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Synthesis of Functionalized Isotactic Polypropylene Dielectrics for Electric Energy Storage Applications

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Introduction. Energy storage has long been a scientifically challenging and industrially important area[1] and is an essential element to energy utilization and management. Capacitors[2] are mostly known as the passive devices in electric circuits that perform a variety of tasks—triggering, filtering, bypassing, smoothing, etc.—which require high power but only a small amount of energy (from static charges). Recently, metalized polymer film capacitors[3] have attracted a great deal of attention for energy storage applications due to their desirable properties, such as lightweight, low cost, safety (no chemical reaction or moving parts), large surface area for charge storage, ability to be packaged into a desirable configuration, and toughness under stress with good reliability. Some capacitors—based on thermoplastic films, such as polypropylene, polyester, and polycarbonate—show self-healing[4] after a puncture, which merely results in a gradual loss of capacitance so that they can be operated closer to the breakdown voltage to maximize their energy storage capacity. However, these metalized polymer film capacitors generally suffer from either low energy density[5] due to a low dielectric constant or unacceptably large energy loss[6] that reduces storage capacity and causes big problems in capacitor stability.

The scientific challenge here is to discover a polymer dielectric that can perform both high energy densities while exhibiting low dielectric loss. On the basis of the linear energy density equation,[5] energy density (J/cm^3) = $^1/_2\varepsilon E^2$, where ε is the dielectric constant that stays constant throughout the applied electric field (E), the desirable dielectric material shall exhibit high ε value, high breakdown strength (E), and very low energy loss during the charging−discharging cycles.[7] In other words, the polarization−depolarization cycle is fully reversible (low hysteresis). The ε value in the polymer is contributed by a combination of induced electronic polarization (σ and π electrons) and segmental motion (including dipole orientation); the former is fast and highly reversible, but the segmental motion is slow and usually not completely reversible in the capacitor application time scale (milliseconds).[6] The slow randomization of the poled polar groups usually causes large hysteresis in the $D-E$ loop (charge displacement vs applied electric field), resulting in large energy loss that significantly limits the capacitor applications. On the other hand, the breakdown strength is strongly dependent on the film quality that is associated with polymer molecular weight, morphology (i.e., crystallinity, crystal size, crystal phase, etc.), impurities, and defects.[8] The state-of-the-art metalized polymer film capacitors[9]—using biaxial oriented polypropylene (BOPP) thin films—show noticeably high dielectric strength (breakdown electric field >600 MV/m). However, because of a low dielectric constant (ε = 2.2) from the induced electronic polarization, BOPP-based thin film capacitors can only offer energy density in the range of 2−3 J/cm^3 after applying to 600 MV/m and exhibit almost no energy loss during the charging−discharging cycles. It is scientifically interesting to understand how it is possible to increase the dielectric activities (high ε value) in PP polymer without altering good polarization reversibility (thin $D-E$ loops) and high breakdown strength (E) in order to achieve higher energy density in PP-based capacitors.

Results and Discussion. In this paper, we systematically investigate a family of isotactic polypropylene copolymers (f-PP) that contain various $-(CH_2)_n-CH_3$ (I), $-(CH_2)_n-O-Si(CH_3)_3$ (II), and $-(CH_2)_n-OH$ (III) side groups. These chemically modified PP polymers were synthesized and fabricated into thin films for comparative dielectric and electric energy storage studies. The major objective here is to correlate the effects of the side-chain groups (comonomer units) and the associated morphological change to their dielectric and capacitor properties.

