Optimizing Nanostructure to Achieve High Dielectric Response with Low Loss in Strongly Dipolar Polymers

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Abstract:

Advances in modern electronics require the development of polymer-based dielectric materials with high dielectric constant, low dielectric loss, and high thermal stability. Fundamental

dielectric theory suggests that strongly dipolar polymers have the potential to realize a high dielectric constant. In order to achieve high thermal stability, these polymers should also possess a high glass transition temperature T_g . However, it has been observed that in many dielectric polymers the dielectric constant decreases markedly at temperatures below T_g due to dipole freezing. This study shows, through combined theoretical and experimental investigations, that nano-structure engineering of a weakly-coupled strongly-dipolar polymer can result in a high energy density polymer with low loss and high operating temperature. Our studies reveal that disorder creates a significantly larger free volume at temperatures far below T_g , enabling easier reorientation of dipoles in response to an electric field in aromatic urea and thiourea polymers. The net result is a substantial enhancement in the dielectric constant while preserving low dielectric loss and very high breakdown field. These results here pave the way for engineering the nanostructure to create high energy density polymers with low loss and high operating temperature.

Highlights

- A nano-engineering approach for achieving high dielectric constant while maintaining low loss and high thermal stability in polymer dielectrics is reported.
- A combined theoretical and experimental study uncovers the critical role of free volume in generating high dielectric response in the glass state of strongly dipolar polymers.
- Disordered structure in strongly dipolar polymers in the glass state can effectively generate large free volume, allowing for easy re-orientation of dipoles.
- High energy density with low loss and high operating temperature was demonstrated in disordered meta-phenylene polyurea polymer films.

Keywords- Nano-dielectrics, energy storage, free-volume effect, high thermal stability.

Introduction

Polymer dielectric materials are ubiquitous in modern power electronic systems^[1–3]. They are highly desirable for applications in the area of capacitive energy storage^[3–8], transistors^[9–11], photovoltaic devices^[12–14] and electrical insulation^[15,16]. The demand for capacitive energy storage has increased due to continuing electrification of land^[1,17] and sea^[18] transportation, as well as military and civilian systems^[18,19]. These applications require capacitors with high energy density, low loss, high efficiency and high operating temperature. Compared to ceramics and electrolytic capacitors, polymer-based capacitors are attractive because they feature low manufacturing cost and low dielectric loss, can be used under high voltage due to high breakdown strength, and fail gracefully with an open circuit^[3]. In many of these devices and systems, capacitors constitute a substantial fraction of volume and weight (> 30% volume and weight)^[1,4,20–22]. To meet the demand of continued miniaturization of modern electrical and electronic devices and systems, the energy density of dielectric polymers must be improved. In general, the energy stored in a capacitor is proportional to the dielectric constant and the square of the electric field. Therefore, the materials of interest should display high dielectric constant and high breakdown strength. The present state-of-the-art high energy density film capacitors use biaxially oriented polypropylene (BOPP), with a low dielectric constant K of 2.2 and operating temperature below 100 °C, due to its low melting temperature ($T_m < 140$ °C)^[21]. Extensive materials development efforts have led to several alternative dielectric polymers, including polycarbonate (PC), poly(ethylene terephthalate) (PET), and poly(phenylene sulfide) (PPS) with high operating temperatures (>125 °C). However, the dielectric constant of these polymers is still below 3.3^[21,23].

The strong coupling among dipoles have led to high dielectric constants of polyvinylidene fluoride(PVDF)-based ferroelectric polymers ($K > 10$)^[4,24–26]. By proper defect modifications of PVDF-based polymers, we showed that these polymers can achieve either a high dielectric constant at room temperature ($K > 50$) or a very high energy density ($> 25 \text{ J/cm}^3$)^[27–29]. However, the strong dipolar coupling in these ferroelectric polymers causes high polarization hysteresis loss. Moreover, the operating temperature is still limited to below 125°C due to low T_m ($< 140^\circ\text{C}$)^[21,23]. Nevertheless, the results demonstrate the potential of tailoring nano- and meso-structures of dielectric polymers to achieve high dielectric performance.

