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Structure-Property Relationship of Polyimides Based on Pyromellitic Dianhydride and Short-Chain Aliphatic Diamines for Dielectric Material Applications

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ABSTRACT: Most polyolefins that are used for dielectric materials exhibit a low dielectric constant and operating temperatures up to 70°C. Polyimides offer a means to a higher dielectric constant material by the introduction of a polar group in the polymer backbone and are thermally stable at temperatures exceeding 250°C. A common dianhydride, pyromellitic dianhydride (PMDA), is reacted with various short-chain diamines to produce polymers with high imide density. Homopolymers and copolymers synthesized had dielectric constants ranging from 3.96 to 6.57. These materials exhibit a dielectric constant twice that of biaxially oriented polypropylene and therefore a twofold increase in capacitance as well as maintaining low dissipation factors that are acceptable for this application. The experimental dielectric constants of these materials are also compared to density functional theory calculations and exhibit a close relationship. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2013

KEYWORDS: dielectric properties; polyimides; structure-property relations

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INTRODUCTION

There is a current push by the industrial complex to move away from traditional pneumatic, hydraulic, and mechanical devices to electrochemical ones which are controlled electrically.[1] Thus, there is a need for a high-energy storage system to operate these new devices. The best solution to this problem is the incorporation of high-energy density capacitor banks in which the electrical energy can be stored over long charging times and released as needed through short pulses.[2] For this system to operate efficiently and to reduce the size of the overall capacitor bank, an insulating material is needed that possesses a large dielectric constant while still maintaining a low dielectric loss. The two benchmark polymer dielectric materials, biaxially oriented polypropylene (BOPP) and polyvinylidene fluoride (PVDF), have dielectric constants of 2.2 and 10, respectively.[3–6]

Polyimides are attractive materials for this application as they have a more polar backbone and thus a higher dielectric constant than polyolefins. The fact that make polyimides even more desirable is that they are thermally stable at temperatures exceeding 250°C, twice the operating temperature of most common dielectric materials, making them able to withstand the heat generation that these capacitor banks will give rise to and there is less need for cooling the entire capacitor bank.[7] Most common polymers used as dielectric materials exhibit severe decrease in dielectric strength around 70°C.[8]

Interestingly, a search of recent literature yields little work being done in this field. Instead, polyimides are being researched as a possible replacement of silicon dioxide in applications such as the insulating material in semiconductors, printed microelectronics, and so forth.[9–13] Most studies of polyimides in electronic applications have looked at ways to reduce the dielectric constant of the material. The reduction of the dielectric constant has been controlled by lowering the polarizability of the polymer through modification of the backbone with the incorporation of bulky, space-filling groups, the replacement of hydrogen with fluorine atoms, or a combination of both. The introduction of space-filling groups, such as aromatics, increases the free volume and thus decreasing the dipolar and atomic polarizability, whereas fluorine replacement will reduce the total polarizability through the heightening of the hydrophobicity of the polymer.[14–22]

In our research, we focus on the opposite end of the polyimide chemical space in which an increase of the dielectric constant of the polymer is sought. This is done by the polymerization of a common aromatic dianhydride with various alkyl diamines producing an overall reduction of the free volume as well as maintaining a high-imide functional group density in the polymer backbone. The experimental results are combined with theoretical dielectric calculations done through density functional theory (DFT) to give a better understanding of the structure–property relationship of these polyimides. A comparison of theoretical and experimental data will then lead to a next generation of polyimides for the ones reported here.

EXPERIMENTAL

Materials

PMDA, 1,3-diaminopropane (1,3-DAP), 1,2-diaminopropane (1,2-DAP), dimethylformamide (DMF), and *N*-methyl-2-pyrrolidone (NMP) were purchased from Aldrich Chemical (St. Louis, Missouri). Jeffamines (Figure 1) EDR-104, HK511, and D230 were provided by the Huntsman (The Woodlands, Texas). PMDA was recrystallized from acetic anhydride, whereas the diamines were used as received. Shim stocks were purchased from McMaster Carr (Princeton, New Jersey) with a diameter of 2″, a thickness of 0.01″, and ASTM A666 stainless steel.