As illustrated in Scheme 1, the f-PP copolymers were prepared by the copolymerization of propylene with various comonomers, using both homogeneous and heterogeneous isospecific Ziegler−Natta catalysts. Both borane and silane functional groups were known to be stable in Ziegler−Natta catalysis systems,[10] and the resulting borane- and silane-containing PP copolymers were further interconverted into the corresponding OH containing polymers (III).[11] Detailed experimental procedures are discussed in the Supporting Information. Table 1 summarizes the results of three copolymer sets, including two sets of poly(propylene-*co*-1-decene) (PP-D) (I) prepared by the homogeneous $Et(Ind)_2ZrCl_2$/MAO catalyst and heterogeneous $TiCl_3AA/Et_2AlCl$ catalyst, respectively, and one set of PP−OH copolymers (III) prepared by the heterogeneous $TiCl_3AA/Et_2AlCl$ catalyst with the undecenyloxytrimethylsilane comonomer. The resulting PP-OSi$(CH_3)_3$ (II) was further hydrolyzed to the corresponding PP-OH copolymer (III) under acidic conditions. In general, the homogeneous metallocene system[12]—with more comparative comonomer reactivity—produces the PP copolymers with higher comonomer content and narrow molecular weight and composition distributions, but with lower molecular weight, isotactivity, and melting temperature. The traditional heterogeneous Ziegler−Natta catalyst is unfavorable for incorporating large comonomers, but it forms high isotactic PP with high molecular weight and high melting temperature.[10] We were fortunate enough to be able to find the reaction condition to prepare PP-OH containing >4 mol % OH comonomer units, which is sufficient for showing the effects of OH groups in dielectric and capacitor properties (discussed later).

Figure 1 shows the ^{1}H NMR spectra of a typical pair of PP copolymers II and III, before and after silane group deprotection. This copolymer pair was chosen for the comparative dielectric study. The disappearance of a sharp $O-Si-(CH_3)_3$ peak at ~0 ppm indicates successful deprotection. The OH group content in the copolymer III was determined by the peak intensity and protons in the $O-Si-(CH_3)_3$ group of the copolymer II or the CH_2-OH group of the copolymer III;

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Table 1. Summary of Poly(propylene-*co*-decene) and Poly(propylene-*co*-undecenol) Copolymers

run[a]	polymer	[Y][b] (mol %)	M_v ($\times 10^{-3}$ g/mol)	T_m (°C)	ΔH_m (J/g)	T_c (°C)	T_g (°C)
control 1	PP-1	0	32	134.6	80.9	95.5	
control 2	PP-2	0	961	160.9	78.0	104.9	
A-1	PP-D-1	1.1	25	127.7	74.0	83.2	−21.7
A-2	PP-D-2	3.8	16	123.7	60.1	65.7	−18.4
A-3	PP-D-3	12.4	12	106.6	48.0	45.8	−13.7
B-1	PP-D-4	0.5	891	151.5	70.6	99.3	−44.5
B-2	PP-D-5	1.4	902	147.93	59.3	95.6	−45.0
C-1	PP-OH-1	0.7	490	156.7	66.1	106.5	−3.1
C-2	PP-OH-2	1.8	592	156.6	65.4	104.9	−2.3
C-3	PP-OH-3	4.2	392	156.2	65.2	102.0	0.73

[a] Runs in set A: 5 umol Et(Ind)$_2$ZrCl$_2$ catalyst/5 mL MAO (10 wt % in toluene), 75 mL toluene, 40 °C, 120 psi of propylene gas. Runs in Sets B and C: 0.200 g of TiCl$_3$. AA, 5 mL of Al(Et)$_2$Cl (10 wt % in toluene), 75 mL toluene, 60 °C, propylene gas pressure: 120 psi for set B and 30 psi for set C. [b] [Y] indicates the comonomer content (mol %) in the copolymers.

