Effect of Fluorine in Redesigning Energy-Storage Properties of High-Temperature Dielectric Polymers

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ABSTRACT: Exploration of novel polymer dielectrics exhibiting high electric-field stability and high energy density with high efficiency at elevated temperatures is urgently needed for ever-demanding energy-storage technologies. Conventional high-temperature polymers with conjugated backbone structures cannot fulfill this demand due to their deteriorated performance at elevated electric fields. Here, in search of new polymer structures, we have explored the effect of fluorine groups on the energy-storage properties of polyoxanorbornene imide polymers with simultaneous wide band gap and high glass transition temperature (T_g). The systematic synthesis of polymers with varying amounts of fluorine is carried out and characterized for the energy-storage properties. The incorporation of fluorine imparts flexibility to the polymer structure, and free-standing films can be obtained. An oxanorbornene copolymer with 25% fluorination exhibits a high breakdown strength of 700 MV/m and a discharged energy density of 6.3 J/cm³ with 90% efficiency. The incorporation of fluorine helps to increase the polymer band gap, as observed using UV–vis spectroscopy, but lowers the polymer $T_{g'}$ as shown by differential scanning calorimetry. Both the displacement–electric field (D-E) hysteresis loop and high-field conduction measurements show increased conduction loss for polymers with higher fluorine content, despite their larger band gap. The presence of excess free volume may play a key role in increasing the conduction current and lowering the efficiency of polymers with high fluorine content. Such an improved understanding of the effect of fluorination on the polymer energy-storage properties, as revealed in this systematic molecular engineering study, broadens the basis of material-informatic proxies to enable a more targeted codesign of scalable and efficient polymer dielectrics.

KEYWORDS: high temperature polymer dielectrics, fluorine, energy-storage properties, capacitors

1. INTRODUCTION

Advancement of energy-storage and electrification technologies plays a key role in the replacement of traditional fossil fuel energy sources with renewable ones such as wind and solar energy.¹⁻⁴ Electrostatic capacitors are fundamental energystorage devices for electric and electronic systems where instantaneous energy/power is required because capacitors allow energy to be stored over a long charging time and released over a very short period of submicroseconds to multimilliseconds.^{5,6} The ever-increasing demand for land and sea transportation electrification and compact, lightweight consumer electronics demands high-energy-density and highefficiency capacitors.^{7,8} The dielectric materials used in a capacitor determine the capacitor's performance. Polymers are the first choice of materials as a dielectric for building capacitors because of their light weight, flexibility, processing scalability, and, most importantly, graceful failure mode.^{9–13}

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Scheme 1. Polymer Synthesis Using the ROMP Technique



The dielectric constant and breakdown strength of a polymer dielectric placed between two conducting plates determine the energy density of the capacitor according to eq 1^{14}

$$U = \frac{1}{2}\varepsilon_0 \varepsilon E^2 \tag{1}$$

where ε is the relative permittivity, E is the breakdown strength of the polymer used, ε_0 is the vacuum permittivity, and U is the total energy density.

Currently, biaxially oriented polypropylene (BOPP) is a state-of-the-art dielectric polymer widely used because of its high breakdown strength of 700 MV/m as a result of a large band gap (~7 eV).¹⁵ Unfortunately, BOPP suffers from a low dielectric constant of 2.2 and a low operating temperature of 85 °C.^{16–18} The latter limits the use of capacitors from applications above 100 °C, unless complex cooling systems are used to withdraw heat from the capacitor for continuous operation.¹⁹ To overcome this issue, a new family of hightemperature polymers has been developed. Unlike conventional high-temperature polymers, which could not perform at high electric fields even at room temperatures due to their low band gaps,²⁰⁻²² these new high-temperature polymers are all designed with large band gaps. The band gap indicates the energy required for an electron to travel from the valence band to the conduction band and is set to withstand the limit of a dielectric-to-interband ionization.^{23,24} For stability at high temperatures, polymers need to have high glass transition temperatures (T_g) . Above $T_{g'}$ polymers lose their mechanical integrity, and prominent electrical conduction can be observed. In our recent studies, we demonstrated the inverse correlation between the polymer glass transition temperature and band gap. We also elucidated the drawbacks of conventional hightemperature polymers at high electric fields and the thermal limitations on traditional high-electric-field polymers.^{25,26} These intercorrelated design constraints make it challenging to design novel dielectric materials.