We note that in earlier studies of strongly dipolar polymers with very weak coupling among dipoles, such as polyurethane, the polymers show a low loss but also low dielectric constant at temperatures below the glass transition temperature. On the other hand, these polymers exhibit a large increase in dielectric constant after undergoing a glass transition at T_g , e.g., $K > 6$ ^[30,31]. The penalty is that the dielectric loss is also increased markedly (loss $> 5\%$). The large increase in the dielectric constant observed above T_g in these strongly dipolar polymers is attributed to an increase of the empty spaces surrounding the dipoles termed “free-volume effect” which makes it easier for dipoles to follow the applied field, and hence reach a higher dielectric constant. However, large-chain-segment motions above T_g , which have long relaxation times, also causes high dielectric loss^[31]. Now the question is whether one can design a strongly dipolar polymer that can generate the “free volume effect” at temperatures below T_g , thus leading to high K while avoiding large-chain-segment motion causing dielectric loss. If T_g is at a high temperature (for example, $T_g > 200^\circ\text{C}$), the polymer may also have a high operating temperature ($> 150^\circ\text{C}$).

In this work, through a combined theoretical and experimental investigation, we show that such a polymer with high T_g can be realized in several recently developed strongly dipolar polymers based on aromatic urea and thiourea units, with dipole moments of 4.5 Debye and 4.89 Debye, respectively, ^[8,32–34] which are much higher than for VDF in PVDF based polymers, with the dipole moment of 2 Debye ^[24–26]. It is the free volume effect (FVE) at temperatures below T_g ($> 200^\circ\text{C}$) that leads to a high dielectric constant ($K > 5.6$) in *meta*-phenylene polyurea (*meta*-PU) (see Scheme 1 for the chemical structure). It also possesses very low loss (high charge/discharge efficiency) even at very high electric fields (> 600 MV/m).

Theoretical and Experimental Methods

Theoretical methods

To obtain the atomic structures of *meta*-PU, we first apply simulated annealing to the four starting geometries. Classical molecular dynamics package LAMMPS^[36] is used, with force field reaxFF^[37]. A periodic simulation cell of 64 monomers (1024 atoms) is employed, and there are 8 polymer chains in the cell. In simulated annealing, the structures are first heated to and equilibrated at 600 K for 1 ns. They are then cooled to 300 K at a rate of 25 K/100 ps. The last step is equilibration at 300 K for 1 ns. The NPT ensemble is used in annealing, with Nose-Hoover thermostat for temperature and pressure control. The ionic contribution to the dielectric constant is given by the following equation, ^[38–42]

$$\varepsilon_{\alpha\beta}(0) - \varepsilon_{\alpha\beta}(\infty) = \frac{4\pi}{\Omega k_B T} \mathbf{M}_{\alpha\beta}, \quad (3)$$

where α and β stand for the three Cartesian directions, Ω is the volume of simulation supercell, k_B is Boltzman constant, and T is temperature. $\mathbf{M}_{\alpha\beta}$ is the covariance of two dipole moment components α and β . To get the matrix $\mathbf{M}_{\alpha\beta}$, the dipole moment is calculated in the NVT

ensemble at 300 K every 10 fs for 1 ns. The electronic permittivity tensor is obtained by density functional perturbation theory (DFPT) calculations.^[43] To save computational time, a 128-atom simulation cell containing 2 chains with 4 monomers in each is employed. The same four starting geometries are used. We first anneal the structures in classical MD, and then re-optimize the structures at the DFT level, using the QuantumEspresso package^[44]. The electronic permittivity tensor is calculated only for the lowest energy structure. We chose ultrasoft^[45] pseudopotentials with exchange-correlation functional PBE+D^[46,47]. Energy cutoffs of 35 and 420 Rydbergs are used for electron wave functions and electron charge density, respectively.

Synthesis and film fabrication

All chemicals were purchased from Sigma-Aldrich. *meta*-PU was synthesized by polycondensation of *meta*-phenylenediamine and diphenyl carbonate as shown in Scheme 1^[33]. After purification, *meta*-PU was isolated as pinkish powder. To prepare the films, *meta*-PU powders were dissolved in dimethylformamide (DMF) to make 1.0 - 2.0 weight % solution. The thin films were prepared by casting the solution onto silicon substrates pre-coated with 40 nm of platinum at 80 °C overnight, and then annealed at 140 °C under vacuum for 12 hours.

