High Dielectric Constant Sulfonyl-Containing Dipolar Glass Polymers with Enhanced Orientational Polarization

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Abstract

Dipolar glass (DG) polymers, which utilize sub-T_g orientational polarization (T_g is the glass transition temperature) to enhance dielectric constant, are promising for advanced electronic and power applications, because conduction of space charges (electrons and impurity ions) is suppressed in the glassy state and thus the dielectric loss is low. In this study, we studied the effects of dipole density and dipole arrangement in sulfonyl-containing side-chain DG polymers on their dielectric performance in terms of dielectric constant, energy density, and dielectric loss. Mono-sulfonyl (i.e., CH3SO2-) and disulfonyl [i.e., CH3SO2(CH2)3SO2-] groups were quantitatively grafted to polyepichlorohydrin (PECH) (mono-substitution) and poly(3,3bis(chloromethyl)oxatane) (PBCMO) (bis-substitution), respectively, in order to vary the dipole density and dipole arrangement in the side chains. As a result of orientation polarization from highly polar sulfonyl (4.5 D) groups, these DG polymers exhibited high apparent dielectric constants (7-11.5) in the glassy state with reasonably low dissipation factors (tan $\delta \sim 0.003-0.02$). It was found that disulfonylated DG polymers exhibited a higher dielectric constant than monosulfonylated DG polymers because of their higher dipole densities. Meanwhile, bis-substituted DG polymers showed a higher dielectric constant than mono-substituted DG polymers. Upon high-field electric poling, reversible transitions between the low-field DG state and the high-field ferroelectric state induced double hysteresis loops, and disulfonylated DG polymers had more significant ferroelectric switching than mono-sulfonylated DG polymers due to stronger dipolar interactions among the disulfonyl groups. On the basis of the experimental results, monosulfonylated DG polymers, whether mono- or bis-substituted, should be more appropriate for electric energy storage applications.

Introduction

High dielectric constant and low loss polymers are highly desirable for new dielectric applications such as gate dielectrics for printable electronics^{1, 2} and polymer film capacitors.^{3, 4} Compared with ceramic materials, dielectric polymers usually exhibit significantly lower dielectric constants. For example, linear dielectric polymers utilizing electronic and atomic (or vibrational) polarizations only have dielectric constants between 2 and 5. To further increase dielectric constant for polymers, one needs to utilize orientational polarization from molecular dipoles.⁵ Small organic molecules can exhibit high dielectric constants (e.g., 180 for N-methylformamide⁶ and 80 for water⁷) with a reasonably low dielectric loss at room temperature. On the contrary, polar polymers, such as cyano (CN)-containing polyimides,⁸ exhibit dielectric constants of only 3-5 and have a broad dipole relaxation peak that directly covers the frequency range of interest for power electronic applications (i.e., ~1-10 kHz). Learning from water,⁹ it is highly desirable to enhance the dielectric constant and increase the dipole relaxation speed towards at least hundreds of MHz for polymers.

To realize this goal, one viable candidate is a dipolar glass (DG) polymer, which is reminiscent of spin glasses in magnetic materials.¹⁰ In a DG polymer, individual mobile dipole groups are confined within the free volume of a glassy polymer matrix. Basically, a DG polymer utilizes the sub-T_g orientational polarization (T_g is the glass transition temperature) to enhance dielectric constant.^{5, 11} Note that the DG polymers here are different from polar molecule-doped glassy polymers.¹²⁻¹⁵ The doped polar molecules are usually too large to freely rotate below the T_g of the matrix polymer. In addition, at high doping concentrations, the dipolar molecules tend to macrophase separate from the matrix polymer. For DG polymers, however, this is not a problem. The interactions of dipolar groups remain weak because there is no translational motion

in the glassy state, and no ferroelectric (FE) domains can form at zero electric field. It is thus expected that their electric displacement - electric field (D-E) loops should be narrow with relatively high dielectric constants. Because of frozen chain dynamics below T_g , DG polymers could exhibit a low electric leakage and a low dielectric loss. The challenge, however, is how to achieve fast dipole rotation at high frequencies, e.g., >1 MHz.

In the past, some DG polymers with relatively high dielectric constant have been studied, and some even commercialized. Most of these DG polymers contain cyanoethyl (-CH₂CH₂CN) or cyanomethyl (-CH₂CN) side groups. When -CH₂CN groups were attached as the side chains in a bisphenol A polycarbonate (i.e., CN-PC), the dielectric constant at 1 kHz increased to 4.0 for CN-PC as compared to that of 2.9 for neat PC.¹⁶ The dissipation factor was reasonably low, i.e., tan $\delta \sim 0.005$ at 130 °C and 1 kHz. However, the dielectric constant was low due to the low density of -CH₂CN dipoles. Cyanoethylated poly(vinyl alcohol) (CN-PVA) exhibited a dielectric constant of ca. 10 and a minimum tan δ of 0.01 at 1 Hz below its T_g of 25 °C.¹⁷ Cyanoethylated poly(2,3-dihydroxylpropyl methacrylate) (CN-PDPMA) exhibited a relatively high dielectric constant (ca. 8) between the β (rotation of -CH₂CH₂CN dipoles at -60 °C) and the α (T_g at 25 °C) transitions at 500 Hz.¹⁸ However, the window between the β and α transitions was narrow, only about 85 °C. Also, the T_gs for CN-PVA and CN-PDPMA (and some cyanoethylated celluloses¹⁹) are too low for applications above room temperature.

The low T_g of cyano-ethylated polymers can be attributed to the relatively long side chains. To overcome this problem, Shin-Etsu Chemical commercialized cyanoethylated pullulan (CEP, ~90% functionality). The original application was for a high dielectric constant coating for the phosphor grains in so-called thick-film electro-luminescent lamps.²⁰ Because of the rigid cellulose backbone structure, the T_g reached ca. 110 °C,²¹ and the dielectric constant at room temperature was between 13 and 18 at frequencies below 10^4 Hz. From the frequency-scan results, the dipole relaxation peak at room temperature was just above 1 MHz.²² Using CEP as the gate dielectric, high mobility (0.43 cm²/V·s) was reported for α -sexithienylene (α -6T) in an organic FET device.²³ Despite these attractive dielectric properties, CEP suffers from relatively low Tg, low dielectric breakdown strength (ca. 80 MV/m), and insufficiently rapid dipole switching speed (i.e., dipoles cannot fully switch above 10^4 Hz). Crosslinking of CEP with multifunctional small molecules has been pursued in order to enhance Tg and mechanical integrity.²⁴⁻²⁶ However, the dielectric constant tended to decrease due to hindered rotation of dipoles in crosslinked samples.

