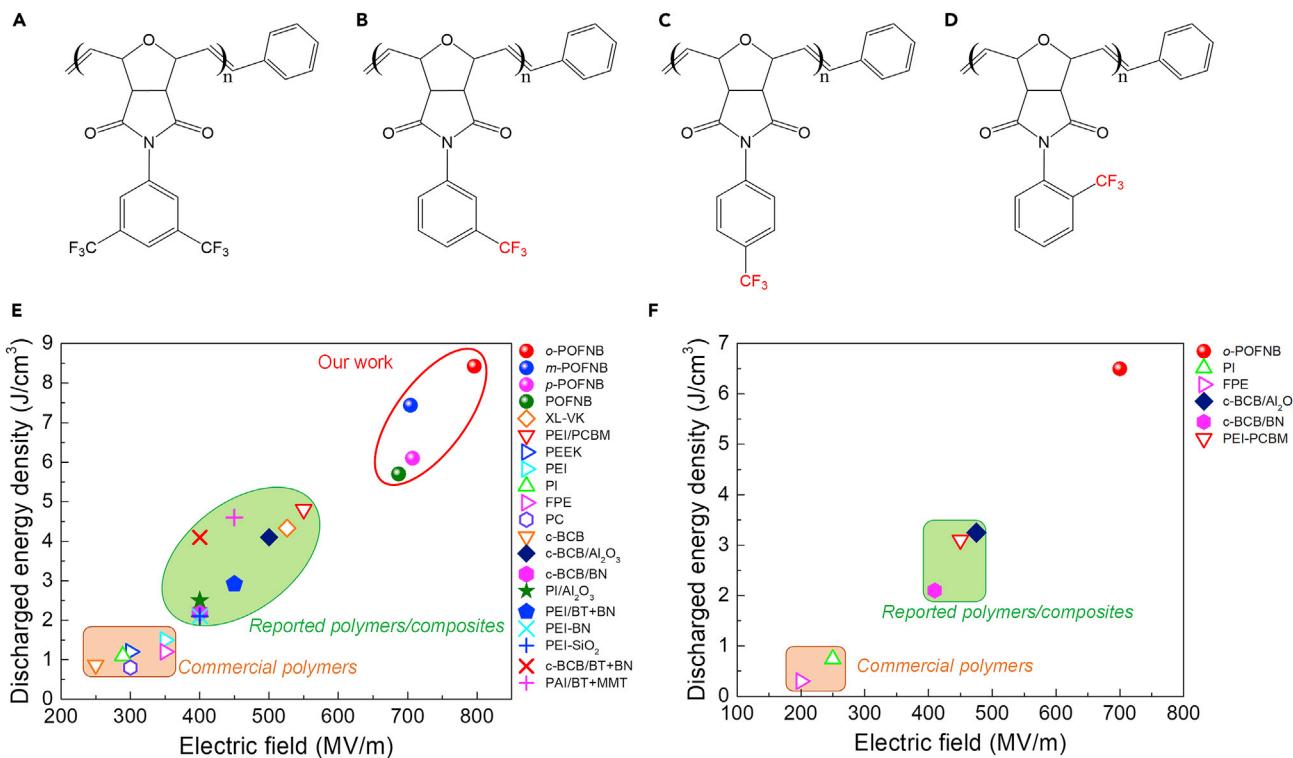


Figure 3. Molecular engineering of flexible high- T_g and large band gap polymers

(A–D) Chemical structure of (A) POFNB, (B) *m*-POFNB, (C) *p*-POFNB, and (D) *o*-POFNB.

(E and F) Discharged energy density of POFNBs at 150°C (E) and 200°C (F) in comparison to established high-temperature and high-field polymers and polymer composites.

