

# Dielectric Polymers for OTFT Application

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## Abstract

A series of new dielectric polymers with phenyl, epoxy, and carboxylic acid functional groups was prepared via free-radical polymerization. The effect of such dielectric polymers with various functional groups on the performance of OTFT was investigated. The nonpolar groups of terpolymer made the surface of the dielectric layer more hydrophobic and improved the crystal growth of pentacene on the gate insulator, resulting in higher mobility. By controlling the functional group, the electric characteristics of OTFT performance was varied, with 0.00017-0.15 cm<sup>2</sup>/V·s mobility.

**Keywords:** dielectric polymer, OTFT, pentacene

## 1. Introduction

The organic thin-film transistor (OTFT) has been drawing much interest of late for use in low-cost electronic devices such as electronic paper, RFID, and smart card, and in the backplane circuitry of active-matrix displays [1-3]. It may help come up with a flexible display due to its flexibility, light weight, and solution processability [4, 5]. Meanwhile, many research works on OTFT have been devoted to the search for high mobility [6-8] and stability [9-11] and for solution-processable organic [12-19] or polymeric [20-23] semiconductors. Although OTFT has desirable features, it may have problems in achieving good interfacial properties and long-term stability. Furthermore, there has been a dearth of research on organic dielectric materials [24]. The OTFT dielectric material requires a high dielectric constant, chemical resistance, pinhole-free thin-film formability, and long-term stability. The electrical characteristics of an OTFT device have been known to depend on the material characteristics of the organic semiconductor and dielectric layer [25]. Many research works have been conducted on OTFTs with dielectric polymers, but there has yet been no attempt to study OTFT's characteristics by varying the composition of its monomer subunit.

In this work, a series of new dielectric polymers with functional groups of phenyl, epoxy, and carboxylic acid (-COOH) were prepared via free-radical polymerization. With the phenyl group, dielectric polymer is expected to improve the interfacial property between the gate insulator and the active pentacene semiconductor. The epoxy group may be used for cross-linking the moiety, and the -COOH group can increase the dielectric constant due to its hydrophilic nature. The effect of dielectric polymer on the performance of OTFT with various functional groups was investigated by varying the monomer composition of the dielectric polymer.

## 2. Experiments

Methyl methacrylate (M), benzyl methacrylate (B), glycidyl methacrylate (G), styrene (S), and methacrylic acid (Ma) were purchased from Aldrich Chemical Co. and were used as received. Series of dielectric copolymers and terpolymers were designed to have different backbone structures: (1) poly(benzyl methacrylate-co-glycidyl methacrylate-co-methacrylic acid) (BGMa series); (2) poly(benzyl methacrylate-co-styrene-co-methacrylic acid) (BSMa series); (3) poly(methyl methacrylate-co-styrene-co-methacrylic acid) (MSMa series); (4) poly(methyl methacrylate-co-styrene) (MS); (5) poly(benzyl methacrylate-co-methyl methacrylate) (BM); and (6) poly(benzyl methacrylate-co-styrene) (BS). The number of polymer series denotes the mole ratios of the monomer composition.

Via free-radical polymerization, the polymers were synthesized in tetrahydrofuran (THF) as a solvent at 70°C,

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**Table 1.** Characteristics of the polymeric gate insulator