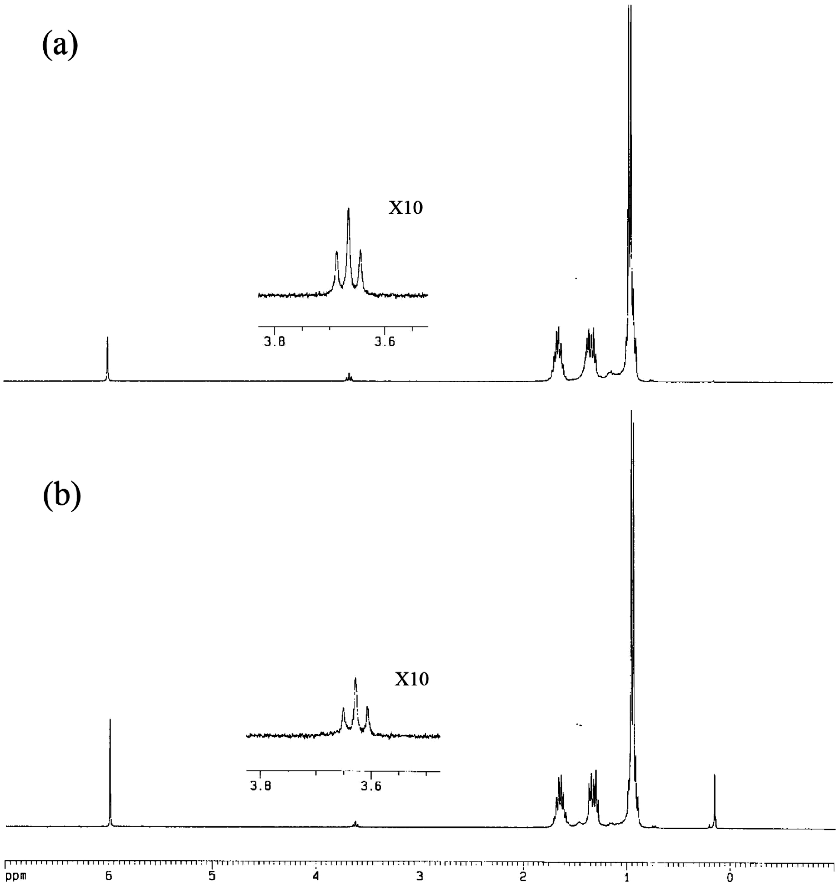
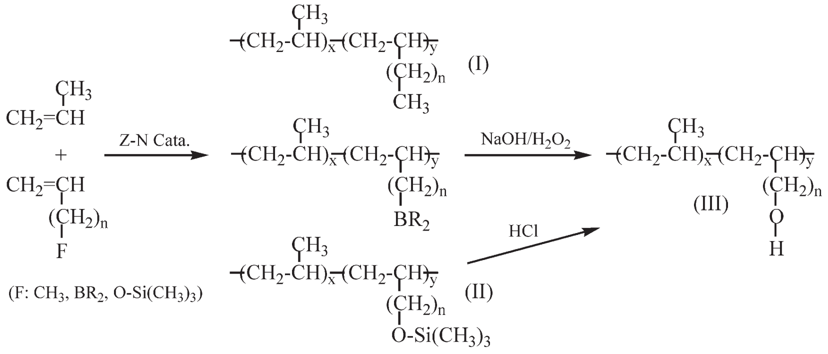


Figure 1. ^{1}H NMR spectra of (a) PP-OH-3 and (b) the corresponding PP-OSi(CH$_3$)$_3$.

Scheme 1



both results are consistent in all runs in Table 1. The crystalline morphology of the copolymers was examined by a combination of DSC (Figure S2), XRD (Figure S3), and polarizing optical microscopy (Figure S4) measurements, shown in the Supporting Information. As expected, the comonomer incorporation reduces PP crystallinity and crystal size, especially for the poly(propylene-*co*-1-decene) copolymers (I). All melting temperature (T_m), heat of fusion (ΔH_m), and crystallization temperature (T_c) decrease proportionally with the increase of the 1-decene incorporation. However, in PP-OH (III) copolymers (set C), both T_m and ΔH_m values show an initial reduction and then subsequently level off at the higher comonomer incorporation. It is interesting to note that PP-OH-3 with 4.2 mol % OH-comonomer units shows sharper XRD peaks (higher crystallinity) than those of PP-D-5 with only 1.4 mol % 1-decene comonomer units (Figure S3). Furthermore, both PP-OH-1 and PP-OH-2 show higher crystallization temperature (T_c) than the PP homopolymer, indicating that the OH groups may also facilitate the crystallization process. It is also interesting to note that due to low comonomer reactivity for the undecenyloxytrimethylsilane comonomer in the heterogeneous Ziegler–Natta catalyst, the resulting PP-OH copolymer (III) may have a tapered molecular structure,[13] with the OH-containing side-chain units concentrated at one end of the copolymer main chain. Therefore, the increase of comonomer content has less effect on the PP chain crystallization.

