Chinese Journal of
POLYMER SCIENCE

REVIEW

https://doi.org/10.1007/s10118-025-3545-x
Chinese J. Polym. Sci. **2026**, *44*, 1959–1983

Design of All-organic Dielectrics for High-temperature Capacitive Energy Storage

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Abstract Polymer film-based dielectric capacitors are required to operate stably and efficiently at extreme temperatures in the emerging applications including underground oil and gas extraction, electrified transportation and space exploration, *etc*. However, the commercial benchmark polymeric dielectric, biaxially oriented polypropylene, can only withstand up to 105 °C, and its electrical insulation performance deteriorates sharply with increasing temperature. Recently, numerous reported strategies, such as surface engineering of polymer films and polymer-inorganic particle blending have reached considerable achievements in balancing the temperature capability and electrical insulation properties of polymeric dielectrics, but show less promise in production scale-up with respect to the all-organic dielectric systems. In this review, we summarize the recent progress of polymer molecular structure design and all-organic composite systems towards high-temperature capacitive energy storage. The correlation of high-temperature capacitive energy storage performance and multi-level structures of all-organic dielectrics is established, and the effect of molecular structures on the charge transport behavior is analyzed. Moreover, the strategy of utilizing materials informatics to design the molecular structure of high-temperature polymers is introduced. Finally, the advantages and limitations of all-organic polymer dielectrics in the field of high-temperature capacitive energy storage are summarized, and the future development directions are highlighted.

Keywords Dielectric capacitors; Dielectric polymers; High-temperature energy storage; Molecular structure

Citation: Wang, R.; Ran, Z. Y.; Meng, L.; Li, Q. Design of all-organic dielectrics for high-temperature capacitive energy storage. *Chinese J. Polym. Sci.* **2026**, *44*, 1959–1983.

1 INTRODUCTION

As the global population surges, alongside rapid economic expansion, intensified industrialization, and the proliferation of energy-intensive sectors, the capacity of conventional non-renewable energy sources is proved inadequate to satisfy the escalating energy demands.[1–3] This inevitability catalyzes the advancement of novel and renewable energy industries, with energy storage and conversion emerging as pivotal challenges on a global scale.[4–6]

Different from traditional electrochemical capacitors and batteries that store energy in chemical form and release it as electricity, dielectric capacitors leverage the polarization properties of dielectric materials to directly store electrical energy.[7,8] Therefore, dielectric capacitors have the characteristics of fast charging and discharging speed, ultra-high power density, and long cycle life, making them highly attractive in energy conversion systems and high-power electrical devices, *e.g.*, electric drive vehicles, medical defibrillators, renewable energy generation, and advanced electromagnetic launch/propulsion systems.[9–12]

Polymer-based dielectric capacitors, thanks to their ultra-high voltage endurance, elegant failure mechanism, flexibility, low cost, light weight, and excellent charging and discharging cycle capabilities, occupy 50% of the market for all capacitors.[13] Emerging applications require dielectric capacitors to have high temperature resistance (defined as ≥120 °C based on applications), *e.g.*, pulse power system (120 °C), hybrid vehicles (150 °C), oil & gas exploration (200 °C), electrified aircraft (250 °C), and geothermal (300 °C).[9] However, polymer-based dielectrics are plagued by the contradiction between electrical insulation property and thermal stability.[14–17] The leakage current of polymer dielectrics tends to increase exponentially with temperature, mainly originating from the electrode-confined charge injection

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Special Topic: Distinguished Young Scholars in Polymer Science
Received November 18, 2025; Accepted December 21, 2025; Published online May 14, 2026

and/or the bulk-confined thermal excitation. For instance, although the conjugated groups in the heat resistant aromatic polymers such as polycarbonate (PC), polyetheretherketone (PEEK), fluoropolyester (FPE), and polyimide (PI) can effectively improve the glass transition temperature (T_g), it is at the cost of reducing the energy bandgap (E_g), which leads to significantly enhanced conduction loss and dramatically reduced breakdown strength.[14] Thus, a trade-off needs to be made between increasing the content of conjugated structural units to improve heat resistance and decreasing the content of conjugated structural units to improve high-temperature insulation. Meanwhile, the pursuit of high-temperature insulation performance also compromises the improvement of dielectric constant (ε) of polymeric dielectrics, as high ε inevitably leads to significant polarization loss and is usually inversely scales with the breakdown strength.[18] For example, even if the ε of the commercial benchmark polymer biaxially oriented polypropylene (BOPP) film is only 2.2, it still has high-temperature capacitive performance far exceeding that of poly(vinylidene fluoride) (PVDF, with the ε of 12).[19,20] Because of the afore-mentioned limitations, it is thus challenging to achieve high energy storage density (U) at high temperature conditions with existing polymeric materials since for linear dielectrics, $U = \frac{1}{2}\varepsilon\varepsilon_0 E^2$, where ε is the dielectric constant, ε_0 is the vacuum permittivity, and E is the applied electric field strength. Apparently, U is strongly dependent on both ε and E, with E limited by the breakdown strength.

The various key parameters that determine the capacitive performance of polymer-based dielectrics under extreme conditions can be classified into two categories: addressing thermal extremes (increasing thermal conductivity and heat resistance) and electrical extremes (increasing electrical resistivity and E_g), respectively (Fig. 1a). Firstly, heat resistance is the primary prerequisite for polymer dielectrics to be applied at high temperatures.[15] In semi-crystalline polymers, the melting temperature is generally used as a reference,[19] while in amorphous polymers, T_g is the decisive factor.[14] When the external temperature exceeds the temperature capability of polymers, polymer chains become flexible to move freely. In this case, the rapidly expanding free volume and degraded mechanical stability lead to an exponential increase in leakage current and ultimately result in electrical breakdown.[21,22] Therefore, polymer dielectrics suitable for thermal extremes typically contain rigid functional groups such as aromatic structures or alicyclic hydrocarbon. Moreover, thermal conductivity is also an important parameter for polymer dielectrics. The thermal conductivity of most polymers ranges from 0.1 $W \cdot m^{-1} \cdot K^{-1}$ to 0.5 $W \cdot m^{-1} \cdot K^{-1}$,[23] resulting in a lack of thermal management capability for capacitors. The waste heat generated by long-term and frequent charging and discharging cannot be promptly dissipated, leading to internal temperature rise in capacitors and seriously threatening their safe operation.

Under the premise of meeting thermal extremes, polymer dielectrics are required to have the ability to withstand electrical extremes. Ideal insulating polymers typically should have a wide E_g and a high Young's modulus (Y) in general. The wide E_g ensures that the valence electrons located in the highest occupied molecular orbital of the polymer are not easily transferred to the lowest unoccupied molecular orbital to form free electrons under electric thermal excitation. The high Y ensures that the polymer can preserve mechanical stability under high electric fields and temperatures, avoiding the electromechanical breakdown caused by thickness changes under the electrostatic force.[21] In addition, trap energy levels and density are also crucial parameters that affect the electrical insulation performance of materials. Deep trap energy levels are beneficial for capturing free charges in materials. However, it should be noted that a higher trap density is not necessarily better, as a high-density trap distribution

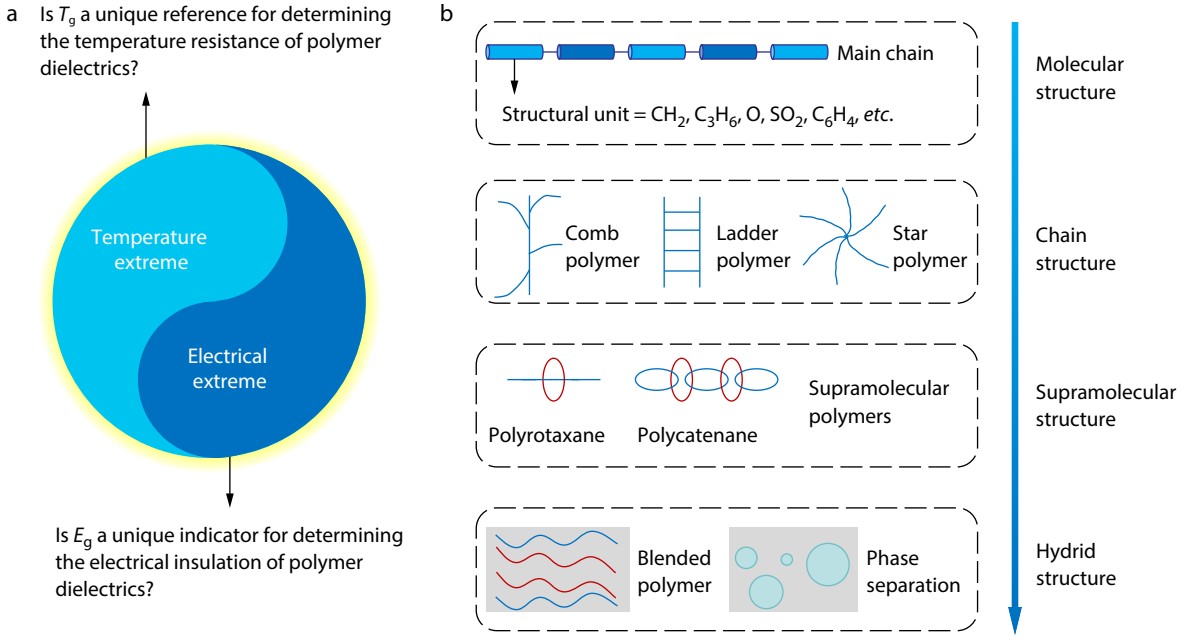

Fig. 1 (a) Doubt about the two parameters used to evaluate the electrical- and thermal-extremes of high-temperature dielectric energy storage polymer dielectrics at current stage; (b) Multi-level structural design of polymer dielectrics from micro to macro scales.

https://doi.org/10.1007/s10118-025-3545-x

will allow the captured free charges to be transported along the traps by tunneling effects. Therefore, when designing polymer molecular structures, it is necessary to comprehensively consider their E_g and trap characteristics.

In the past decade, there are mainly four strategies being developed for the design of high-temperature energy storage polymer dielectrics, including polymer-inorganic particle blending, surface engineering of polymer films, all-organic blending, and polymer molecular structure optimization. Among them, the polymer-inorganic particle blending strategy and surface engineering of polymer films strategy effectively compensate for the shortcomings of organic polymer matrix by either utilizing inorganic micro/nano-structures (*e.g.*, wide E_g inorganic nanostructures such as aluminum oxide, silicon oxide, magnesium oxide and boron nitride nanosheets) for extending the charge transfer path,[14,24–26] or leveraging the surface inorganic coatings for blocking injected charges from electrodes.[27,28] Unfortunately, these strategies suffer from high manufacturing cost (expensive micro/nano-structures and complex process) and inconsistent performance, seriously hindering industry-scale production. In contrast, all-organic composites and polymer molecular structure optimization strategies can achieve consistent quality control of thin films, and the manufacturing process is straightforward, showing broad industrial prospects.[29,30]

Previously, there have been numerous review articles summarizing the research progress of polymer-based dielectrics for film capacitor applications, focusing mainly on the polymer nanocomposite strategies,[31–35] multi-layer engineering and surface modification engineering,[36,37] large-scale preparation and device design,[38] targeted performance enhancement,[39] trap control,[40] polyimide modification.[41] Compared to these, there is few reviews of the progress in pure polymers or all-organic polymers in the field of dielectric capacitive energy storage at high temperatures.[42] This review article summarizes the recent progress of polymer molecular structure design and all-organic composite systems towards high-temperature capacitive energy storage. Different from previous review articles, the structural optimization strategies are classified from micro to macro levels, namely primary structure (structural units), secondary structure (chain morphology), tertiary structure (supramolecular chemical structure), and quaternary structure (composites). These four molecular structure optimization scales are interrelated. The design concept of a high-temperature polymer is generally carried out in a step-by-step manner following these four structure scales. For instance, we need to determine the basic molecular structure of the polymer first, then design the conformation of the chain and the interaction between chains, and finally try other components or design a multilayer structure. In each section, we discuss the correlation of high-temperature capacitive energy storage performance and multi-level structures (Fig. 1b) of all-organic dielectrics, and the effect of molecular structure on the charge transport behavior was also analyzed, which can provide theoretical guidance for researchers to design customized performance dielectric polymers. Subsequently, the potential of using artificial intelligence in designing the molecular structure of dielectric energy storage polymers is discussed. In the final section, the prospects for the future development of all-organic polymer dielectrics in the field of high-temperature capacitive energy storage are proposed.

2 IMPORTANT ASPECTS RELATED TO HIGH-TEMPERATURE CAPACITIVE PERFORMANCE OF POLYMERS

2.1 Heat Resistance of Polymers

A basic requirement for polymer dielectrics used in high-temperature energy storage is the ability to withstand thermal extremes, which is related to the application temperature of capacitors. In the past decade, the mainstream insight has been recognized that the heat resistance of polymers is strongly correlated with their T_g (for amorphous polymers) and melting temperature (T_m, for semi-crystalline polymers). Therefore, a large number of novel polymers with high T_g have been derived, such as PI, fluorinated polyimides (F-PI), poly(phenylquinoxaline) (PPQ), poly(phenylene sulfide) (PPS), FPE, cross-linked divinylsiloxane-dibenzocyclobutene (*c*-BCB), PEEK, polytetrafluoroethylene (PTFE), and polyetherimide (PEI). Among them, the T_g of PEEK from Victrex in the UK is 150 °C, the T_g of PEI from General Electric in the US is 218 °C, the T_g of FPE from 3M in the US is 335 °C, and the T_g of *c*-BCB from Dow Chemical and PI from DuPont in the US are even higher than 350 °C. However, is T_g really the only criterion that determines the heat resistance of polymers Is the maximum temperature under the premise of maintaining stable electrical insulation performance of polymers more suitable than T_g/T_m to define the heat resistance of polymers For instance, the T_m of BOPP is as high as 160 °C, but its maximum operating temperature is limited to below 105 °C, which obviously means that the latter is more suitable as a heat resistance index.