Sample	Slope	S.S. V/decade	$I_{on}/I_{off}$ ratio	$V_{TH}/V$	Mobility /cm <sup>2</sup> /Vs	Dielectric Constant	$C_i$ / nF/cm <sup>2</sup>	Channel Length (L/mm)/Width (W/mm)	Contact Angle
BGMa511	$-3.2 \times 10^{-5}$	9.6	$1.1 \times 10^4$	-16.2	0.082	2.7	7.5	0.3/1	80
BGMa512	$-3.0 \times 10^{-5}$	8.4	$1.7 \times 10^4$	-17.1	0.061	2.7	8.9	0.3/1	78
BGMa522	$-4.7 \times 10^{-5}$	9.0	$5.1 \times 10^4$	-17.2	0.15	3.3	8.7	0.3/1	74
BSMa511	$-2.8 \times 10^{-5}$	9.6	$2.7 \times 10^3$	-15.8	0.0017	3.6	23	0.02/0.8	82
MSMa522	$-9.6 \times 10^{-6}$	31	$1.9 \times 10^1$	-4.1	0.00017	3.5	27	0.02/0.8	76
MS11	$-2.7 \times 10^{-5}$	34	$5.4 \times 10^2$	5.8	0.038	2.3	9.8	0.05/0.2	78
BM11	$-3.0 \times 10^{-5}$	35	$3.0 \times 10^3$	4.1	0.041	2.5	11	0.05/0.2	74
BS11	$-3.3 \times 10^{-5}$	38	$3.0 \times 10^3$	1.4	0.059	3.4	9.3	0.05/0.2	83

under a N<sub>2</sub> atmosphere. AIBN was used as an initiator. After 24 h, the polymers were precipitated in hexane and were dried in a vacuum oven. A 5-10% polymer solution was prepared using PEGMEA as a solvent, and was filtered with a 0.2-  $\mu$ m-membrane filter. To measure the dielectric constants of the polymers or to come up with OTFT, a highly-p-doped Si wafer (0.005  $\Omega$ ) was used as a substrate. For OTFT device fabrication, the polymer's dielectric layer was first spin-coated on a Si wafer, and 80-nm pentacene was deposited at a rate of 0.1 nm/s on top of the gate dielectric, through a shadow mask, via thermal evaporation (JBS International, South Korea). Top-contact Au electrodes were then deposited via the evaporation method. The capacitance values of the dielectric polymers were measured using an Agilent 4284A LCR meter, and the dielectric constants were calculated from the film thickness by profiler and electrode area.

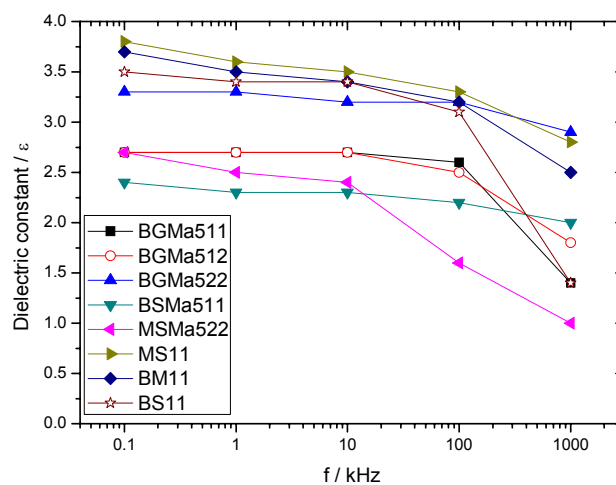
All the OTFTs had a top-contact geometry whose channel length (L) and width (W) are given in Table 1. The film topology and roughness were measured via atomic-force microscopy (N8 ARGOS, Bruker-Nano, Germany). Electrical characterization of the devices was performed in the dark, and the current-voltage (I-V) characteristics of the OTFTs were measured with an Agilent 4156C semiconductor parameter analyzer.

