Cross-Linked Polymer Gate Dielectric Films for Low-Voltage Organic Transistors

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Received March 5, 2009. Revised Manuscript Received April 6, 2009

Cross-linked polymer films were investigated as new gate dielectric materials for low-voltage thin-film transistors. Poly(4-vinylphenol) (PVP) was cross-linked through esterification reactions with commercially available bifunctional anhydrides, acyl chlorides, and carboxylic acids. The polymer dielectric films were evaluated based on surface morphology, capacitance, leakage current, and their compatibility with organic semiconductors. Thin insulating PVP films cross-linked with dianhydrides yielded a capacitance as high as 400 nF/cm^2 with leakage currents below 10^{-8} A/cm^2. Organic thin-film transistors (OTFTs) fabricated on these gate dielectric layers exhibited charge carrier mobilities as high as 3 cm^2/(V s) for p-channel pentacene on octadecyltriethoxylsilane (OTS)-modified PVP and 0.045 cm^2/(V s) for n-channel perfluorinated copper phthalocyanine (FCuPc).

Introduction

Over the past two decades, interest in organic materials for electronic applications has been steadily increasing due to their advantages of inexpensive, large area processing and compatibility with flexible, plastic substrates. Organic thin-film transistors (OTFTs) are particularly interesting owing to simple fabrication methods and facile integration with electronic components.[1,2] While extensive consideration has been given to the semiconductor materials with respect to understanding and improving charge transport, only modest attention has been paid to the gate dielectric material. However, the realization of commercial electronics driven by organic transistors will greatly benefit from the development of new insulating materials and processing capabilities.

Low-voltage transistor operation has attracted interest for many reasons, particularly for low power applications,[3] portable electronics, and most recently, chemical detection in aqueous media.[4,5] For most circuit-based electronics, the critical device metric is the output current (I_{DS}) relative to the input voltage (V_G). The saturation current in organic thin-film transistors is generally calculated by $I_{DS} = (WC_i/2L)\mu(V_G - V_T)^2$, where μ is the charge carrier mobility, C_i is the capacitance per unit area of the insulator, V_T is the threshold voltage, and W and L are the OTFT channel width and length, respectively. Significant gains, with respect to I_{DS} relative to V_G, can be made by increasing C_i through design and engineering of the insulating layer. The capacitance, C, is defined by $C = k\varepsilon_0 A/d$, where ε_0 is the permittivity of free space, A is the area of the capacitor, and d is the thickness of the dielectric. While new or composite materials are necessary to increase the dielectric constant, the simplest approach to increase the capacitance is decreasing the film thickness. A reduction in thickness, however, is often accompanied by a decrease in uniformity and an increase in leakage current owing to pinholes extending through the film.

The use of polymer gate dielectric layers has been pivotal in reducing OTFT operating voltages, which has been accomplished by incorporating known insulator materials or developing new systems based on cross-linkable polymers. The benefits of integrating cross-linked polymer films based on poly(4-vinylphenol) (PVP) was initially shown by Klauk et al.[6] Other polymeric dielectric layers, which generally consist of cross-linked systems, have been used for organic thin-film transistors, including polyimides,[7] glass resins,[8]

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10.1021/cm900637p CCC: $40.75

poly(methyl methacrylate) (PMMA),[9] poly(vinyl alcohol),[10] and photo-alignment layers.[11] A commercially available interlayer dielectric from the silicon industry, divinyltetramethyldisiloxane−bis(benzocyclobutene) (BCB), was used to show general ambipolar characteristics for common organic semiconductors and demonstrate transistor operation below 5 V.[12] High-*k* polymeric gate dielectrics were developed using cross-linked cyanoethylated poly(vinyl alcohol) (CR-V) yielding good insulator properties and transistor characteristics for operating biases below 3 V.[13] Low-voltage OTFTs based on ultrathin polymer films were demonstrated using PVP and polystyrene films cross-linked with trichlorosilanes,[14,15] resulting in ideal characteristics for organic transistors at biases below 1 V. The main limitations of the polymer gate dielectrics investigated thus far include high annealing temperature, which limits their compatibility with plastic substrates, or the use of moisture sensitive cross-linking agents, which may have adverse effects related to environmental changes.

In addition to polymer dielectric films, self-assembled monolayer (SAM) and multilayer dielectrics have been used to achieve low-voltage operation and low-power complementary circuits. Thin molecular gate dielectric films with a precisely controllable thickness were demonstrated using a layer-by-layer, self-assembly method from solution for low-voltage OTFTs.[16] Polymer dielectric surface grafting has also been demonstrated using other approaches, such as ring-opening metathesis polymerization initiated from a ruthenium-modified SAM.[17] Phenylene-terminated SAMs[18] and docosyltrichlorosilanes[19] on silicon and alkane SAMs on alumina[3] have been used as the gate dielectric to fabricated low-power organic devices. Additionally, OTFTs have been fabricated with thin metal-oxide dielectric layers, such as alumina,[20] titania,[21] tantalum oxide,[22] or alumina films with a thin polymer layer[23] for low-voltage transistor operation. Finally, polyelectrolyte dielectrics have been used to fabricate low voltage TFTs leading to devices with extremely high carrier densities while suffering from low-switching speeds.[24]

Previously, we reported low-voltage OTFT operation by incorporating ultrathin films of poly(4-vinylphenol) cross-linked with 4,4′-(hexafluoroisopropylidene)diphthalic anhydride (HDA). Here, we evaluate the thermal cross-linking of poly(4-vinylphenol) with a variety of commercially available, ambient stable bifunctional anhydrides, acylchlorides, and carboxylic acids. With the low temperature cross-linking requirements for these materials, we remain within the processing limits of plastic substrates, and the stability toward organic solvents is necessary for subsequent solution-deposition methods. The influence of the cross-linker material, concentration, processing conditions, and surface treatment on the insulating physical and electronic properties is presented. Additionally, OTFTs are fabricated with various vacuum and solution-processed semiconductors and characterized to determine the relationship between the insulator properties and the transistor performance.