Another very typical example is the classic PI film (Kapton), which has a much higher T_g than other polymer dielectrics and is considered one of the best polymer dielectrics. Although Kapton can withstand high temperatures of 150 and 200 °C, its electrical insulation performance is severely degraded in such conditions.[14,29] On the contrary, the classic PEI film (Ultem) with a T_g of only 218 °C has several orders of magnitude higher electrical resistivity than Kapton at 200 °C.[30] Therefore, a higher T_g may not necessarily be better for high-temperature energy storage polymers, as excessively high T_g may have a negative impact on electrical performance due to the introduction of additional aromatic groups.[29,43] Similarly, PC exhibits excellent high-temperature energy storage performance in temperatures similar to its T_g.[44]

Recently, the coefficient of thermal expansion (CTE) has been revealed to be a key performance parameter instead of T_g affecting the thermal stability of polymers.[45,46] Even if the ambient temperature is lower than T_g, the CTE of the polymer in the glass state will have an obvious inflection point with the increase of temperature. Coincidentally, the temperature-dependent leakage current of most high-temperature resistant polymers matches well with the CTE trend. The CTE reflects the volume change of the material, so even trace changes have a huge impact on the stacking of polymer chains as well as the internal free volume. The high free volume causes the free electrons to gain more energy under the

https://doi.org/10.1007/s10118-025-3545-x

applied electric field, which makes it easier to transition and tunnel without being trapped. Therefore, the molecular structure design of materials not only needs to ensure the stability of macro-structure, but also needs to pay attention to the stability of micro-structure.

The thermal conductivity of polymer dielectrics is related to the thermal management of capacitors during operation to prevent the thermal breakdown of devices caused by thermal runaway.[14,47] The current pure polymer suitable for high temperature capacitors has a thermal conductivity of up to 2 $W \cdot m^{-1} \cdot K^{-1}$, about 10 times that of conventional polymers.[47] However, it should be noted that as the voltage of the capacitor increases, the waste heat increases sharply. Taking BOPP as an example, the electric field strength of the capacitor in the hybrid electric vehicle is 200 $MV \cdot m^{-1}$, and the waste heat energy density of BOPP is about 0.02 $J \cdot cm^{-3}$ under the premise of 95% charge-discharge efficiency. When the applied field intensity is further increased to 600 $MV \cdot m^{-1}$, the waste heat energy density of BOPP will increase to about 0.18 $J \cdot cm^{-3}$ at the same efficiency. Therefore, the reported thermal conductivity of polymers is still insufficient, and it is more noteworthy in high dielectric constant polymers and high electric field application scenarios.

2.2 Electrical Tolerance of Polymers

The electrical extreme tolerance assessment of solid-state dielectrics can be divided into breakdown strength and electrical conductivity. High breakdown strength is beneficial for thin films to achieve larger energy density under higher electric fields, while low electrical conductivity can reduce Joule heating during charge-discharge processes. At present, the mainstream understanding is that the breakdown mechanisms of polymer dielectrics are mainly divided into electrical breakdown, thermal breakdown, and electro-mechanical breakdown (Fig. 2a).[48] Among them, electrical breakdown refers to when the applied electric field exceeds a certain strength, the electrons in the dielectric obtain sufficient energy to transition from the bound state to the conductive state, resulting in a sharp increase in current and the formation of a conductive path. Unlike the typical instantaneous characteristic of electrical breakdown, the process of thermal breakdown is relatively slow and requires a long time to accumulate heat. The electro-mechanical breakdown is strongly correlated with the Y and ε of materials, suggesting that soft, high ε polymer dielectrics should pay attention to this breakdown mechanism. However, to this day, there is still no consensus on which breakdown mechanism dominates polymer dielectrics at high temperatures, or perhaps multiple breakdown mechanisms work together. In addition, the current method used to evaluate the breakdown strength of polymer dielectrics is Weibull statistics. However, it should be noted that the breakdown strength of polymers in different regions has dispersion, and capacitor devices generally do not allow for a large number of weak breakdown points. This inspired us to consider whether it is reasonable to use Weibull characteristic breakdown strength to evaluate polymer dielectrics rather than minimum breakdown strength in multiple breakdown tests Furthermore, it is necessary to understand how much higher the breakdown strength of polymer dielectrics needs to be than in actual application scenarios to ensure the safe operation of capacitors.

Generally, the mainstream polymer dielectrics used for high-temperature capacitive energy storage have relatively low ε and high Y. Therefore, theoretically, electrical breakdown and thermal breakdown contribute more to actual breakdown compared to electro-mechanical breakdown. In this case, electrical conductivity plays a crucial role in the breakdown process due to its significant impact on both electrical and thermal breakdown.

The traditional understanding is that the electrical conductivity of solid-state dielectrics is determined by the E_g, which is often used to explain the electrical properties of inorganic semiconductor materials. However, when the object is transformed into an organic polymer or organic semiconductor, energy band theory has certain limitations. At present, the field of organic semiconductors has provided a very detailed insight of the charge transport mechanism.[49,50] As shown in Fig. 2(b), based on the intermolecular transfer integral (the ability of charge transfer between molecules) and non-local

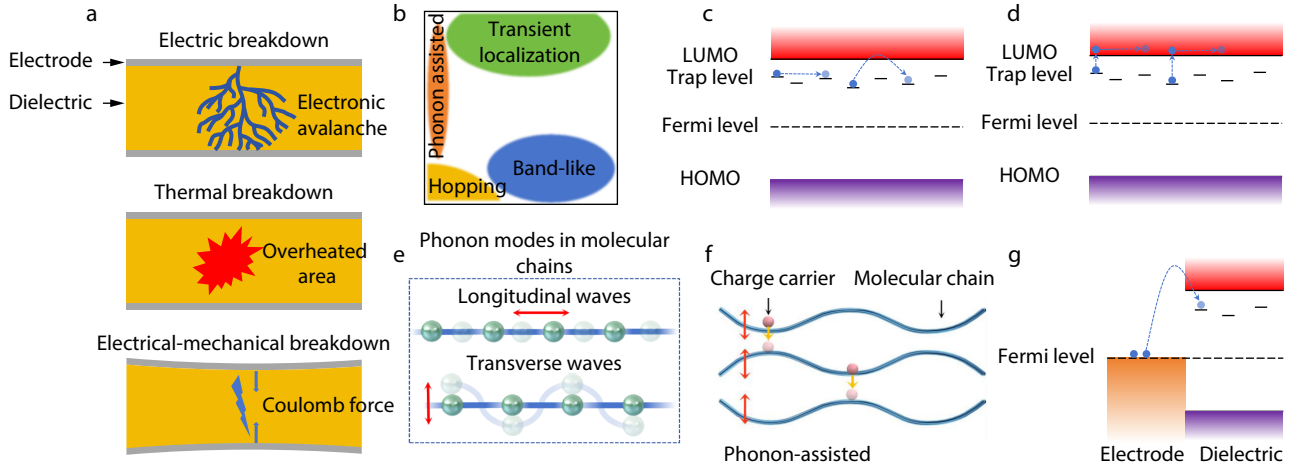

Fig. 2 (a) Schematic diagram of three types of dielectric breakdown; (b) A schematic regime diagram on the (transfer integral, electron–phonon coupling) plane for the carrier mobility of the Holstein–Peierls model; (c) Schematic diagram of charge tunneling under Hopping conduction mechanism; (d) Schematic diagram of charge migration under P-F emission conduction mechanism; (e) A schematic diagram of phonon models in polymers; (f) A schematic diagram of phonon-assisted interchain charge transfer in dielectric polymers; (g) Schematic diagram of electrode charge injection related to Schottky barrier.

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electroacoustic coupling of organic molecules, there are four types of charge transfer mechanisms: hopping, band-like, phonon-assisted, and transient localization.

Hopping conduction is a reliable mechanism to explain charge transfer in materials with weak electroacoustic coupling and weak intermolecular charge transfer (Fig. 2c).[51] In hopping conduction, the carriers captured by energy traps cannot derive enough energy to be excited into the conduction band, but they can still "hopping" between nearby traps through tunneling effects. Therefore, once the charge transfer of polymer dielectrics belongs to the jump conductivity mode, theoretically the bandgap of the material should have a weak correlation with its conductivity. In other words, the bandgap of the material no longer has a decisive impact on conductivity.

As the electric field strength increases, the intermolecular charge transfer within the material intensifies, leading to a shift in the charge transfer mechanism from hopping to band like transport, which is very common in most polymer dielectrics. The charge transfer mechanism of free charge in the material through conduction band under high temperature and high electric field can be described by Poole-Frenkel (P-F) emission (Fig. 2d).[52] P-F emission refers to the process in which electrons captured by energy traps are thermally excited into the conduction band of the dielectric, forming a current.

If increasing the electric field and temperature cannot excite electrons into the conduction band, phonon-assisted charge conduction will become the main physical mechanism.[53] Phonon-assisted current results from the interaction of phonons (lattice vibrations) with charge carriers (electrons or holes).[54–57] When a lattice vibration (phonon) collides with a carrier, the phonon can transfer energy and momentum to the carrier, thereby changing its state of motion. Phonon-assisted hopping conduction is strongly related to the vibration direction and amplitude of phonons (Fig. 2e). For instance, the vibration direction of phonons affecting electron conduction needs to be consistent with the direction of electron conduction, and a large vibration amplitude is conducive to phonon-assisted hopping conduction. In high temperature energy storage dielectric polymers, the ultrahigh ambient temperature means violent molecular vibration, which is bound to promote the phonon-assisted hopping conduction of charge in the polymer matrix (Fig. 2f).

In addition to the charge conduction mechanism within polymers, electrode charge injection is another key source of increased conductivity under high temperature and strong electric fields, which we refer to as electrode limited conduction mechanism. The conduction mechanisms of electrode limitation include Schottky injection (also known as hot electron emission), Fowler-Nordheim (F-N) tunneling, direct tunneling, and field emission. The conductivity current generated by hot electron emission is highly dependent on temperature, while the tunneling effect and the field emission are almost temperature independent.

The difference between the conduction band (LUMO energy level) of the dielectric film and the Fermi energy level (Work Function) of the metal electrode is the potential barrier for electron injection from the electrode into the interior of the dielectric, which is denoted as the electron injection barrier (Fig. 2g).[27] If the electron energy is not sufficient to overcome the potential barrier at the interface for Schottky injection, there is still a probability of electron injection when the potential barrier is thin enough (<100 Å), which is called quantum tunneling effect.

3 PRIMARY MOLECULAR STRUCTURE DESIGN OF POLYMERS

Many efforts have been reported to optimize the molecular structure of polymers. This section will review the design of primary structures in polymers for improving high-temperature dielectric energy storage performance. The primary structure refers to a polymer molecular structure composed of basic structural units linked by covalent bonds,[58] *e.g.*, polyethylene is composed of methylene structural units. The chemical structure of polymer chains determines their basic chemical properties and structural characteristics.

Designing the main chain molecular structure of polymers is the most effective and fundamental strategy to achieve the desired performance.[59] To draw inspiration from the comparison of performance between commercial high-temperature dielectric PI (Kapton) and PEI (Ultem). In contrast to PI with ultra-high T_g, the introduction of flexible ether bonds in PEI main chains weakens the intrachain charge transfer complex, significantly improving high-temperature insulation performance at the expense of T_g.

Transforming aromatic polymers into non-aromatic polymers to obtain non-conjugated high-temperature resistant polymers with wide E_g appears to be a highly effective strategy (Fig. 3a). For instance, compared to the original polyimide, non-aromatic polyimide can not only achieve an E_g of over 4 eV, but also retain high T_g, which is attractive for the high-temperature capacitive performance (Fig. 3b).[60] It is worth noting that the proportion of C to H/O in non-aromatic polyimides is significantly reduced, endowing them with self-cleaning performance, which is beneficial for their long-term reliability. However, by carefully designing the combination of structural units in the molecular structure, E_g was overturned as the key factor determining high-temperature insulation performance (Fig. 3c). In fact, when E_g exceeds an experimental value (3.3 eV), it has a marginal effect on the high-temperature insulation performance of dielectric polymers.[29] This can be attributed to the fact that the conduction mechanism will transition from P-F emission to hopping conduction as the E_g increases. In this case, the high-temperature energy storage performance of the polymer is closely related to the dihedral angle between adjacent conjugated planes in the chemical structure (Fig. 3d). Based on this new insight, dielectric polymers with excellent high-temperature energy storage performance at 150, 200, and 250 °C can be designed through tailored assembly of structural units, *e.g.*, at an extreme temperature of 250 °C, the U_d reaches 2.1 J·cm^{-3} with η≥90%, which is currently the highest reported level in main chain modified polymer (Figs. 3e and 3f).[29]

Apart from optimizing the main chain, side-chain or side-group engineering has a significant impact on the electrical and thermal performances of polymers, depending on the properties of the side-group and its spatial hindrance on the movement of the molecular. Although the design space is not