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Molecular engineering of flexible all-organic high- T_g and large-bandgap polymers

A flexible all-organic polymer, polyoxafluoronorbornene (POFNB), was successfully developed based on the molecular engineering principle in which repeat units of fairly rigid fused bicyclic structure and alkenes, separated by freely rotating single bonds, are designed to break the aforementioned design constraints for concurrent high T_g and large bandgap, as shown in Figures 2 and 3A.⁴ The piston-like crankshaft structure endows the system with a large bandgap of $\approx 5 \text{ eV}$, almost twice that of Kapton. Coupled with the high T_g of 186°C , POFNB exhibits a superior energy density of $5.1 \text{ J}/\text{cm}^3$ at 170°C .

Moreover, the POFNB polymer is highly flexible while being temperature invariantly stable. Its piston and pendant structure allows further engineering for dipolar polarization for energy storage. By keeping the backbone structure and adjusting the pendant group, a class of POFNBs was synthesized to optimize the thermal stability, high field endurance, and energy density (Figures 3B–3D).^{38–40} Among these polymers, *ortho*-POFNB has the highest T_g of 244°C , which can function well at 200°C with the highest energy density of $6.5 \text{ J}/\text{cm}^3$ among flexible polymer dielectrics reported, as presented in Figures 3E and 3F.

HIGH DIELECTRIC CONSTANTS FOR HIGHER ENERGY DENSITY

Challenge: Inverse relationship of dielectric constants and bandgap

To tailor the polarization processes for higher dielectric constants and higher energy density, close attention should be paid to the impact on bandgap. Designs to