Experimental Section

Materials. All materials were purchased from Aldrich and used as received unless otherwise noted. Propylene glycol monomethyl ether acetate (PGMEA) was purchased from Alfa Aesar and *N*,*N*-dimethylformamide (DMF) was purchased from Mallinckrodt Baker. Hexamethyldisilazane, trimethylsilyl chloride, and octadecyltrimethoxysilane were purchased from Gelest, Inc. Pentacene and 5,5′-bis-(7-dodecyl-9*H*-fluoren-2-yl)-2,2′-bithiophene (DDFTTF)[25] were purified by vacuum sublimation ($P \sim 10^{-6}$ Torr) in a three-zone furnace 2−3 times. The three-zone temperature settings for pentacene and DDFTTF were 230, 190, and 120 °C and 350, 280, and 180 °C, respectively. FCuPc was washed repeatedly with acetone and methanol prior to use.

Dielectric Film Preparation. Standard solutions of poly-4-vinylphenol (PVP) were prepared with a cross-linking agent (CL) in a ratio of 10:1 (PVP:CL) by weight in propylene glycol monomethyl ether acetate (PGMEA). The concentrations of PVP and the CL are varied between 10 and 50 mg/mL and 0.2 and 20

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mg/mL, respectively. A catalytic amount of organic base (2−5% based on the number of PVP monomers) was added to the solutions of PVP with anhydride cross-linkers to promote the esterification reaction. The solutions were filtered through a 0.2 μm syringe filter and spin-coated onto highly doped n^{++} Si(100) substrates ($R < 0.008$ Ω cm) at rates of 2K−7K RPM for 1 min on a spin-coater (Headway Research, Inc.). Prior to spin-coating, the substrates were treated with UV−ozone (Jelight, Model 42) for 20 min and blown dry with filtered (Mykrolis) nitrogen. The substrates were then cured at 60−100 °C in air for 2 h and stored under vacuum for at least 1 h before use.

Device Fabrication. Polymer dielectric films were deposited on highly doped silicon substrates according to a previously reported method.[4] All semiconductor films, other than 4TTMS,[4] were deposited by thermal evaporation (Angstrom Engineering, Inc.) at a rate of 0.3−0.5 Å/s under a pressure of 5.0×10^{-7} Torr. The substrate temperature (T_{sub}) was controlled by heating a copper block during deposition. Pentacene, DDFTTF, and FCuPc were deposited at a T_{sub} of 65 °C, 90 °C, and 105 °C, respectively, to a thickness of 40 nm (30 nm for DDFTTF). The top-contact devices were completed with gold electrodes thermally evaporated at 1 nm/s onto a rotating substrate. The electrode dimensions were defined by a shadow mask with a channel width (W) and length (L) of 1 mm and 50 μm, respectively. The deposition of 4TTMS[4] and carbon nanotube networks were reported elsewhere.[27]

Chemical Modification. The polymer dielectric layers were briefly treated by UV−ozone for 3−5 min and then modified with silanes by spin coating neat solutions of either hexamethyldisilazane (HMDS) or trimethylchlorosilane (TMSCl) at 3K rpm for 1 min. The films were cured on a hot plate at 90 °C for 10 min and stored under nitrogen before the semiconductor deposition. Octadecyltriethoxysilane (OTS) treatment was performed on polymer samples in a glass desiccator evacuated to 30 mTorr at 100 °C for 48 h. The substrates were annealed at 100 °C for 10 min and then rinsed with toluene, acetone, and ethanol.

Characterization. Film thicknesses were determined using ellipsometry (Optrel GdBR Multiscope at a 70° angle of incidence under nulling conditions with a 532 nm laser with a beam diameter and spot size of 0.6 mm and 20 mV, respectively). Contact angle measurements were recorded using a First Ten Angstroms FTA200 equipped with a CCD camera. Roughness and thickness corroborations were performed with atomic force microscopy (AFM) (Digital Instruments Nanoscope IV) operated in tapping mode (~350 kHz frequency, Si tip). Capacitance measurements were carried out using a sandwich electrode configuration with an HP 4192 LF Impedance Analyzer or an Agilent E4980A Precision LCR Meter for frequencies ranging between 5 Hz and 100 kHz. Transistor electrical characterization was performed with a Keithley 4200SCS semiconductor parameter analyzer connected to a standard probe station setup.

