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Bio-based poly(hydroxy urethane)s for efficient organic high-power energy storage

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ABSTRACT: Fast, low-cost and efficient energy storage technologies are urgently needed to balance the intermittence of sustainable energy sources. High-power capacitors using organic polymers offer a green and scalable answer. They require dielectrics with high permittivity (ε_r) and breakdown strength (E_B), which bio-based poly(hydroxy urethane)s (PHUs) can provide. PHUs combine high concentrations of hydroxyl and carbamate groups, thus enhancing their ε_r, and a highly tuneable glass transition (T_g), which dictates the regions of low dielectric losses. By reacting erythritol dicarbonate with bio-based diamines, fully bio-based PHUs were synthesised with $T_g \sim 50$ °C, $\varepsilon_r > 8$, $E_B > 400$ MV·m^{-1} and low losses (tan $\delta < 0.03$). This results in energy storage performance comparable with the flagship petrochemical materials (discharge energy density, $U_e > 6$ J·cm^{-3}) combined with a remarkably high discharge efficiency, with $\eta = 85\%$ at E_B and up to 91% at 0.5 E_B. These bio-based PHUs thus represent a highly promising route to green and sustainable energy-storage.

INTRODUCTION

The increasing energy demand combined with the need for reduced fossil fuels consumption has led to significant investments in more sustainable energy platforms, such as wind or solar power. The intermittence of these energy sources has made the necessity for fast, low-cost and efficient energy storage technologies critical.[1] Dielectric-based capacitors are strong candidates, due to the high power density (> 1 MW·kg^{-1}) that they inherently afford, resulting from their fast charge and discharge cycles.[1] These capacitors are especially promising for applications where pulse-power is needed such as electric vehicles, most notably for inverters, but also in the food industry, where high power discharges are used to enhance seed germination and sterilize, and in medicine, where they power surgical lasers and defibrillators.[1–4]

The energy density discharged from a dielectric capacitor (U_E) is defined as

$$U_E = \int_{D_{max}}^{0} E \, \mathrm{d}D \qquad (1)$$

Where D is the dielectric displacement and E the electric field, [1] which for linear dielectrics can be simplified as:

$$U_E = \frac{1}{2} DE = \frac{1}{2} \varepsilon_0 \varepsilon_r E^2 \qquad (2)$$

Where ε_r is the relative permittivity and ε_0 is the permittivity of vacuum.

Therefore, an ideal candidate for dielectric energy storage requires a high permittivity and the ability to withstand high electric fields, *i.e.* a high breakdown strength E_b.

Inorganic ceramics of highly polar perovskites, show huge permittivity values,[5,6] but low breakdown fields and high volumetric densities, thus limiting their potential to contribute to the weight reduction required in applications such as electric vehicles. Polymers can typically withstand significantly stronger electric fields, with breakdown strengths 10-100 higher than ceramics, and are also lighter and cheaper to produce. The commercially available organic material of choice is biaxially oriented polypropylene (BOPP), which registers an $E_b \sim 700$ MV·m^{-1}, however, its energy density is ~ 2-4 J·cm^{-3} due to its low permittivity ($\varepsilon_r = 2.2$),[1] which is common for linear dielectrics. Further increasing this energy density would decrease both the environmental impact and the weight of these capacitors, which currently accounts for ~ 25% of the weight of inverters in electric vehicles.[7] Alternatives include non-linear dielectrics, such as ferroelectrics or relaxor ferroelectrics, which show higher permittivities and thus high macroscopic polarization, P. This leads to enhanced U_E as $P \sim D$ in these materials where $\varepsilon_r >> \varepsilon_0$. Polar VDF-derived homo-, copo- and ter-polymers have been intensively studied, especially poly(vinylidenefluoride-*ter*-trifluoroethylene-*ter*-chlorofluoroethylene) P(VDF-*ter*-TrFE-*ter*-CFE), which is a prime candidate for various energy-related applications due to its room-temperature permittivity > 50.[8,9] It has been reported to display high energy densities, with U_e = 5-10 J·cm^{-3} in intrinsic polymers. [10–13] Unfortunately, non-linear dielectrics suffer from high polarization hysteresis, which induces significant dielectric losses and limits the efficiency of the discharged process, η, which can be defined as:

$$\eta = \frac{U_E}{U_E + U_l} \qquad (3)$$

Where U_l is the energy density lost during the discharge process.