General Procedure for Homopolymerization

A three-neck flask equipped with a Teflon^{TM}-coated magnetic stir bar was fitted with a reflux condenser, a glass stopper, and a glass apparatus for trapping evolved water. The entire apparatus is flame dried under vacuum to remove moisture and placed under an inert atmosphere. To the flask, the appropriate amount of diamine, 0.02 mL of isopropylamine (IPAm) and 50 mL of NMP, was added. The solution was stirred for 30 min at room temperature to disperse the amine equally in solution. To the solution, the appropriate amount of dianhydride was added and this mixture was stirred at 50–100°C for 2 h. Once all of the solids were dissolved, the temperature was increased to 180°C and the solution was stirred for 10 h. The polyimide was precipitated out of solution by the addition of methanol. The solvent was decanted off and the polymer was dried at 75°C *in vacuo*.

Polymer 4. FTIR (cm^{-1}): 1774, 1717, 1664, 1395, and 1363. Differential scanning calorimetry (DSC) results: T_g = not observed; T_m = not observed. Thermogravimetric analysis (TGA) (10°C min^{-1}): N_2 (onset): 258°C.

Polymer 7. ^{1}H NMR ((CD$_3$)$_2$S=O, ppm): $\delta = 1.23$ (m, 12H), 2.94 (m, 11H), 4.23 (m, 2H), 8.11 (m, 2H). FTIR (cm^{-1}): 2976, 2878, 1771, 1716, 1460, 1380, 1355, 1265, 1105, and 917. DSC results: $T_g = 75°C$; T_m = not observed. TGA (10°C min^{-1}): N_2 (onset): 262°C.

General Procedure for Copolymerization

A three-neck flask equipped with a Teflon^{TM}-coated magnetic stir bar was fitted with a reflux condenser, a glass stopper, and a glass apparatus to trap evolved water and a rubber septum stopper. The apparatus was then flame dried under vacuum to remove moisture and placed under an inert atmosphere. To the flask, the appropriate amount of the two diamines, 0.04 mL of IPAm and 25 mL of DMF, was added. The solution was stirred for 30 min at room temperature to disperse the diamines equally in DMF. The appropriate amount of PMDA was added to an Erlenmeyer flask and stored under inert atmosphere. To the flask, 75 mL of DMF was added. The flask is heated slightly until all of the PMDA is dissolved. The amine solution is heated to 50°C and the PMDA/DMF solution is then canulated into the three-neck flask. After the addition of PMDA/DMF solution is complete, the temperature is raised to 150°C and the solution is stirred until the polyamic acid is dissolved. After complete dissolution of the polyamic acid, the temperature is raised to 180°C and the solution is refluxed for 12–24 h to form the polyimide.

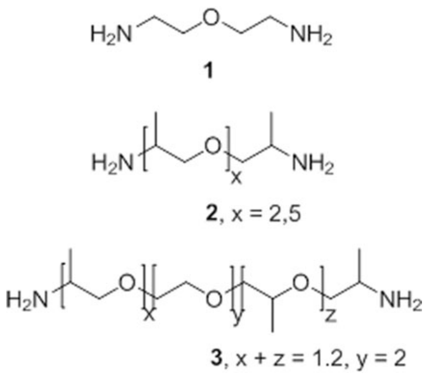


Figure 1. Structure of Jeffamines EDR-104 (top), D230 (middle), and HK511 (bottom).

Polymer 9. ^{1}H NMR ((CD$_3$)$_2$S=O, ppm): $\delta = 1.01$ (m, 10H), 1.28 (m, 8H), 3.64 (m, 10H), 4.43 (m, 3H), 8.14 (m, 4H). FTIR (cm^{-1}): 2975, 2936, 2873, 1771, 1717, 1458, 1358, 1266, 1157, 1110, 1067, 1040, 916, 828, and 731. DSC results: $T_g = 54°C$; T_m = not observed. TGA (10°C min^{-1}): N_2 (onset): 349°C.