PEEU was prepared from (*m*-phenylenedioxy) dianiline and diphenyle carbonate by thermal polycondensation as shown in Scheme 2. The mixture of the two monomers was stirred at 150 °C in vacuum for 4 hours, and PEEU powder was obtained through purification with ethanol for multiple times. PEEU films were prepared by dissolving the powders in DMF at elevated temperature, and solution cast at 80 °C for 2 days, followed by annealing at 150 °C for 2 days.

Measurement of dielectric properties of Polymer Powders (ordered structures)

It is not easy to directly measure the dielectric constant of polymer powders. Here a composite approach, i.e., mixing the powder with a fluid that does not affect the powder, was employed for

the dielectric characterization. Gold-sputtered glass slides were used as the electrodes to form a parallel-plate capacitor. The electrodes were separated by Kapton tape spacers with thickness of 64 μm . The area of the electrode was 1 cm x 1 cm (and repeated with 0.5 cm x 0.5 cm electrode area). Fluid (castor oil) with dielectric constant of 4.7 was chosen to make slurry with meta-PU powder. The rationale behind this approach was that if the capacitance of a cell filled with the reference fluid is lowered by adding powder, the dielectric constant of the powder is lower than that of the fluid. The dielectric constant of the mixture was measured as 4.6. The dielectric constant of PEEU powders was measured in the same way.

Electrical Characterization

The dielectric properties at variable temperature were measured using an HP 4284 impedance analyzer, which was connected to an environmental test chamber (Delta 9023). The Polarization-Electric field (P-E) response was measured with a modified Sawyer-Tower circuit. The charged (stored) energy density, discharged (released) energy density and efficiency were calculated from the P-E loop. The x-ray diffraction data were collected using a Panalytical Xpert Pro MPD diffractometer.

Results and discussion

We first present the theoretical results. A computer simulation study of *meta*-PU is carried out by first constructing trial structures and performing simulated annealing in classical molecular dynamics to find possible crystalline configurations. Four initial guesses of the crystal structures are created as shown in Fig. S1. Interestingly, only one of the four structures converges to an ordered crystal-like structure after simulated annealing, see Fig. 1. This ordered structure has an antiparallel arrangement of dipole directions of the chains. The other three structures converge to

disordered structures, in which the chains are misaligned in the xy-plane. However, there is no entanglement of the chains. All chains are parallel to the z-axis but are misaligned. The tendency of *meta*-PU to be disordered may be attributed to the weak dipole-dipole interaction.

The calculation of dielectric constant is divided into two parts, the ionic and electronic contributions. The diagonal elements of electronic permittivity tensor of ordered structure are $\epsilon_{xx}(\infty)=3.09$, $\epsilon_{yy}(\infty)=2.63$, and $\epsilon_{zz}(\infty)=4.36$. The electronic permittivity tensor is averaged spherically and $\epsilon_{avg}(\infty)=3.36$. We use the same numbers for all *meta*-PU structures, since the electronic contributions are similar for different configurations and are not affected much by the arrangement of chains. The ionic contributions are shown in Table 1 for the four *meta*-PU structures. Significantly larger ionic permittivities are found in the misaligned disordered structures. Fig. 2 presents a comparison of the ionic contributions of the disordered (averaged over the 3 disordered structures) and the ordered structures. The total dielectric constants of ordered and disordered structures are presented in Table 2.

The ionic permittivity is proportional to the variation of the dipole moment. Therefore, a larger dipole motion could lead to a larger permittivity. The specific volume is ~12% larger in the disordered structures compared to the ordered structure. The larger volume gives urea units more free space to vibrate. In both the ordered and disordered structures, the dipole moment of the urea lies in the xy-plane (randomly oriented in the disordered structure). Two types of the single-urea motion cause variation of the dipole moment as shown in Fig. 3: (i) wiggling in the plane containing the chain, and (ii) rotation in the xy-plane. Intuitively, the rotation causes larger dipole-moment variation. Therefore, we define the direction of the dipole in the xy-plane to be its orientation angle, and use the variation of this angle to represent the activity of urea units. The disordered structures have the variation 70~100% larger than the ordered structure.