In addition to intrinsic parameters of $T_{\rm g}$ and band gap, extrinsic parameters also have profound effects on dielectric breakdown.²⁷ Due to the complicated interplay of various electronic, thermal, chemical, and mechanical factors, understanding the dielectric breakdown phenomenon is still far from complete. Another approach to improving the breakdown strength for high-temperature polymers is using large-band-gap inorganic materials to make either composites or coatings. However, this approach faces flexibility and processing difficulties along with the cost issue.^{1,28–32} Because the maximum capacitor energy density is proportional to the square of the electric breakdown strength, as mentioned in eq 1, better ideas and studies focused on parameters influencing

the intrinsic electrical breakdown strength of high-temperature polymers are truly needed.³³ This will further advance the innovation of polymer dielectrics with enhanced energy densities at elevated temperatures and high electric fields.

Previous studies have reported that the presence of polar groups or dipoles in the polymer structure influences the dielectric breakdown strength. Dipoles in the polymer structure can act as scattering centers for injected hot electrons and inhibit runaway of the hot electron, leading to an improved breakdown field of the polymers.^{34,35} However, the presence of polar groups, for example, C-F bonds, could introduce defects such as free volume in the polymer structure that could result in deteriorated polymer breakdown strength because excess free volume provides ease of transport of injected hot electrons.³⁶ Experimental work with a systematic polymer design needs to be carried out to better understand this phenomenon and its practical influence on the dielectric properties. Our recently designed polymer dielectrics based on a polyoxanorbornene imide system allow us to systematically study the influence of polar groups on the dielectric properties of polymers with high T_{σ} and large band gap.^{25,37}

In this study, novel polyoxanorbornene imide-based polymers are synthesized. The number of fluorine groups in the polymer structures is varied by the copolymerization of two monomers. The polymer system used here itself demonstrates simultaneous high T_g and large band gap, unlike other high-temperature polymers, and is hence suitable for applications where an elevated temperature is required.

2. MATERIAL SYNTHESIS AND PROCESSING

2.1. Pentafluorooxanorbornene Imide Monomer Synthesis. The monomer was synthesized according to the synthesis scheme shown in Scheme S1 using the Diels-Alder reaction. The reaction was carried out in a flame-dried 500 mL two-neck round-bottomed flask, equipped with a magnetic stir bar. All reactions are carried out under an argon atmosphere. In the first step, the flask was charged with 1.0 equiv of maleic anhydride, to which anhydrous toluene was added using the cannula transfer method to dissolve maleic anhydride. To this solution was added dropwise via syringe with stirring 1.5 equiv of 2,3,4,5,6-pentafluoroaniline dissolved in toluene. The reaction mixture was then stirred at 50-60 °C for 5-6 h and then cooled to room temperature to give a white residue. The obtained solid white precipitate was then filtered and washed with an excess of pentane or hexane to remove excess pentafluoroaniline to give a white amic acid powder. The obtained amic acid powder was vacuum-dried and used for subsequent reactions without further purification.

The obtained amic acid (1.0 equiv) and anhydrous sodium acetate (0.5 equiv) were placed in a one-neck round-bottomed flask equipped with a magnetic stir bar. Anhydrous acetic anhydride was then added to this mixture, and the mixture was heated at 70 °C for 8 h under an argon atmosphere. The reaction mixture turned dark brown. The mixture was then cooled to room temperature and poured into a conical flask containing ice and a magnetic stir bar. The flask was then placed in an ice bath and further stirred for 30 min; an off-white solid precipitated from the brown solution, which was then collected by filtering under vacuum. The collected solid was then washed with excess water and recrystallized in an ethanol/hexane (5:95) mixture to give a white crystal imide product, which was further dried under vacuum to remove excess solvent.

In the next step, the Diels–Alder reaction was used to make a final product. Here, 1 equiv of imide obtained in the previous step was dissolved in acetonitrile. To this solution was added 2 equiv of furan under an argon atmosphere. The reaction was carried out at 50-60 °C for 24 h, and then the mixture was cooled to room temperature. Excess furan and acetonitrile were then removed from the reaction mixture using a rotary evaporator under vacuum. The obtained solid product was further recrystallized using an ethanol/hexane mixture to give a white crystal product, which was dried under vacuum to remove excess solvent and to obtain the final pentafluorooxanorbornene imide product.

2.2. Oxanorbornene Imide Monomer Synthesis. Oxanorbornene imide monomer was synthesized using a previously reported reaction method using *exo-3,6-epoxy-1,2,3,6-tetrahydrophthalic anhydride and aniline.* The reaction scheme is shown in Scheme S2.