Figure 2 compares dielectric constant (ε) profiles between PP and two copolymers of PP-D (I) and PP-OSi(CH_3)$_3$ (II)—having ~4 mol % of comonomer units—over a wide range of temperatures (from 20 to 100 °C) and frequencies (100 to 1 M Hz). A systematical dielectric constant comparison between PP and three poly(propylene-*co*-1-decene) copolymers containing 1.1 mol % (run A-1), 3.8 mol % (run A-2), and 12.4 mol % (run A-3) 1-decene units (vs frequency and temperature) is also shown in Figures S5 and S6 of the Supporting Information. Both side chains slightly increase the PP ε value (polarizability) with the level proportional to the comonomer content, which are accompanied by the increase of frequency and temperature dependency. The increase in polarizability is due to increased chain flexibility, since reduced crystallinity (discussed before) allows for more segmental motion in amorphous phase,[14] which increases dipole alignment along the applied electric field direction. However, under high-frequency conditions, this relatively slow segmental motion is significantly limited. The ε value proportionally decreases with the increase of frequency, which becomes almost constant ($\varepsilon = \sim 3$) at 1 M Hz frequency. This reduced dielectric activity may only be from the quick induced electronic polarization mechanism. On the other hand, the ε value also continuously decreased with increasing temperature, especially in the low-frequency range. The molecular alignment, by applied electric field, may be retarded due to the increase of general molecular motion from the increased temperature and reduced crystallinity.

Figure 3 shows dielectric constants of several PP-OH copolymers (III) containing 0, 0.7, 1.8, and 4.2 mol % OH comonomer units, respectively, over a temperature range from −20 to 100 °C and a frequency range from 100 to 1 M Hz. The dielectric constant increases proportionally with the OH content. The ε value of PP-OH-3 with 4.2 mol % of the OH comonomer content reaches about 4.6 (more than 2 times that of PP), which is significantly higher than the values of PP-D (I) and PP-OSi(CH_3)$_3$ (II) with similar comonomer contents—especially in the high-frequency range. In fact, this PP-OH-3 polymer was directly prepared from the interconversion of PP-OSi(CH_3)$_3$ (II) shown in Figure 2. The OH groups clearly contribute to the polarizability of the PP-OH (III) copolymer, which may be originated from the induced electronic polarization of OH groups or local dipole orientation of OH groups along the electric field direction. It is a