To search for better alternatives to CEP, we recently developed methylsulfonyl-containing DG polymers because the sulfonyl group has an even higher dipole moment (~4.5 D) than that of the cyano group (3.9 D). In a recent study, a new DG polymer, poly[2-(methylsulfonyl) ethyl methacrylate] (PMSEMA) showed a high dielectric constant of 11-12 at room temperature with a reasonably low tanð of 0.02 at 10 Hz.²⁷ Most recently, methylsulfonyl-containing poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) was synthesized to further enhance the T_g above 210 °C.²⁸ For a 25% sulfonyl-functionalized PPO sample (i.e., SO₂-PPO₂₅), the dielectric constant was 6.2, the energy density was 22 J/cm³, and the minimum tanð was as low as 0.003 in the glassy state.

Despite the above achievements, it is still desirable to explore new opportunities to further enhance dielectric constants for DG polymers. In this study, we propose disulfonyl-containing DG polymers, and the disulfonyl side group is CH₃SO₂(CH₂)₃SO₂CH₂-. Because there are three methylene units between two sulfonyl groups, they can point to the same direction in an all trans conformation. If the polar disulfonyl groups can be rotated together by the poling electric field, the orientational polarization can be quadrupled according to the Langevin equation.²⁹ Therefore, even higher dielectric constant should be expected. To test this hypothesis, we grafted disulfonyl groups into side chains of polyepichlorohydrin (PECH) (i.e., mono-substitution) and poly(3,3bis(chloromethyl)oxatane) (PBCMO) (i.e., bis-substitution) using post-chemical modification. For comparison, methylsulfonyl (i.e., mono-sulfonyl) groups were also attached to PECH and PBCMO, respectively. The effects of dipole density and dipole arrangement in the side chains were studied using broadband dielectric spectroscopy (BDS) and D-E loop tests.

Experimental Section

Materials. 3,3-Bis(chloromethyl)oxetane (BCMO, 97%, PharmaBlock, Inc., Sunnyvale, CA) and triethlyamine (Et₃N, 99%, Fisher Scientific, Pittsburgh, PA) were freshly distilled over phosphorus pentoxide (P₂O₅) and calcium hydride (CaH₂), respectively, before use. All other solvents were used as received from Fisher Scientific. Sodium thiomethoxide (95%), 3-(methylthio)-1-propanol (98%), 3-chloroperbenzoic acid (*m*-CPBA, \leq 77%), methanesulfonyl chloride (MsCl, 99.7%), thioacetic acid (96%), sodium ethoxide (EtONa, 21 wt.% in ethanol), tetrapropylammonium bromide (TPAB, 98%), boron trifluoride diethyl etherate (BF₃·Et₂O, 46.5% BF₃ basis), P₂O₅ (99%), CaH₂ (99.9%), and PECH [number-average molecular weight (M_n) = 5.22×10^5 g/mol with a molecular weight distribution of 2.93 by size-exclusion chromatography (SEC)] were purchased from Sigma-Aldrich (St. Louis, MO) and used as received.

Measurements and Instrumentation. Proton (¹H) and carbon-13 (¹³C) NMR spectra were recorded using a Varian Inova 600 (¹H)/150 (¹³C) MHz and a Bruker Ascend III 500 (¹H)/125 (¹³C) MHz NMR instruments equipped with a prodigy probe, respectively, using tetramethylsilane (TMS) as the internal standard, and deuterated chloroform (CDCl₃) or dimethylsulfoxide (DMSO*d*₆) as the solvent. Differential scanning calorimetry (DSC) was recorded using a TA Instruments Q100 DSC. The scanning rate was 10 °C/min and about 3 mg sample was used to avoid possible thermal lag. Thermogravimetric analysis (TGA) was recorded on a TA Instruments Q500 TGA with a heating rate was 10 °C/min. SEC was performed using a Waters 515 high performance liquid chromatography (HPLC) pump equipped with a Waters 2414 differential refractive index (RI) detector. Tetrahydrofuran (THF) was used as the eluent at a flow rate of 1.0 mL/min at 40 °C. Linear PS standards were employed for conventional calibration.

All polymer samples were purified by Soxhlet extraction with methanol for 3 days before film-casting from solution. Thin films (ca. 3-6 μ m thick) were obtained by casting from 5 wt.% dimethylacetamide (DMAc) solutions, followed by a stepwise heating process; room temperature for 4 h, 110 °C for 10 h, and 140 °C for 10 h in a vacuum oven. BDS was performed using a Novocontrol Concept 80 broadband dielectric spectrometer with temperature control (Montabaur, Germany). The applied voltage was 1 V_{rms} (root-mean square voltage) with frequencies ranging from 1 to 10⁶ MHz and temperatures ranging from -150 to 150 °C. Silver electrodes (ca. 50 nm thick with an area of 78.5 mm²) were evaporated onto both sides of the film using a thermal evaporator (EvoVac Deposition System, Angstrom Engineering, Inc., Kitchener, ON, Canada).

D-E hysteresis loop measurements were carried out using a Premiere II ferroelectric tester (Radiant Technologies, Inc., Albuquerque, NM) equipped with a Trek 10/10B-HS high voltage amplifier (0-10 kV AC, Lockport, NY). The applied voltage had a bipolar sinusoidal waveform at 1 kHz. Tests were performed in a silicon oil bath at room temperature. Silver electrodes with 50 nm thickness and an area of 5.15 mm² were coated on both sides of the film.



Scheme 1. Syntheses of various dipolar glass (DG) polymers, DG1-DG4.

Polymer Syntheses. As shown in Scheme 1, syntheses of DG1 and DG2 were modified from a reported procedure.³⁰ DG3 and DG4 were synthesized according to previous methods,³¹ except that PBCMO (P3) was synthesized via a cationic ring-opening polymerization of BCMO using BF₃ as catalyst.³² Detailed experimental procedures are described below.