### 3. Results and Discussion

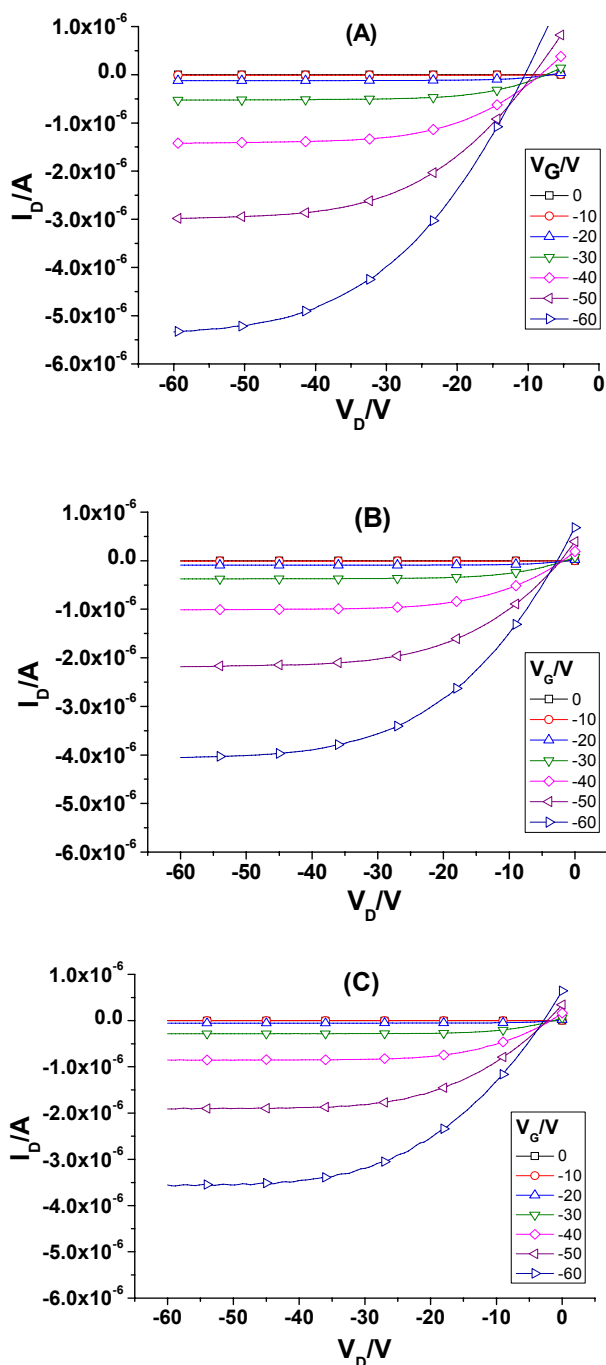
The frequency dependence values of the dielectric constants for various polymers are shown in Fig. 1. The dielectric constant at 1 kHz was 3.5-2.5, which is the ex-

pected value for most organic-based materials. The minor variation is due to the polar groups, such as the -COOH or ester group, in methacrylic acid (Ma) or methyl methacrylate (MMA). As such, copolymers containing an Ma or MMA subgroup have slightly higher dielectric constants. In the case of the BGMa series terpolymers, the dielectric constant of BGMa522 slightly increased compared with those of the BGMa series terpolymers due to its methacrylic-acid content.

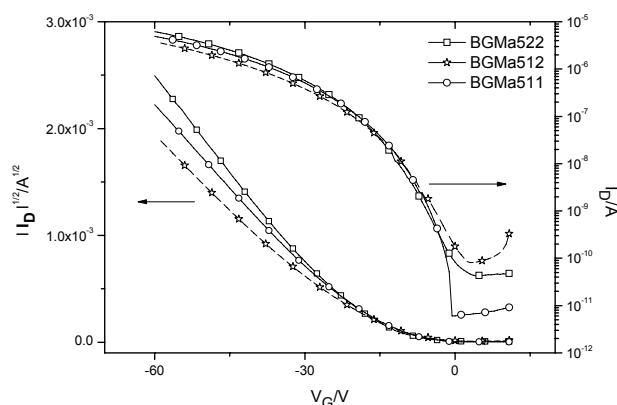
Fig. 2 and 3 show the output and transfer characteristics, respectively, of the OTFTs with different mole ratios in the BGMa series. The overall characteristics of the other polymer gate insulator showed a similar I-V behavior. Fig. 2 showed a significant non-ohmic behavior, which may be due to a bulk-limited parasitic resistance caused by the transition regions next to S/D, by an injection barrier between

**Fig. 1.** Frequency dependence of the dielectric constant for various polymers

S/D and pentacene, or by the combination of both effects [26]. The electric characteristics of the BGMa, BSMa, and MSMa terpolymers and of the MS, BM, and BS copolymers are summarized in Table 1. The observed mobilities of pentacene reported here are relatively low compared with the others [27-30]. The reason for this observation is not yet



**Fig. 2.** Output characteristic of the OTFT with different mole ratios in the BGMa series: (a) BGMa511; (b) BGMa512; and (c) BGMa522.