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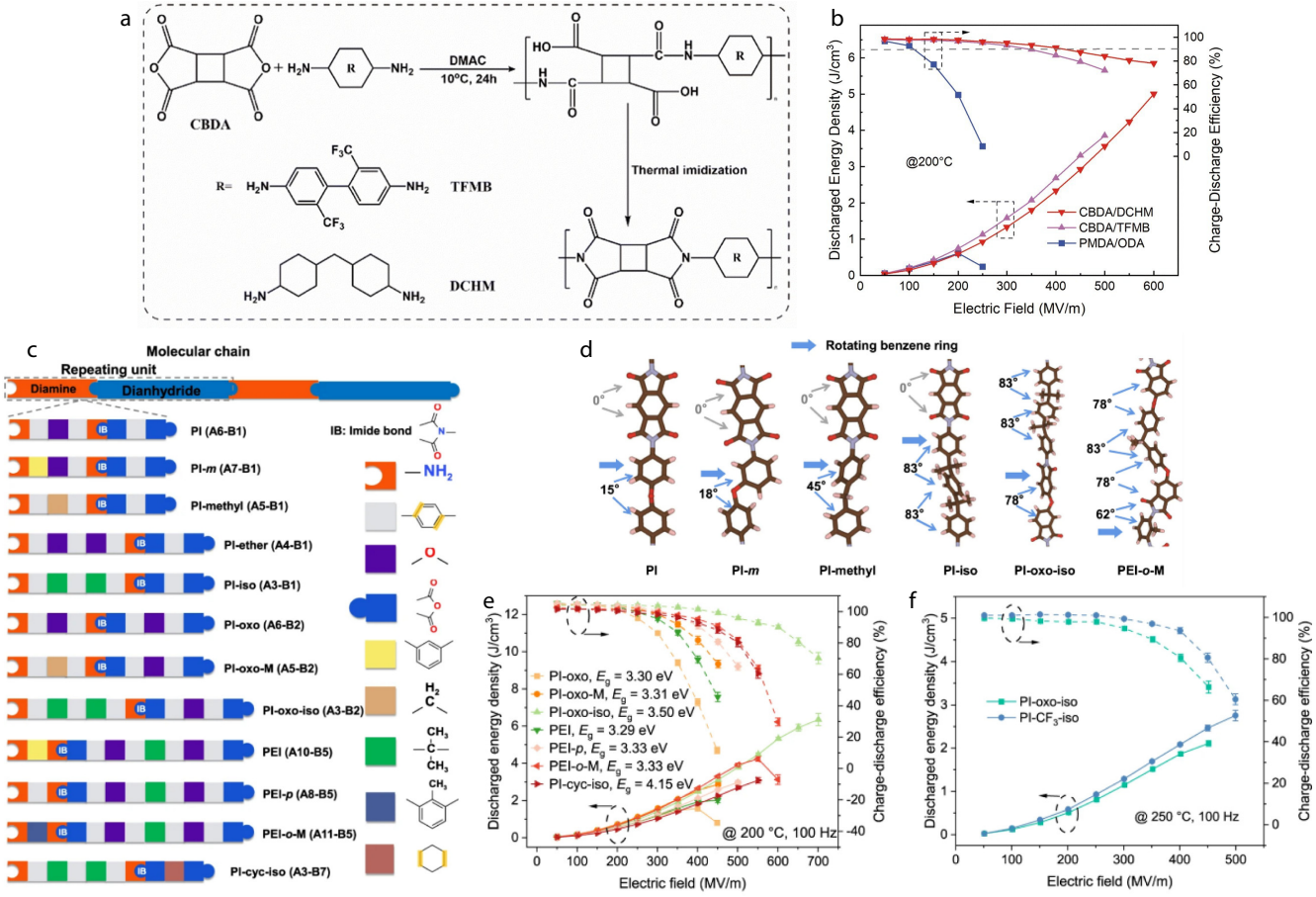
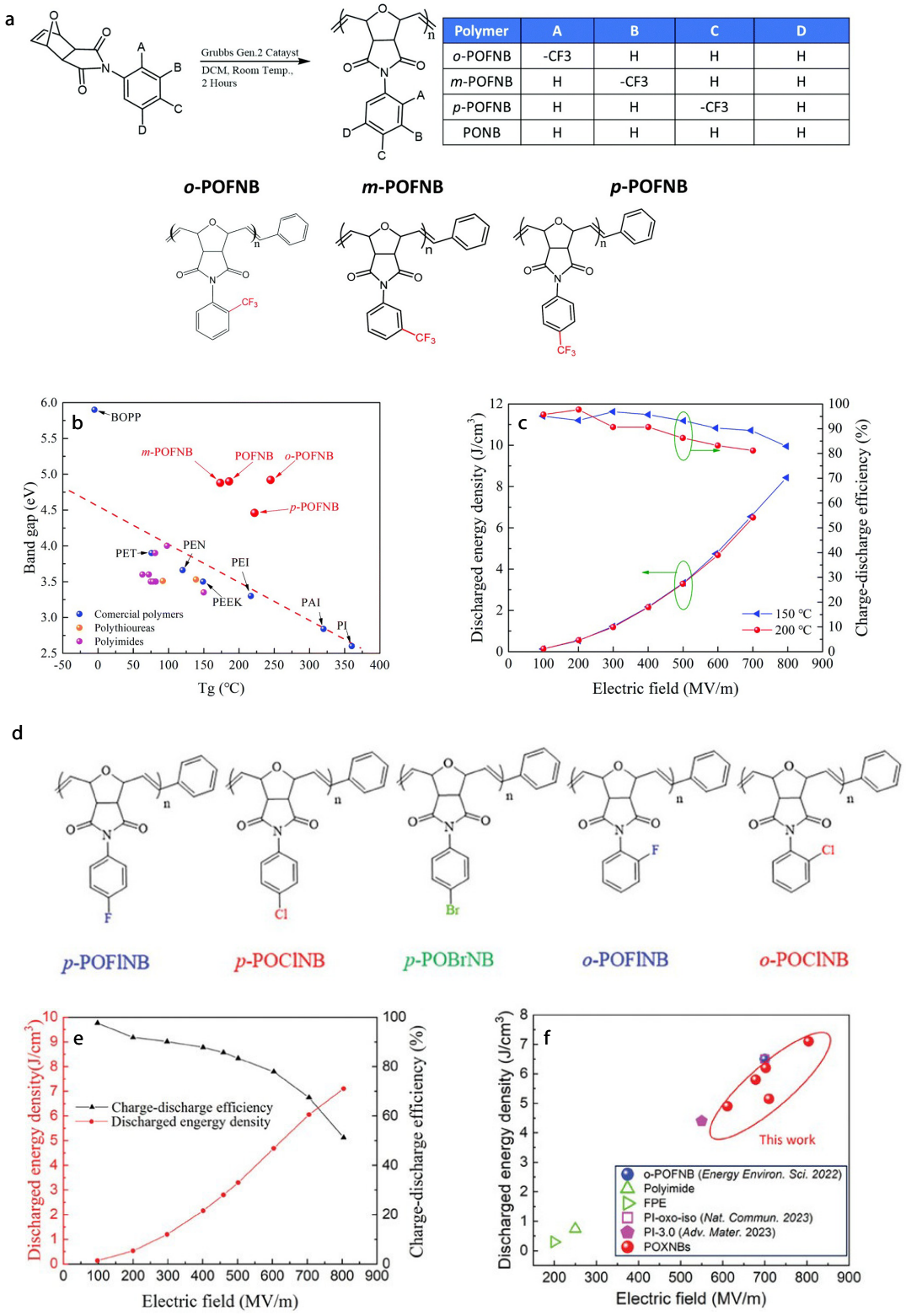


Fig. 3 (a) Molecular structure design of semi-aliphatic polyimide; (b) High temperature energy storage performance of semi-aliphatic polyimide; (a, b: reproduced with permission from Ref. [60]; Copyright (2023), The Royal Society of Chemistry). (c) Modular assembly strategy of structural units for designing polyimide; (d) Adjacent conjugated plane dihedral angles in polyimide molecular structure. High temperature energy storage performance of different polyimide derivatives at (e) 200 °C and (f) 250 °C. (c–f: reproduced with permission from Ref. [29]; Copyright (2023), Nature).

as diverse as the main-chain engineering, it can be integrated with the main-chain structure design to form complementary and synergistic effects. A very typical example is that by simply changing the position of the trifluoromethyl group on the side benzene ring of cyclic olefin polymers, the E_g and T_g of the polymer can be easily adjusted (Figs. 4a–4c).[61] Furthermore, the halogen substituents of the aromatic side-chains hanging on the double-ring backbone polymer also have a significant impact on the high-temperature energy storage performance of polymer dielectrics, mainly due to the change in the free volume of the polymer caused by the halogen substituents (Figs. 4d–4f).[62] This strategy can significantly affect the T_g without changing the E_g and dielectric constant, making it highly attractive for the molecular structure design of polymers applied at extreme temperatures.

Another important contribution of side-chain engineering is the ability to design the dielectric constant of dielectric polymers through different groups. Trifluoromethyl as a side group has been proven to be used to reduce the dielectric constant of polymers, and it monotonically decreases with increasing fluorine content, *e.g.*, the dielectric constant of polymers decreases from 3.2 to 2.4 as the fluorine content increases to 30.7 wt% (Fig. 5a).[63] The decrease in dielectric constant was found to be due to the weakening of chain mobility and dipole density by $-CF_3$. On the contrary, cyan groups (—CN) with large dipole moments have been shown to effectively increase the dielectric constant of polymers, which is very attractive for improving energy storage density (Figs. 5b–5d).[64] In the PI-derived polymer platform, where changing the structure of diamines or dianhydride can easily adjust the polymer structure, the effect of the position and quantity of —CN groups on the dielectric properties of the polymer was discussed in detail.[64–67] It was found that the dielectric constant is positively correlated with the number of —CN groups, and para —CN groups exhibit higher dipole moments compared to meta —CN groups due to their easier dipole rotation. Polymers with —CN groups as side groups exhibit the potential to achieve high dielectric constant and low dielectric loss. Based on the Clausius-Mossotti equation, the essence of this strategy is revealed, *i.e.*, the rigid polymer skeleton achieves tight chain stacking to reduce losses, and the small-sized side groups with large dipole moment at suitable sites endow high dielectric constants (Fig. 5e).[67]

The copolymerization of multiple molecular structures to form random or block copolymers is a strategy that can combine the advantageous properties of polymers with different



Polymer	A	B	C	D
o-POFNB	-CF3	H	H	H
m-POFNB	H	-CF3	H	H
p-POFNB	H	H	-CF3	H
PONB	H	H	H	H

Fig. 4 (a) Molecular structure design of polyolefins; (b) The bandgap versus T_g for polymers synthesized in this study and for established polymers with high electric field and/or high temperature stability; (c) Energy storage performance of *o*-POFNB at 150 and 200 °C; (a–c: reproduced with permission from Ref. [61]; Copyright (2022), The Royal Society of Chemistry). (d) The position and element design of the pendant groups in polyolefins; (e) Energy storage performance of *p*-POCINB at 200 °C; (f) Comparison of energy storage performance between POXNBs and other published all-organic pure homopolymers. (d–f: reproduced with permission from Ref. [62]; Copyright (2024), Wiley).

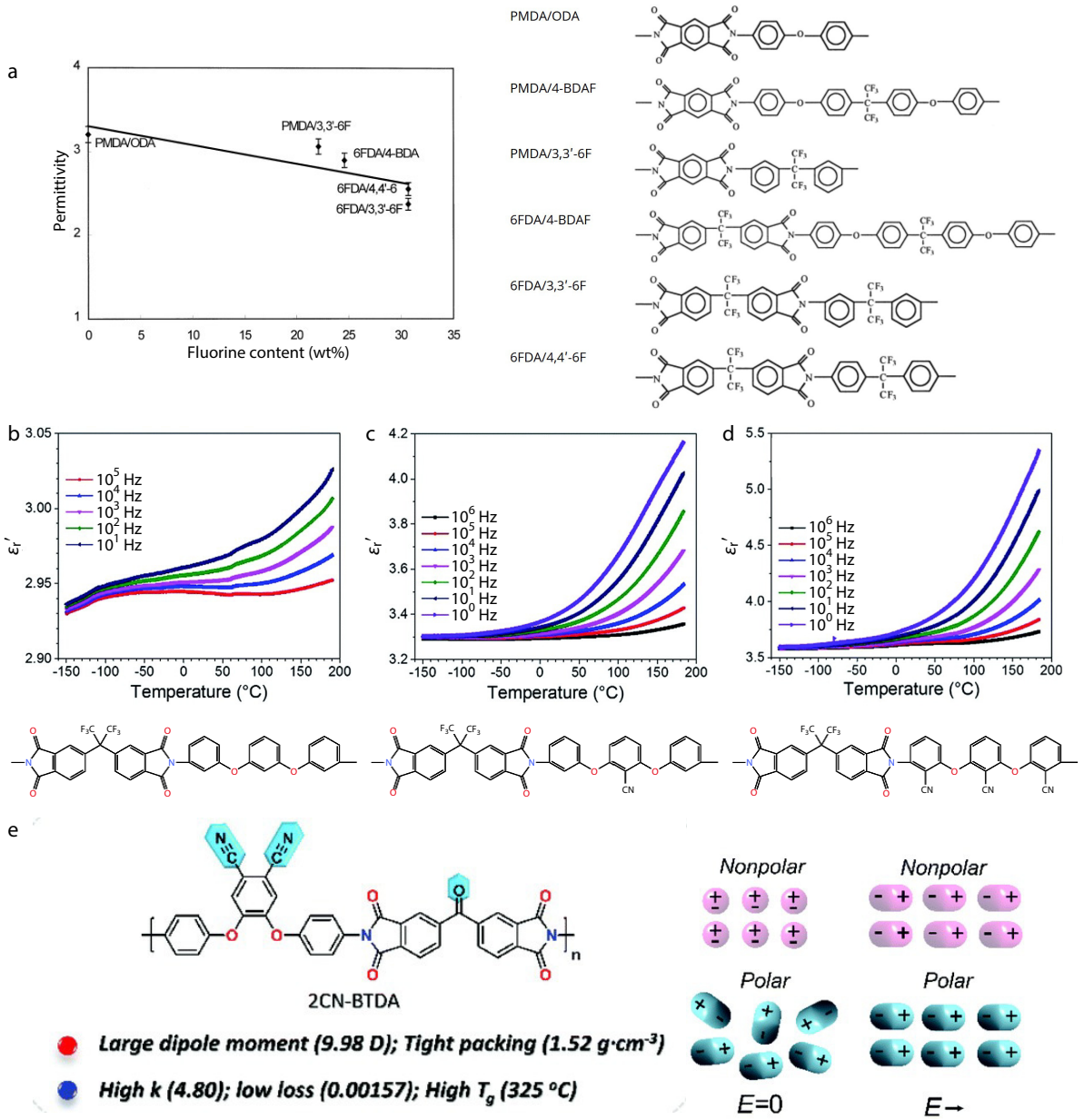


Fig. 5 (a) Dielectric constant versus fluorine content of polyimides (Reproduced with permission from Ref. [63]; Copyright (2001), Wiley); Dielectric constant as a function of temperature for samples contain (b) 0, (c) 1, and (d) 3 –CN groups, respectively (Reproduced with permission from Ref. [64]; Copyright (2014), The Royal Society of Chemistry). (e) Schematic illustration of designing high-performance polyimide dielectrics based on the orientational polarization (Reproduced with permission from Ref. [67]; Copyright (2021), The Royal Society of Chemistry).

molecular structures and regulate chain conformation. This strategy is very common in ferroelectric polymers, such as copolymerizing TrFE structural unit in PVDF to obtain an all-*trans* (β) conformation.[68,69] At present, this strategy is also widely used in high-temperature resistant dielectric polymers.[70] The purpose of designing copolymer molecular structures in high-temperature resistant dielectric polymers can be mainly divided into two aspects. On the one hand, the copolymerization utilizes energy band mismatch between different molecular structures to construct intrachain electron barriers (Figs. 6a–6d).[71] It should be noted that although copolymerization of high electron affinity monomers and low electron affinity monomers can form a high charge barrier, it will also lead to strong electrode charge injection due to the decrease in Schottky barrier, as the LUMO energy level of high electron affinity monomers is close to the work function of the metal electrode. This suggests that the copolymerization strategy requires tailored control of the ratio of high electron affinity monomers (Figs. 6e and 6f).[72] On the other hand, the copolymerization can assembles some polar units onto the backbone to improve the dielectric constant. Introducing electron donating pyrrolidine and electron withdrawing trifluoromethyl or nitro groups into block copolymers with push-pull azobenzene pendants can even achieve higher ε than ferroelectric polymer (PVDF, ε is about 12) (Figs. 7a–7c).[73] It should also be noted that the dielectric