Synthesis of 3-Methylsulfonyl-1-Propanol. 3-Methylthio-1-propanol (5.00 g, 47.0 mmol) and 100 mL of CHCl₃ were charged into a 250 mL flask. Using an ice/water bath, *m*-CPBA (34.8 g, 141 mmol) was slowly added into the solution. After warming to the ambient temperature, the mixture was allowed to stir for 2 h. White powder was obtained by evaporating the solvent and washing with diethyl ether, followed by vacuum-drying; yield: 80%. ¹H NMR (δ , CDCl₃): 3.82 (s, HOCH₂CH₂-, 2H), 3.19 (t, HOCH₂CH₂-, 2H), 2.95 (s, -SO₂CH₃, 3H),

2.10-2.14 (m, HOCH₂CH₂CH₂-, 2H), 1.81 (s, *H*O-, 1H) (Figure S1 in the Supporting Information). ¹³C NMR (δ, CDCl₃): 60.3, 51.7, 40.7, 25.3. MS (ESI): (M-H + H₂O)⁻/*z*: calculated 155.0 and found 155.2.

Synthesis of 3-(Methylsulfonyl)propyl Methanesulfonate. Triethylamine (2.58 g, 25.5 mmol) was added dropwise to a dichloromethane (DCM) solution (30 mL) of 3-(methylsulfonyl)-1-propanol (2.35 g, 17.0 mmol) and MsCl (2.53 g, 22.1 mmol) in a 100 mL flask. The mixture was stirred at ambient temperature for 1 h, followed by washing twice with 20 mL of 3 wt.% HCl solution. After drying with anhydrous Na₂SO₄ for 30 min, the solvent was evaporated under vacuum, giving a yellow liquid; yield: 88%. ¹H NMR (δ , CDCl₃): 4.40 (t, CH₃SO₃OCH₂CH₂-, 2H), 3.19 (t, CH₃SO₃CH₂CH₂CH₂-, 2H), 3.05 (s, CH₃SO₃-, 3H), 2.96 (s, -SO₂CH₃, 3H), 2.33-2.36 (m, CH₃SO₃CH₂CH₂-, 2H) (Figure S2). ¹³C NMR (δ , CDCl₃): 67.4, 50.6, 41.1, 37.5, 22.4. MS (ESI): (M+Na)⁺/z: calculated 239.0 and found 239.1.

Synthesis of 3-(Methylsulfonyl)propyl Thioacetate. Et₃N (1.79 g, 17.7 mmol) was added dropwise to a CHCl₃ solution (30 mL) of 3-(methylsulfonyl)propyl methanesulfonate (2.75 g, 12.7 mmol) and thioacetic acid (1.73 g, 22.7 mmol). The mixture was then refluxed for 3 h, followed by washing twice with 3 wt.% HCl solution and ammonium hydroxide (10 wt.%), respectively. After drying with anhydrous sodium sulfate for 30 min, the solvent was evaporated under vacuum. The crude product was purified by passing through a silica gel column with ethyl acetate and hexanes (v:v = 1:2) as the eluent, giving a pink red solid; yield: 65%. ¹H NMR (δ , CDCl₃): 3.08 (t, CH₃COSCH₂-, 2H), 3.03 (t, -CH₂SO₂CH₃, 2H), 2.92 (s, -SO₂CH₃, 3H), 2.36 (s, CH₃CO- 3H), 2.13-2.18 (m, -CH₂CH₂CH₂-, 2H) (Figure S3). ¹³C NMR (δ , CDCl₃): 194.3, 52.3, 39.7, 29.7, 26.4, 21.9. MS (ESI): (M+Na)⁺/*z*: calculated 219.0 and found 219.2.

Synthesis of Poly[oxy(3-(methylsulfonyl)propylthiomethyl)ethylene] (P2). 3-

(methylsulfonyl)propyl thioacetate (0.300 g, 1.53 mmol) was added to a DMAc (5 mL) solution of EtONa (0.110 g, 0.530 mmol). After stirring at ambient temperature for 20 min, a DMAc solution (5 mL) of PECH (P1, 71.0 mg) was added to the mixture, followed by reacting at 60 °C under nitrogen for 3 h. Distilled water (30 mL) was added to the slurry after most solvent was evaporated under vacuum. The filtered cake was purified by precipitation from CHCl₃ into methanol, and then dried under high vacuum at 40 °C overnight; yield: 95%. ¹H NMR (δ , DMSO-*d*₆): 3.48-3.87 (br, -CH₂CHO-), 3.18 (t, -CH₂SO₂CH₃), 2.98 (s, -SO₂CH₃), 2.59-2.80 (br, -CH₂SCH₂-), 1.91-2.02 (br, -CH₂CH₂CH₂-) (see Figure S4). ¹³C NMR (δ , CDCl₃:DMSO-*d*₆ = 1:1 v/v): 79.1, 69.2-70.0, 59.8, 54.4, 52.9, 44.2, 40.8, 33.1, 31.1, 22.5, 15.9. Because P2 was not soluble in THF, SEC was not performed.

Synthesis of PBCMO (P3). Freshly distilled BCMO (10.0 g, 64.5 mmol) was charged into a dry 20 mL flask under dry nitrogen. 10 μ L of BF₃·Et₂O was injected to the flask, and the mixture was allowed to stir at ambient temperature for 2 h. As the polymerization proceeded, the polymer precipitated from the solution due to crystallization. The precipitated polymer was washed with methanol several times, followed by vacuum drying at 40 °C until reaching a constant weight. Finally, 7.50 g of white solid was obtained; yield: 75%. ¹H NMR (δ , CDCl₃): 3.60 (s, -CH₂CCH₂O-, 4H), 3.47 (s, -CCH₂Cl, 4H) (see Figure S5). ¹³C NMR (δ , CDCl₃:DMSO-d₆ = 1:1 v/v): 74.2, 50.7, 49.4. SEC result showed that the M_n of PBCMO was 13 kg/mol with a polydispersity index (PDI) of 1.74 (see Figure S8).

Synthesis of Poly[oxy-2,2-bis(3-(methylsulfonyl)propylthiomethyl) trimethylene] (P4). This polymer was prepared as described for P2, except that PBCMO (P3) was used instead of PECH (P1); yield: 90%. ¹H NMR (δ, DMSO-d₆): 3.22-3.40 (br, -CH₂CCH₂O-), 3.18 (t, -CH₂SO₂CH₃), 2.98 (s, -SO₂CH₃), 2.54-2.71 (br, -CCH₂SCH₂CH₂-), 1.91-2.03 (br, -CH₂CH₂CH₂-) (see Figure S5). 13 C NMR (δ , CDCl₃:DMSO-d₆ = 1:1 v/v): 71.9-70.3, 52.9, 45.5, 44.8, 32.3, 22.8. Because P4 was not soluble in THF, SEC was not performed.