Polymer 10. ^{1}H NMR ((CD$_3$)$_2$S=O, ppm): $\delta = 1.08$ (m, 16H), 4.18 (m, 10H), 8.17 (m, 4H). FTIR (cm^{-1}): 2975, 2936, 2873, 1771, 1717, 1458, 1358, 1266, 1157, 1110, 1067, 1040, 916, 828, and 731. DSC results: $T_g = 54°C$; T_m = not observed. TGA (10°C min^{-1}): N_2 (onset): 349°C.

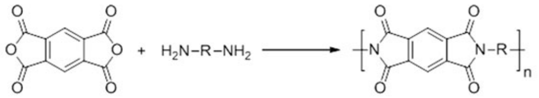
Polymer 11. ^{1}H NMR ((CD$_3$)$_2$S=O, ppm): $\delta = 0.93$ (m, 10H), 1.28 (m, 12H), 3.56 (m, 10H), 4.43 (m, 4H), 8.15 (m, 4H). FTIR (cm^{-1}): 2867, 1770, 1716, 1355, 1105, 1036, and 728. DSC results: $T_g = 58°C$; T_m = not observed. TGA (10°C min^{-1}): N_2 (onset): 350°C.

Instrumentation

Solution ^{1}H NMR was performed on a Bruker DMX500 high-resolution digital NMR spectrometer. All chemical shifts were referenced to (CD$_3$)$_2$S=O (^{1}H = 2.50 ppm). DSC was done with a TA instruments DSC Q series with a heating rate of 10°C min^{-1}. Samples were sealed in an aluminum pan with an empty pan used as a reference. TGA was performed using a TA instruments TGA Q500. Dielectric measurements were made with an Imass Time Domain Dielectric Spectrometer.

General Procedure for Generation of Polyimide Thin Film

An appropriate amount of polyimide and DMF is added to a scintillation vial to produce a 10% wt/wt mixture. The mixture is heated until the polyimide dissolves and the solution is then filtered. The filtered solution is drop casted onto a stainless steel



4: R = $-(CH_2)_3-$
5: R = $-CH_2CH(CH_3)-$
6: R = $-(CH_2)_2O(CH_2)_2-$
7: R = $-(CH(CH_3)CH_2O)_xCH_2CH(CH_3)-$
8: R = $-(CH(CH_3)CH_2O)_x(CH_2CH_2O)_y(CH_2CH(CH_3)O)_zCH_2CH(CH_3)-$
9: R = $-[(CH_2)_3]_{0.2}-$, $-[(CH(CH_3)CH_2O)_xCH_2CH(CH_3)]_{0.8}-$
10: R = $-[(CH_2)_3]_{0.2}-$, $-[(CH(CH_3)CH_2O)_x(CH_2CH_2O)_y(CH_2CH(CH_3)O)_zCH_2CH(CH_3)]_{0.8}-$
11: R = $-[CH_2CH(CH_3)]_{0.2}-$, $-[(CH(CH_3)CH_2O)_xCH_2CH(CH_3)]_{0.8}-$
12: R = $-[CH_2CH(CH_3)]_{0.5}-$, $-[(CH(CH_3)CH_2O)_xCH_2CH(CH_3)]_{0.5}-$
13: R = $-[CH_2CH(CH_3)]_{0.5}-$, $-[(CH(CH_3)CH_2O)_x(CH_2CH_2O)_y(CH_2CH(CH_3)O)_zCH_2CH(CH_3)]_{0.5}$

Figure 2. Structures of synthesized polyimides.

shim stock and covered with a glass petri dish slightly opened to the air and allowed to dry overnight to produce a tacky film. The shim stock with the tacky film is then placed into a vacuum oven and heated at 165–175°C for 24 h to evaporate all of the solvents. Isothermal TGA is run at 170°C on a dried part of the film to determine the level of solvent remaining

RESULTS AND DISCUSSION

Homopolymers

Solubility and Thermal Properties. The homopolymers shown in Figure 2 were all synthesized from the same condensation procedure. Polymers **4**, **5**, and **6** proved to be insoluble in most organic solvents with the exception of *m*-cresol. However, even after extensive drying under vacuum, the minute amount of *m*-cresol remaining caused the films casted from this solvent to be too conductive. Polymers **7** and **8** proved to be more soluble stemming from the increase in distance between rigid aromatic functionalities in the polymer backbone.