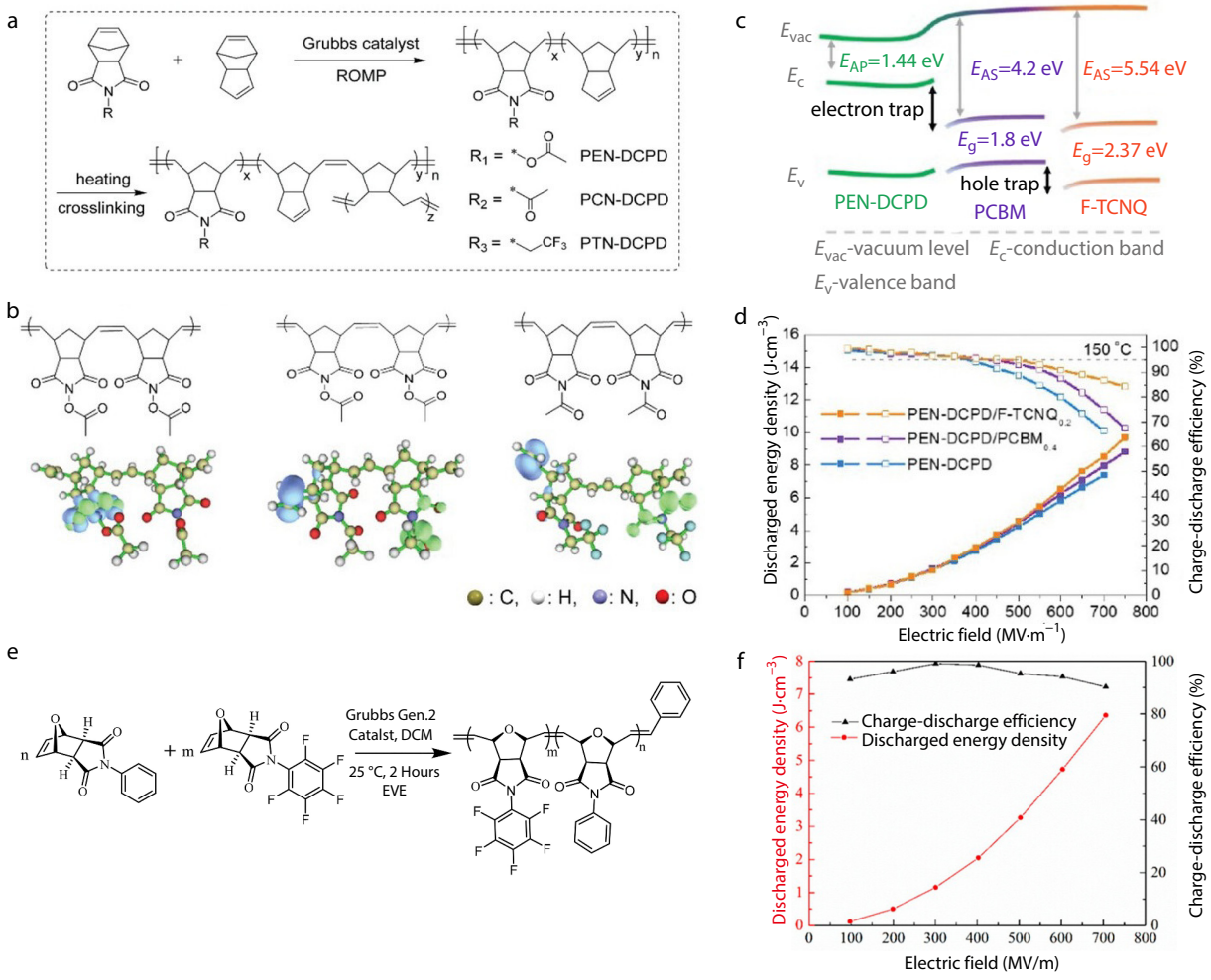


Fig. 6 (a) Synthesis of PEN-DCPD, PCN-DCPD, and PTN-DCPD by ROMP and thermo-crosslinking; (b) Diagram of the DFT simulation of the electron-hole pairs of EN-EN, CN-CN, and TN-TN unit under the applied electric fields, where the blue ones represent electrons, and the green ones represent holes; (c) Deep charge trap energy created by PEN-DCPD and trace PCBM or F-TCNQ; (d) Discharged energy density and charge-discharge efficiency of PEN-DCPD, PEN-DCPD/$PCBM_{0.4}$, and PEN-DCPD/F-$TCNQ_{0.2}$ films; (a–d: reproduced with permission from Ref. [71]; Copyright (2023), Wiley). (e) Polymer synthesis using the ROMP technique; (f) Discharged energy density analysis of POF25 (e, f: reproduced with permission from Ref. [72]; Copyright (2023), American Chemical Society).

constant of the polymer can be adjusted through the photoisomerization of azobenzene groups in the molecular structure (Figs. 7d and 7e).[74] Although high ε is attractive for low electric field applications (*e.g.*, the operation electric field of the capacitor in the inverter of a hybrid electric vehicle is 200 MV·m^{-1}), it cannot adapt to pastry factory applications (≥ 400 MV·m^{-1}). In this case, additional copolymerization of some cycloaliphatic monomers is required to enhance its high field insulation at the expense of sacrificing some dielectric constant (Figs. 7f and 7g).[74]

4 MOLECULAR CHAIN MORPHOLOGY DESIGN OF POLYMERS

The secondary structure of polymers (remote structure) refers to the various shapes of individual polymers in space, also known as the conformation and configuration of polymers. The morphology of polymer chains includes but is not limited to ladderphane polymers, grafted polymers, and cross-linked polymers. In the past decade, it has been proven that the design of molecular chain morphology has a significant impact on the thermal and electrical properties of polymers.

Among all secondary structures, ladderphane polymers belong to an extremely special structure that covalently binds two long chains through short molecular monomers (Fig. 8a).[47,75–79] Ladderphane molecular chains with strong π-π interactions are prone to dense stacking to form semi-crystalline polymers (Fig. 8b), thereby facilitating phonon transport and achieving high thermal conductivity. Chen and his collaborators developed a ladderphane polymer based on polycyclic olefins, which achieved an ultra-high thermal conductivity of 1.9 W·m^{-1}·K^{-1} due to π-π stacking.[47] It is worth noting that this ladderphane polymer also decouples the long-term contradiction between high thermal conductivity and high insulation performance (Figs. 8c and 8d). At 200 °C, it exhibits a resistivity two orders of magnitude higher than commercial PEI, resulting in a U_d of up to 5.34 J·cm^{-3} with efficiency of 90% (Figs. 8e and 8f). The tightly stacked structure

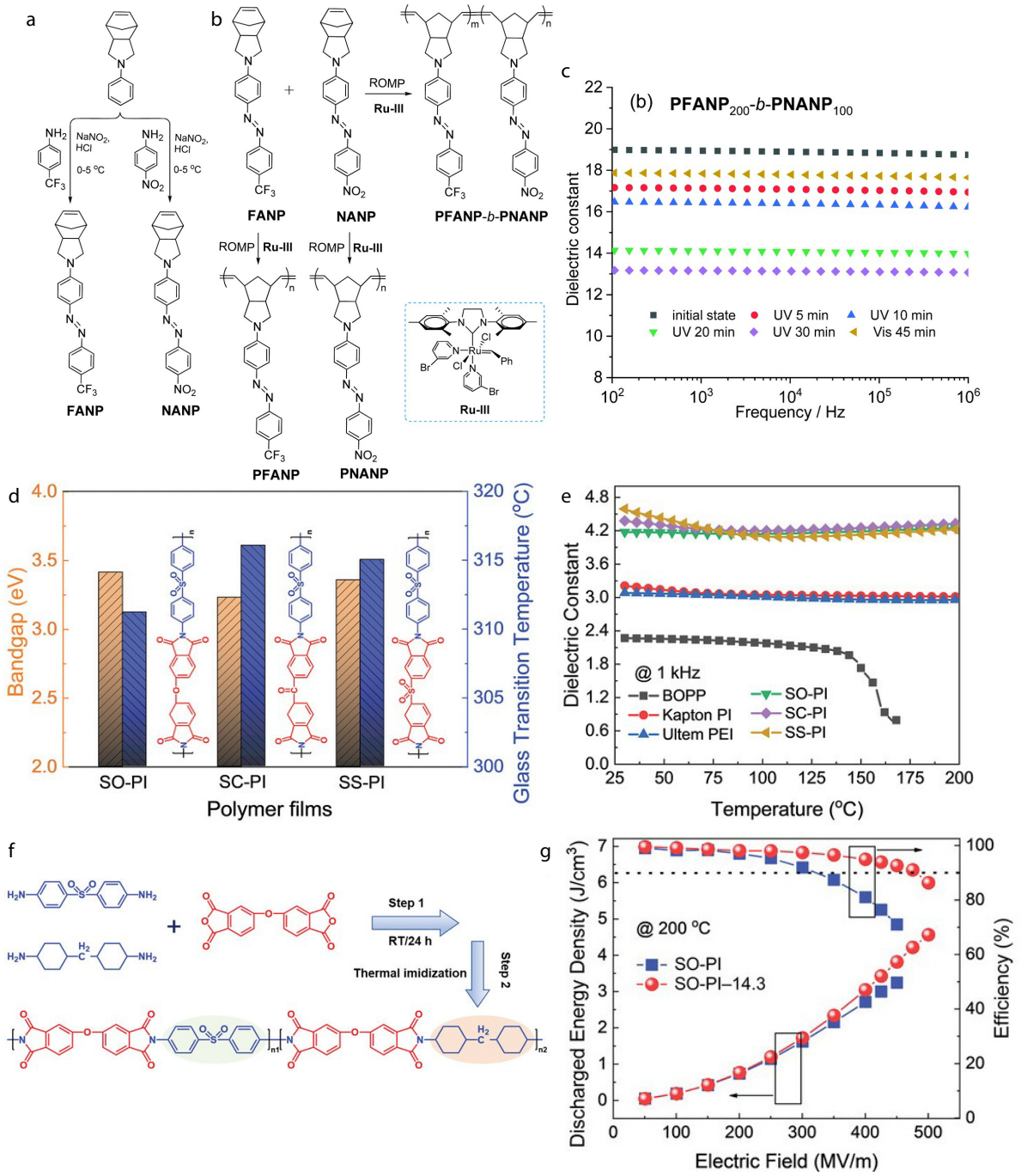


Fig. 7 Syntheses of (a) monomers and (b) polymers; (c) Dielectric constant of the films made from the polymer solution in THF versus frequency under ultraviolet irradiation at 365 nm and visible light irradiation at 440 nm in turn; (a–c: reproduced with permission from Ref. [73]; Copyright (2019), Royal Society of Chemistry). (d) Bandgap and glass transition temperature for SO-PI, SC-PI, and SS-PI film; (e) Temperature dependence of dielectric constant at 1 kHz for SO-PI, SC-PI, SS-PI, and commercial dielectric polymers, *e.g.*, Ultem PEI, Kapton PI, and BOPP; (f) Schematic diagram for the synthesis route of copolymer; (g) Capacitive properties for neat SO-PI and SO-PI–14.3 copolymer film at 200 °C; (d–g: reproduced with permission from Ref. [74]; Copyright (2024), Wiley).

of ladderpane polymers suppresses chain movement over a wide temperature range, which is beneficial for improving breakdown strength.[78] Meanwhile, the higher affinity structure in the connected molecular structure compared to the main chain can effectively prevent charge hopping, thereby reducing leakage current. Consequently, the excellent high-temperature energy storage performance and thermal conductivity of ladderpane polymers have shown great potential and prospects in the field of high-temperature capacitors, in spite of their research is just in its infancy (Figs. 8g–8i).

Connecting different functional side chains to the main chain of the original polymer through chemical bonds to