Synthesis of Poly[oxy(3-(methylsulfonyl)propylsulfonylmethyl)ethylene] (DG1). m-CPBA (254 mg, 1.03 mmol) was added slowly to P2 (100 mg, 0.413 mmol) in DMAc (2 mL). After stirring at ambient temperature for 2 h, the mixed solution was precipitated in diethyl ether. After several times precipitations from hexafluoroisopropanol into methanol followed by vacuum drying at 40 °C overnight, a white solid was obtained quantitatively. ¹H NMR (δ , DMSO- d_6): 3.90-4.13 (br, -CH₂CHO-), 3.58-3.85 (br, -CH₂CHO-), 3.20-3.58 (br, -CH₂SO₂CH₂-), 3.02 (s, -SO₂CH₃), 2.07-2.25 (br, -CH₂CH₂CH₂-) (see Figure S4). ¹³C NMR (δ , DMSO- d_6): 73.01-75.23 (m), 68.12-70.47 (m), 54.28 (s), 51.53-52.84 (m), 40.26 (s), 15.28 (s). ¹³C NMR (δ , DMSO- d_6): 73.3-74.8, 68.3-70.2, 54.6, 51.5-52.9, 15.6. Because DG1 was not soluble in THF, SEC was not performed.

Synthesis of Poly[oxy-2,2-bis(3-(methylsulfonyl)propylsulfonylmethyl) trimethylene]

(*DG2*). DG2 was prepared in the same manner as described for DG1, except that P4 was used instead of P2, with a doubled molar ratio of *m*-CPBA per repeat unit of the polymer. ¹H NMR (δ , DMSO-*d*₆): 3.68-4.07 (br, -CH₂CCH₂O-), 3.45-3.68 (br, -CCH₂SO₂-), 3.16-3.40 (br, -CH₂CH₂CH₂SO₂CH₃), 3.01 (s, -SO₂CH₃), 2.02-2.28 (br, -CH₂CH₂CH₂SO₂CH₃) (see Figure S5). ¹³C NMR (δ , DMSO-*d*₆): 68.49-74.43 (m), 51.13-55.20 (m), 42.59 (s), 42.34 (s), 42.29 (s). ¹³C NMR (δ , DMSO-*d*₆): 70.3-73.5, 52.5-55.2, 51.8-52.5, 44.0-44.8, 15.0-16.3. Because DG2 was not soluble in THF, SEC was not performed.

Synthesis of Poly[oxy(methylthiomethyl)ethylene] (P5). Sodium thiomethoxide (0.500 g, 7.14 mmol) and TPAB (10.0 mg, 0.0376 mmol) were added to a solution of P1 (0.220 g, 2.38 mmol of Cl) in DMAc (20 mL). After stirring at ambient temperature for 2 h, the mixture was

poured into deionized water (100 mL). The precipitate was purified by several precipitations from THF solution into methanol and then drying under vacuum at 40 °C overnight. A white solid was obtained quantitatively. ¹H NMR (δ , CDCl₃): 3.75–3.69 (m, -CH₂CHO-), 3.57–3.69 (m, -CH₂CHO-), 2.61–2.79 (m, -CH₂SCH₃), 2.15 (s, -SCH₃) (see Figure S6). ¹³C NMR (δ , CDCl₃): 79.2-79.3, 70.6-71.3, 35.9-36.0, 16.8. SEC results for P5: M_{n,P5} = 767 kg/mol and PDI = 1.71 (see Figure S8).

Synthesis of poly[oxy(methylsulfonylmethyl)ethylene] (DG3). P5 (1.00 g, 9.60 mmol) was dissolved in DMAc (40 mL) at room temperature, and the polymer solution was cooled in an ice/water bath. An excess of *m*-CPBA (4.97 g, 28.8 mmol) was added to the polymer solution slowly. The reaction solution was stirred for 2 h and then precipitated into methanol. After several precipitations from hexafluoroisopropanol into methanol followed by vacuum drying at 40 °C overnight, a white solid was obtained quantitatively. ¹H NMR (δ , DMSO- d_6): 3.86–4.24 (br, -CH₂CHO-), 3.55–3.84 (br, -CH₂CHO-), 3.20–3.55 (br, -CH₂SO₂CH₃), 2.95–3.20 (br, -SO₂CH₃) (see Figure S6). ¹³C NMR (δ , DMSO- d_6): 73.33–74.75 (m), 68.20–70.38 (m), 55.09–56.60 (m), 43.92 (s), 40.21 (s), 15.36 (s), 15.07 (s). ¹³C NMR (δ , DMSO- d_6): 73.6-75.0, 68.6-70.3, 55.7-57.1, 42.4-43.5. Because DG3 was not soluble in THF, SEC was not performed.

Synthesis of poly[oxy-2,2-bis(methylthiomethyl)trimethylene] (P6). Sodium thiomethoxide (3.14 g, 19.4 mmol) was added to a solution of P3 (1.00 g, 12.9 mmol of Cl) in DMAc (20 mL). The mixture was heated to 140 °C, stirred for 0.5 h, and then poured into deionized water (100 mL). The precipitate was purified by several precipitations of its THF solution into methanol and then dried under vacuum at 40 °C overnight. A white solid was obtained quantitatively. ¹H NMR (δ , CDCl₃): 3.36 (s, -CH₂CCH₂O-), 2.66 (s, -CCH₂S-), 2.13 (s, -SCH₃) (see Figure S7). ¹³C NMR (δ , CDCl₃): 72.0, 45.4, 38.3, 18.1. SEC results for P6: M_n =

15 kg/mol and PDI = 1.74 (see Figure S8).

Synthesis of poly[oxy-2,2-bis(methylsulfonylmethyl)trimethylene] (DG4). P6 (1.00 g, 5.61 mmol) was dissolved in DMAc (40 mL) at room temperature, and the polymer solution was cooled in an ice/water bath. An excess of *m*-CPBA (4.85 g, 28.1 mmol) was added to the polymer solution slowly. The reaction solution was stirred at 80 °C for 0.5 h and then precipitated into methanol. After several precipitation from hexafluoroisopropanol into methanol followed by vacuum drying at 40 °C overnight, a white solid was obtained quantitatively. ¹H NMR (δ , DMSO-*d*₆): 3.72 (br, -CH₂CCH₂O-), 3.63 (br, -CCH₂SO₂-), 3.06 (br, -SO₂CH₃) (see Figure S7). ¹³C NMR (δ , DMSO-*d*₆): 69.04-73.82 (m), 58.25 (s), 53.40-55.87 (m), 43.20-44.71 (m), 15.04 (s). ¹³C NMR (δ , DMSO-*d*₆): 70.8-73.1, 54.6-56.0, 43.8-44.8, 15.5. Because DG4 was not soluble in THF, SEC was not performed.