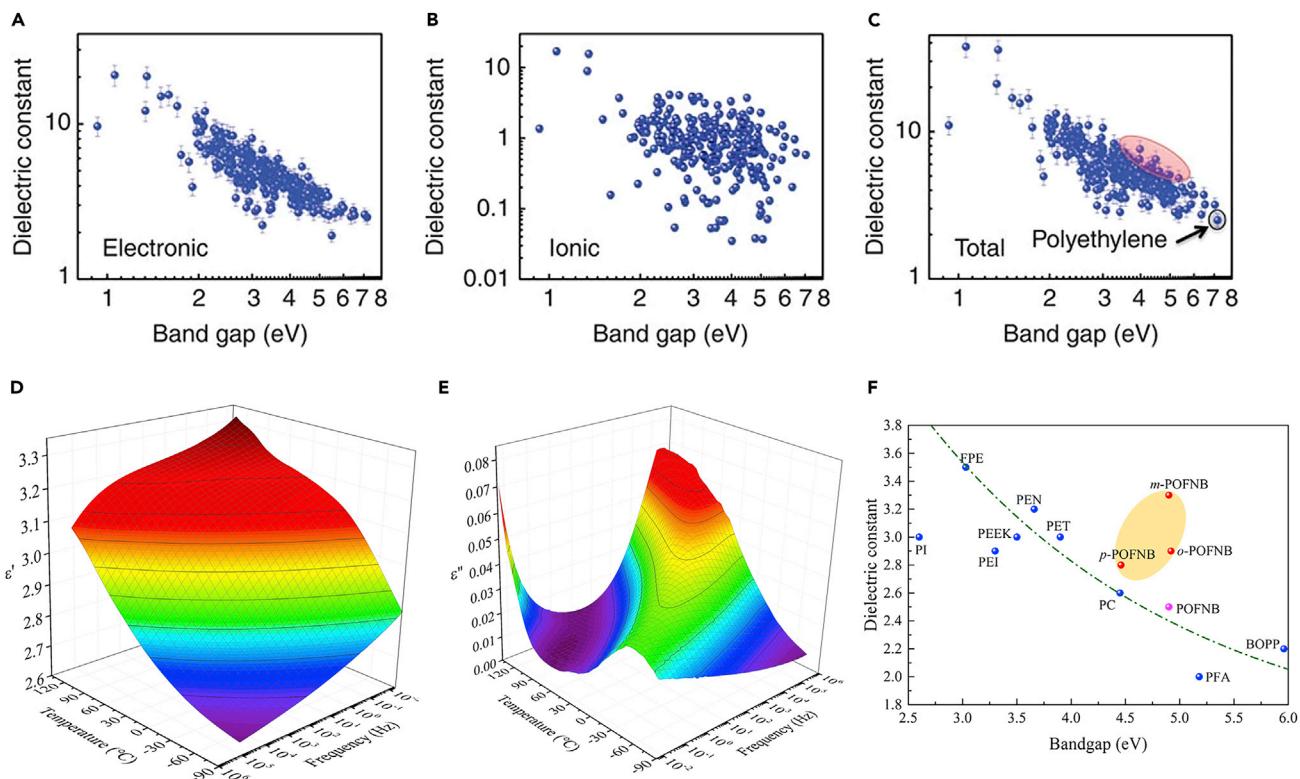


Figure 4. Dielectric polarization and its interactions with band gap of dielectric polymers

(A–C) Computed (A) electronic, (B) ionic, and (C) total dielectric constant as a function of the band gap. The highlighted region corresponds to the most “promising repeat units,” composed of at least one of $-\text{NH}-$, $-\text{CO}-$, and $-\text{O}-$ and at least one of $-\text{C}_6\text{H}_4-$ and $-\text{C}_6\text{H}_2\text{S}-$ blocks. Band gap was computed using the HSE06 electronic exchange-correlation functional. Reprinted with permission from Sharma et al., Nat. Comm. 523, 576–579 (2015).⁴¹

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(D) Relationship of measured dielectric constant and band gap for conventional polymer dielectrics and POFNBs.

(D and E) The real part (D) and imaginary part (E) of the relative permittivity.³⁹

(F) Relationship between the measured dielectric constant and band gap for POFNBs and other commercial polymer dielectrics. Reproduced from Deshmukh et al.³⁸ with permission from the Royal Society of Chemistry.

increase the dielectric constants of typical polymer dielectrics shall avoid the reduction of bandgap. For instance, detailed studies shown in Figures 4A and 4B suggest that the electronic dielectric constants have a clear inverse relationship with bandgaps while ionic dielectric constants have little correlation with band gaps.^{2,41}