Phonon densities of states are calculated for the ordered and disordered structures of *meta*-PU and are shown in Fig. S2. Low frequency phonons contribute more significantly to the total dielectric constant,

$$\epsilon_{\alpha\beta}(0) = \epsilon_{\alpha\beta}(\infty) + \frac{4\pi}{\Omega_0} \sum_m \frac{S_{m,\alpha\beta}}{\omega_m^2}, \quad (1)$$

where $S_{m,\alpha\beta}$ is the mode-oscillator strength tensor, ω_m is the phonon eigen frequency and $\epsilon_{\alpha\beta}$ is the permittivity tensor. Therefore, the disordered structures 2 and 3 have much larger ionic permittivities, because the lowest phonon peaks have shifted to lower frequencies. The misaligned geometries in the disordered structures introduce slow collective motions, therefore allowing lower energy optical phonons.

The increase in free volume in the disordered structure gives rise to an enhancement in permittivity. More importantly, this mechanism does not introduce high loss, as shown by the experimental data on *meta*-PU. To further confirm that disorder is responsible for the high dielectric constant, we have also performed simulations for aromatic polyurea (ArPU), see the molecular structure in Scheme S1. The simulations led to four ordered structures, corresponding to the four starting geometries. To mimic a disordered structure of ArPU, we artificially mixed the four initial ordered structures and did simulated annealing. As shown in Table S1, the disordered structure has a higher dielectric constant than the ordered one. To test this procedure, the same mixed disordered structure is created for *meta*-PU. After simulated annealing, the three “annealed” *meta*-PU disordered structures and the blended *meta*-PU disordered structure have almost the same total energies and similar ionic permittivities.

The simulation results show unequivocally that the presence of large free volume in the disordered structure can lead to higher ionic permittivity, compared with that of the ordered structure. A large free volume enables easier reorientation of dipoles in response to an electric

field. Moreover, the lack of long-range order removes a lower bound on the energies of optical phonons and enables longer wavelength vibrations, which also increase permittivity.

To compare with the theoretical results, *meta*-PU with ordered (crystalline) and disordered phases were prepared. It is interesting to note that the as synthesized *meta*-PU powder shows relatively sharp X-ray diffraction peaks, visible in Fig. 4(a), indicating the presence of a crystalline phase in addition to an amorphous component. The crystalline structure from computer simulations (shown in Fig. S3) and its lattice constants match well with the lattice spacing (the X-ray peaks) in Fig. 4(a). In contrast, the films made from solution casting display a broad X-ray peak centered at $2\theta = 9.5^\circ$, shown in Fig. 4(b), indicating an amorphous (disordered) structure. TGA and DSC data (see supporting online materials, Fig. S4 and S5) show no sign of weight loss and transition below 200°C.

The dielectric properties of *meta*-PU films are presented in Fig. 5(a) for the room temperature dielectric properties as function of frequency and Fig. 5(b) for dielectric properties vs. temperature measured at 1 kHz. The results show a high dielectric constant ($K > 5.6$) and low loss (loss tangent $\sim 1.5\%$) over a broad temperature range, due to the high glass transition temperature. Even more importantly, the *meta*-PU films exhibit a linear dielectric response and very low loss even at very high electric field, see Fig. 5(c) for the charge/discharge curve at electric field close to 700 MV/m, measured at room temperature at 10 Hz.

In order to measure the dielectric constant of the *meta*-PU powder, we mixed the powder with dielectric fluids of different dielectric constants and used the Lorentz-Lorentz equation (Equation (2))^[35] to deduce the dielectric constant of the *meta*-PU powder from the dielectric constant of the mixture K_e . It is noted that these dielectric fluids do not dissolve the *meta*-PU powder (as verified by the X-ray diffraction data of the mixture). In the case of a two-phase, three-

dimensional medium, the Lorentz-Lorentz theory yields the following expression for K_e in terms of the dielectric constant K_1 (*meta*-PU powder), K_2 (the fluid) and the powder volume fraction p_1 of the mixture.

$$\frac{(K_e - K_2)}{K_e + 2K_2} = \frac{p_1(K_1 - K_2)}{(K_1 + 2K_2)} \quad (2)$$

High precision data can be obtained if the dielectric constant of the fluid is close to that of the powder. As shown in Fig. S6, the dielectric constant of the mixture of *meta*-PU powder ($p_1 = 25$ vol %) and castor oil ($K_2 = 4.75$) is 4.5 (at 1 kHz), lower than that of the dielectric fluid, indicating that the *meta*-PU powder dielectric constant is smaller than 4.5. Using Equation (2) yields a $K_1 = 3.8$, which is smaller than $K = 5.7$ measured in the disordered structures (films). The dielectric loss data is presented in Fig. S7. The results indicate that *meta*-PU in the disordered structure possesses a higher dielectric constant than that in the ordered phase, confirming the theoretical results.