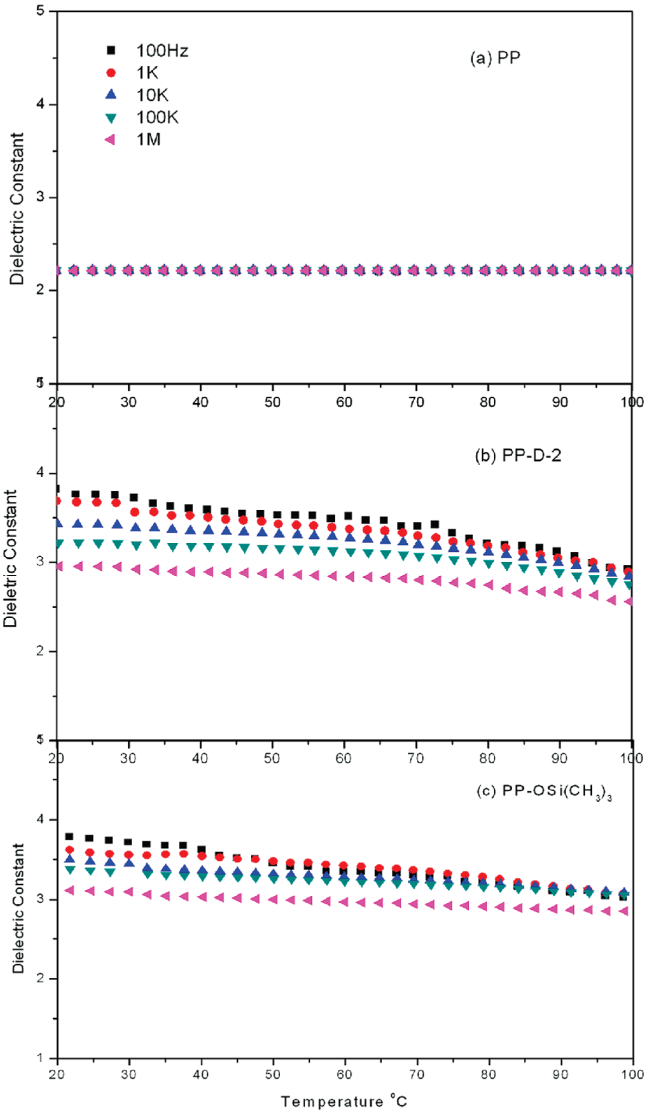


Figure 2. Dielectric constants (vs frequency and temperature) for (a) PP, (b) PP-D-2 with 3.8 mol % 1-decene comonomer units, and (c) PP-OSi(CH_3)$_3$ with 4.2 mol % undecenyloxytrimethylsilane comonomer units.

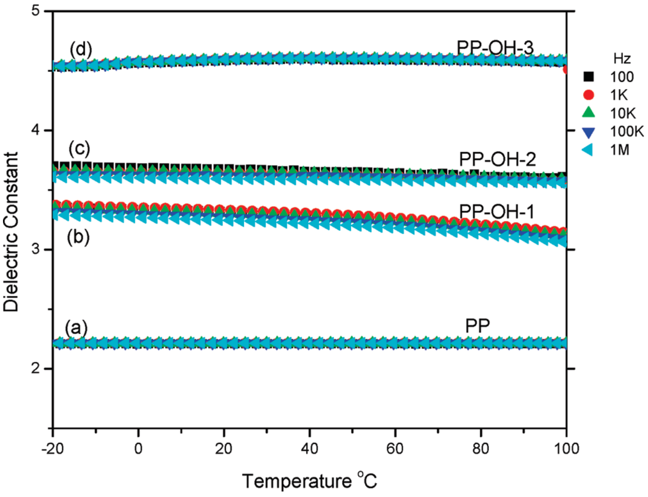


Figure 3. Dielectric constants (vs frequency and temperature) for (a) PP and three PP-OH copolymers containing (b) 0.7, (c) 1.8, and (d) 4.2 mol % OH content.