Thus, only efficiency values < 70 % were reported near E_b in these high-permittivity petrochemical fluorinated polymers.

A new class of other promising petrochemical polymers have recently emerged as alternatives, referred to as dipolar glass polymers.[14–16] They combine highly polar side groups such as hydroxyl or sulfonyl groups with a high-temperature glass transition (T_g), which increases their operating temperature and decreases the dielectric losses near RT. Contrary to highly crystalline polymers such as BOPP, these amorphous dipolar glasses are more prone to conduction losses from mobile space charges; they are thus operated below their T_g where this mobility is drastically limited. Thus, they display high discharge energy density values, U_e = 4-10 J·cm^{-3}, and can reach efficiencies over 80%.[14–16] Due to their high concentration of hydroxyl groups and highly tuneable T_g, poly(hydroxy urethane)s (PHUs) could meet these criteria, with the added benefits of being isocyanate-free and potentially bio-based.[17] Recently, PHUs have even been considered for energy-related applications, including energy harvesting.[18] Bio-based polymers synthesised from erythritol dicarbonate (EDC) look especially promising as EDC is low-cost, highly reactive and can be produced on large scale, with high conversion yields and in soft conditions from a natural sugar alcohol (i.e. erythritol).[17,19]

In this paper, we demonstrate the potential of bio-based PHUs for energy storage. A series of 100% bio-based PHUs is synthesised from reacting EDC with bio-based diamines (H_2N-$(CH_2)_n$-NH_2) by polyaddition in DMSO at 80 °C. Their dielectric and energy storage performance are then evaluated and compared with "state of the art" intrinsic polymers for dielectric energy storage.[10,11]

RESULTS AND DISCUSSION

The route used to synthesise the 100% bio-based PHUs, which is based on our previously reported work, is shown in Fig. 1a.[19] In addition to being isocyanate-free, these PHUs provide a high density of polar groups with two hydroxyl and two carbamate functions per repeating unit, which is expected to result in significant dielectric properties. Three different PHUs were synthesised, with various α,ω-diamine alkyl chain lengths, namely n = 6, 8 and 12, referred to as PHU6, PHU8 and PH12, respectively. The chemical structure of the PHUs was confirmed by ^{1}H NMR (Fig. 1b and Fig S1). Full conversion of the cyclic carbonates and amines was assumed since no remaining signals at 5.15 ppm (proton of the methine carbon of EDC) and 2.68 ppm (α-proton of NH_2) were detected. As expected, the ratios of secondary to primary alcohols are of about 85 : 15 for the three polymers.[17,19] The number average molecular weight, M_n, and the dispersity, $Đ$, were determined by size exclusion chromatography in DMF (SEC, Fig. S2) and found to be M_n = 8.6, 4.4 and 3.4 kg·mol^{-1} and $Đ$ = 2.2, 3.1 and 2.8, for n = 6, 8 and 12, respectively.

The influence of the diamine alkyl chain length on the glass transition (T_g) was evaluated by differential scanning calorimetry (DSC, Fig. 1c). It revealed that T_g decreases with increasing values of n, from 50 °C, to 40 °C and 22 °C for n = 6, 8 and 12, respectively, as shown in the inset of Fig. 1c. Though this trend is to be expected, it should be noted that some of these variations may also be attributed to the differences in molecular weight, which also influences the position of T_g. It is worth noting that PHU12 exhibits a melting temperature, T_f =59 °C, as a result of the longer and more flexible alkyl chain, which facilitates the packing of polymer chains required for the growth of crystalline lamellae. As it displays both the highest T_g and the highest density of dipolar groups, PHU6 was selected for the rest of the study.