Results and Discussion

Syntheses of Various DG Polymers. As shown in Scheme 1, the syntheses of DG1 and DG2 were modified from a reported procedure.³⁰ Syntheses of DG3 and DG4 had been reported before;³¹ similar procedures were used and the resulting polymers were obtained with satisfactory yields. Since the starting polymer, P3 (i.e., Penton by Hercules, Inc.), for DG4 was not commercially available anymore, it was synthesized by cationic ring-opening polymerization in bulk (ca. 75% yield). Although the M_n of 13 kg/mol for P3 was significantly lower than that (~190 kg/mol) of the commercial product (possibly due to the presence of impurities containing hydroxyl groups),³³ it still formed decent films for the dielectric property study. The syntheses of DG1 and DG2 employed the same thioester intermediate, AcS(CH₂)₃SO₂CH₃, which was synthesized in three steps with good yields. Then, an SN2 substitution reaction of P1 or P2 with

the hydrolyzed thioester followed by oxidation with *m*-CPBA resulted in DG1 or DG2, respectively. Because P3 was crystalline, the substitution and oxidation reactions were carried out at elevated temperatures (i.e., 100 °C). The chemical structures of all DG polymers were confirmed by ¹H and ¹³C NMR (see the Polymer Syntheses section above). ¹H NMR results (Figures S4-S7) indicated that all the post-modification reactions were nearly quantitative. ¹H NMR spectra for DG1 and DG2 are shown in Figure 1. All protons could be assigned with expected integration values. For the four intermediated polymers that were soluble in THF (i.e., P1, P3, P5, and P6), SEC results suggested that the molecular weight increased slightly after SN2 substitution reactions, and no chain scission of P1 or P3 was observed under the reaction conditions (see Figure S8). All DG polymers are soluble only in strongly polar solvents, such as N,N-dimethylformamide (DMF), DMAc, DMSO, and hexafluoro-2-propanol, because of the high polarity and high grafting density of the sulfonyl or disulfonyl groups in the side chains.



Figure 1. ¹H NMR spectra of DG1 (upper panel) and DG2 (bottom panel) in DMSO- d_6 . Symbol * indicates the solvent peak. A trace amount of trifluoroacetic acid was added to shift the water peak to lower fields.



Figure 2. (A) TGA and (B) DSC thermograms for various DG polymers. For both TGA and DSC, the heating and cooling rates were 10 °C/min under dry nitrogen. The degradation temperatures at 5% weight loss ($T_{d,5\%}$) are shown in (A) and the T_g values are shown in (B).

Thermal Properties of DG Polymers. Thermal stability of the DG polymers was

evaluated by TGA (Figure 2A). All samples exhibited a single-step decomposition with the 5% weight loss ($T_{d,5\%}$) around 290 °C, except for DG2, whose $T_{d,5\%}$ was only 254 °C. It was likely that the strong electron-withdrawing disulfonyl groups destabilized DG2, which exhibited the highest char yield of 16 wt.% at 600 °C. Considering the highest sulfonyl density for DG2, the sulfonyl groups should be responsible for the high char yield.^{34, 35}

Thermal transitions of the DG polymers were investigated by DSC, as shown in Figure 2B. Only glass transitions were observed for all samples within the temperature range studied. X-ray diffraction results showed only amorphous halos (data not shown), indicating the amorphous nature of these polymers. From Figure 2B, the Tgs of DG1-DG4 were found at 73, 86, 85, and 122 °C, respectively, when the heating rate was 10 °C/min. In general, disulfonylated polymers (DG1 and DG2) had lower Tgs than mono-sulfonylated polymers (DG3 and DG4). Meanwhile, the bis-substituted polymers (DG2 and DG4) had higher Tgs than the mono-substituted polymers (DG1 and DG3). Note that Tgs of DG3 and DG4 were consistent with those reported before.³¹



Figure 3. (A,B,C,D) Real (ε_r') and (E,F,G,H) imaginary (ε_r'') relative permittivities as a function of temperature at different frequencies for various DG polymers: (A,E) DG1, (B,F) DG2, (C,G) DG3, and (D,H) DG4. Insets in (E-H) show logarithmic maximum frequency (f_{max}) as a function of 1/k_BT for various DG polymers.

Dielectric Properties of DG Polymers. Temperature-scan BDS experiments were conducted for solution-cast DG films to investigate the sub-T_g transitions; the results are shown in Figure 3. In general, two transitions were observed for the side-chain DG polymers, namely, β and α (or glass) transitions. The α transitions were often obscured by significant conduction of impurity ions in polar polymers, when the temperature was near and above the Tgs.^{27,28} Therefore, DSC should be better than BDS to determine the Tg for polar polymers unambiguously. Well-defined β transitions were observed at low temperatures (-100 ~ -75 °C at 1 Hz), which could be attributed to the rotation of sulfonyl side groups in response to the applied electric field.^{27,28} All transition peaks shifted to higher temperatures as the frequency increased due to the slower kinetics of the sulfonyl dipoles in following the increasing frequency of electric field. As a result of the sub-Tg orientational polarization, the ε_r' values increased above the β transitions for all DG polymers.



Figure 4. (A) T_g and (B) T_β for DG1-DG4. (C) Proposed local chain conformations for DG1-DG4 with different dipole-dipole interactions, I - IV. Sulfonyl dipoles are shown as red arrows. Rotation of the sulfonyl side groups is responsible for the β transition.