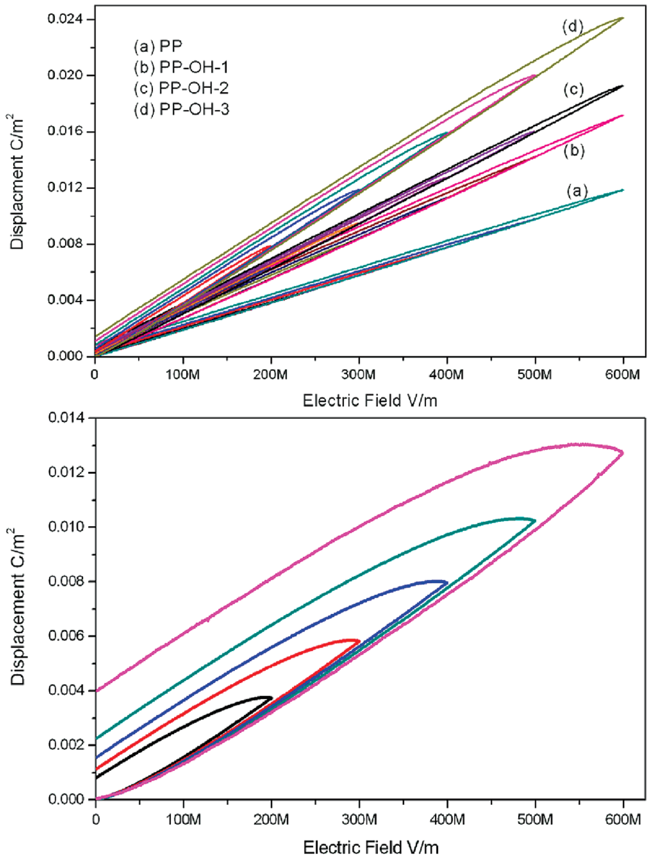


Figure 4. $D-E$ hysteresis loops vs the applied electric field (top) for (a) PP and three PP-OH copolymers containing (b) 0.7, (c) 1.8, and (d) 4.2 mol % OH content and (bottom) PP-OSi(CH$_3$)$_3$ copolymer with 4.2 mol % undecenyloxytrimethylsilane comonomer units.

pleasant surprise for us to observe all PP-OH dielectric profiles resembling the PP profile, with a dielectric constant (ε) that is independent over a wide range of frequencies (between 100 and 1 M Hz) and temperatures (between −20 and 100 °C). These overlapped and flat dielectric constant lines imply a fast polarization response for the PP-OH (III) copolymer, even under a relatively low electric field condition. The interchain H-bondings between OH groups offer not only high crystallinity (Table 1) but also a network structure that provides segment stability (immobility and reversibility) even when the temperature rises up to 100 °C. A FTIR spectrum of PP-OH-3 (Figure S7 in the Supporting Information) clearly shows a broad OH absorption band peaked at 3300 cm^{-1}, indicating H-bonding between OH groups in the PP-OH copolymer.[15]

Figure 4 (top) compares $D-E$ loops of PP and three PP-OH (III) copolymers (shown in Figure 3). For comparison purposes, the $D-E$ loops of a corresponding PP-OSi(CH$_3$)$_3$ (II) used to prepare PP-OH-3 are also shown in Figure 4 (bottom). For each sample, a dc electric field was applied across the polymer film with an initial amplitude of 100 MV/m, which was then increased 100 MV/m intervals until reaching 600 MV/m. As expected, the PP displays a linear $D-E$ loop with very low hysterises, indicating a constant dielectric constant (ε = 2.2 estimated from slope) and completely reversible polarization−depolarization over the whole applied electric fields. Most interestingly, all the PP-OH copolymers also exhibit similar linear and slim $D-E$ loops; the slope of the $D-E$ loop increases with the OH content. Consistent with the dielectric results in Figure 3, the dielectric constant (slope) increases with the OH content in PP-OH copolymers. In addition, it maintains constant over a wide range of applied electric fields, up to E = 600 MV/m. The charge displacement of PP-OH-3 reaches 0.024 C/m^2 at 600 MV/m, which is double that of PP under the same applied electric field. Evidently, the dielectric loss maintains very small, with even the PP-OH copolymers exhibiting significantly higher dielectric activities. On the other hand, the broad hysterises in the $D-E$ loops were observed in the corresponding PP-OSi(CH$_3$)$_3$ (II) copolymer (Figure 4, bottom), which increases with the applied electric field. The pending side chains containing OSi(CH$_3$)$_3$ groups reduce crystallinity and polarization reversibility (molecular structure) under the applied electric field. During the depolarization cycle, the poled groups and/or chain segments cannot be entirely randomized in the time scale of the process. Overall, the combination of the dielectric constant (vs temperature and frequency) and polarization loops (vs applied electric field) results clearly indicates the unique contribution of OH polar groups in PP-OH dielectric thin film; this not only increases polarizability but also provides a stable PP-OH structure and morphology under a wide range of applied electric fields and elevated temperatures. This polar PP-OH polymer shall have a physical network structure for performing fast polarization−depolarization cycles with low hysteresis and low energy loss.