Increasing the dielectric constants through enhancing the dipolar relaxation

Similar to ionic dielectric polarization, proper enhancement of dipolar polarization also has no negative impact on bandgaps, which can be utilized to improve the dielectric constants, while additional care should be taken to restrict the dipolar relaxation loss. Dipolar relaxation loss stems from interactions of dipoles with adjacent groups. For instance, fluorine has strong polarity while the strong interactions of dipoles give rise to high polarization loss for polyvinylidene fluoride (PVDF) and its copolymers, higher even than 30%.^{42–45} Copolymerization or multilayer compressed structures are proposed to restrict the large scales of motion of dipolar groups, but the loss at elevated temperatures remains high.⁴⁶ To decouple the interactions of dipoles, rigid segments are incorporated to create a larger free volume. Nevertheless, rigid groups themselves cannot rotate flexibly. Accordingly, a strategy that combines rigid and flexible segments is proposed to explore polymers with strong dipolar relaxation and low loss.^{47,48} The rigid segments contribute to high glass

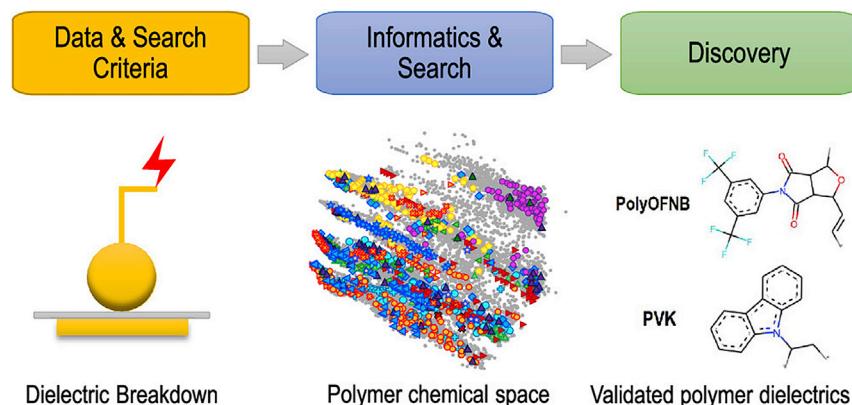


Figure 5. Integrated and informatics-experimental philosophy for rational material exploration and design