2.3. Polymer Synthesis. All polymers were synthesized using the ring-opening metathesis polymerization (ROMP) technique, as shown in Scheme 1. For example, to synthesize POF100 homopolymer, 2.5 g of pentafluoronorborneneimide monomer was weighed in a 100 mL round-bottomed flask equipped with a magnetic stirrer. The monomer was then dissolved in 25 mL of anhydrous dichloromethane (DCM). The monomer solution was then stirred under an argon atmosphere at room temperature. In the next step, Grubbs second-generation catalyst was weighed in a 20 mL scintillation vial, and 5 mL of DCM was added to dissolve the catalyst. The prepared catalyst solution was then added to the monomer solution under an argon atmosphere in one shot at room temperature. The reaction mixture started to become viscous; the reaction was allowed to continue for 2 h. At the end, the reaction was terminated by adding excess ethyl vinyl ether (EVE) and allowed to stir for an extra 20 min. The prepared polymer was then precipitated by the dropwise addition of a polymer solution into vigorously stirring methanol. The solid polymer was then separated using vacuum filtration to give a brownish solid polymer. The obtained polymer was further purified by dissolving in tetrahydrofuran and precipitating in methanol to give a white polymer product, which was further dried under vacuum at 60-70 °C for 48-72 h to give pure polymer. Similarly, copolymers were synthesized using an appropriate mole ratio of fluorinated and oxygenated norbornene (FNB and ONB) monomers.

2.4. Film Processing. Polymer films were processed by using the solution-casting method. Polymers were first dissolved in a dimethylacetamide solvent with a 12% concentration. This solution was then filtered through a

0.45- μ m gel permeation chromatography (GPC) filter. The doctor blade assembly was used to cast the film from the filtered solution on the glass plate using a 380 μ m applicator, where the glass substrate was preheated at 40 °C. The cast wet film was then allowed to dry at 40 °C for 2 h and then at room temperature for 12 h. The film was then removed from the glass substrate by using water and a blade to obtain a flexible freestanding polymer film. The film was further vacuum-dried to remove excess solvent.

3. RESULTS AND DISCUSSION

3.1. Structural Characterization. The chemical structures of synthesized monomers and polymers were charac-



Figure 1. (a) DSC analysis and (b) TGA (5% weight loss temperature) of synthesized polymers.

terized by using ¹H and ¹⁹F NMR analysis (Figures S1–S4). ¹H NMR of polymers in a dimethyl sulfoxide solvent was used to calculate the practical amount of fluorine in the copolymer structures, and the copolymer composition was determined. As shown in Figure S2a, the ¹H NMR spectrum for POF100 does not show any peak in the aromatic region of 7.50 ppm. As the fluorine amount was decreased, the area under the aromatic region around 7.50 ppm continued to increase, as shown in Figures S1–S4. The ratio of peaks of the area under the aromatic region and the area under double bonds at 3.75–3.50 ppm was used to calculate the practical copolymer composition, and it matches closely with the theoretical



Figure 2. Band-gap measurement of (a) POF25, (b) POF50, and (c) POF100 and (d) T_g versus band gap comparison for synthesized polymers.

ratio. All fluorine-containing polymers show similar peaks at around -142, -150, and -161 ppm for 19 F NMR.

3.2. Thermal Characterization. T_{g} analysis is another way of verifying the copolymer composition. Theoretical T_g values for the copolymers were calculated using the Flory-Fox equation and compared with practical T_g values from differential scanning calorimetry (DSC) analysis. It was observed that the $T_{\rm g}$ values match closely. As shown in the polymer structure in Scheme 1, synthesized polymers contain a backbone with aliphatic cyclic groups, which imparts rigidity to the polymer structure to some extent. The presence of rigid aromatic side groups helps in the further improvement of T_{g} Comparing the T_g values of POF100 and PONB homopolymers indicates that the substitution of hydrogen atoms on the side benzene groups with fluorine results in a substantial decrease in $T_{\rm g}$ from around 228 to 204 °C. The repulsive forces between fluorine groups due to partial negative charges on the fluorine introduces free volume in the polymer structure, which leads to reduced $T_{g'}$ whereas the rigid

structure of the PONB polymer shows higher T_g . As the fluorine amount is increased, the T_g value decreases and follows the sequence POF100 < POF50 < POF25 < PONB. Theoretical T_g values for POF25 and POF50 are 220.98 and 214.63 °C, respectively, calculated using the Flory–Fox equation, which is very close to the practical T_g values of 222.92 and 214.49 °C. Single T_g values with close proximity to theoretical T_g values indicate that the polymer obtained is a random copolymer. Thermogravimetric analysis (TGA) shows that all polymers show an onset of the degradation temperature above 350 °C, confirming the high thermal stability of the polymers (Figure 1). The presence of fluorine does not have a drastic effect on the polymer degradation temperature.