Results and Discussion

Polymer Dielectric Layers. Cross-linked polymer films were formed through the esterification of (4-vinylphenol) (PVP) with bifunctional anhydrides, acyl chlorides, and carboxylic acids. PVP was chosen for its proven dielectric characteristics[14] and compatibility with many organic semiconductors.[6,28] Additionally, PVP is a unique polymer for chemical cross-linking because of the presence of the peripheral hydroxyl groups. For simplicity, only commercially available cross-linkers were investigated, including HDA, benzophenone-3,3′,4,4′-tetracarboxylic dianhydride (BCD), ethylenediaminetetraacetic dianhydride (EAD), diethylenetriaminepentaacetic dianhydride (DAPD), 3,3′,4,4′-biphenyltetracarboxylic dianhydride (BPD), biphenyl-4,4′-dicarboxylic acid (BCA), suberic acid (SA), and suberoyl chloride (SC). Figure 1 shows a schematic of an OTFT and PVP cross-linked with HDA in addition to the molecular structures of the cross-linker molecules. To ensure cross-linking with the polymer matrix rather than the formation of an interpenetrating network, cross-linking materials that self-react were not used. Other materials that were considered for the polymer matrix include poly(vinylalcohol) and poly(allylamine). However, they are only soluble in water, which is not useful for our choice of water-insoluble or water-sensitive cross-linkers.

Table 1. Electrical Characteristics of Cross-Linked Polymer Films

CL	concn [mg/mL]	surface	Ci [nF/cm^2]	κ
HDA	2	bare	166	4.1
	2	HMDS	160	4.1
	2	TMS	157	4.1
EAD	1	bare	159	4.4
	1	HDMS	157	4.4
	1	TMS	154	4.4
BCD	2	bare	156	4.5
	2	HDMS	152	4.5
	2	TMS	154	4.5
DAPD	0.5	bare	174	4.8
BPD	2	bare	156	4.2
SCl	2	bare	180	4.2
SA	2	bare	159	4.0

The cross-linked polymer films were spin-coated from a solution of propylene glycol monomethyl ether acetate (PGMEA) owing to the good solubility of both the PVP and the cross-linkers. The solubility of EAD and DAPD in PGMEA was less than 1 mg/mL; therefore, solution formulations with these materials used solvent mixtures of 3:1 (v/v) PGMEA with dimethylformamide (DMF). Many solvents, such as acetone, alcohols, acetic acid, and acetic anhydride were excluded on the basis of the limited solubility of the CLs. While other polar solvents, such as dimethyl sulfoxide (DMSO), DMF, and tetrahydrofuran (THF) were sufficient with regard to solubility, spin-coating from PGMEA produced the most uniform films. Low quality films with streaks and pinholes were formed with low-boiling point solvents, such as THF. The AFM of cross-linked PVP films deposited from a solution in THF is shown in the Supporting Information, Figure S1.

PVP cross-linking with anhydrides and carboxylic acids required a catalytic amount of organic base, such as triethylamine (TEA), triethanoylamine, diethylamine, or pyridine. Without the addition of the base, which is used to deprotonate the weakly acidic phenol hydrogen, the deposited films were easily dissolved by sonication following the curing

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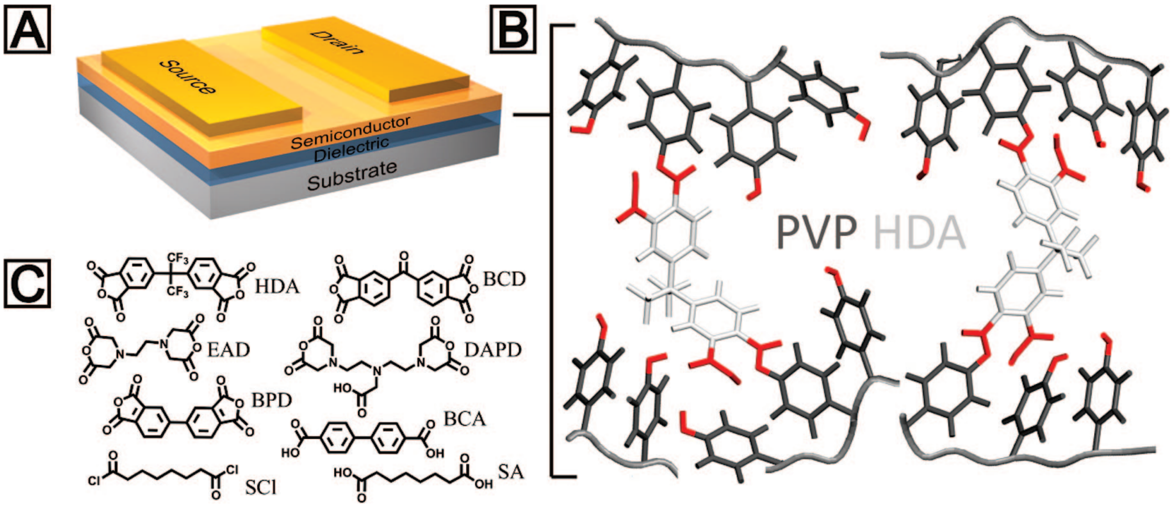

Figure 1. Schematic of an organic thin-film transistor (A) with the molecular structure of the cross-linked PVP with HDA (B). The molecular structure of a variety or dianhydrides and bifunctional carboxylic acids and acylchlorides is shown in C.