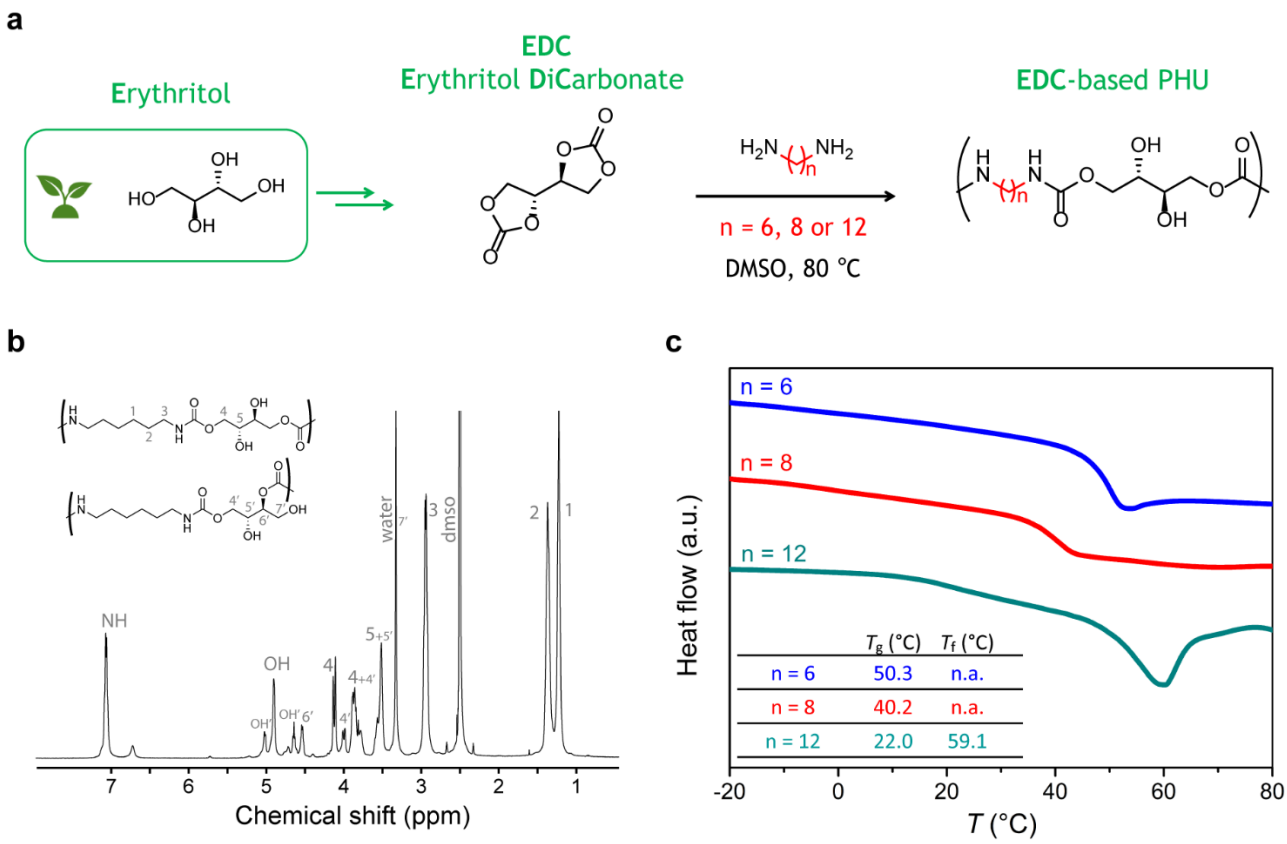

Figure 1. (a) Synthesis route to EDC-based PHUs. (b) ^{1}H NMR spectrum of PHU6. (c) DSC thermograms for the various EDH PHUs (10 °C/min, second heating).

The dielectric properties of PHU6 were evaluated by casting capacitors from solutions in DMSO. A permittivity of 8.4 was measured on PHU6 at 1 kHz in the vicinity of room temperature (Fig. 2a). While it is lower than that of the semi-crystalline fluorinated polymers ($\varepsilon_r \sim 50$),[9–11] it is high when compared with other amorphous polymers which typically display $\varepsilon_r \sim 2$-4. Furthermore, this high permittivity was found to be accompanied with low dielectric losses, with tan $\delta < 0.03$ measured in the same conditions, thus promising stable properties at high electric fields for PHU6. Although lower than that of BOPP, dielectric losses in that range can provide the high discharge efficiencies required for reliable operation.[20] The high-field stability was confirmed by its breakdown strength (E_b).[21] The two-parameter Weibull distribution analysis[21] of PHU6 revealed a high $E_b = 428$ MV·m^{-1}, which is comparable with that measured for fluorinated polymers (270-490 MV·m^{-1}).[10,11] The relatively high shape parameter, $\beta = 5.9$, also indicates a narrow breakdown strength distribution, which is be expected to increase performance reliability of the devices made from this EDC-based PHU. The high breakdown field of PHU6 allows for high polarization values to be reached, despite its linear dielectric behaviour, with $P_{max} = 3.2$ μC·cm^{-2} measured at E_b (Fig. S4a). This remains low compared to fluorinated polymers, in which $P \sim 10$ μC·cm^{-2} can be reached at E_b, even if their permittivity decreases significantly at higher field due to their non-linear behaviour.[10,11]