To further confirm that the results obtained here are not an isolated case, we also synthesized poly (arylene ether urea) (PEEU) polymer (Scheme 2), which has an ordered structure in the as synthesized powder, and see sharp x-ray peaks for the PEEU powder, Fig. 4(c). In contrast, the solution-cast films display a broad x-ray peak, Fig. 4(d), indicating an amorphous structure. The dielectric constant of PEEU films is 4.7, while the dielectric constant of PEEU powder deduced from Equation (2) using PEEU powder/fluid mixture is 3.65, which is smaller than that of the disordered structure.

Conclusions

In conclusion, through combined theoretical and experimental studies, we show that in *meta-PU* and several other strongly dipolar polymer dielectrics, disordered phases exhibit higher dielectric constants compared with those of ordered phases, due to the large built-in free volumes in the disordered structures. Larger free volumes in disordered phases of these strongly dipolar polymers at temperatures far below the glass transition enable easier reorientation of dipoles in response to an electric field, leading to high dielectric constants while preserving low dielectric loss. At the same time, disorder enables longer wavelength vibrations, which also increases permittivity. These concepts and the experimental results demonstrate a new and promising approach for developing dielectric polymers with high dielectric constant, low loss, and high operating temperature.

ACKNOWLEDGEMENTS

The authors thank the support of this work by ONR under Grants No. N00014-14-1-0109, N00014-14-1-0106 and N00014-13-1-0719.

Table 1. Spherically averaged ionic contributions to the dielectric constants for ordered and disordered structures.

	Ordered	Disordered 1	Disordered 2	Disordered 3
$\epsilon_{avg}(ionic)$	2.48	2.81	4.76	4.00

Table 2. Simulated dielectric constants of *meta*-PU. $\epsilon_{avg}(ionic)$ is average ionic contributions to the dielectric constants. $\epsilon_{avg}(0)$ is the total static dielectric constant (ionic + electronic).

	Ordered structure	Disordered structures
$\epsilon_{avg}(ionic)$	2.48	3.85
$\epsilon_{avg}(0)$	5.84	7.21

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Figure Captions:

Scheme 1. Schematic of synthesis of *meta*-PU.

Scheme 2. Schematic of synthesis of PEEU.

Fig. 1. Snap shots of *meta*-PU cells after simulated annealing. Only the structure 1 is ordered.
(Colors represent chains. In structure 1 the chains occupy “lattice” sites, so it is ordered.)

Fig. 2. The disorder effect on the ionic dielectric response. The plot shows the convergence of the ionic contribution to permittivity with simulation time. The black curve is the ordered structure, while the red curve is the average of the three disordered structures. The disordered structures have much higher ionic contributions.

Fig. 3. Single-urea motion contributions to dipole moment variation in the ordered *meta*-PU structure. (a) Antiparallel dipole pairs aligned along the x-axis. (b) Rotation of a single urea unit in xy-plane. (c) Wiggling of a single urea unit in xz-plane.

Fig. 4. X-ray data for (a) ordered *meta*-PU structures; (b) films of disordered *meta*-PU structure; (c) ordered PEEU structures, powder; (d) films of disordered PEEU structure.

Fig. 5. (a) Dielectric constant vs. frequency, measured at room temperature; (b) Dielectric constant vs temperature, measured at 1 kHz; (c) P-E loop of *meta*-PU film.

Scheme 1

Scheme 2

Fig. 1.

Fig. 2.

Fig. 3.

Fig. 4.

Fig. 5

Vitae

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a giant electrocaloric effect over a broad temperature range in a class of defects modified ferroelectric polymers. He is the recipient of the 2008 Penn State Engineering Society Premier Research Award and a Fellow of IEEE and a Fellow of APS.