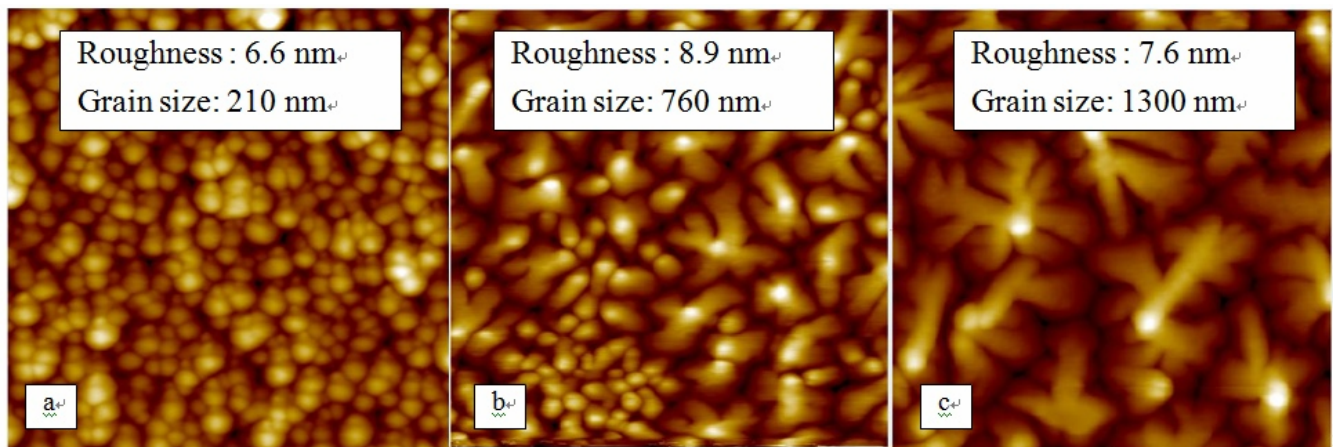


**Fig. 3.** Transfer characteristics of the OTFT with different mole ratios in the BGMa series at  $V_D = -30$  V.

clear. The device geometry was perhaps poor and had somewhat relatively larger leakage current and low mobility values. This may be due to the large electrode contact pads of the source and drain electrodes. Nevertheless, a qualitative comparison of the given datasets is still possible.

Since the BGMa series had glycidyl methacrylate (GM), the  $-\text{COOH}$  in Ma could react with the epoxy group in GM, resulting in crosslinked materials. With these functional groups, a patterned dielectric layer can be generated for future application. The phenyl group in benzyl methacrylate (B) could interact with pentacene to assist in the initial growth of pentacene. BGMa522 yielded better results than the other compositions, as shown in Table 1. The BGMa series had a small dielectric-constant variation, but the mobility of OTFT changed from 0.06 to 0.15 depending on the composition.

One may think that the dielectric constant will influence the mobility of OTFT, or more importantly, the interfacial property of the dielectric polymers. The performance of OTFTs and the functionality of dielectric polymers may be related to the interfacial property between the organic semiconductor and the dielectric layer [31, 32]. The surface of the gate dielectric layer influences the initial growth mechanism of pentacene. The influence of monomer moiety on pentacene growth may be checked using two different terpolymers, BSMa511 and MSMa522. As BSMa511 has about four times more phenyl moiety than MSMa522 does, the interfacial interaction with pentacene will promote the growth of pentacene on the gate insulator surface. Although it is qualitative, the phenyl group has an aromatic nature, which will help stack pentacene molecules on top of



**Fig. 4.** Atomic-force microscopy images ( $5 \times 5 \mu\text{m}$ ) of pentacene deposited on (a) a bare Si substrate; (b) an MSMa522-coated substrate; and (c) a BSMA511-coated substrate. The thickness of pentacene was about 80 nm, and its deposition rate was 0.1 nm/s.

the gate insulator. The difference in backbone (i.e., methyl methacrylate (M) and benzyl methacrylate (B)) will be reflected on the difference in contact angle, as shown in Table 1, as well as in crystal growth. Fig. 4 shows the pentacene images on the bare substrates MSMa522 and BSMA511. As expected, the BSMA-coated sample had the biggest crystal size due to the interactions between the pentacene and phenyl moiety of the BSMA polymer. This in fact resulted in a tenfold difference in mobility, as shown in Table 1.