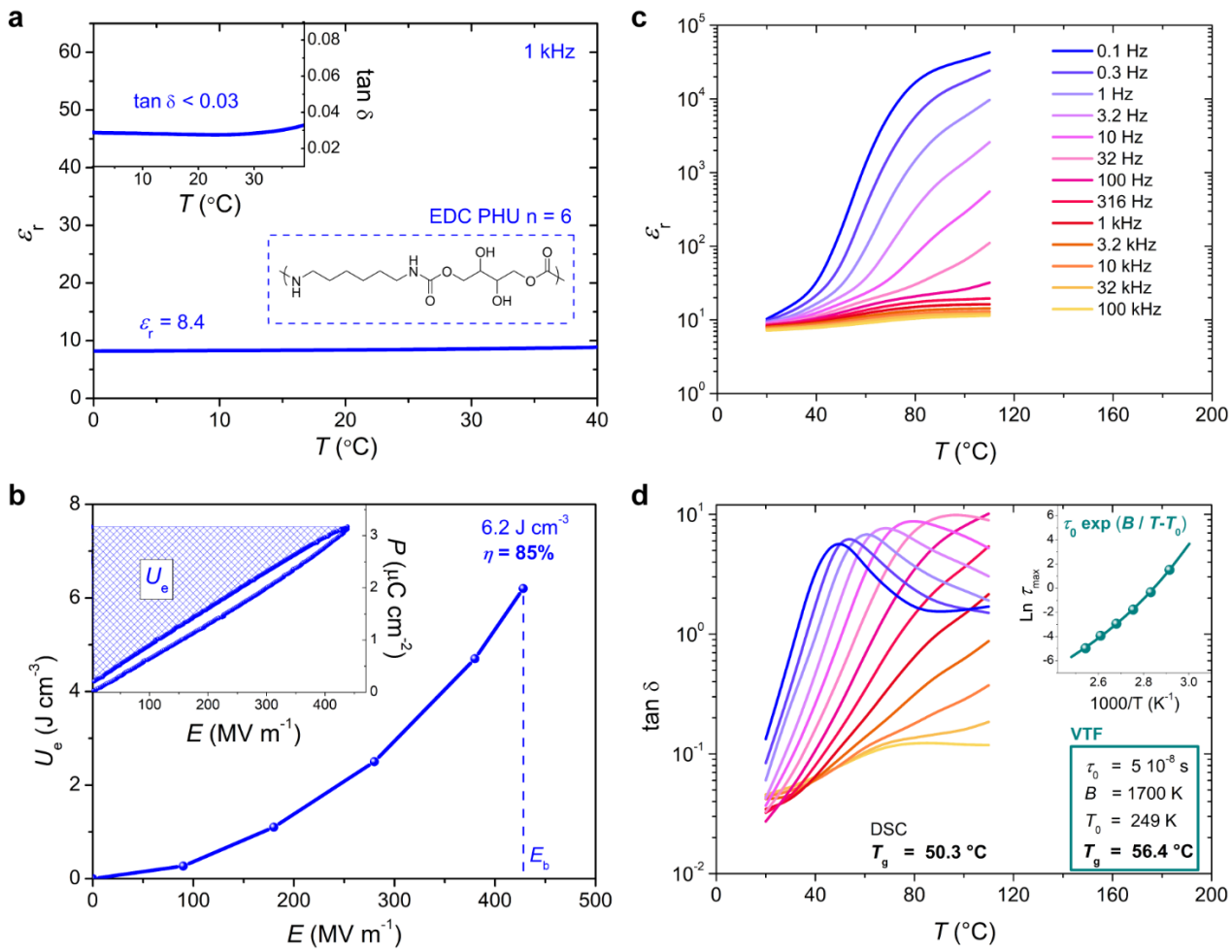

Figure 2. (a) real part of the low-field permittivity versus temperature at 1 kHz (dynamic, 10 °C min^{-1}). (b) Polarization versus electric field at E_b (inset, 100 Hz, room temperature) and corresponding efficiency versus discharged energy measured on PHU6. (c-d) Broadband dielectric spectroscopy versus temperature measured on PHU6: (c) real part of the permittivity and (d) loss tangent. The inset of (d) displays the Vogel-Tammann-Fulcher fit of the maximum relaxation time and the corresponding factors extracted from the equation.