4. BAND-GAP AND DIELECTRIC PROPERTIES

4.1. Band-Gap Measurement. As mentioned earlier, the band gap is an important parameter for breakdown strength determination as well as to control the conduction when a high



Figure 3. Dielectric constant and dielectric loss of (a) POF25, (b) POF50, and (c) POF100.

electric field is applied. Hence, the study of parameters affecting the polymer band gap becomes crucial. All synthesized polymers in this study show band gaps of >4.5 eV, which is high compared to other high-temperature polymers. Traditional high-temperature polymers maintain their high T_g values because of the large number of aromatic groups in their backbone; however, this highly conjugated aromatic system leads to a diminished band gap. For the polymers studied in this work, unlike other high-temperature polymers, the backbone consists of aliphatic cyclic groups. In addition, aromatic benzene is a side group instead of the main polymer backbone. This leads to reduced conjugation or crossconjugation, and a higher band gap is achieved. In our previous study, to accelerate the process of dielectric polymer design, we used a machine-learning approach to predict $T_{\rm g}$ and the band gap for 13000 polymer systems (Figure 2d). As shown in the figure, polymers synthesized in this study show simultaneous large band gap and high $T_g^{38,39}$ Here, we also observe some effect of the fluorine amount on the polymer band gap. The POF100 polymer shows a higher band gap of 4.79 eV

compared to those of POF50 (4.59 eV) and POF25 (4.46 eV) (Figure 2a-c). The band gap was measured using UV-vis spectroscopy on the polymer film. Because a freestanding film could not be made from the PONB polymer, its band-gap measurement was not performed. There is no drastic difference in the band gaps of POF25 and POF50, perhaps because of a small difference in the fluorine amount of the two polymers. However, POF100 shows a noticeable blue shift in the absorption spectra and an increase in the band-gap value. The introduction of electron-withdrawing fluorine leads to an increased electron cloud density on fluorine atoms, reducing the conjugation effect; hence, an increased optical band gap is observed.⁴⁰ This strategy of incorporating strong electronwithdrawing groups along with an unconjugated polymer backbone design can be used to make materials with simultaneous high T_g and high band gap.

4.2. Dielectric Spectroscopy. Dielectric spectroscopy was carried out on the fluorine-containing polymer films with an applied electric field of 100 kV/m. As mentioned earlier, because of the rigid nature of the PONB polymer, freestanding



Figure 4. D-E hysteresis loop and discharged energy density analysis of (a) POF25, (b) POF50, and (c) POF100 at room temperature.



Figure 5. Conduction performance of the synthesized polymers. The solid curves are fitted results using the Schottky law.

films could not be obtained and the dielectric properties of the polymer were not measured. The presence of fluorine imparts flexibility, and freestanding films are obtained. It is observed that the incorporation of free volume with the introduction of fluorine, which is confirmed from DSC analysis, causes a decrease in the concentration of reorientable dipoles, and hence a reduction in the dielectric constant value is observed. The presence of free volume also creates voids (air, dielectric constant ~ 1) in the polymer structure, which results in an overall reduction in the dielectric constant as the fluorine amount is increased. Furthermore, due to the high electronegativity of fluorine, the introduction of fluorine reduces an overall electronic polarization and hence the total dielectric constant of polymer. The POF25 polymer shows a dielectric constant close to 3.00 at 1 kHz (Figure 3a), and the POF100 polymer shows a dielectric constant close to 2.75 at 1 kHz and room temperature (Figure 3c). It is also observed that the dielectric loss at 1 kHz for POF25, especially at elevated temperatures, is less than the dielectric loss for POF50 and POF100 (Figure 3). More large-scale segmental motions in POF50 and POF100 than in POF25 might have led to higher

dielectric-polarization losses. It shall be noted that all polymers studied here show low dielectric losses of <1% at elevated temperatures as well in the frequency range of 1–1 kHz. Looking at the polymer structures, repeat units of the polymer are separated by alternate single and double bonds, where there is no restriction on the rotation of the single bonds, also the side benzene group is free to rotate around the C–N bond. This unique repeat unit structure resembles a piston attached to the crankshaft with freedom of rotation at the molecular level. Hence, stable dielectric constant and low dielectric loss are observed over broad frequency and temperature ranges.