The DSC data summarized in Table I show that polymers **4**, **5**, and **6** do not exhibit a glass transition temperature even down to −90°C. A melting temperature is either absent or is above the point of thermal degradation and thus not observed. The incorporation of a longer alkyl ether chain between aromatic imide groups gives rises to a T_g but again there is an absence of a melting temperature.

Dielectric Properties. The insoluble polymers were pressed into a pellet to test the dielectric properties of the material with polymer **4** being cohesive enough and did not fall apart when placed in the sample holder. Figure 3 (top) shows the dielectric spectra of polymer **4**. The dielectric constant is stable above 5.5, whereas the loss factor remains below 2% even as the temperature is increased to 100°C. Polymer **4**, exhibits a dielectric constant that is 2.5 times larger than BOPP while still being well under the 5% dielectric loss threshold which constitutes capacitor failure.[23] When the longer ether chains are added instead of the short alkyl chains, the dielectric constant is reduced as there is an increase in free volume stemming from the protruding methyl groups. The loss factor, which is below 1% at room temperature, increases significantly when the polymer is heated to T_g and the instrument short circuits as soon as the polymer is heated above T_g.

Copolymers

As the polymers that contain the longer ether chains are more soluble in high boiling solvents, it was decided to copolymerize them with the shorter alkyl diamines. The introduction of the shorter alkyl diamine served a twofold purpose (1) by increasing the percent functionality of imide there should be an increase in dielectric constant and (2) the loss factor should also be reduced through an increase in rigidity of the polymer, that is less response by the polymer to the switching electric field.

Thermal Properties and Film Formation. Combining the short alkyl diamine with the long ether diamines caused a reduction in the T_g versus a polymer solely made with the ether linkage. The solubility of these copolymers, made with 20% of the alkyl and 80% of the ether diamines, in high boiling solvents was maintained compared to the homopolymers and the films produced looked like a sheet of glass over the shim stock. Changing the feed of the diamines to a 50/50 mixture created polymers with reduced solubility in DMF. Instead of a smooth, clear film, a dispersion in DMF was obtained at a much reduced concentration (1–5%). Upon cooling the film, cracks appeared and the film peeled off of the shim stock.

Dielectric Properties. Figure 3 (bottom) shows the typical dielectric results for the copolymers. There is an increase in the dielectric constant with copolymers constructed from 1,3-DAP and either Jeffamine 2 or 3. Using 1,2-DAP instead caused a reduction in the dielectric constant which can be explained by the free volume increase from the methyl group. Even with the incorporation of alkyl diamine, the loss factor remains on the same order as the homopolymer, whereas increasing the temperature to the T_g of the polymer does not cause as significant increase in the loss as compared to the homopolymer. Raising the temperature above the T_g of the polymer causes the loss factor to increase well above 5% at high frequencies and above 10% at low frequencies.

Table I. Thermal and Dielectric Properties of Polyimides

Polymer	T_g (°C)[a]	T_m (°C)	T_d (°C)[b]	k_{calc}	$k_{60\ Hz}$[c]	$k_{1\ kHz}$[c]	tan(δ)$_{60\ Hz}$[c]	tan(δ)$_{1\ kHz}$[c]
4[d]	n/o	n/o	258	4.0 ± 0.5	5.61	5.60	0.000869	0.000553
7	75	n/o	262	3.8 ± 0.4	4.20	4.18	0.00357	0.00518
9	54	n/o	349	TBD[e]	6.57	6.55	0.00362	0.00626
10	58	n/o	350	TBD[e]	5.15	5.12	0.00363	0.00460
11	51	n/o	378	TBD[e]	3.96	3.92	0.00477	0.00608

[a] Values taken from the midpoint, [b] Values taken from onset, [c] Values at room temperature, [d] Pressed pellet, [e] To be determined.