Nonetheless, the combination of high E_b, linear non-coercive behaviour (confirmed by the bipolar loops in Fig. S4(b)) and low losses (the area inside the "P-E loop" is minimal) maximises the discharged energy density U_e in PHU6, which corresponds to the highlighted area above the "P-E loop", as shown in the inset of Fig. 2b. Monitoring U_e versus E reveals that U_e is much lower in PHU6 than in fluorinated polymers at low fields (E < 300 MV·m^{-1}), as expected from the differences in low-field dielectric permittivity.[10–13] However, when E reaches the vicinity of E_b, the quadratic dependence in E allows PHU6 to reach an impressive value of U_e > 6 J·cm^{-3} and thus to catch up with the state-of-the-art fluorinated polymers. Due to the low volumetric mass density of PHU6, this corresponds to a specific energy of 2 Wh·kg^{-1}, which is comparable with the performances recorded in electrochemical capacitors,[22] but with a far greater power density of ~ 10^8 W·kg^{-1}, assuming a full discharge time, $\tau = 5RC$, through a

resistor R = 100 kΩ, with C the capacitance of the polymer-based device. Furthermore, the low dielectric losses in PHU6, combined with reduced conduction losses (Fig. S5), induce a highly efficient discharge process, with a remarkably high efficiency, η = 85 %, measured in the bio-based PHU at E_b, which is much higher than the efficiencies typically measured in high performance fluorinated polymers, with η < 70 % as shown in Fig. 3.[10–13] For a more reliable field of operation, E ~ 0.5 E_b (235 MV·m^{-1}), η = 91 % was measured in PHU6. This remarkable efficiency ranks among the best reported values intrinsically measured on linear dielectrics, including biaxially oriented polypropylene (BOPP)[20,23–25] and dipolar glasses (DG).[15,16,25–28] With the exception of BOPP, the performance reported in Fig. 3 were limited to intrinsically measured materials at E_b. We excluded polymers subjected to material processing or device architecture specifically dedicated to high-field applications (sandwich multilayers, stretching, crosslinking, nanocomposites, …) where U_e > 15 J·cm^{-3} can be reached while maintaining high discharge efficiencies.[7,29–31] It is worth noting that, such strategies could also be applied to the PHUs presented here to further improve their energy density, by increasing E_b, but also bring their efficiencies even closer to that of BOPP, by limiting conduction losses. The large discrepancies between reported results on fluorinated polymers, even for similar compositions, with U_e ~ 5-10 J·cm^{-3} and η = 50-70 % at E_b, are most probably due to the strong influence on the dielectric properties of their structural parameters, especially the crystallinity, which are highly dependent on the casting/annealing conditions.[32]