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transition temperature, and the flexible chains give rise to flexible rotation. The synthesized polymers exhibit obvious sub-glass transition β and γ relaxations and have high dielectric constants of 4.8–6.6.^{47,48} The low activation energy suggests that the structure imparts polymers with a low-energy barrier for rotation of dipoles and thus contributes to lower dielectric loss.

Based on the aforementioned concept of molecular engine, flexible segments and rigid segments were combined strategically in POFNBs. Asymmetrically fluorinated aromatic pendant groups with strong polarizability are bridged to the piston-like backbone with flexible single bonds, endowing the system with strong dipolar relaxation (Figures 4D and 4E). For instance, *m*-POFNB exhibits high dielectric constants (3.2) and a large bandgap of 4.84 eV simultaneously, relative to established high-temperature polymers, e.g., 2.6 eV for PI and 3.3 eV for PEI. Coupled with the high glass transition temperature of 178°C, data points of *m*-POFNB appeared as outliers in the mutual inverse relationship of glass transition temperature, dielectric constant, and bandgap (Figures 2 and 4F).³⁹

BEYOND POFNBs: SCREENING POLYMER STRUCTURES USING THE INFORMATICS-BASED APPROACH

The mutual inverse relationships among bandgap, T_g , and dielectric constant indicated the complexity of polymer dielectrics design for high-temperature and high-density energy storage. Purely based on empirical rules, it is challenging to design a specific polymer with multiple paradoxically desired parameters. Besides, the process of design, synthesis, and electrical characterization of a novel dielectric polymer is tedious and inefficient. Such issues can be well addressed with the integrated informatics-experimental approach for material exploration,^{2,29,32,41,49–52} as illustrated in Figure 5.³² Bandgaps, dielectric constants, and glass transition temperatures of polymers can all be predicted through machine learning according to the repeat unit of polymers.^{49,53,54} Based on appropriate screening criteria, polymers with large bandgap, high T_g , and relatively high dielectric constants can be screened from a big design space of 13,000 polymers with diversified chemical structures. The informatics-based approach can greatly decrease the cost of following synthetic validation and electrical characterization of polymer dielectrics.

REMARKS AND OUTLOOK

In summary, restricted by the mutual constraints originating from the inverse relationship of bandgap versus T_g and bandgap versus dielectric constant, a concerted molecular engineering co-designs approach is elucidated for novel polymer dielectrics with balanced key parameters. In commodity high-temperature polymers, aromatic structure contributes to the superior thermal stability of polymers, while the conjugation can also reduce the bandgap, leading to high conduction loss, low breakdown strength, and poor energy-storage performance. Decoupling of the conjugation through molecular design unleashes a new route to maintaining a large bandgap. Dipolar relaxation can be utilized to further improve the dielectric constants without sacrificing the bandgap. Beyond POFNBs, to accelerate the targeted exploration of polymer dielectrics, material informatics based on first-principle computations and data-driven investigation shall be pursued to assist and accelerate the novel polymer dielectrics design. Lastly, flexibility and ease of processing should always be paid close attention for designing polymer dielectrics.

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AUTHOR CONTRIBUTIONS

Conceptualization, R.R., G.A.S., and Y.C.; investigation, C.W., A.A.D., and L.C.; writing – original draft, C.W.; writing – review & editing, C.W., A.A.D., L.C., R.R., G.A.S., and Y.C.; funding acquisition, R.R., G.A.S., and Y.C.