It is desirable to understand these thermal transitions at the molecular level in terms of dipolar interactions among sulfonyl groups in DG polymers (Figure 4). From Figures S9D and S11D, the T_g values were -25 and 9 °C for P1 (PECH) and P3 (PBCMO), respectively. The higher T_g of P3 compared to that of P1 could be attributed to a stronger dipole-dipole interaction and thus chain stiffness because of the smaller distance between neighboring -CH₂Cl groups along the main chain.^{30, 36, 37} After replacing the -CH₂Cl groups in P1 and P3 with -CH₂SCH₃ groups, P5 and P6 exhibited decreased T_g values (-38 °C for P5 and -6 °C for P6; DSC data not shown),^{31, 33} because the dipole moment of the -CH₂SCH₃ (~1.5 D) group is lower than that of the -CH₂Cl group (~1.87

D) and they have a longer flexible side chain. After substitution with disulfonyl groups for DG1/DG2 or sulfonyl groups for DG3/DG4, the Tg values substantially increased (Figure 4A), which could be explained by the enhanced dipolar interaction I and certain steric hindrance among inner sulfonyl groups (4.5 D) directly attached to the main chain (see the proposed local chain conformations in Figure 4C). In other words, it is this strong intramolecular interaction (at least locally) that increased the rigidity/stiffness of DG polymer chains and their T_gs. Comparing mono- with bis-substitution, DG2 and DG4 exhibited higher T_{gs} than DG1 and DG3. This is because of the stronger dipolar interaction I and increased main-chain rigidity due to the smaller distance between neighboring sulfonyl groups in DG2 and DG4 (i.e., ideally every repeat unit) than that in DG1 and DG3 (i.e., ideally every other repeat unit). Alternatively, the dipolar sulfonyl interactions can also be directed orthogonally to the main chains (i.e., intermolecular rather than intramolecular interaction that is perpendicular to the paper). If this was the case, the distance between adjacent sulfonyl groups from neighboring chains should be similar for all DG polymers, and there should not be any difference in Tg for mono- (DG1 and DG3) and bissubstituted polymers (DG2 and DG4). However, this was not the case based on our experimental results. In addition, DG1 and DG2 with bis-substitution showed lower Tg values than DG3 and DG4 with mono-substitution, respectively. This could be explained by the poorer packing and thus larger free volume due to the longer side chains in DG1 and DG2.

Increasing ε_r'' was seen for each DG polymer as the temperature approached the T_g (Figures 3E-H); the lower the frequency, the more significant was the increase in ε_r'' . This increase could be attributed to the conduction of impurity ions, as reported in previous reports.^{27, 28} Note that ions could still conduct even when the temperature is somewhat below the T_g.³⁸

The activation energies for the β transition (E_{a, β}) were determined from the peak frequency

 (f_{peak}) , vs. 1/k_BT (see insets in Figures 3E-H). Intriguingly, the E_{a,β} values were nearly the same for DG1-DG4, i.e., ~0.6 eV (also see Table 1 later). This result suggests that the observed β transitions should be largely ascribed to the rotation of only one sulfonyl group per side chain, regardless of the bis- or mono-substitution. Otherwise, if the two sulfonyl groups rotated together in the disulfonyl side chains, as we suggested originally, the $E_{a,\beta}$ values for DG1 and DG2 would be different from those for DG3 and DG4, because the disulforyl group has a larger volume than the mono-sulfonyl group. Given the stronger dipolar interaction I among the inner sulfonyl groups than the dipolar interaction II among the outer sulforyl groups (see Figure 4C), we consider that only the methylsulfonyl groups should be easy to rotate and the sulfonyl groups adjacent to the main chain were difficult to rotate freely due to steric hindrance. Comparing DG1 with DG3 and DG2 with DG4, DG1 and DG2 exhibited lower T_{β} values, especially at 10⁵ Hz. This suggests that the methylsulfonyl dipoles in the disulfonyl groups of DG1 and DG2 are much easier to rotate than those in DG3 and DG4, because the mobility of the methylsulfonyl dipoles in DG3 and DG4 are hindered by the stronger dipolar interaction I than dipolar interaction II when they are directly attached to the main chain. Meanwhile, the T_{β} values at 10⁵ Hz were lower for DG1 and DG3 This could be attributed to the smaller distances between than DG2 and DG4, respectively. adjacent sulfonyl groups and thus stronger dipolar interactions for DG2 and DG4.

Polymer	Tg / Tm ^a (°C)	$\epsilon_{r,\infty} b$	εr' / Τ _{βα} ^c (1000 Hz)	peak εr' ^d (100 Hz)	$ \tan \delta_{\min} / T_{\beta \alpha} e \\ (1 \text{ Hz}) $	$E_{a,\beta} (eV)^{f}$
P1	-25 / -	2.4	2.9 / -70°C	11	0.006 / -70°C	0.35±0.01
P2	2 / -	4.0	5.9 / -50°C	32	0.02 / -50°C	$0.57{\pm}0.02$
P3	9 / 166	3.6	3.8 / -20°C	4.2	0.006 / -20°C	$0.43{\pm}0.01$
P4	17 / -	4.4	7.6 / -35°C	26	0.02 / -35°C	$0.71 {\pm} 0.01$
DG1	73 / -	4.0	8.1 / 25°C	50	0.023 / 25°C	0.61 ± 0.02
DG2	88 / -	4.6	9.1 / 25°C	43	0.019 / 25°C	$0.59{\pm}0.01$
DG3	85 / -	4.4	6.8 / 25°C	32	0.003 / 60°C	$0.62{\pm}0.01$
DG4	123 / -	4.4	7.7 / 25°C	21	0.020 / 60°C	$0.56{\pm}0.01$

Table 1. T_g/T_m , Dielectric Constants, Minimum Dissipation Factor (tan δ), and Activation Energy for the β Transition (E_{a, β}) of Various DG Polymers.

^{*a*} Obtained from DSC results.

^{*b*} Obtained from the ε_r' values at -140 °C and 1 MHz. Supposedly, only electronic and atomic polarizations contribute to the $\varepsilon_{r,\infty}$.

 c Obtained from the ϵ_{r}' values at 1 kHz for $T_{\beta\alpha}$ between the β and α transitions.

^{*d*} Obtained from the peak ε_r' values at 100 Hz (i.e., slightly above the glass transition). Supposedly, the contribution from ionic conduction is almost negligible.

^{*e*} Minimum dissipation factor, tan δ , at 1 Hz, and the T_{$\beta\alpha$} is also given (see Figure S13).

^{*f*} Activation energy for the β transition (E_{a, β}) obtained from the ln*f*_{peak} vs. 1/k_BT plots.