Although both BGMA and BSMA had a  $-\text{COOH}$  group in their polymers, BSMA had lower mobility than BGMA. This may be explained by the hydrophilic nature of the  $-\text{COOH}$  group, whereas pentacene is hydrophobic. The  $-\text{COOH}$  group in BGMA could react with the epoxy group in glycidyl methacrylate during heat treatment, as explained earlier. Hence, the hydrophilic group in the BGMA series would be eliminated, and the pentacene mobility of the BGMA series was larger than that of the BSMA series.

As the phenyl group affects the growth of pentacene, the fine-tuning of the monomer composition will increase the mobility and will improve the performance of pentacene-based OTFT. In terms of the overall performance of OTFT devices, it may not be dramatic, but organic-based dielectrics offer many choices, such as one that is full of monomers to tune the performance of OTFT. Further researches related to dielectric polymer will benefit the future OTFT technology.

#### 4. Conclusions

Several polymers were synthesized via free-radical polymerization and were tested as OTFT gate insulators. When pentacene was used as an organic semiconductor, their mobility ranged from 0.0017 to 0.15  $\text{cm}^2/\text{V}\cdot\text{s}$ . This may be attributed to the initial interfacial interaction between the gate insulator moiety and pentacene. With the introduction of functional groups and the fine-tuning of the monomer composition of dielectric polymer, the performance of OTFT is expected to improve.

#### References

- [ 1 ] S. R. Forrest, *Nature* **428**, 911(2004).
- [ 2 ] T. W. Kelley, P. F. Baude, C. Gerlach, D. E. Ender, D. Muires, M. A. Haase, D. E. Vogel and S. D. Theiss, *Chem. Mater.* **16**, 4413( 2004)
- [ 3 ] A. Facchetti, M.-H. Yoon and T. J. Marks, *Adv. Mater.* **17**, 1705(2005).
- [ 4 ] S. Pyo, S. Lee, and S. Kwon, *J. Appl. Phys.* **99**, 99 (2006).
- [ 5 ] M. C. Chen, C. Kim, S. Y. Chen, and T. J. Marks, *J. Mater. Chem.* **18**, 1029 ( 2008).
- [ 6 ] C. Rolin, K. Vasseur, S. Schols, M. Jouk, G. Duhoux, R. Muller, J. Genoe, and P. Heremans, *Appl. Phys. Lett.* **93**, 033305 (2008).
- [ 7 ] L. Burgi, M. Turbiez, R. Pfeiffer, F. Bienewald, H.-J. Kirner, and C. Winnewisser, *Adv. Mater.* **20**, 2217 (2008).