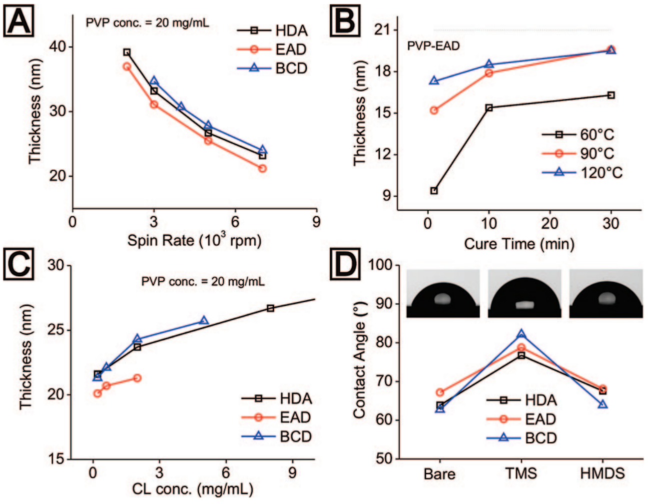

Figure 2. Physical characteristics of the cross-linked polymer films. (A) Thickness versus spin rate of PVP films cross-linked with HDA (black squares), EAD (red circles), and BCD (blue triangles). (B) Film stability of PVP−EAD films as a function of curing time for temperatures of 60 °C (black), 90 °C (red), and 120 °C (blue). (C) Thickness versus cross-linker concentration. (D) Water contact angle of PVP films with surface treatment.

process. The polymer solutions mixed with the cross-linker and the organic base catalyst were very stable at room temperature—no precipitation was observed even after many weeks. However, when the solutions were heated (e.g., on a hot plate at 60 °C), they became cloudy owing to the reaction between the polymer and cross-linker. The morphology of the PVP films cross-linked with HDA is shown in the Supporting Information, Figure S3, for different organic base catalysts.

Physical Properties of Polymer Films. Thin insulating films were deposited from solution via spin-coating with rates between 2000 and 7000 rpm. The film thickness is plotted versus spin-coating rate in Figure 2A for HDA, EAD, and BCD. For similar cross-linker concentrations, the film thickness is nearly independent of cross-linker material. However, the thickness of films consisting of EAD or DAPD was slightly lower since they were deposited using PGEMA:DMF solvent mixtures. After deposition, the films were cured at a temperature ranging between 60 and 120 °C, depending on the cross-linking agent. Most cross-linking systems required a cure temperature of at least 100 °C for stability toward subsequent chemical processing. Mixtures based on either SC or EAD could be cross-linked at temperatures as low as 60 °C. As shown in Figure 2B, a curing temperature of 90 °C resulted in improved film stability. It was not beneficial to further increase the temperature. PVP cross-linking with dianhydrides required slightly higher temperatures of 100 °C−120 °C. Fourier transform infrared (FTIR) spectroscopy was used to determine the formation of the ester linkage of the stable films. The film thickness was slightly dependent on cross-linker concentration, which is illustrated in Figure 2C for HDA, EAD, and BCD.

The surface energy of the polymer dielectric can be modified through silane treatment. Cross-linked polymer films based on HDA, EAD, and BCD were modified with hexamethyldisilazane (HDMS) and trimethylchlorosilane (TMSCl) to improve adhesion with the organic semiconductor and passivate the hydroxyl traps along the surface. Only a slight change in capacitance was observed as a result of the increase in thickness, which is discussed in the following section (Table 1). Figure 2D shows the change in contact angle for these films modified with HMDS and TMSCl. An increase in water contact angle of up to 20 °C was observed for treatment with TMSCl, while the change was negligible for HDMS.

The morphology of the polymer dielectric films was evaluated with atomic force microscopy (AFM). Surface analysis with AFM was critical in identifying which cross-linkers produced uniform, pinhole-free films. Initially, we found that the use of linear diacylchlorides as cross-linker materials gave films with good stability toward subsequent solvent treatment. However, AFM analysis revealed that phase separation occurred between the polymer and the cross-linker resulting in porous films. The porosity could be decreased with a reduction in chain length between the reactive groups, but the resultant films were still rough. The morphology of these films is shown in the Supporting Information, Figure S2.