DECLARATION OF INTERESTS

The authors declare no competing interests.

REFERENCES

- Pan, H., Li, F., Liu, Y., Zhang, Q., Wang, M., Lan, S., Zheng, Y., Ma, J., Gu, L., Shen, Y., et al. (2019). Ultrahigh – energy density lead-free dielectric films via polymorphic nanodomain design. *Science* 365, 578–582.
- Mannodi-Kanakkithodi, A., Treich, G.M., Huan, T.D., Ma, R., Tefferi, M., Cao, Y., Sotzing, G.A., and Ramprasad, R. (2016). Rational Co-design of polymer dielectrics for energy storage. *Adv. Mater.* 28, 6277–6291.
- Li, Q., Chen, L., Gadinski, M.R., Zhang, S., Zhang, G., Li, H., Iagodkine, E., Haque, A., Chen, L.Q., Jackson, T., and Wang, Q. (2015). Flexible high-temperature dielectric materials from polymer nanocomposites. *Nature* 523, 576–579.
- Wu, C., Deshmukh, A.A., Li, Z., Chen, L., Alamri, A., Wang, Y., Ramprasad, R., Sotzing, G.A., and Cao, Y. (2020). Flexible temperature-invariant polymer dielectrics with large bandgap. *Adv. Mater.* 32, 2000499.
- Feng, Q.K., Zhong, S.L., Pei, J.Y., Zhao, Y., Zhang, D.L., Liu, D.F., Zhang, Y.X., and Dang, Z.M. (2022). Recent progress and future prospects on all-organic polymer dielectrics for energy storage capacitors. *Chem. Rev.* 122, 3820–3878.
- Liu, X., Zheng, M., Chen, G., Dang, Z., and Zha, J. (2021). High-temperature polyimide dielectric materials for energy storage: theory, design, preparation and properties. *Energy Environ. Sci.* 15, 56–81.
- Ho, J.S., and Greenbaum, S.G. (2018). Polymer capacitor dielectrics for high temperature applications. *ACS Appl. Mater. Interfaces* 10, 29189–29218.
- Chu, B., Zhou, X., Ren, K., Neese, B., Lin, M., Wang, Q., Bauer, F., and Zhang, Q.M. (2006). A dielectric polymer with high electric energy density and fast discharge speed. *Science* 313, 334–336.
- Watson, J., and Castro, G. (2015). A review of high-temperature electronics technology and applications. *J. Mater. Sci. Mater. Electron.* 26, 9226–9235.
- Liu, X.J., Zheng, M.S., Chen, G., Dang, Z.M., and Zha, J.W. (2022). High-temperature polyimide dielectric materials for energy storage: theory, design, preparation and properties. *Energy Environ. Sci.* 15, 56–81.
- Li, H., Gadinski, M.R., Huang, Y., Ren, L., Zhou, Y., Ai, D., Han, Z., Yao, B., and Wang, Q. (2020). Crosslinked fluoropolymers exhibiting superior high-temperature energy density and charge-discharge efficiency. *Energy Environ. Sci.* 13, 1279–1286.
- Zhou, Y., Li, Q., Dang, B., Yang, Y., Shao, T., Li, H., Hu, J., Zeng, R., He, J., and Wang, Q. (2018). A scalable, high-throughput, and environmentally benign approach to polymer dielectrics exhibiting significantly improved capacitive performance at high temperatures. *Adv. Mater.* 30, 1805672.
- Azizi, A., Gadinski, M.R., Li, Q., AlSaud, M.A., Wang, J., Wang, Y., Wang, B., Liu, F., Chen, L., Alem, N., and Wang, Q. (2017). High-performance polymers sandwiched with chemical vapor deposited hexagonal boron nitrides as scalable high-temperature dielectric materials. *Adv. Mater.* 29, 1701864.
- Li, H., Ai, D., Ren, L., Yao, B., Han, Z., Shen, Z., Wang, J., Chen, L., and Wang, Q. (2019). Scalable polymer nanocomposites with record high-temperature capacitive performance enabled by rationally designed nanostructured inorganic fillers. *Adv. Mater.* 31, 1900875.
- Ai, D., Li, H., Zhou, Y., Ren, L., Han, Z., Yao, B., Zhou, W., Zhao, L., Xu, J., and Wang, Q. (2020). Tuning nanofillers in *in situ* prepared polyimide nanocomposites for high-temperature capacitive energy storage. *Adv. Energy Mater.* 10, 1903881.
- Yuan, C., Zhou, Y., Zhu, Y., Liang, J., Wang, S., Peng, S., Li, Y., Cheng, S., Yang, M., Hu, J., et al. (2020). Polymer/molecular semiconductor all-organic composites for high-temperature