- [ 8 ] A. Babel, Y. Zhu, K.-F. Cheng, W.-C. Chen, and S. A. Jenekhe, *Adv. Funct. Mater.* **17**, 2542 (2007).
- [ 9 ] H. Usta, A. Facchetti, T. J. Marks, *J. Am. Chem. Soc.* **130**, 8580(2008).
- [ 10 ] B. Jones, A. Facchetti, M. R. Wasielewski, T. J. Marks, *Adv. Funct. Mater.* **18**, 1329 (2008).
- [ 11 ] H. Tian, J. Shi, D. Yan, L. Wang, Y. Geng, and F. Wang, *Adv. Mater.* **18**, 2149 (2006).
- [ 12 ] T. Kojima, J.-I. Nishida, S. Tokito, and Y. Yamashita, *Chem. Lett.* **36**, 1198 (2007).
- [ 13 ] M. L. Tang, M. E. Roberts, J. J. Locklin, M. M. Ling, and Z. Bao, *Chem. Mater.* **18**, 6250 (2006).
- [ 14 ] R. Schmidt, S. Goettling, D. Leusser, D. Stalke, A.-M. Krause, and F. Wurthner, *J. Mater. Chem.* **16**, 3708 (2006).
- [ 15 ] M. Mas-Torrent and C. Rovira, *Chem. Soc. Rev.* **37**, 827 (2008).
- [ 16 ] H. Yan, Y. Zheng, R. Blache, C. Newman, S. Lu, J. Woerle, and A. Facchetti, *Adv. Mater.* 9999, 1 (2008).
- [ 17 ] Z. Wang, C. Kim, A. Facchetti, and T. J. Marks, *J. Am. Chem. Soc.* **129**, 13362 (2007).
- [ 18 ] S. E. Koh, J. E. Mendvedeva, A. Facchetti, B. Delley, A. J. Freeman, T. J. Marks, and M. A. Ratner, *J. Phys. Chem. B.* **110**, 24361 (2006).
- [ 19 ] B. Yoo, D. Basu, T. Jung, D. Fine, B. A. Jones, A. Facchetti, M. R. Wasielewski, T. J. Marks, K. Dimmier, and A. Doda-balapur, *Adv. Mater.* **19**, 4028 (2007).
- [ 20 ] J. A. Letizia, M. R. Salata, C. M. Tribout, A. Facchetti, M. A. Ratner, and T. J. Marks, *J. Am. Chem. Soc.* **130**, 9679 (2008).
- [ 21 ] H. Kong, D. H. Lee, I.-N. Kang, E. Lim, Y. K. Jung, J.-H. Park, T. Ahn, M. H. Yi, C. E. Park, and H.-K. Shim, *J. Mater. Chem.* **2008**, 1895(2008).
- [ 22 ] Lu, H. Usta, C. Risko, L. Wang, A. Facchetti, M. A. Ratner, and T. J. Marks, *J. Am. Chem. Soc.* **130**, 7670(2008).
- [ 23 ] H. Yan, Z. Chen, Y. Zheng, C. E. Newman, J. Quin, F. Dolz, M. Kastler, and A. Facchetti, *Nature* **457**, 679(2009).
- [ 24 ] Y. W. Choi, I. D. Kim, H. L. Tuller, and A. I. Akinwande, *IEEE Trans. Electron Dev.* **52**(12), 2819(2008).
- [ 25 ] S. Pyo, M. Lee, J. Jeon, J. H. Lee, M. H. Yi, and J. S. Kim, *Adv. Func. Mater.* **15**(4), 619 (2005).
- [ 26 ] Y. Hong, F. Yana, P. Migliorato, S. H. Han, J. Jang, *Thin Solid Films*, **515**, 4032(2007).
- [ 27 ] C. D. Dimitrakopoulos, A. R. Brown, and A. Pomp, *J. Appl. Phys.* **80**(4), 2501 (1996).
- [ 28 ] D. J. Gundlach, Y. Y. Lin, T. N. Jackson, S. F. Nelson, and D. G. Schlom, *IEEE Electron Device Lett.* **18**(3), 87(1997).
- [ 29 ] Y. Y. Lin, D. J. Gundlach, S. F. Nelson, and T. N. Jackson, *IEEE Electron Device Lett.* **18**(12), 606(1997).
- [ 30 ] D. Knipp, R. A. Street, A. Volkel, and J. Ho, *J. Appl. Phys.* **93**(1), 347 (2003).
- [ 31 ] H. Klauk, M. Halik, U. Zschieschang, G. Schmid, W. Radlik, and W. Weber, *J. Appl. Phys.* **92**(9), 5259(2002).
- [ 32 ] H. Sirringhaus, N. Tessler, D. S. Thomas, P. J. Brown, and R. H. Friend, *Adv. Solid State Phys.* **39**, 101(1999).