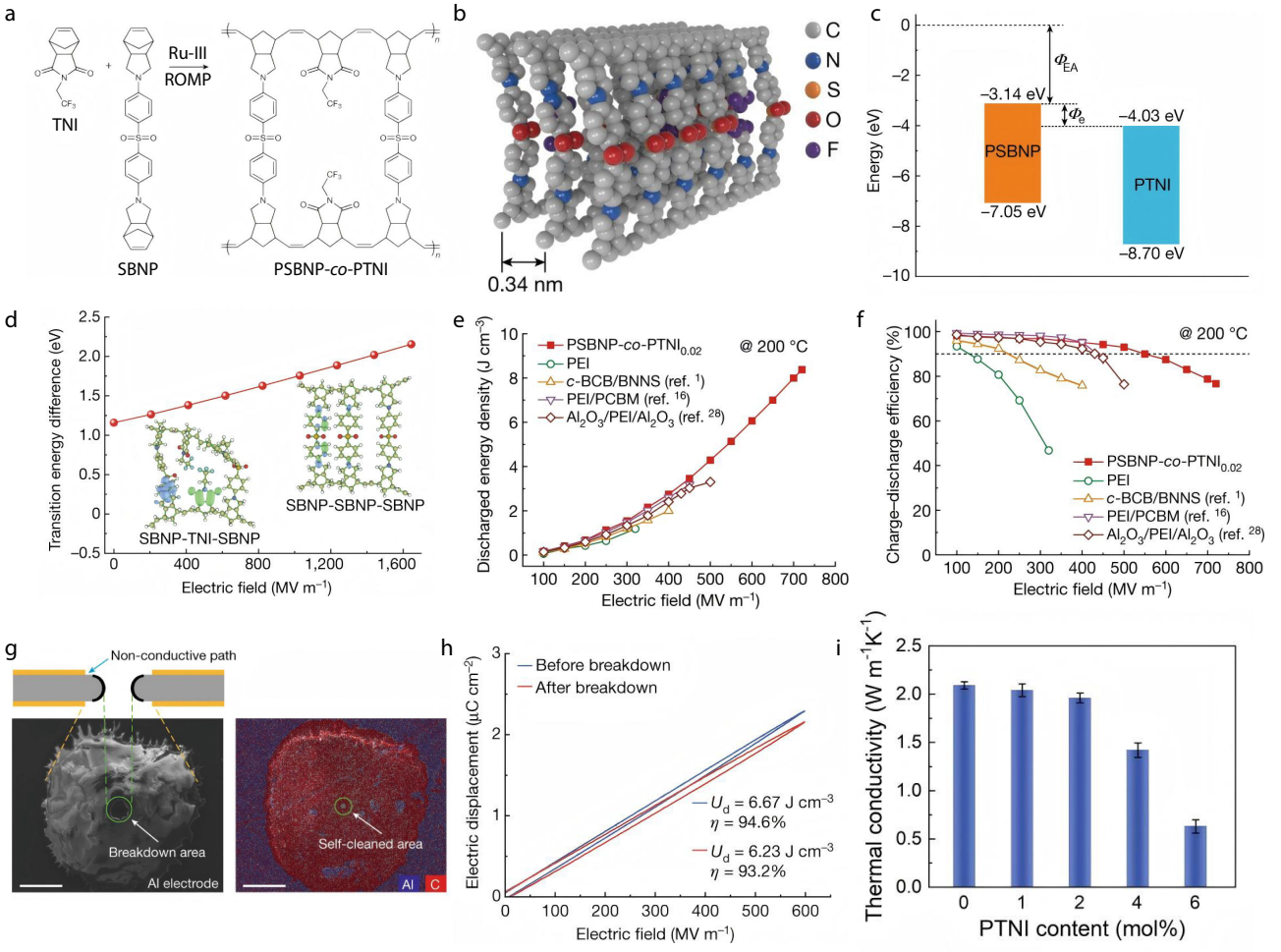


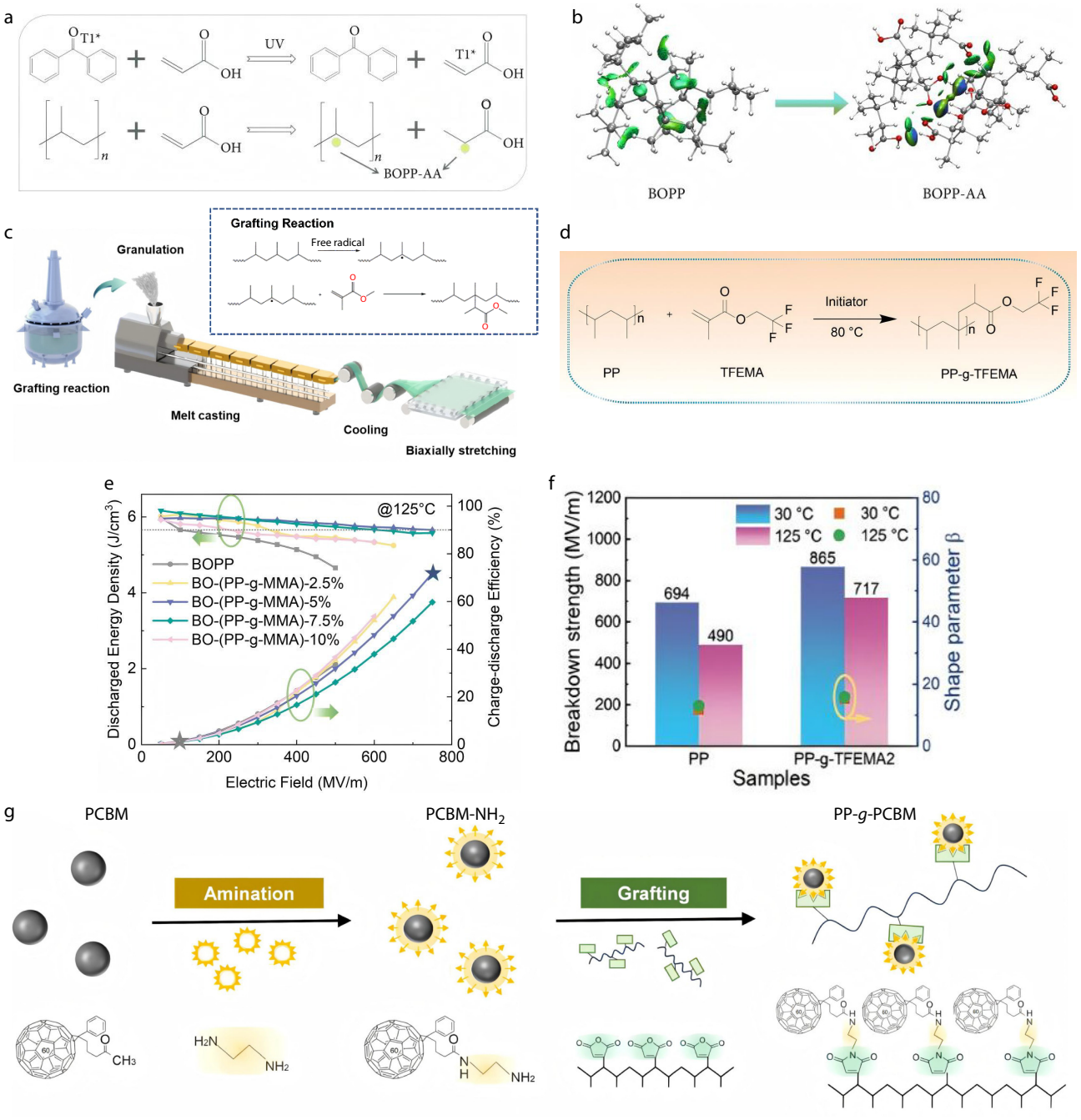
Fig. 8 (a) Molecular structure design, (b) lattice spacing and (c) energy level structure of ladderphane polymers; (c) Energy-band diagram of PSBNP and PTNI; (d) Simulated electron transition energy difference between SBNP-SBNP-SBNP and SBNP-TNI-SBNP units under the applied electric fields; (e) Discharged energy density and (f) charge-discharge efficiency of PSBNP-*co*-PTNI$_{0.02}$ and other polymer and composite films measured at 200 °C; (g) SEM image and EDS analysis of PSBNP-*co*-PTNI$_{0.02}$ film after electrical breakdown. Scale bars, 100 μm; (h) Electric displacement–electric field loops of PSBNP-*co*-PTNI$_{0.02}$ film before and after electrical breakdown at room temperature; (i) Thermal conductivity of PSBNP-*co*-PTNI with different PTNI content. (Reproduced with permission from Ref. [47]; Copyright (2023), Nature).

form grafted polymers is an important means of optimizing polymer molecular structure. Similar to nanocomposites, grafted polymers can also compensate for the shortcomings of the original polymer properties by leveraging the advantages of grafted components. The influence of different grafting components on polymer properties varies greatly. For example, acrylic acid (AA) as a grafting phase can form deep chemical traps in BOPP-based polymers and generate built-in electric fields to suppress electrode charge injection (Figs. 9a and 9b).[80] Similarly, methyl methacrylate (MMA)[19] and trifluoroethyl methacrylate (TFEMA)[81] are used as grafting phases to introduce charge trapping sites (Figs. 9c and 9d). Compared with the original polymer, this grafting structure can reduce the leakage current density by more than an order of magnitude, thereby significantly improving the high-temperature capacitive performance of the polymer (Figs. 9e and 9f). It is worth noting that this type of grafting engineering can perfectly adapt to existing BOPP film industrial production lines, with simple process, environmental protection, and high productivity. In addition to grafting polymers, organic small molecules with strong electron affinity can also be used as grafting components, *e.g.*, ammoniated [6,6]-phenyl-C61-butyric acid methyl ester (PCBM),[82] which utilizes the strong electron withdrawing effect of PCBM to firmly confine free electrons at the grafting site (Figs. 9g–9i). Overall, the electrical properties, dispersibility, content, and molecular weight of the grafted components need to be thoroughly optimized, while paying attention to the influence of different components on the mechanical or processing properties of the polymer, in order to determine the optimal grafted polymer suitable for high-temperature energy storage.

Crosslinking is a prominent strategy to enhance the high-temperature energy storage performance of polymer dielectrics by constructing three-dimensional network molecular structures. Firstly, cross-linking can significantly improve the thermal stability of polymers by restricting the mobility of polymer chains, thereby preventing polymer thermal degradation or melting at high temperatures and enabling poly-

mers to maintain their capacitive performance over a higher temperature range. In addition, cross-linked structures can significantly enhance the mechanical strength and modulus of polymers, maintaining the mechanical integrity of the material and avoiding deformation and fracture. In terms of dielectric properties, cross-linking strategies can reduce dielectric loss by reducing the polarization and movement of polymer chains. In terms of thermal conductivity, cross-linking can also enhance intermolecular interactions to promote phonon transfer. The influence of comprehensive thermal conductivity, dielectric and mechanical properties on the three breakdown mechanisms of polymer thermal breakdown, electrical breakdown, and electro-mechanical breakdown, cross-linking can significantly enhance the breakdown strength of dielectric polymers at high temperatures, thereby obtaining higher energy storage density.

Based on the various advantages of cross-linking engineering, even PVDF-CTFE, a kind of relaxor ferroelectric polymer used at room temperature, can be modified into high-temperature resistant dielectrics that can withstand 150 °C (Fig. 10a).[83] Moreover, the cross-linking center in polymers can effectively limit carrier transfer as a charge capture center, which has great attraction for reducing the electrical conduction loss of dielectrics under extreme conditions. By customizing the molecular structure of crosslinking components, such as introducing aromatic crosslinking components into non



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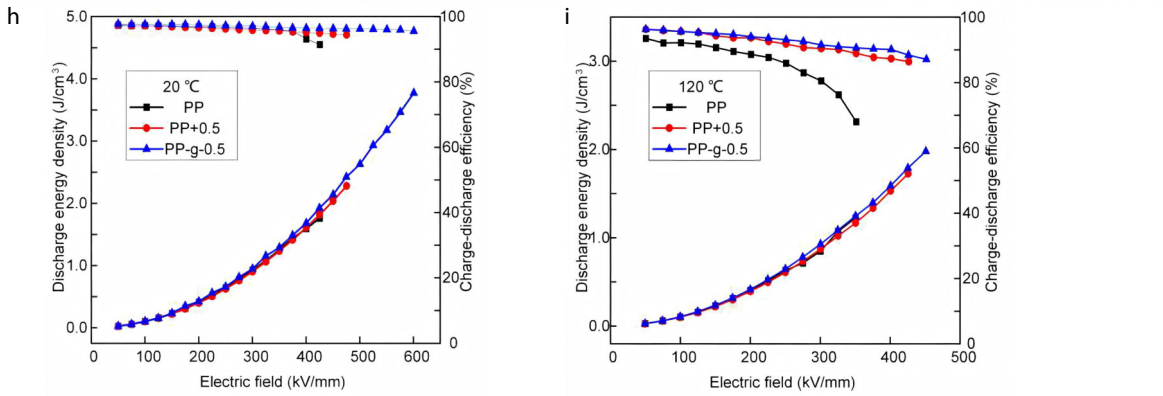

Fig. 9 (a) The process of bonding BOPP with acrylic acid; (b) Simulation of interaction forces between BOPP-AA molecule chains; (a, b: reproduced with permission from Ref. [80]; Copyright (2022), Institute of Electrical and Electronics Engineers). Process roadmap for grafting (c) methyl methacrylate (MMA) and (d) trifluoroethyl methacrylate (TFEMA) onto BOPP; (e) Capacitive performance of BOPP-MMA with different MMA contents; (c, e: reproduced with permission from Ref. [19]; Copyright (2023), The Royal Society of Chemistry). (f) Comparison of breakdown strength between PP and PP-*g*-TFEMMA2 (d, f: reproduced with permission from Ref. [81]; Copyright (2024), Wiley); (g) Process roadmap for covalent grafting of PCBM onto PP molecular chains. Energy storage performance of PP, PP/PCBM blends, and PP-*g*-PCBM at (h) 20 °C and (i) 120 °C; (g–i: reproduced with permission from Ref. [82]; Copyright (2023), Elsevier).

aromatic polymers, the trap energy levels and density in the polymer can be finely controlled (Fig. 10b).[84] UV irradiation is another effective strategy to promote cross-linking of molecular chains. Thanks to its no chemical additives, simplicity, and continuous processing ability, it can be perfectly integrated into the process of preparing thin film capacitors. However, UV crosslinking requires the molecular structure to contain functional groups similar to double bonds. Although the carbonyl groups and crosslinking points generated can significantly enhance the dielectric properties of polymers, they inevitably have destructive and uncontrollable effects on the molecular backbone.[85] Considering this drawback, introducing UV reactive sites on the molecular side chains may be a more secure strategy (Figs. 10c and 10d).[86] In addition, radiation on the surface of polymers, which only destroys the main chain structure of the polymer surface through high-energy photons to generate oxygen-containing groups for limiting electrode charge injection without damaging the insulation stability inside the polymer, is also a strategy worth promoting due to its universality.[87]

5 SUPRAMOLECULAR CHEMICAL STRUCTURE DESIGN OF POLYMERS

Supramolecular chemical structure refers to the assembly of molecules or ions into complex structures through non covalent bonds (such as hydrogen bonds, van der Waals forces, electrostatic interactions, π-π interactions, *etc.*). These non-covalent bonds are weak in strength, but due to their large number, they can form stable and functionally specific structures. Supramolecular chemistry emphasizes intermolecular interactions and self-assembly processes, thereby constructing complex systems with specific forms and functions. Taking hydrogen bonding as an example, whether in ferroelectric polymers[20] suitable for room temperature or linear polymers[88] suitable for high temperature, hydrogen bonding has been proven to serve as charge trapping sites to suppress conduction current loss. In general, people believe that hydrogen bonds will dissociate at high temperatures. However, in glassy polymers, hydrogen bonds still exist and play an important role due to the freezing of molecular chains. When aromatic polyamide PNFA is incorporated into PEI matrix and a hydrogen bond network is introduced, even at high temperatures, the dipole rotation induced β relaxation in PEI is significantly suppressed by hydrogen bonds, thereby suppressing leakage current.[88]

Besides hydrogen bonding, the physical cross-linking network of electrostatic interactions can also serve as charge trapping sites.[89] Without any additional processes, the electrostatic interactions between chains can effectively strengthen polymer chains, combined with their capture effect on charge carriers, significantly enhancing the breakdown strength of polymers at high temperatures.