- dielectric energy storage. *Nat. Commun.* 11, 3919.
17. Wang, Y., Li, Z., Wu, C., and Cao, Y. (2020). High-temperature dielectric polymer nanocomposites with interposed montmorillonite nanosheets. *Chem. Eng. J.* 401, 126093.
 18. Zhang, B., Liu, J., Ren, M., Wu, C., Moran, T.J., Zeng, S., Chavez, S.E., Hou, Z., Li, Z., LaChance, A.M., et al. (2021). Reviving the "Schottky" barrier for flexible polymer dielectrics with a superior 2D nanoassembly coating. *Adv. Mater.* 33, 2101374.
 19. Dong, J., Hu, R., Xu, X., Chen, J., Niu, Y., Wang, F., Hao, J., Wu, K., Wang, Q., and Wang, H. (2021). A facile *in situ* surface-functionalization approach to scalable laminated high-temperature polymer dielectrics with ultrahigh capacitive performance. *Adv. Funct. Mater.* 31, 2102644.
 20. Zhang, T., Yang, L., Zhang, C., Feng, Y., Wang, J., Shen, Z., Chen, Q., Lei, Q., and Chi, Q. (2022). Polymer dielectric films exhibiting superior high-temperature capacitive performance by utilizing an inorganic insulation interlayer. *Mater. Horiz.* 9, 1273–1282.
 21. Rabuffi, M., and Picci, G. (2002). Status quo and future prospects for metallized polypropylene energy storage capacitors. *IEEE Trans. Plasma Sci. IEEE Nucl. Plasma Sci. Soc.* 30, 1939–1942.
 22. Zhang, T., Chen, X., Thakur, Y., Lu, B., Zhang, Q., Runt, J., and Zhang, Q.M. (2020). A highly scalable dielectric metamaterial with superior capacitor performance over a broad temperature. *Sci. Adv.* 6, x6622.
 23. Kremer, F., and Schönhals, A. (2002). *Broadband Dielectric Spectroscopy* (Springer).
 24. Ho, J., and Jow, T.R. (2012). High field conduction in biaxially oriented polypropylene at elevated temperature. *IEEE Trans. Dielectr. Electr. Insul.* 19, 990–995.
 25. Xu, D., Xu, W., Seery, T., Zhang, H., Zhou, C., Pang, J., Zhang, Y., and Jiang, Z. (2020). Rational design of soluble polyaramid for high-efficiency energy storage dielectric materials at elevated temperatures. *Macromol. Mater. Eng.* 305, 1900820.
 26. Pan, J., Li, K., Chuayprakong, S., Hsu, T., and Wang, Q. (2010). High-temperature poly(phthalazinone ether ketone) thin films for dielectric energy storage. *ACS Appl. Mater. Interfaces* 2, 1286–1289.
 27. Dissado, L.A., and Fothergill, J.C. (1992). *Electrical Degradation and Breakdown in Polymers* (Peter Peregrinus Ltd.).
 28. Ieda, M. (1984). Electrical conduction and carrier traps in polymeric materials. *IEEE Transactions on Electrical Insulation* EI-19, 162–178.
 29. Shen, Z.H., Wang, J.J., Jiang, J.Y., Huang, S.X., Lin, Y.H., Nan, C.W., Chen, L.Q., and Shen, Y. (2019). Phase-field modelling and machine learning of electric-thermal-mechanical breakdown of polymer-based dielectrics. *Nat. Commun.* 10, 1843.
 30. Sun, Y., Boggs, S.A., and Ramprasad, R. (2012). The intrinsic electrical breakdown strength of insulators from first principles. *Appl. Phys. Lett.* 101, 132906.
 31. McPherson, J., Kim, J., Shanware, A., Mogul, H., and Rodriguez, J. (2002). Proposed universal relationship between dielectric breakdown and dielectric constant. In *Digest. International Electron Devices Meeting (IEEE)*, pp. 633–636.
 32. Wu, C., Chen, L., Deshmukh, A., Kamal, D., Li, Z., Shetty, P., Zhou, J., Sahu, H., Tran, H., Sotzing, G., et al. (2021). Dielectric polymers tolerant to electric field and temperature extremes: integration of phenomenology, informatics, and experimental validation. *ACS Appl. Mater. Interfaces* 13, 53416–53424.
 33. Sun, Y., Boggs, S., and Ramprasad, R. (2015). The effect of dipole scattering on intrinsic breakdown strength of polymers. *IEEE Trans. Dielectr. Electr. Insul.* 22, 495–502.
 34. Kamal, D., Wang, Y., Tran, H.D., Chen, L., Li, Z., Wu, C., Nasreen, S., Cao, Y., and Ramprasad, R. (2020). Computable bulk and interfacial electronic structure features as proxies for dielectric breakdown of polymers. *ACS Appl. Mater. Interfaces* 12, 37182–37187.
 35. Thakur, Y., Dong, R., Lin, M., Wu, S., Cheng, Z., Hou, Y., Bernholc, J., and Zhang, Q. (2015). Optimizing nanostructure to achieve high dielectric response with low loss in strongly dipolar polymers. *Nano Energy* 16, 227–234.