The origin of the dielectric enhancement in PHU6 was elucidated by performing broadband dielectric spectroscopy (BDS) at various temperatures (Fig. S6). BDS confirms that the high permittivity of PHU6 near RT is maintained over a broad range of frequencies. The dielectric properties are remarkably stable with frequency, even at high frequencies with ε_r = 8.6, 8.4 and 7.7 at 100 Hz, 1 kHz and 10 kHz, respectively (Fig. 2c). Rising the temperature results in a significant change in permittivity with ε_r increasing by several orders of magnitude, especially at low frequencies. However, a closer inspection of the dielectric losses (Fig. 2d) reveals that this jump in ε_r is accompanied with a massive increase in tan δ. This behaviour is related to the increased mobility of space charges, afforded by the proximity of the glass transition temperature. The maximum in dielectric losses gradually shifts to higher temperatures with increasing frequency. Its attribution to the glass transition is confirmed by the Vogel-Tammann-Fulcher (VTF) dependency of the maximum relaxation time τ_{max} with inverse temperature (inset of Fig. 2d). The extrapolation of the VTF equation to τ_{max} = 100 s, defined as τ_{max} (T_g) by Angell et al.,[33] reveals a glass transition temperature T_g = 56 °C, which is in good agreement with the static value of T_g = 50 °C obtained by DSC measurements. These results highlight the importance of tuning the glass transition temperature in order to keep it well over the temperature range of interest, in order to minimize the energy dissipated during the discharge process, through the suppression of electronic and ionic conductions in the glassy state. The position of T_g is all the more important for high temperature applications (T > 100 °C), such as inverters in electric vehicles, which have recently garnered significant attention.[24,25,28,34–36] While the PHUs presented here are not suitable for applications where T > 50 °C, the wide variety of available precursors (i.e. polyamines and polycarbonates) to access to this family of materials can also offer high temperature solutions. The use of a more rigid bio-based diamine, such as isophorone diamine (IPDA), could significantly increase the T_g, with reported values up to 140 °C,[37,38] while remaining 100%-

bio-based and still benefiting from the highly polar hydroxy urethane group. Reacting IPDA with sorbitol-derived trifunctional cyclic carbonates could even produce bio-based thermosets,[37] in which the crosslinking would further decrease conduction losses and enhance the E_b.

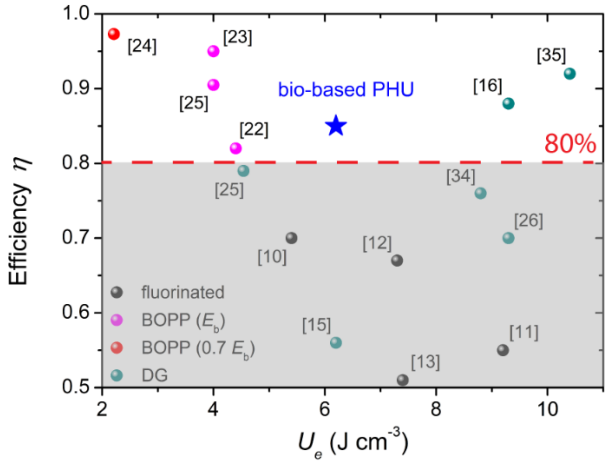

Figure 3. Comparison between the energy storage performance, efficiency η vs. discharge energy density U_e, of our bio-based PHU with recent literature reports measured intrinsically on state-of-the-art petrochemical polymers at E_b, including fluorinated polymers, biaxially oriented polypropylene (BOPP) and dipolar glasses (DG).

The high frequency loss tangent data also reveal another peak, especially visible near 70 °C at 100 kHz. It suggests the presence of a sub-T_g local β relaxation, which would thus play an important role in the dielectric enhancement measured near RT, by allowing a degree of dipole mobility below T_g. Such transitions have been previously observed in polyurethanes and attributed to the movements of the polar carbonyl groups of the urethane hydrogen-bonded to water molecules in these particularly hygroscopic materials.[39] Understanding and controlling these phenomena will be key to further enhancing the energy storage performances of these highly promising bio-based polymers.

CONCLUSIONS

In summary, we have synthesised an isocyanate-free 100%-bio-based poly(hydroxy urethane) with a glass transition temperature near 50 °C and a high density of polar groups, granting it high dielectric permittivity and low losses near room temperature. The combination of its high breakdown strength, with $E_B > 400$ MV·m^{-1}, linear dielectric behaviour and low losses, enables this PHU to reach energy storage performance comparable with the state-of-the-art petrochemical polymers with a remarkably high discharge efficiency with $\eta = 85\%$ at E_B and up to 91% at 0.5 E_B. While this efficiency remains lower than BOPP, the possibility to reduce the mass/volume of plastic used,

afforded by the increased discharge energy density (U_e > 6 J·cm^{-3}) and their 100%-bio-based origin, highlight that these PHUs represent a promising route to environmentally-friendly energy-storage.

ASSOCIATED CONTENT

Supporting Information

Materials and methods, ^{1}H NMR spectra, SEC traces,
two-parameter Weibull distribution analysis of the breakdown strength, *P-E* loops, leakage current density, broadband dielectric spectroscopy.

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Notes

The authors declare no competing financial interests.

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