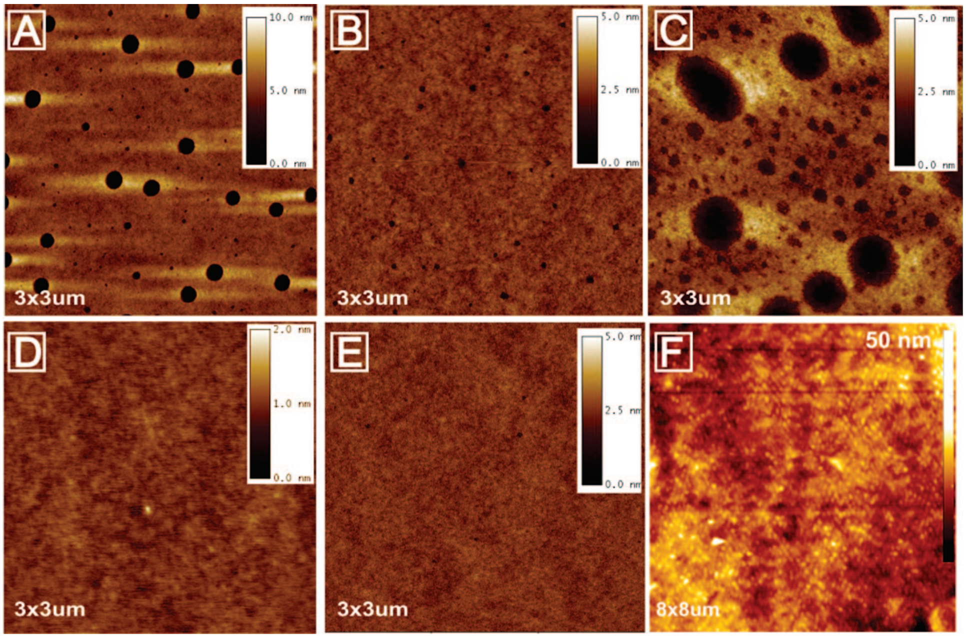

Figure 3. Polymer dielectric film morphology. AFM micrographs of 20 mg/mL PVP with: 20 mg/mL HDA and 2 μL/mL TEA (A), 2 mg/mL EAD (B), 5 mg/mL BPD and 1 μL/mL TEA (C), 2 mg/mL HDA and 1 μL/mL TEA (D), 1 mg/mL EAD (E), and 2 mg/mL HDA deposited on planar silicon substrates. The standard PVP−HDA (20/2) formulation deposited on ITO/PET substrates is shown in panel F.

The most uniform films were achieved for PVP cross-linked with HDA, EAD, and BCD cross-linkers, with surface roughness, rms, values as low as 0.2−0.3 nm. It should be noted that increasing the cross-linker to polymer ratio, based on mass, above the standard value (2:20 for HDA and 1:20 for EAD) resulted in films with pinholes and/or phase separation as determined by AFM. Figure 3A shows the morphology of PVP−HDA films with a 10-fold increase in HDA concentration compared to the standard (Figure 3E) indicating the potential for phase separation at high cross-linker concentrations. Similarly, Figure 3B shows films with nanometer sized pinholes resulting from a 2-fold increase in EAD concentration compared to the standard concentration (Figure 3E). Polymer films cross-linked with BPD contain highly nonuniform pinholes and pores. Finally, films consisting of DAPD and SA were unstable toward PGMEA (i.e., delaminated upon sonication) after curing and, therefore, were not imaged. The morphology of the PVP films formed from solutions with these cross-linking agents is shown in the Supporting Information (Figure S3D), revealing many large and small pinholes.

The cross-linked polymer films, PVP−HDA in particular, were compatible with plastic transistor substrates.[29] We use poly(ethylene terephthalate) (PET) sheets with an indium tin oxide (ITO) coating as conductive transparent substrates. Because of the increased roughness of these ITO/PET substrates compared to silicon substrates, two sequential PVP−HDA layers were deposited resulting in a film with a roughness of 2.6 nm.

Electrical Properties of Polymer Films. The principal electrical characteristics for gate dielectric films are the capacitance and leakage current. The capacitance, which is a measure of the amount of charge separated at a given potential, determines the number of charge carriers that can be induced in the semiconductor layer at a particular gate bias. The leakage current through the polymer layer should be as low as possible and has a significant impact on the key transistor parameters, including on/off ratio. The capacitance and leakage current of the cross-linked polymer films were measured in two-terminal devices consisting of a sandwich electrode structure. Gold pads (0.88 mm^2, 0.22 mm^2, and 0.09 mm^2) were thermally evaporated on polymer dielectric films on degenerately doped silicon substrates. The capacitance of cross-linked PVP−HDA dielectric films showed slight frequency dependence that scaled with thickness, as shown in Figure 4A. The relative dielectric constant was extracted from the slope of the capacitance versus inverse thickness (Figure 4B), yielding values of 4.2 and 4.1 for HDA and SCl, respectively. A capacitance as high as 400 nF/cm^2 was observed for 10 nm PVP−HDA films; however, the 22 nm film with a capacitance of 165 nF/cm^2 (average C_i between 5−20 Hz) was selected as the standard for OTFT characterization. The leakage current for a variety of PVP−HDA films is shown in Figure 4C, with current densities below 10^{-6} A/cm^2 and 10^{-8} A/cm^2 for 22 and 56 nm films, respectively, for biases below 2 V. The cross-linked polymer films with a thickness of 20−25 nm electrically broke down between 3 and 4 V. Films of 50 and 150 nm thickness could withstand biases of 10 and 25 V, respectively, yielding an average breakdown voltage of 1.7−2.0 MV/cm.

The frequency dependent capacitance per unit area, C_i, for HDA and SCl is shown in Figure 4D for three difference electrode dimensions. C_i scaled properly with electrode size for the PVP−HDA films, however, a slight variation was observed for the less-uniform SCl films owing to significant parasitic current. The corresponding capacitance versus frequency measurements for PVP−EAD films is shown in