 36. Zhang, Z., Wang, D.H., Litt, M.H., Tan, L.S., and Zhu, L. (2018). High-temperature and high-energy-density dipolar glass polymers based on sulfonylated poly(2, 6-dimethyl-1, 4-phenylene oxide). *Angew. Chem., Int. Ed. Engl.* 57, 1528–1531.
 37. Zhang, Z., Zheng, J., Premasiri, K., Kwok, M.H., Li, Q., Li, R., Zhang, S., Litt, M.H., Gao, X.P.A., and Zhu, L. (2020). High-k polymers of intrinsic microporosity: a new class of high temperature and low loss dielectrics for printed electronics. *Mater. Horiz.* 7, 592–597.
 38. Deshmukh, A.A., Wu, C., Yassin, O., Mishra, A., Chen, L., Alamri, A., Li, Z., Zhou, J., Mutlu, Z., Sotzing, M., et al. (2022). Flexible polyolefin dielectric by strategic design of organic modules for harsh condition electrification. *Energy Environ. Sci.* 15, 1307–1314.
 39. Wu, C., Deshmukh, A.A., Yassin, O., Zhou, J., Alamri, A., Vellek, J., Shukla, S., Sotzing, M., Casalini, R., Sotzing, G.A., and Cao, Y. (2021). Flexible cyclic-olefin with enhanced dipolar relaxation for harsh condition electrification. *Proc. Natl. Acad. Sci. USA* 118, e2115367118.
 40. Wu, C., Deshmukh, A.A., Li, Z., Chen, L., Alamri, A., Wang, Y., Zhou, J., Yassin, O., Ramprasad, R., Sotzing, G.A., and Cao, Y. (2021). 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, 1468–1470.
 41. Sharma, V., Wang, C., Lorenzini, R.G., Ma, R., Zhu, Q., Sinkovits, D.W., Pilania, G., Oganov, A.R., Kumar, S., Sotzing, G.A., et al. (2014). Rational design of all organic polymer dielectrics. *Nat. Commun.* 5, 4845.
 42. Qian Wang, C.W. (2021). Bulk charge transport and interfacial polarization of P(VDF-HFP) investigated by dielectric response. *IEEE T. Dielectr. El. In.* 28, 1247–1254.
 43. Wang, Y., Cui, J., Yuan, Q., Niu, Y., Bai, Y., and Wang, H. (2015). Significantly enhanced breakdown strength and energy density in sandwich-structured barium titanate/poly(vinylidene fluoride) nanocomposites. *Adv. Mater.* 27, 6658–6663.
 44. Zhang, X., Jiang, J., Shen, Z., Dan, Z., Li, M., Lin, Y., Nan, C.W., Chen, L., and Shen, Y. (2018). Polymer nanocomposites with ultrahigh energy density and high discharge efficiency by Modulating their nanostructures in three dimensions. *Adv. Mater.* 30, 1707269.
 45. Li, Q., Han, K., Gadinski, M.R., Zhang, G., and Wang, Q. (2014). High energy and power density capacitors from solution-processed ternary ferroelectric polymer nanocomposites. *Adv. Mater.* 26, 6244–6249.
 46. Yin, K., Zhang, J., Li, Z., Feng, J., Zhang, C., Chen, X., Olah, A., Schuele, D.E., Zhu, L., and Baer, E. (2019). Polymer multilayer films for high temperature capacitor application. *J. Appl. Polym. Sci.* 136, 47535.
 47. Li, Z., Treich, G., Tefferi, M., Wu, C., Nasreen, S., Scheirey, S.K., Ramprasad, R., Sotzing, G.A., and Cao, Y. (2019). High energy density and high efficiency all-organic polymers with enhanced dipolar polarization. *J. Mater. Chem. A Mater.* 7, 15026–15030.
 48. Wu, C., Li, Z., Treich, G.M., Tefferi, M., Casalini, R., Ramprasad, R., Sotzing, G.A., and Cao, Y. (2019). Dipole-relaxation dynamics in a modified polythiourea with high dielectric constant for energy storage applications. *Appl. Phys. Lett.* 115, 163901.
 49. Chen, L., Kim, C., Batra, R., Lightstone, J.P., Wu, C., Li, Z., Deshmukh, A.A., Wang, Y., Tran, H.D., Vashishta, P., et al. (2020). Frequency-dependent dielectric constant prediction of polymers using machine learning. *Npj Comput. Mater.* 6, 61.
 50. Sha, W., Li, Y., Tang, S., Tian, J., Zhao, Y., Guo, Y., Zhang, W., Zhang, X., Lu, S., Cao, Y., and Cheng, S. (2021). Machine learning in polymer informatics. *Info* 3, 353–361.
 51. Ramprasad, R., Batra, R., Pilania, G., Mannodi-Kanakkithodi, A., and Kim, C. (2017). Machine learning in materials informatics: recent applications and prospects. *Npj Comput. Mater.* 3, 54.
 52. Batra, R., Song, L., and Ramprasad, R. (2020). Emerging materials intelligence ecosystems propelled by machine learning. *Nat. Rev. Mater.* 6, 655–678.
 53. Kim, C., Chandrasekaran, A., Jha, A., and Ramprasad, R. (2019). Active-learning and materials design: the example of high glass transition temperature polymers. *Mrs Commun.* 9, 860–866.
 54. Kim, C., Chandrasekaran, A., Huan, T.D., Das, D., and Ramprasad, R. (2018). Polymer genome: a data-powered polymer informatics platform for property predictions. *J. Phys. Chem. C* 122, 17575–17585.