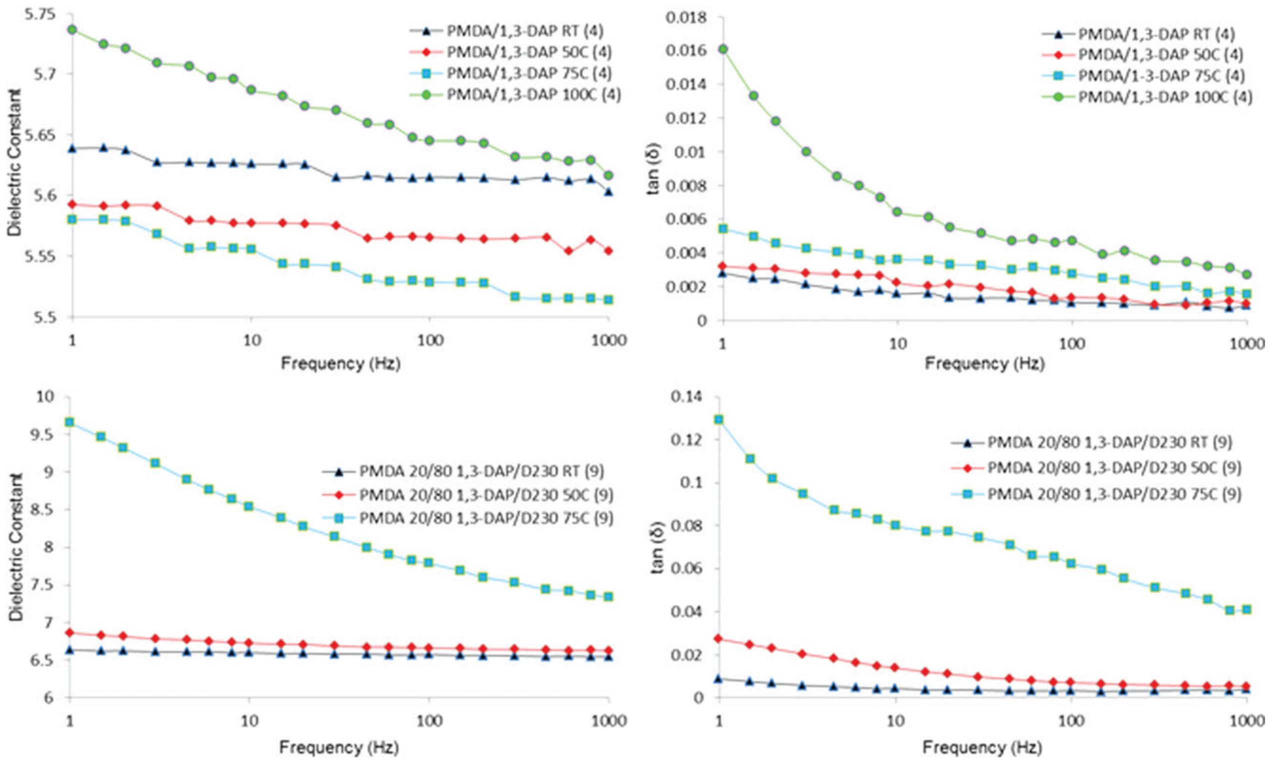


Figure 3. Temperature effects on dielectric properties. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Comparison to Theoretical Calculations

Theoretical Calculations. Given that the synthesized polyimides have complex structures, it is difficult and time-intensive to perform DFT calculations. Therefore, we considered a few polyimides (Figure 4) with simpler but similar structures compared to those synthesized polyimides. In this way, we can give a qualitative view on the structure–property relationship of synthesized polyimides. To mirror the experimental work, the repeat unit of A-1 is exactly the same as synthesized polymer **4**, and polymer A-3 which is very similar to synthesized polymer **7**. By considering A-3, we can identify the effect of incorporating methyl groups and increasing the number of —CH2— units in the repeat unit.