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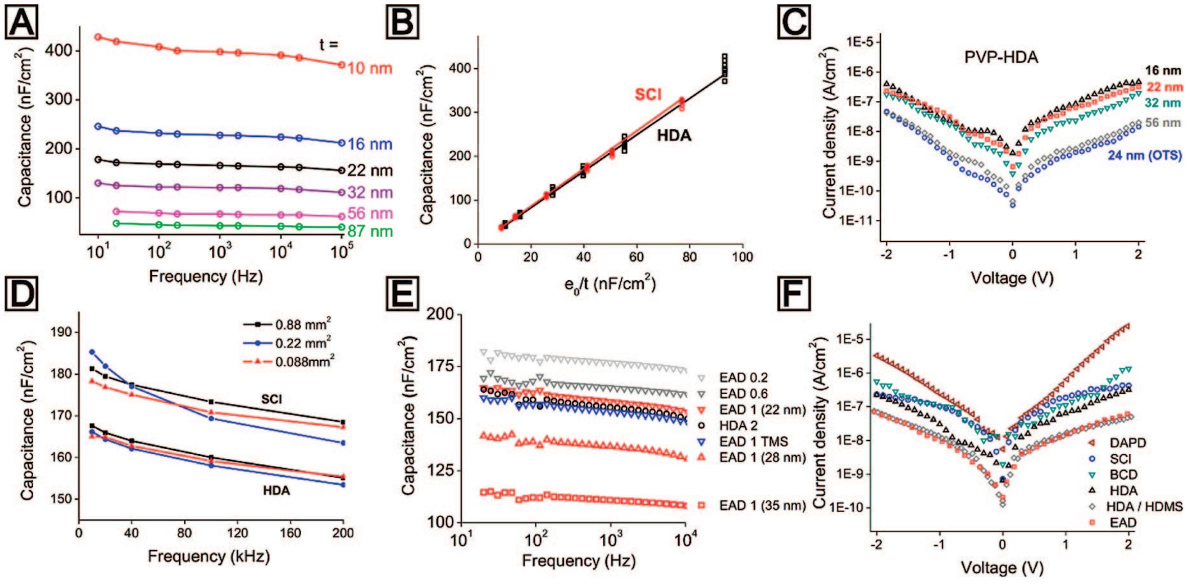

Figure 4. Electrical characteristics of cross-linked PVP films. (A) Capacitance vs frequency for PVP−HDA films with different thicknesses. (B) Capacitance vs inverse thickness for polymer films with HDA and SCl. (C) Leakage current of PVP−HDA films. (D) Capacitance vs frequency for HDA and SCl with electrode areas of 0.88 mm^2, 0.22 mm^2, and 0.09 mm^2. (E) Capacitance vs frequency for PVP−EAD films with different thickness, EAD concentration, and surface treatment. (F) Leakage current for various cross-linked PVP films with a thickness of ∼20−25 nm.

Table 2. Transistor Parameters for Pentacene, DDFTTF, and FCuPc Semiconductors on Various Cross-Linked Polymer Films

		μ [cm^2/(V s)]			V_T [V]			on/off ratio		
OS	CL	bare	HMDS	TMS	bare	HMDS	TMS	bare	HMDS	TMS
pentacene	HDA	0.7	0.5	0.5	−0.16	−0.2	−0.22	9.5×10^4	8.9×10^4	1.2×10^4
	EAD	1.23	0.47	0.35	−0.35	−0.36	−0.17	4.0×10^5	2.7×10^5	4.4×10^4
	BCD	0.9	0.7	0.47	−0.05	−0.26	0.13	1.2×10^5	5.1×10^4	1.3×10^4
	DAPD	0.55			0.38			3.3×10^4		
	SA	0.5			0.32			2.1×10^4		
DDFTTF	HDA	0.17	0.16	0.17	−0.08	−0.081	−0.083	5.0×10^4	5.3×10^4	1.5×10^5
	EAD	0.14	0.14	0.16	−0.11	−0.11	−0.11	1.4×10^5	6.0×10^4	1.5×10^5
	BCD	0.2		0.19	−0.21		−0.25	1.6×10^4		1.0×10^5
FCuPc	HDA	0.003	0.001	0.0008	0.48	0.92	0.88	1.1×10^4	5.6×10^3	1.1×10^3
	EAD	0.001	0.0014	0.0008	0.71	0.51	0.65	4.8×10^3	1.3×10^3	1.2×10^3

Figure 4E, illustrating its dependence on thickness, EAD concentration, and surface treatment. Finally, the leakage current for a variety of cross-linkers is shown in Figure 4F.

Table 1 shows the dielectric constants of the cross-linked polymer films and the dependence of surface treatment on capacitance. After silane treatment, the thickness, as determined by ellipsometry, increased on average by 0.5−1.0 nm, which translates to the observed decrease in capacitance. The dielectric constant does not vary significantly with cross-linker and is most influenced by the PVP matrix. The values are slightly higher than the κ reported for PVP.[28]

OTFTs were fabricated on various cross-linked polymer films using the p-channel materials pentacene and 5,5′-bis-(7-dodecyl-9*H*-fluoren-2-yl)-2,2′-bithiophene (DDFTTF)[30,31] and the common n-channel material copper(II) 1,2,3,4,8,9,10,11,15,16,17,18,22,23,24,25-hexadecafluoro-29*H*,31*H*-phthalocyanine (FCuPc). N- and p- channel materials were used to demonstrate the compatibility of different semiconductor materials with the polymer dielectrics. Top-contact OTFTs of all materials exhibited excellent linear and saturation regime characteristics with only slight $I_{DS}-V_G$ hysteresis while stably operating at low voltages, generally below 2 V. Additionally, the device yield was very high, with nearly every device working on smooth Si/SiO$_2$ substrates when the films were prepared according to the optimized procedure. The average capacitance between 5 and 20 Hz was used for the transistor parameter analysis providing a reasonable approximation for DC TFT characterization. The transistor parameters of these devices were determined from the $I_{DS}-V_G$ curves and are presented in Table 2.