However, it should still be noted that these weak interactions often weaken at high temperatures, which limits the application of supramolecular chemical structures at higher temperatures (such as 250 °C). Very recently, Wang *et al*. discovered a new physical mechanism for charge conduction at high temperatures in insulating polymers, known as phonon-assisted current (Figs. 11a–11c).[90] In the field of organic semiconductors, there have been very comprehensive studies on the phonon assisted current conduction mechanism. The phonon assisted current is related to local chain vibration. As the temperature increases, the molecular chain vibration intensifies and eventually forms electroacoustic coupling with electrons. At this time, electrons will jump between chains with the vibration of phonons. Wang *et al.* were inspired by cable-stayed bridges to insert cyclic small molecule crown ethers into PI molecular chains as a molecular damper. Cyclic crown ethers can limit the vibration of molecular chains at high temperatures through special supramolecular interactions (mechanical bonds) with PI chains (Fig. 11d). The correlation between molecular chain vibration and inter chain charge transfer has been confirmed through comprehensive experiments and simulation simulations (Figs. 11e and 11f). Thanks to limited local vibration, PI-M/C_{34} exhibits a resistivity four orders of magnitude higher

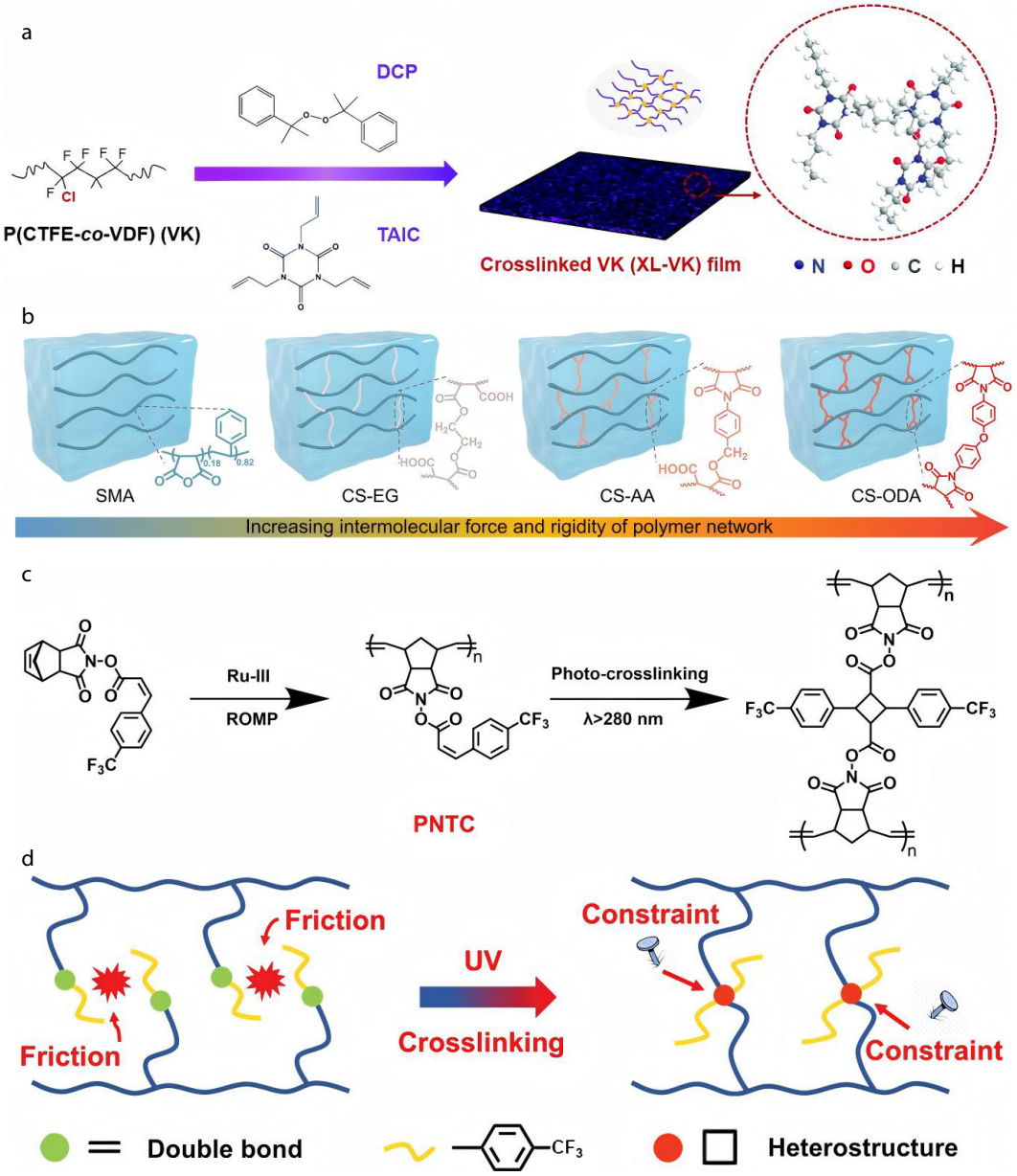

Fig. 10 (a) Schematic of the preparation of XL-VK films (Reproduced with permission from Ref. [83]; Copyright (2020), The Royal Society of Chemistry); (b) Schematic of the preparation of SMA, CS-EG, CS-AA, and CS-ODA films (Reproduced with permission from Ref. [84]; Copyright (2023), Wiley); (c) Schematic of the preparation of photo-crosslinking PNTC films; (d) The pinning effect in photo-crosslinking PNTC; (c, d: reproduced with permission from Ref. [86]; Copyright (2023), Wiley).

than commercial polyimide at 250 °C, with an unprecedented U_d of 4.1 J·cm^{-3} and a η of 90%, far exceeding all current dielectric polymers and polymer composites (Fig. 11g). The discovery of this new physical mechanism and the diversity of chemical topological structures with mechanical bonds are very likely to break through the current temperature limit of high-efficiency capacitive energy storage.

6 ALL-ORGANIC POLYMER COMPOSITES

Unlike the strategies for optimizing molecular structures mentioned above, blended multi-polymer systems belong to composites, and their physical mechanisms have many similarities with traditional nanocomposites, especially in terms of interfaces. Blending have been developed for polymer dielectrics with high dielectric constant, high breakdown strength, and high energy density, aiming to regulate the aggregation state structure, polarization, and charge transfer process, which comprehensively affect the dielectric energy storage performance. Amorphous regions within polymers, often harboring various structural defects, pose as potential electrical vulnerabilities. For instance, the interchain spacing can be adjusted by meticulously modulating the interactions between polymer chains, leading to a notably higher dielectric constant as well as a suppressed tanδ of the composites.[91] In addition, by blending PEI with PEMEU, the regulation of chain spacing and free volume results in an enhancement of polarization without sacrificing the dielectric loss, thus reinforcing the significant impact of

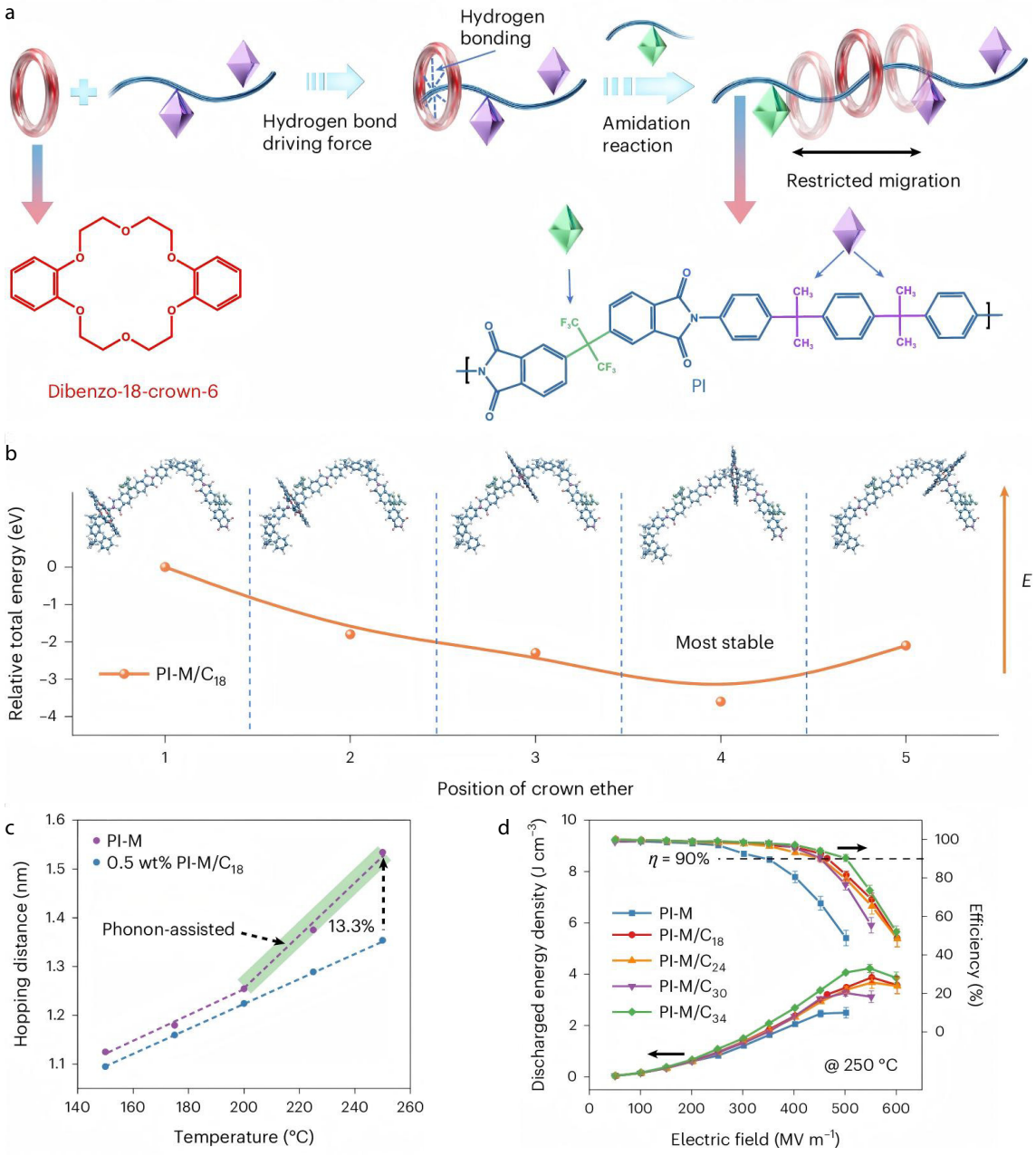

Fig. 11 (a) The synthesis of the polymer with mechanical bonds driven by hydrogen bonding, in which the large-volume side groups (isopropyl or hexafluoroisopropyl) carried in dianhydride and diamine monomers can prevent crown ether derivatives from detaching from the molecular chain. The green and purple octahedra represent hexafluoroisopropyl and isopropyl groups, respectively. (b) The relative total energy changes of molecular systems corresponding to different crown ether positions in the V-shaped PI molecular chain; (c) Temperature-dependent hopping distances of the pristine PI-M and 0.5 wt% PI-M/C_{18}; (d) Discharged energy densities and charge-discharge efficiencies of PI-M with different crown ether derivatives at 250 °C. (Reproduced with permission from Ref. [90]; Copyright (2025), Nature).

molecular packing structure on dielectric properties.[92] The amplified electrostatic interaction arising from the opposing polarities of phenyl charges in PI and PEI enables the polymer chains within the blends to achieve an intensified chain packing, ultimately resulting in a substantial augmentation of DC breakdown strength of 1000 MV·m^{-1} at ambient temperature and 650 MV·m^{-1} at elevated temperatures (Figs. 12a–12c).[93] Ferroelectric polymers, as doped polymers, can also have a positive effect on the energy storage performance of high-temperature linear polymers, especially in improving the dielectric constant, although the breakdown strength and resistivity values slightly decrease with the content of ferroelectric polymers. When the mass ratio of P(VDF-HFP) to PI is 1:4, the corresponding U_d of PI-20 can reach 2.25 J·cm^{-3} even at 150 °C, which is 670% of that of pure PI film.[94] This is attributed to the increase in dielectric constant and the suppression of space charge at the interface. Recently, a polymer blend dielectric composed of ordinary polyimide and bifunctional dipole glass polymer has been reported,

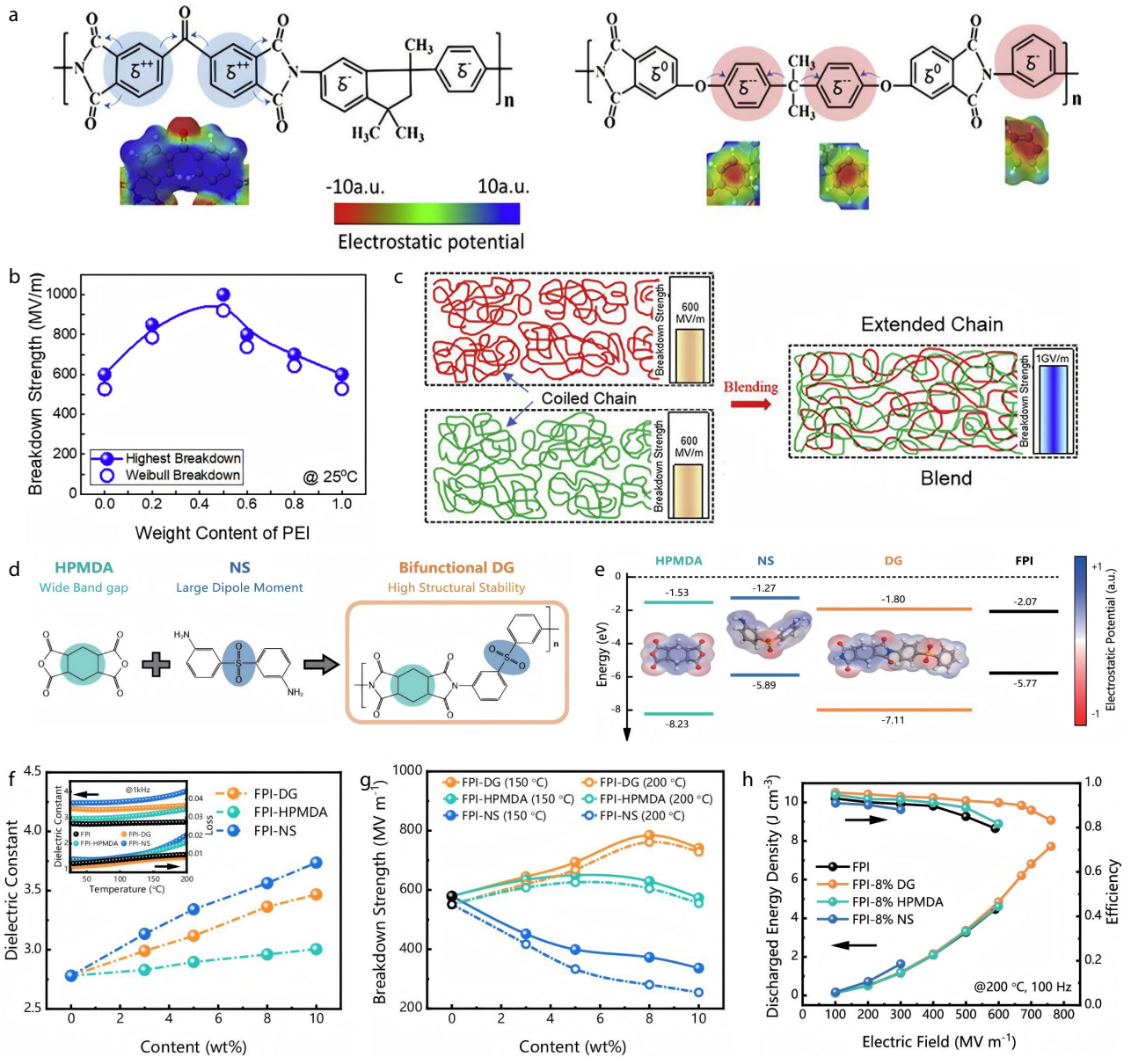

Fig. 12 (a) Chemical structure and electrostatic potential of PI and PEI; (b) The breakdown strength of films with different PEI contents; (c) Schematic illustration of the PI/PEI blend strategy in enhancing the electrostatic interaction and engineering the extended chain packing; (a–c: reproduced with permission from Ref. [93]; Copyright (2021), Elsevier). (d) Schematic diagram of the synthesis of bifunctional DG; (e) Band structures and electrostatic potential distribution of 1,2,4,5-cyclohexanetetracarboxylic dianhydride (HPMDA), 3,3′-sulfonyldianiline (NS), DG, and fluorinated polyimide (PI); (f) Dielectric constant of FPI-DG, FPI-HPMDA, FPI-NS at 1 kHz and 25 °C; (g) High temperature Weibull breakdown strength of FPI-DG, FPI-HPMDA, FPI-NS; (h) Discharged energy density and efficiency versus electric field of FPI, FPI-8 wt% DG, FPI-8 wt% HPMDA, and FPI-8 wt% NS at 200 °C; (d–h: reproduced with permission from Ref. [95]; Copyright (2024), Nature).