DFT, as implemented in the Vienna *ab initio* simulation package (VASP), was used to determine the structural and electronic properties of the polymers.[24] The Perdew, Burke, and Ernzerhof functional (PBE), projector-augmented wave frozen-core potentials, and a cutoff energy of 400 eV for the plane wave expansion of the wave functions were used.[25–27] The PBE-optimized geometry was then used to determine the dielectric constant tensor using density functional perturbation theory (DFPT).[28] In this study, we considered an isolated infinite chain of the polyimides. The true dielectric permittivity of the polymer chain alone was then extracted by combining the DFPT computation of the supercell (containing a significant amount of vacuum) with effective medium theory, using a recently developed method.[29,30] The band gap and dielectric constant results of polyimides are shown in Figure 5 in which the filled symbol represents the electronic

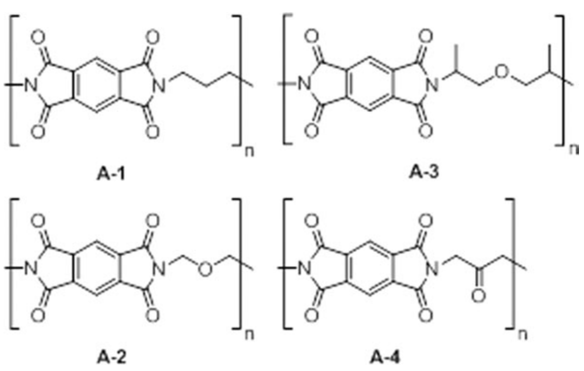


Figure 4. Repeating units of polyimides calculated using DFT.

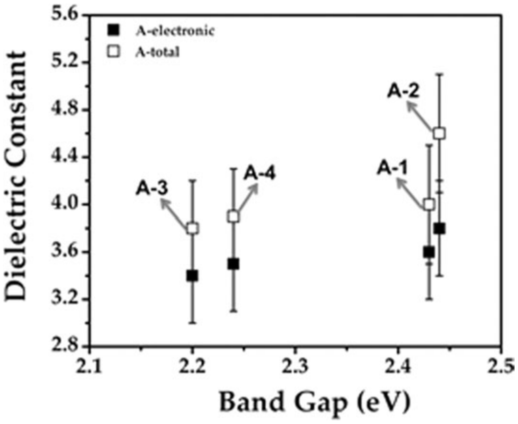


Figure 5. Band gap and dielectric constant results.

dielectric constant, whereas the open symbol is for total dielectric constant. When changing the linker from —CH2— to —O—, the band gap remains almost the same, but both the electronic and the total dielectric constant increase, but when the linker is changed to —CO—, both the band gap and the dielectric constant decrease. Also, in Figure 5, when comparing A-3 with A-2, we can see that incorporating methyl groups and increasing the number of —CH2— units in the repeating unit will decrease the band gap and the dielectric constant.

Polymer **4** has an experimentally higher, about a factor of 1.4, than the calculated dielectric constant, whereas the calculated and experimental dielectric constant is the same for polymer **7**. The difference in accuracy for the two calculations could be owing to how well the polymer chains are ordered as polymer **4** is a pressed pellet and polymer **7** is a thin film. The ordering of polymer chains could be different and this difference is not taken into account in DFT calculations.

CONCLUSIONS

A series of high-functionality polyimide homopolymers and copolymers featuring PMDA with various short-chain aliphatic diamines were synthesized and dielectric properties were measured. The homopolymers with the densest functionality proved to be insoluble, whereas the soluble homopolymers had a large increase in dielectric loss and could not be measured at temperatures near or above T_g. A reduction in loss of the soluble homopolymers is accomplished by copolymerization with a shorter alkyl diamine which also allows for the measurements to be made above T_g, but again the loss is quite significant above this temperature. Still, the dielectric constant of all of the polymers was higher than biaxially oriented polypropylene and possessed operating temperatures well above that of BOPP. Future work will look at processing a film of polymer **4** from the more soluble poly(amic) acid form and then performing thermal imidization.

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