The semiconductor materials evaluated generally displayed the highest electrical performance on the polymer films without surface treatment. The reduced performance on HMDS-treated films can be attributed to the increase in surface roughness, from 0.2−0.3 nm for bare PVP−HDA to 0.5 nm after HDMS treatment (see Supporting Information, figure S4). Additionally, the low density of the reactive hydroxyl groups on the surfaces leads to an incomplete coverage of the HDMS and TMSCl monolayers. In addition

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(30) Meng, H.; Zheng, J.; Lovinger, A. J.; Wang, B. C.; Van Patten, P. G.; Bao, Z. N. Oligofluorene-thiophene derivatives as high-performance semiconductors for organic thin film transistors. *Chem. Mater.* **2003**, *15* (9), 1778–1787.

(31) DeLongchamp, D. M.; Ling, M. M.; Jung, Y.; Fischer, D. A.; Roberts, M. E.; Lin, E. K.; Bao, Z. Thickness dependence of microstructure in semiconducting films of an oligofluorene derivative. *J. Am. Chem. Soc.* **2006**, *128* (51), 16579–16586.

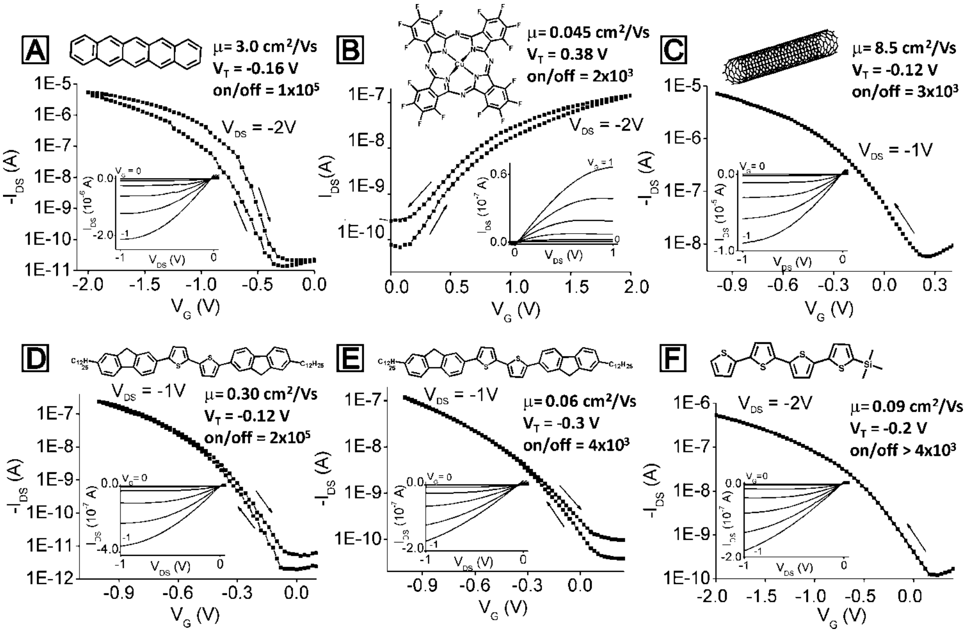

Figure 5. Electrical characteristics of organic thin-film transistors (OTFTs) on PVP−HDA dielectric layers with a source-drain electrode geometry of *W*/*L* = 20. Transfer and output (inset) characteristics of OTFTs with 40 nm thermally evaporated films of pentacene (A), FCuPc (B), sorted carbon nanotube networks (C), DDFTTF (D), DDFTTF on PET/ITO substrates (E), and solution-processed 4TTMS (F).

to an increase in surface roughness, the silanol groups can add additional trap sites for the positive charge carriers, possibly explaining the increase in threshold voltage for pentacene and, to a lesser extent, for DDFTTF.

OTFTs fabricated with pentacene (40 nm) on PVP−EAD showed exceptional device characteristics with a field-effect mobility of 1.23 cm^2/(V s) and an on/off ratio of 4 × 10^5 at a gate bias of 1 V. From the same pentacene deposition, OTFTs on PVP cross-linked with HDA and BCD had a slightly lower performance with mobilities of 0.7 and 0.9 cm^2/(V s), respectively. The highest thin-film mobility, 3 cm^2/(V s), was achieved for devices with pentacene films on octadecyltriethoxysilane (OTS) monolayers on PVP−HDA; however, these devices exhibited an increased hysteresis in the $I_{DS}-V_G$ scans compared to bare PVP−HDA. Lower performance was observed for polymer films cross-linked with SA and DAPD presumably due to larger leakage current through the gate dielectric. The performance of DDFTTF films did not significantly vary with cross-linker or surface treatment, with mobilities ranging between 0.14 and 0.2 cm^2/(V s) and on/off ratios around 1 × 10^5. Similarly, the performance of FCuPc was similar for PVP−EAD and PVP−HDA films regardless of surface treatment with an average mobility on the order of 0.001 and an on/off ratio slightly greater than 10^3 for gate biases of 2 V. As shown in Figure 5, these devices exhibited low hysteresis, except in the off-state, presumably due to the polarization of mobile ions at the interface.