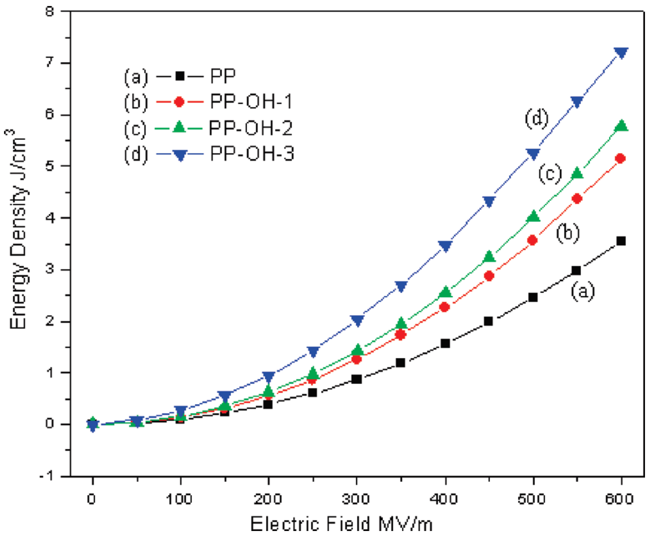


Figure 5. Releasing energy density for (a) PP and three PP-OH copolymers containing (b) 0.7, (c) 1.8, and (d) 4.2 mol % OH content.

Figure 5 compares the energy density of the same four polymers, including PP and three PP-OH (III) copolymers containing 0, 0.7, 1.8, and 4.2 mol % OH comonomer units. The energy density ($U_e = \int E \, dD_{\mathrm{discharing}}$) is estimated from the discharging cycle in Figure 4 (left), which clearly increases with the OH content and exponentially increases with the applied electric field (E). At the applied electric field E = 600 MV/m, the energy density for PP-OH-3 reaches 7.42 J/cm^3—more than double that shown in BOPP capacitors. Most importantly, the increase of energy density does not cause an increase in energy loss (the area enclosed by the charging−discharging cycle), which remains very low (similar to PP) for all PP-OH copolymers.

Conclusion. In this paper, we systematically examine the structure−property relationship of PP copolymers containing various comonomer units that change the semicrystalline morphology and increase dielectric properties. Seemingly, most of the side chains (comonomer units) reduce PP crystallinity and increase the molecular motion that allows for dipole alignment with the applied electric field. However, this molecular motion is not fully reversible in the time scale of the measurement, which results in the dielectric sensitivity to frequency, temperature, and applied electric field, as well as big dielectric loss in $D-E$ loops. On the other hand, the high molecular weight, characteristically tapered PP-OH copolymer (III)—prepared by the heterogeneous Ziegler–Natta catalyst—shows high crystallinity with a unique network structure, via interchain OH groups dimerization (H-bonding), offering not only higher polarizability but also good reversibility. Its dielectric constant maintains constant over a wide range of temperatures (between −20 and 100 °C), frequencies (between 100 and 1 M Hz), and applied electric fields (> 600 MV/m). The PP-OH (having 4.2 mol % OH content) based thin film capacitor displays a linear reversible charge storage capacity with high releasing energy density > 7 J/cm^3 (2−3 times of BOPP) after an applied electric field at $E = 600$ MV/m, without showing any significant increase in energy loss and remnant polarization at zero electric field.

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Supporting Information Available: Polymerization procedures and DSC curves of copolymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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