4.3. High-Field Energy-Storage Performance. The discharged energy density as a function of the electric field can be measured by using a displacement–electric field (D-E)hysteresis loop. The D-E loop measurement was performed by using a Sawyer-Tower polarization loop tester with a unipolar positive half-sinusoidal wave of 100 Hz. In D-Eloops, the measured integral charge (equal to D) includes the contribution of the conduction component, so the area between charging and discharging cycles indicates the total energy loss (conduction loss and polarization loss) during the charging-discharging process; i.e., a tighter loop indicates higher efficiency. At room temperature, with an applied electric field of 700 MV/m, POF25 shows a discharged energy density of 6.3 J/cm³ with around 90% efficiency (Figure 4a). As the fluorine content is increased to 50%, no drastic change is observed in the discharged energy density of POF50, and a slight widening of the D-E loop is observed (Figure 4b). However, in the case of POF100, where all of the hydrogen atoms of the pendant benzene groups are replaced with fluorine, the D-E loop widens, and a drop in the discharged energy density (5.5 J/cm^3) is observed with a drastic drop in the charge-discharge efficiency (~50%; Figure 4c). The presence of sufficient free volume in POF100 to transport the injected hot electrons from electrodes causes a drastic reduction of the discharged energy density of the POF100 polymer. POF25 and POF50 polymers were further characterized at 150 °C to investigate their high-field energy-storage performance at elevated temperature. At 150 °C, POF25 and POF50 perform well with a high charge-discharge efficiency of >95% at electric fields of <500 MV/m (Figure S5), outperforming previously reported polymers with a wellbalanced $T_{\rm g}$ and large band gap coupling with optimized fluorination.

4.4. High-Field Conduction. Conduction losses play a major role in the total energy loss at high electric fields due to the nonlinear increase of the conduction current with an increase of the electric field. To further understand the energy losses observed in the D-E hysteresis loop, polymer films were characterized using a designed high-field conduction measurement system.⁴¹ As shown in Figure 5, POF25 shows the lowest conduction current even at a high electric field of 650 MV/m. POF50 shows higher conduction than POF25, and conduction starts even at low electric fields of around 225 MV/m for POF100. These results explain the higher energy losses observed in POF100. The solid curves in Figure 5 are the fitted results using the Schottky law, which indicated that the conduction was attributed to the injected carrier rather than electrons excited from the valence band. As mentioned earlier, the availability of excess free volume in POF100 could help in the ease of transport of injected carriers and lead to increased conduction. Although POF100 exhibits a higher band gap than other polymers, which would suggest lower conduction, the

increase in conduction due to the availability of free volume dominates.

4.5. Conclusion. In summary, we have systematically studied the effect of the incorporation of polar fluorine groups on the structural and electrical properties of high- $T_{\rm g}$ and largeband-gap dielectric polymers. The introduction of fluorine groups imparts flexibility to the polymer film, and free-standing films can be obtained; however, it has an adverse effect on the polymer T_{g} . Due to high electronegativity, fluorine can be used to improve the band gap, especially for high-temperature polymers. It is observed that an increase in the amount of fluorine results in a lowering of the dielectric constant because of a decrease in the total dipole density. Further study of the energy-storage properties indicates that excess fluorine amount in POF100 shows lower energy density and charge-discharge efficiency. Excess free volume in POF100 might have led to ease of transport of the injection of excess carriers and resulted in a lower charge-discharge efficiency.

5. METHODS

5.1. Material Characterization. NMR analysis of synthesized monomers and polymers was carried out using a Bruker AVANCE 500 MHz spectrometer. The T_g values of the synthesized polymers were measured by DSC analysis using a TA Instruments DSC Q-100 differential scanning calorimeter with a heating and cooling rate of 10 °C/min. The degradation temperature of the polymers was carried out by TGA using a TA Instruments TGA Q-500 analyzer with a heating rate of 20 °C/min. UV–vis spectroscopy to measure the polymer band gap was done using an Agilent 5000 UV–vis/near-IR spectrometer. GPC analysis was performed for the molecular weight characterization of the polymers.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.3c08858.

Material synthesis (monomer synthesis schemes and POF100 polymer synthesis scheme), material characterization (NMR spectra of synthesized monomers and polymers and GPC analysis of synthesized polymers), and electrical characterization (D-E hysteresis loop analysis of POF25 and POF50 polymers at 150 °C) (PDF)

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G.S., Y.C., and R.R. directed the research. A.A.D. and C.W. contributed equally to the experiments and manuscript preparation. A.A.D., O.Y., S.S., and A.R.K. contributed to the monomer and polymer synthesis and characterization. C.W. and J.Z. performed the electrical experiments. C.W., T.L., and X.L. did the formal analysis of the conduction. L.C. and R.G. contributed to the plotting of the machine-learning-predicted $T_{\rm g}$ versus band-gap graph. A.A.D. and C.W. wrote the first manuscript, and all authors participated in editing of the manuscript.

Notes

The authors declare no competing financial interest.

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