The influence of cross-linker concentration on the transistor performance is shown in Table 3. The optimal cross-linker concentrations for HDA and EAD are 2 mg/mL and 1 mg/mL, respectively, for a solution with a PVP concentration of 20 mg/mL. At higher concentrations, the polymer and cross-linker tend to phase separate as illustrated by the AFM images in Figure 3, resulting in rougher films with lower charge-carrier mobilities. The electronic performance also decreases for lower cross-linker concentrations owing to less dense films and an increased presence of charge-trapping surface phenol groups.

Table 3. Transistor Parameters for Pentacene on PVP−HDA and PVP−EAD Films with Cross-Linker Concentration

OS	CL	concn [mg/mL]	μ [cm^2/(V s)]	V_T [V]	on/off
pentacene	HDA	0.2	0.45	−0.2	4.1 × 10^5
		2	0.7	0.16	9.5 × 10^4
		8	0.35	−0.13	5.3 × 10^5
		20	0.35	−0.08	4.6 × 10^3
	EAD	0.2	0.45	−0.26	4.0 × 10^4
		0.6	0.43	0.08	4.8 × 10^4
		1	1.23	−0.35	4.0 × 10^5
		2	0.76	−0.18	7.1 × 10^4

Figure 5 shows the electric characteristics of various semiconducting materials deposited on PVP−HDA substrates. Each panel shows the transfer characteristics ($I_{DS}-V_G$) with output curves ($I_{DS}-V_{DS}$) displayed in the insets. All devices consist of 22 nm polymer dielectric films with a capacitance of 165 nF/cm^2, except for 4A, which uses an OTS surface-modified polymer film, and 4E, which consists of a two-layer dielectric film with a capacitance of 105 nF/cm^2 on the rough ITO/PET substrates. In addition to vacuum deposited films of pentacene, FCuPc, and DDFTTF, solution-processed carbon nanotube networks and 4TTMS films showed ideal characteristics with high charge carrier mobilities. Highly crystalline films of 4TTMS showed a mobility close to 0.1 cm^2/(V s), and sorted nanotube networks yielded an effective mobility of 8.5 cm^2/(V s) with an on-current of 10 μA at 1 V. Details on TFTs based on sorted nanotube networks will be reported elsewhere.[27]

Low-voltage OTFTs were demonstrated on flexible ITO/PET substrates and aluminum foil (Reynolds). The characteristics of DDFTTF on a 35 nm two-layer PVP−HDA film are presented in Figure 4E. On aluminum foil, which functioned as the substrate and gate electrode, an 80 nm, two-layer PVP−HDA film was deposited from a solution

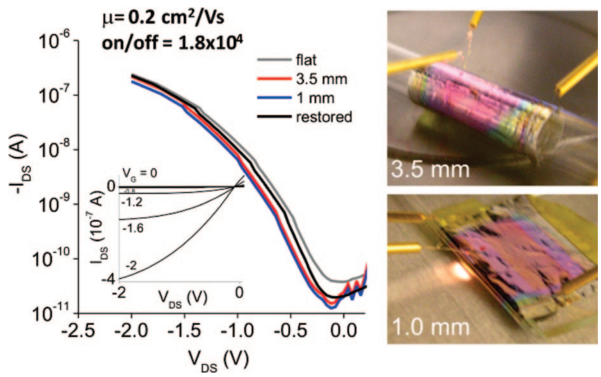

Figure 6. Influence of bending on the electrical characteristics of flexible transistors fabricated on aluminum foil substrates. The transfer characteristics of an OTFT with pentacene are shown as a function of bending radius with an inset of the output characteristics after the device was restored to the initial planar condition.

of 50 mg/mL PVP to compensate for the substrate roughness. Immediately after fabrication, the Al-foil device with a pentacene active layer demonstrated nearly ideal transistor characteristics. A slight decrease in the source-drain current was observed when the substrate was rolled around a 3.5 mm radius glass rod, as shown in Figure 6, with the channel direction oriented parallel to the bending direction. A further decrease in I_{DS} was obtained at very low bending radii, such as 1 mm. However, I_{DS} was partially recovered after removing the strain. The influence of physical stress from bending on the transfer characteristics is shown in Figure 6 with an inset of output characteristics measured after the bending sequence. The device performance remained reasonably stable with a $\mu \sim 0.2$ and an on/off ratio of 1.8×10^4.

Conclusion

In this report, we presented a new cross-linkable solution-processable polymer dielectric material based on stable precursors with low temperature curing. The cross-linked polymers, based on poly(4-vinylphenol) and dianhydride linkers, were compatible with several organic n- and p-channel semiconductors with mobilities as high as 3.0 cm^2/(V s) for pentacene on OTS-modified polymer films. The influence of surface treatment and cross-linker concentration on OTFT performance was shown for a variety of cross-linked polymer systems. Additionally, these polymer films could be incorporated with flexible substrates, such as Al-foil and ITO/PET, and solution-processable semiconductors, including 4TTMS and carbon nanotube networks.

Acknowledgment. M.R. acknowledges partial financial support from the NASA Graduate Fellowship Program. Z.B. acknowledges financial support from the Stanford Center for Polymeric Interfaces and Macromolecular Assemblies (NSF-Center MRSEC), the NSF-EXP-SA sensor project (Award no. ECCS 0730710), and the Sloan Research Fellowship.

Supporting Information Available: Atomic force micrographs (AFM) of additional polymer films deposited under various conditions (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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