achieving optimized bandgap and polarizability (Figs. 12d and 12e).[95] Surprisingly, bifunctional dipole glasses with high molecular weight exhibit more significant dielectric performance improvements than any single component, including dielectric constant and breakdown strength (Figs. 12f and 12g). At the same time, the dipole glass can maintain the thermal stability of the polymer even at a high load of 10 wt%. Therefore, even at 200 °C, the blended polymer can still exhibit 6.21 J·cm^{-3} and maintain a η of over 90% (Fig. 12h). The interactions between molecular chains also significantly affect the migration of charges in polymers. Recent reports suggest the need to weaken the π-π stacking between molecules and introcture hydrogen bonding.[96] Based on this principle, a high film crystallinity polymer composite (PTFMB) was designed, which has a wide E_g and low charge transfer energy (0.554 eV). Consequently, the crystalline polyamide film achieved high mechanical strength (378.3 MPa), breakdown strength (682 MV·m^{-1}), and discharged energy density (6.06 J·cm^{-3} at η=90%, with a peak value of 10.29 J·cm^{-3}).

Multilayer structured polymers have garnered substantial attention owing to their exceptional properties in terms of dielectric constant, breakdown field strength, and energy stor-

age properties. Research shows that the breakdown strength of multilayered polymers surpasses that of randomly blended linear and ferroelectric polymers. The electric field distribution will be affected by the dielectric contrast including the DC conductivity and dielectric constant between different polymer materials. Furthermore, the corresponding electric field formed by the charges at the interface between material layers could significantly prevent the migration of injected and emitted electrons. The optimization of layer numbers also has an influence on the charge transport, which jointly leads to the enhanced breakdown strength and reduced conduction loss, ultimately benefiting the energy storage performance (Figs. 13a and 13b).[97] In polyetherimide/polysulfone multilayer dielectrics, it was found that a large number of deep traps were formed at the interlayer interface, which can effectively suppress the development of breakdown paths (Figs. 13c–13e).[98]

Compared with polymer doping, organic small molecules are more easily able to design the energy levels and densities of charge traps by regulating their band structure (Fig. 14a). Generally speaking, substances with high electron affinity have narrow band gaps. If a polymer with high electron affinity is used as the doping phase, free electrons can easily conduct through the doping phase. However, at low doping levels, adjacent organic small molecules cannot form a continuous conductive path, but instead form isolated charge islands due to the band barrier between them and the insulating matrix,[99–103] resulting in excellent high-temperature capacitance performance (Figs. 14b–14g).[30] Importantly, these all-organic polymer composites exhibit remarkable homogeneity in their properties, avoiding challenges associated with filler dispersion. Furthermore, the all-organic polymer offers notable advantages in terms of scalability of the manufacturing process and the facile control of film quality. The

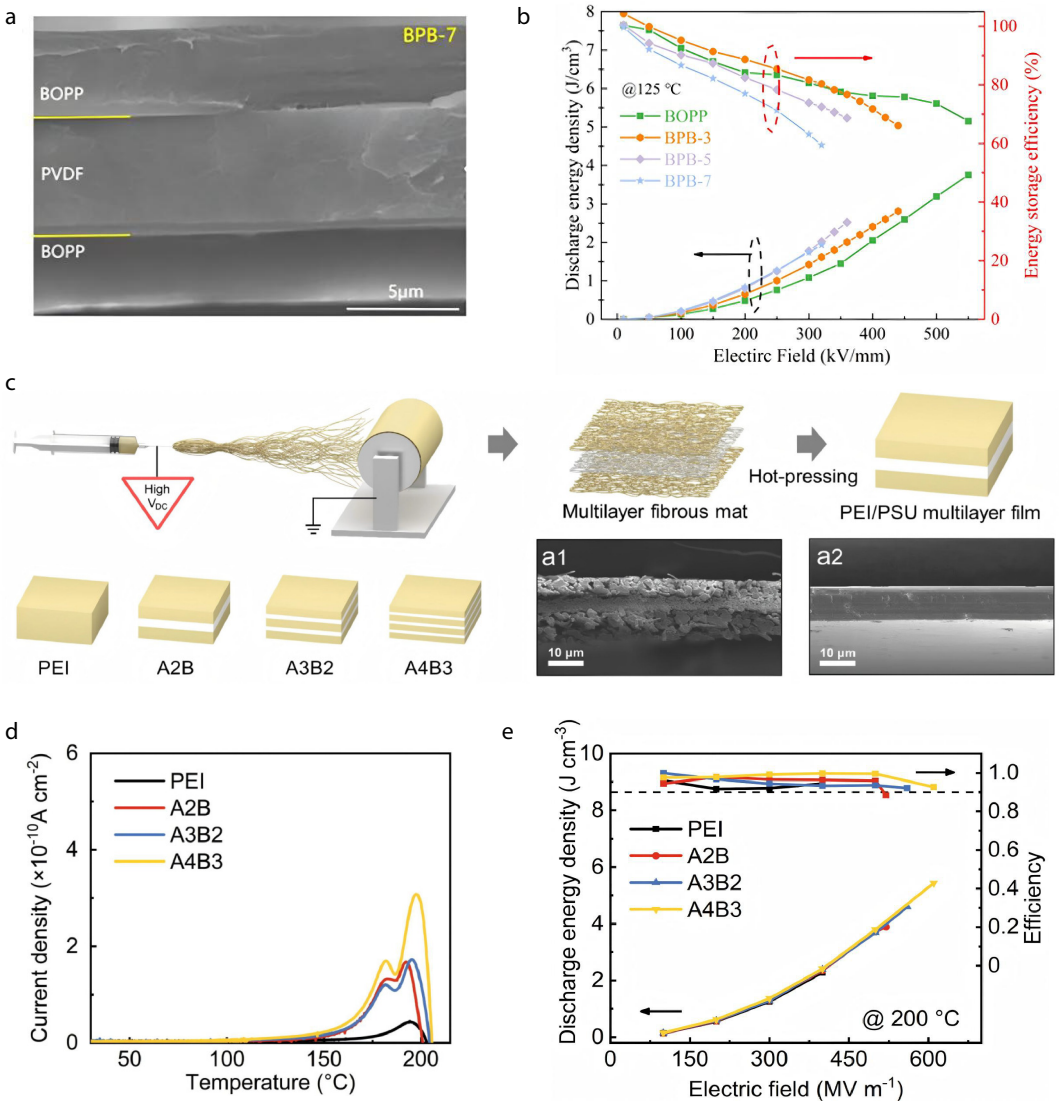

Fig. 13 (a) Microstructure of BPB sandwich composite films; (b) Energy storage performance of BP multilayer films; (a, b: reproduced with permission from Ref. [97]; Copyright (2023), Elsevier). (c) Schematic illustration of the synthesis procedure of preparing PEI/PSU multilayer composite film; (d) Thermally stimulated depolarization current of PEI, A2B, A3B2, and A4B3 films; (e) Discharged energy density and efficiency as a function of electric field at 200 °C; (c–e: reproduced with permission from Ref. [98]; Copyright (2024), Elsevier).

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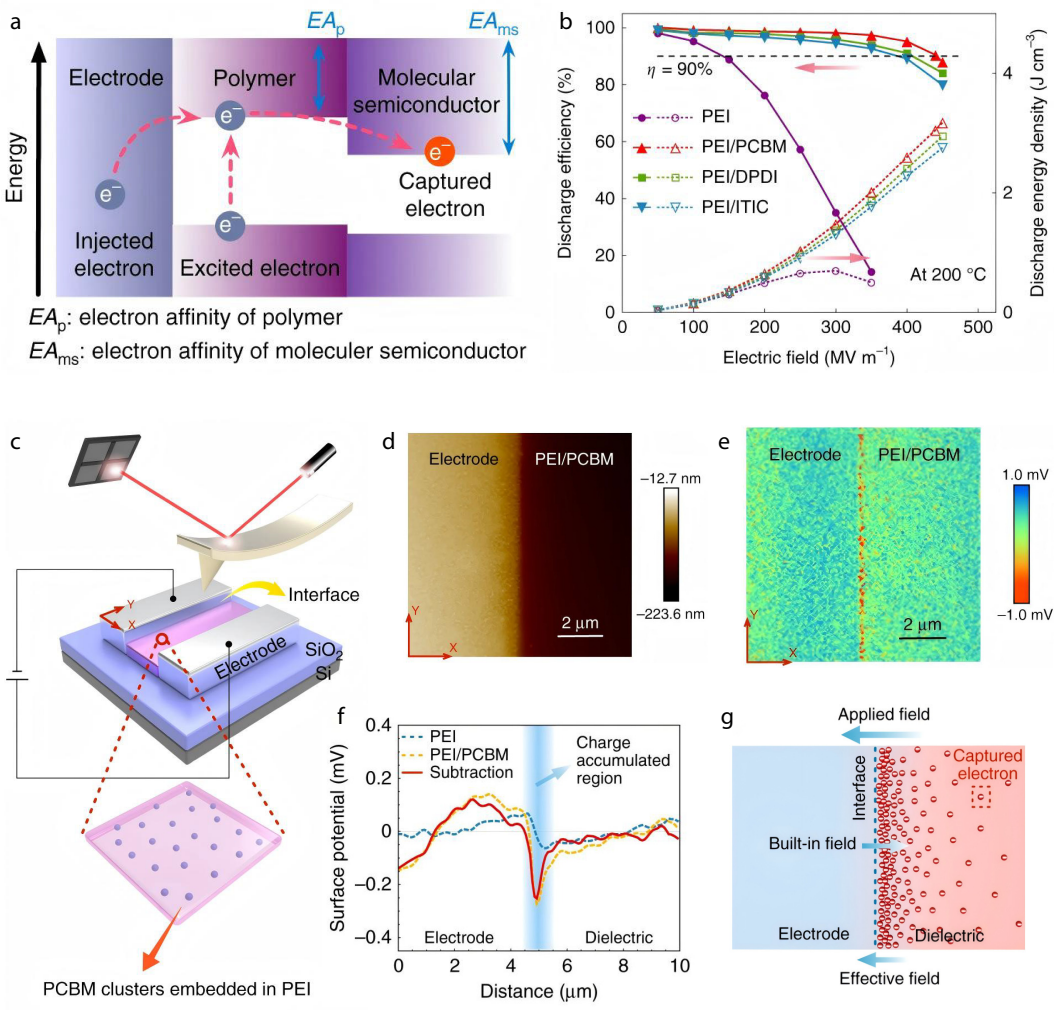

Fig. 14 (a) Band diagram showing the possible charge transfer in the all-organic composite; (b) Field-dependent energy density and discharge efficiency of PEI and PEI/PCBM (0.5 vol% PCBM), PEI/DPDI (0.75 vol% DPDI), and PEI/ITIC (0.25 vol% ITIC) composites at 200 °C; (c) Schematic diagram of the KPFM testing; (d) Topography of the PEI/PCBM composite; (e) Surface potential mapping of the PEI/PCBM composite; (f) Surface potential profiles along the horizontal axis derived from the surface potential mappings; (g) Schematic illustration of the built-in electric field formed by the molecular semiconductor captured electrons. (Reproduced with permission from Ref. [30]; Copyright (2020), Nature).

currently known high electron affinity organic small molecules include ITIC, PCBM, and DPDI, all of which exhibit effective insulation enhancement effects.[30] And it has been proven that atomic level modification can more effectively limit charge transport,[44] and this charge limiting effect has been shown to be universal in different polymers.[102] Although molecular semiconductors perform well in limiting charge transport, it is worth noting that when the content of molecular semiconductors exceeds 1%, the number of cycles cannot reach 5×10^4 at 300 MV·m^{-1} at 180 °C, indicating that the content of organic molecular semiconductor should be carefully controlled.[103] Note that increasing the E_g of organic small molecule components to transform them from semiconductors to insulators can appropriately increase the loading capacity. The 4,6-dinitrobenzene-1,3-dicarbonititrile (DNBDC) with an electron affinity of –4.59 eV and a E_g of 5.11 eV has been selected as a trap for free charges.[104] At a content of 1 wt%, the best high-temperature energy storage performance has been achieved to date.