Thermal and dielectric properties for P1-P4 and DG1-DG4 are summarized in Table 1. Comparing with P2 and P4, DG1 and DG2 exhibit significantly higher T_g values, indicating that the inner sulfonyl groups are responsible for the chain rigidity as a result of strong dipolar interaction I and certain steric hindrance. From the BDS results (Figures 3 and S9-S12), the $\varepsilon_{r,\infty}$ values, i.e., the dielectric constant at infinite frequencies with only contributions from electronic and atomic polarizations, are obtained. First, the $\varepsilon_{r,\infty}$ values for P1 and P3 are 2.4 and 3.6, respectively. When sulfonyl groups are present, the $\varepsilon_{r,\infty}$ values increase to 4.0-4.6 for P2, P4, and DG1-DG4, regardless of mono- or bis-substitutions. This is consistent with previous understanding that dielectric constants from electronic and vibrational polarizations are between 2 and 5 for hydrocarbon-based polymers.⁵ At a temperature above the β but below the α transitions, these polymers can be considered as DG polymers. Usually, relatively low tan δ can be achieved between the β and α transitions (i.e., around T_{$\beta\alpha$}) for dipolar glass polymers, because polymer chains are largely frozen and only the side groups can rotate. For most sulfonyl polymers, the minimum tand values at 1 Hz are around 0.02, except that DG3 shows a minimum tand as low as 0.003 at 60 °C (see Table 1 and Figure S13). The ε_r' values for P2 and P4 at 1 kHz and $T_{\beta\alpha}$ are 5.9 and 7.6, whereas they are 8.1 and 9.1 for DG1 and DG2; the increments are only 2.2 and 1.5, respectively. These results are consistent with the above consideration that the outer sulfonyl groups should be largely responsible for the enhanced dielectric constant in glassy P2/DG1 and P4/DG2. Right above the glass transition, all polymers should exhibit a peak in ε_r' . The ε_r' peak at 100 Hz for P2 and P4 are 32 and 26, whereas they are 50 and 43 for DG1 and DG2; the increments are 18 and 17, respectively. Obviously, both inner and outer sulfonyl groups can contribute to the peak ε_r' values above the T_g, with the outer sulfonyl groups contributing more than the inner sulfonyl groups. Although dielectric constants are as high as 20-50 right above Tg due to the orientational polarization of sulfonyl dipoles in DG polymers, molten polymers are not suitable for electric energy storage because of a high dielectric loss from conduction of space charges (both electrons and impurity ions) (see Figures 3 and S9-S12).



Figure 5. Representative bipolar D-E loops for solution-cast films of (A) DG1, (B) DG2, (C) DG3, and (D) DG4 at room temperature and 1 kHz (with a sinusoidal waveform). Film thicknesses were around 3-6 μ m for all samples.

To investigate the dielectric properties of the DG polymers under high electric fields, bipolar D-E loop study was carried out for solution-cast film samples (3-6 μ m thick). Figure 5 shows bipolar D-E loops of the DG polymers at room temperature and 1 kHz. The apparent dielectric constant (ε_r) was obtained from the linear range when the poling field was within ±100 MV/m, i.e., $\varepsilon_r = D/(\varepsilon_0 E)$. At room temperature and 1 kHz, the ε_r values of DG1, DG2, DG3, and DG4 were 9.0, 11.5, 7.2, and 8.0, respectively. These values were slightly higher than those obtained from the BDS measurements (i.e., 8.1, 9.1, 6.8, and 7.7 for DG1, DG2, DG3, and DG4 at room temperature and 1 kHz). This could be attributed to the higher poling electric field in D- E loop tests, which were able to polarize additional dipoles that were difficult to polarize at low electric fields in BDS measurements. Upon increasing the poling field above 200 MV/m, double hysteresis loops (DHLs) appeared for all samples; the higher the poling field, the more obvious the DHLs. This could be attributed to the formation of metastable FE domains upon high-field poling. The obvious DHL behavior was somewhat different from the linear dielectric behavior for other DG polymers reported recently.^{27, 28} Similar DHL behavior was also reported recently for even-numbered nylons (nylon-6 and nylon-12) at elevated temperatures recently.³⁹ Supposedly, paraelectric even-numbered nylons should not exhibit any DHLs. However, upon high field-poling, metastable FE domains formed. After removing the poling electric field, field-induced FE domains disappeared and the polarization returned to nearly zero. Here, we consider that a similar situation happened for these DG polymers. These FE domains were so short-lived that the remnant polarization returned to nearly zero when the poling field decreased to zero. Obviously, the formation of metastable FE domains would cause a higher dielectric loss.

Comparing with DG3 and DG4, DG1 and DG2 started to show broadened loops at lower poling fields, indicating that longer side chains and weaker dipolar interaction **II** facilitated the orientation of sulfonyl groups and the formation of field-induced FE domains. DG2 exhibited the broadest loops, namely, the highest dielectric loss, among all DG polymers due to its long disulfonyl groups with a high dipole density. This is certainly undesirable for electric energy storage.



Figure 6. (A) Stored and (B) discharged energy densities (U_{e,stored} and U_{e,discharged}) and (C) loss% for all DG polymers at room temperature. Results are extracted from the D-E loops in Figure 5.

Stored and discharged energy densities (U_{e,stored} and U_{e,discharged}) for all DG polymers at room temperature were extracted from the D-E loops in Figure 5. The loss% was calculated from the U_{e,stored} and U_{e,discharged} with a definition of loss% = $100(1 - U_{e,discharged}/U_{e,stored})$ %.⁴⁰ As shown in Figure 6A, the U_{e,stored} values for DG1 and DG2 showed a similar increasing trend, and as did those for DG3 and DG4. At the same electric field, especially above 200 MV/m, DG1 and DG2 exhibited a higher U_{e,stored} than DG3 and DG4, indicating a higher orientational polarization for the disulfonyl side chains than the mono-sulfonyl side chains. The U_{e,discharged} followed similar trends as the U_{e,stored} for DG1/DG2 and DG3/DG4, respectively (Figure 6B). Basically, disulfonylated DG1/DG2 discharged more energy than mono-sulfonylated DG3/DG4. However, due to its high breakdown strength (note that this breakdown strength is obtained from the maximum poling field shown in Figure 5D, not from a separate Weibull statistic analysis), DG4 exhibited a high U_{e,discharged} of 15.4 J/cm³ at 546 MV/m, which is more than 5 times that for current state-of-the-art dielectric film, biaxially oriented polypropylene (i.e., 3.0 J/cm³ at 550 MV/m).

For dielectric losses in Figure 6C, bis-substituted DG2/DG4 exhibited higher loss% than mono-substituted DG1/DG3. Moreover, the loss% for disulfonylated DG1/DG2 increased faster than mono-sulfonylated DG3/DG4 as the electric field increased. For most dielectric applications such as film capacitors and gate dielectrics, the applied electric field usually does not

exceed 200-300 MV/m.³ Also, considering the low loss requirement for polymer dielectrics,⁴ we consider that DG3 had an optimal performance at room temperature, namely, a high dielectric constant of 7.2, a U_{e,discharged} of 9.3 J/cm³ at 445 MV/m, and the loss% of only 12%.

Conclusions

In this study, a series of sulfonyl-containing DG polymers were designed and synthesized to investigate the influence of dipole density and dipole arrangement in side chains on their dielectric behavior and electric energy storage. Among them, DG1/DG3 were mono-substituted, and DG2/DG4 were bis-substituted. Meanwhile, DG1/DG2 were disulfonylated, and DG3/DG4 were mono-sulforylated. As a result of sub-T_g β transitions and rotation of highly polar sulforyl groups, these DG polymers exhibited high apparent dielectric constants (7-11.5) in the glassy state with reasonably low dissipation factor (tan $\delta \sim 0.003$ -0.02). However, these DG polymers exhibited differences in dielectric behaviors. First, bis-substituted DG2/DG4 showed higher dielectric constants than mono-substituted DG1/DG3 due to higher dipole densities in bissubstituted polymers. Second, disulfonylated DG1/DG2 had higher dielectric constants than mono-sulfonylated DG3/DG4. However, the increments were not large, indicating that the orientational polarization in disulforylated polymers mostly originated from the outer sulforyl groups, rather than the inner sulforyl groups. This was a result of weaker dipolar interactions **II** between outer sulfonyl groups than the dipolar interactions I between inner sulfonyl groups. In addition, the strong dipolar interactions I between inner sulfonyl groups and certain steric hindrance increased the rigidity/stiffness of polymer chains. As a result, the Tg values for these DG polymers were significantly higher than their precursor polymers such as P1-P4. Third, under high-field poling, all DG polymers exhibited DHLs at high enough electric fields, which could be attributed to the formation of metastable field-induced FE domains. The disulfonylated DG1/DG2 displayed more significant FE switching than the mono-sulfonylated DG3/DG4 because of strong dipolar interactions among disulfonyl groups. However, FE switching contributed to high dielectric or hysteresis losses, and were thus undesired. From the point of view of high energy density and low loss requirements, mono-sulfonylated DG3 and DG4 demonstrated better dielectric performance than disulfonylated DG1 and DG2.

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Supporting Information. The Supporting Information is available free of charge on the ACS Publications website at DOI: xxxxxxxxxx.

¹H NMR spectra for various small molecule intermediates and polymers; SEC traces for P1, P5, P3, and P6; BDS and DSC results for P1, P2, P3, and P4; temperature-scan tanδ results for DG1-DG4.

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TOC Graphics

High Dielectric Constant Sulfonyl-Containing Dipolar Glass Polymers with Enhanced Orientational Polarization

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dipolar interactions: I > II DG3, ε,=7.2 DG4, ε_r=8.0 DG2, ε_r=11.5 DG1, ε,=9.0

Supporting Information

High Dielectric Constant Sulfonyl-Containing Dipolar Glass Polymers with Enhanced Orientational Polarization

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Figure S1. ¹H NMR spectra for 3-methylsulfonyl-1-propanol in CDCl₃. Solvent peak at 7.25 ppm is labeled with "*".



Figure S2. ¹H NMR spectra for 3-(methylsulfonyl)propyl methanesulfonate in CDCl₃. Solvent peak at 7.25 ppm is labeled with "*".



Figure S3. ¹H NMR spectra for 3-(methylsulfonyl)propyl thioacetate in CDCl₃.



Figure S4. ¹H NMR spectra of P1, P2, and DG1 in DMSO- d_6 . Solvent DMSO peaks at 2.5 ppm are labeled with "*". A trace amount of trifluoroacetic acid (TFA) was added to shift the water peak to lower fields.



Figure S5. ¹H NMR spectra for P3 (CDCl₃), P4 (DMSO-*d*₆), and DG2 (DMSO-*d*₆). Solvent DMSO peaks at 2.5 ppm are labeled with "*". A trace amount of TFA was added to shift the water peak to lower fields.



Figure S6. ¹H NMR spectra for P1 (DMSO-*d*₆), P5 (CDCl₃), and DG3 (DMSO-*d*₆). Solvent DMSO peaks at 2.5 ppm are labeled with "*". A trace amount of TFA was added to shift the water peak to lower fields.



Figure S7. ¹H NMR spectra for P3 (CDCl₃), P6 (CDCl₃), and DG4 (DMSO-*d*₆). Solvent DMSO peak at 2.5 ppm is labeled with "*". A trace amount of TFA was added to shift the water peak to lower fields.



Figure S8. SEC traces for P1, P5, P3, and P6. Tetrahydrofuran (THF) was used as solvent at a flow rate of 1.0 mL/min. Polystyrene standards were used for conventional calibration.



Figure S9. Temperature-scan BDS results of (A) ε_r' , (B) ε_r'' , and (C) tan δ for P1 (i.e., PECH). The heating rate was 2 °C/min. α and β transitions are shown in the plots. (D) First-cooling and second-heating DSC thermograms for P1. The scanning rate was 10 °C/min.



Figure S10. Temperature-scan BDS results of (A) ε_r' , (B) ε_r'' , and (C) tan δ for P2. The heating rate was 2 °C/min. α and β transitions are shown in the plots. (D) First-cooling and second-heating DSC thermograms for P2. The scanning rate was 10 °C/min.



Figure S11. Temperature-scan BDS results of (A) ε_r' , (B) ε_r'' , and (C) tan δ for P3 (i.e., PBCMO). The heating rate was 2 °C/min. α and β transitions are shown in the plots. (D) First-cooling and second-heating DSC thermograms for P3. The scanning rate was 10 °C/min.



Figure S12. Temperature-scan BDS results of (A) ε_r' , (B) ε_r'' , and (C) tan δ for P4. The heating rate was 2 °C/min. α and β transitions are shown in the plots. (D) First-cooling and second-heating DSC thermograms for P4. The scanning rate was 10 °C/min.



Figure S13. Dissipation factor $(\tan \delta)$ as a function of temperature at different frequencies for various DG polymers: (A) DG1, (B) DG2, (C) DG3, and (D) DG4.