7 MATERIALS INFORMATICS-ASSISTED POLYMER MOLECULAR STRUCTURE DESIGN

The Nobel Prize in Chemistry and Physics in 2024 are both awarded to the field of artificial intelligence, which is becoming the hottest research topic at the intersection of materials science. In recent years, the application of machine learning (ML) in materials science has gradually increased.[105,106] With the development of big data technology and the improvement of computing power, material researchers can design new materials faster, optimize existing material properties, and accelerate the process of material discovery. Although traditional experimental and simulation methods can provide a deep understanding of material properties, they are often time-consuming and costly, while machine learning can find patterns in big data and complex parameter spaces, improving research efficiency.[107–109]

For high-temperature energy storage polymer dielectrics, machine learning strategies can help researchers predict the

basic properties of materials, such as E_g, T_g, and ε, through their chemical structure. The current machine learning models, whether targeting the molecular structures of polyimide derivatives,[29] polynorbornene derivatives,[110] or polysulfides derivatives (Figs. 15a and 15b),[111] have predicted performance results that are highly consistent with experimental performance. However, it should still be noted that machine learning can generally only predict based on the primary chemical structure of materials. Once it involves the secondary and tertiary structures of polymers, it cannot accurately predict them. Therefore, it is necessary to continue enriching the experimental database of polymer with secondary/tertiary structures in order to obtain more accurate machine learning models. In addition to screening the intrinsic chemical structure of polymers, the chemical structure and electrical properties of organic doped components are another direction that can be optimized using machine learning. As mentioned before, organic semiconductors with high E_a can attract free electrons and constrain their migration, but the narrow E_g makes their LUMO energy level easily filled by excited electrons, weakening the ability to attract charges. Machine learning can screen out molecular structures with both high E_g and high E_a from a large number of organic molecules, and has been proven to have significant advantages in improving the high-temperature capacitive performance of polymer dielectrics (Fig. 15c).[104] However, it should be noted that the limitations of existing theories can lead to biases in machine learning results, ultimately resulting in a mismatch between the predicted results and experimental patterns. For instance, machine learning can effectively screen polymers with wide E_g, but previous theories suggest that increasing the E_g has marginal effects when it exceeds 3.3 eV.[29] Moreover, the screening principle for all-organic composites are wide E_g and high electron affinity, but it is not clear whether this screening principle has limitations and lacks multitude experimental evidence to verify.

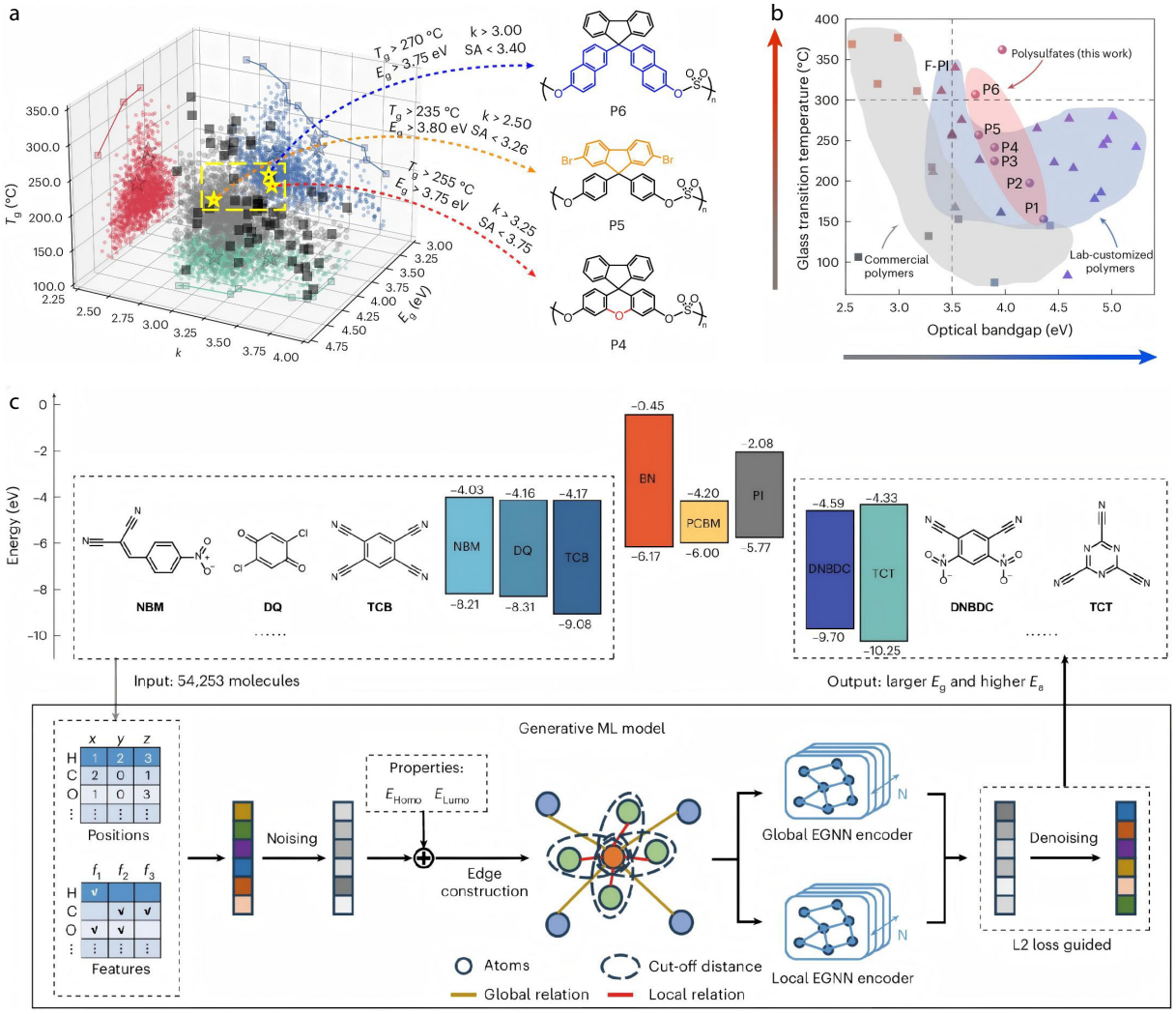

Fig. 15 (a) Selection criteria for machine learning predicted glass transition temperature, bandgap and dielectric constant of 49731 polymers, leading to three top polysulfates P4, P5 and P6; (b) Plot of glass transition temperature and optical bandgap of polysulfates P1–P6 and other commercial and lab-customized dielectric polymers (a, b: reproduced with permission from Ref. [111]; Copyright (2025), Nature); (c) Schematic diagram of generative ML model for outputting fillers of larger E_g and higher E_a (Reproduced with permission from Ref. [104]; Copyright (2025), Nature).

Machine learning has brought new ideas and tools to the research of materials science, which can significantly improve the efficiency of material design, optimization, and characterization.[112–114] However, issues such as the quality of data and models, and the interpretability of models still need to be further addressed. With the continuous advancement of technology and the deepening of research, machine learning will play a more important role in the field of materials science, making significant contributions to promoting technological innovation and industrial development.[115,116]

8 OUTLOOK

High-temperature polymer dielectrics are crucial for capacitors in applications requiring high heat resistance, such as electrified transportation and deep oil & gas exploration. This review focuses on the multi-scale structural design of all-organic polymer dielectrics, which have the advantage of large-scale production prospects compared to other strategies. The most critical challenge is the inherent contradiction between the heat resistance and the electrical insulation performance of polymer dielectrics, but existing strategies can not fully address this issue. Therefore, we put forward the following aspects for future research and development.

(1) Unlike the band theory in ordered structure of crystals, the physical mechanism of charge conduction cannot be accurately described in the matrix of polymers with disordered structures. At present, various physical mechanisms of charge conduction have been proven to exist in disordered polymers, such as hopping conduction, P-F emission, conjugated plane dihedral angle, space charge conduction, phonon assisted current, and trapping theory. However, based on these physical mechanisms, it is still difficult to design a satisfactory high-temperature polymer dielectric. Therefore, further exploration is needed towards understanding the physical mechanism of charge conduction in polymers.

(2) This review has already summarized the effect of multiple scales of polymer molecular structure on different parameters of high-temperature capacitive performance, as shown in Table 1. Apparently, the optimization strategies at different scales focus on different parameters, *e.g.*, the design of the main chain significantly changes almost all parameters, which requires elaborate design to trade-off, while the scale of the supramolecular structure can significantly enhance electrical insulation performance without affecting other parameters. Meanwhile, the synergistic relationship between the optimization strategies at different molecular structure scales is still unclear. It should be noted that although combining multiple optimization strategies may further optimize the high-temperature capacitive performance of polymers, the complexity of processing and/or the economy of raw materials cannot be ignored. The above issues are the main constraints that prevent high-temperature dielectric polymers from replacing BOPP.

(3) Most reports only focus on the discharged energy density and charge-discharge efficiency at high temperatures, which are generally achieved under high electric field. We believe that it is necessary to pay attention to achieve high discharged energy density under low electric fields, *i.e.*, how to simultaneously achieve high dielectric constant and high insulation performance, which can expand its application scenarios. Moreover, high thermal conductivity is another key parameter of polymer films, but it is only achieved in ladderphane polymers. For the evaluation of dielectric strength, although Weibull statistics is a good strategy, it seems to be only suitable for dielectric films with self-healing properties, such as polypropylene and cyclic olefins. For dielectric films with high carbon hydrogen ratios such as polyimide, we suggest increasing the comparison of minimum breakdown strength to ensure the safe operation of capacitors. And it is also necessary to ensure the mechanical properties of the polymer, such as tensile strength and toughness, which are crucial for industrial production of capacitor films.

(4) Machine learning has shown immense potential in predicting the performance of high-temperature dielectric polymers, but the accuracy is relatively low due to the insufficient database size and data diversity. Existing databases mostly focus on chemical structures and static dielectric constants at room temperature, lacking data reflecting dynamic structural characteristics such as chain relaxation, side chain orientation, π-π stacking, hydrogen bonding, and charge localization at high temperatures. In addition, traditional models generally rely on simplified molecular fingerprints or descriptors, which fail to fully reflect the effects of molecular conformational evolution and multi-scale thermal excitation processes on breakdown strength, dielectric constant, and thermal resistance. Future development should focus on establishing a cross-scale and multi-dimensional high-temperature polymer database, including multi-source data fusion from first principles, molecular dynamics to phase-field simulation, as well as developing graph neural network algorithms to ex-

Table 1 The effect of molecular structure optimization at different scales on parameters related to high-temperature capacitive performance.

Optimize scale		Effect on the properties			
		T_g	E_g	Dielectric constant	Electrical conductivity
Molecular structure	Main chain	High	High	High	High
	Side chain	Medium	Medium	High	High
	Copolymer	High	High	Medium	Medium
Chain structure	Ladder	Medium	Low	Low	High
	Graft	Medium	Low	Medium	High
	Crosslink	High	Low	Low	Medium
Supramolecular structure	Hydrogen bond	Low	Low	Low	High
	Mechanical bond	Low	Low	Low	High
Hydrid structure	Multi-layer	Medium	medium/low	medium/low	Medium
	Blend	Medium	medium/low	medium/low	Medium

https://doi.org/10.1007/s10118-025-3545-x

plicitly embed molecular stacking order, chain segment orientation, and thermal vibration characteristics into the model, thereby achieving accurate prediction of capacitive performance and reverse design of polymer dielectrics.

In summary, polymer-based dielectrics are the primary choice for dielectric energy storage in extreme conditions, but there are still numerous scientific, technical, and engineering challenges that need to be addressed. Although the all-organic dielectric strategies reported in the past decade have achieved exciting results, there has yet to be a dielectric with comprehensive excellent high-temperature capacitive performance, graceful failure mechanism, and compatible process preparation. A machine learning strategy-based material informatics has emerged to assist in predicting the electrical and thermal properties of materials, thereby guiding the design of multi-level polymer molecular structures and greatly saving time-cost. The development of machine learning algorithms with more predictive and accurate results, as well as the expansion of experimental databases for high-temperature resistant polymers, require the joint efforts of a large number of researchers. The intersection of chemistry, physics, materials science and engineering, electrical engineering, and computer science can rapidly promote the development of high-temperature capacitors from theory to application. This is also the development direction of many material fields in the future, not limited to polymer energy storage dielectrics.

BIOGRAPHY

Qi Li is a professor in the Department of Electrical Engineering at Tsinghua University. He received his Ph.D. degree in materials science at Wuhan University of Technology. He was a postdoctoral fellow at the Department of Materials Science and Engineering of the Pennsylvania State University before joining Tsinghua University. His research interests include dielectric polymers for capacitive energy storage, smart dielectric materials, and ferroelectric polymers for energy conversion and harvesting.

Conflict of Interests

The authors declare no interest conflict.

ACKNOWLEDGMENTS

This work was financially supported by the National Natural Science Foundation of China (Nos. 52525303, 92466301 and 52307025).

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Graphical Abstract

Design of All-organic Dielectrics for High-temperature Capacitive Energy Storage

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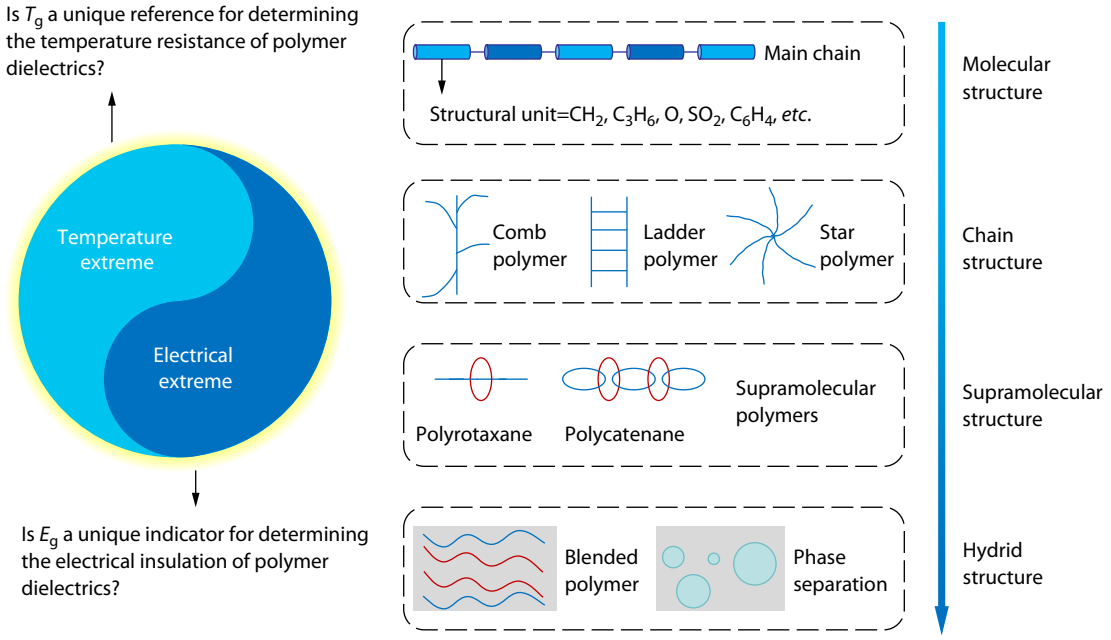
This work reviews all-organic dielectric development for high-temperature capacitive energy storage, with a focus on multiscale-structural strategies in decoupling thermal stability from insulation.



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https://doi.org/10.1007/s10118-025-3545-x