Supplementary Information

Side-chain Modification in Dielectric-Constant of Polymer: Toward High-k Materials Synthesis and Application for Low-Voltage Operating Printed Electronics

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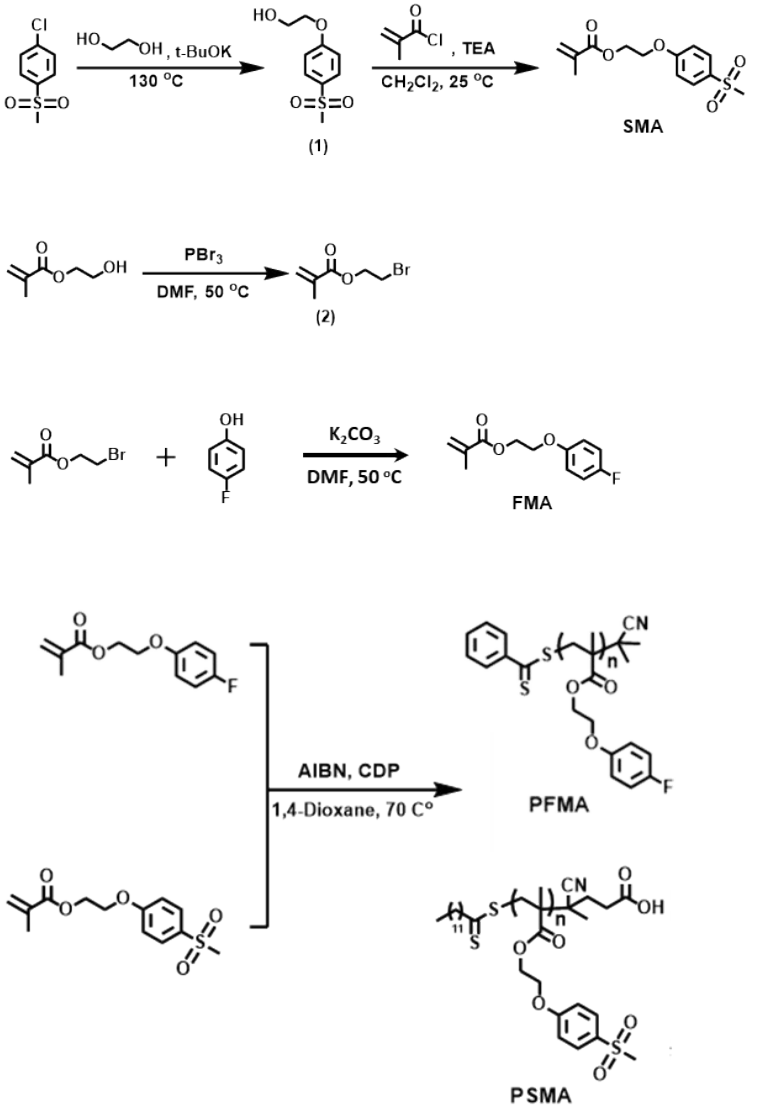


Scheme S1. Synthetic routes of **monomers** and **polymers**

Experimental Section.

Synthesis of 2-(4-(methylsulfonyl)phenoxy)ethanol written as (1)

Potassium *tert*-butoxide (*t*-BuONa) (6.18 g, 55.07 mmol) was dissolved in 30mL of ethylene glycol and the mixture was heated to 50 °C. Then, 1-chloro-4-(methylsulfonyl) benzene (7.0 g, 36.72 mmol) and 5mL of ethylene glycol were added. The mixture was stirred at 130 °C for 6 h. After cooling, the mixture was filtered and washed with 200 mL of dichloromethane and 200 mL of water. The organic layer was dried over $MgSO_4$ and filtered. The solvent was removed by a rotary evaporator and the crude product was purified by silica gel column chromatography with *n*-hexane:ethyl acetate (1:2) to afford the white powder. The results powder was recrystallized from ethyl acetate and petroleum ether to afford the desired compound (6.8 g, 85 % yield). ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.88 (d, 2H), 7.05 (d, 2H), 4.24 – 4.10 (m, 2H), 4.06 – 3.97 (m, 2H), 3.03 (s, 3H), 1.99 (t, 1H).

Synthesis of 2-(4-(methylsulfonyl)phenoxy)ethyl methacrylate (SMA)

2-(4-(methylsulfonyl)phenoxy)ethanol (1) (6.0 g, 27.75 mmol) and triethylamine (3.2 g, 30.52 mmol) were dissolved in 40 mL of dichloromethane and stirred at 0 °C. Then, A solution of methacryloyl chloride (2.8 g, 27.75 mmol) in dichloromethane (20 mL) was slowly dropwise. After the addition of methacryloyl chloride was complete, the mixture was stirred at RT for 4h. After then, the mixture was poured into 200 mL of water and extracted with dichloromethance. The organic layer was dried over $MgSO_4$ and filtered. The solvent was removed by a rotary evaporator and the crude product was purified by silica gel column chromatography with *n*-hexane:ethyl acetate (1:1) to afford the white powder. The results powder was recrystallized from ethyl acetate and petroleum ether to afford the desired

compound (4.85 g, 61 % yield). ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.87 (d, 2H), 7.05 (d, 2H), 6.13 (s, 1H), 5.60 (s, 1H), 4.56 – 4.49 (m, 2H), 4.33 – 4.24 (m, 2H), 3.03 (s, 3H), 1.95 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 167.32, 161.94, 135.97, 134.19, 126.42, 119.17, 115.46, 104.68, 66.34, 62.69, 18.39. HRMS (ESI, *m/z*): $[M+Na]^+$ calcd for $C_{13}H_{16}O_5SNa$, 307.0612; found 307.0618

Synthesis of 2-bromoethyl methacrylate written as (2)

2-Hydroxyethyl methacrylate (35.5 g, 272.78 mmol) was dissolved in 400mL of DMF and stirred at 50 °C. Then, phosphorus tribromide (36.9 g, 136.39 mmol) was dropwise and the mixture was stirred for 24 h. After cooling, the mixture was filtered and washed with 500 mL of ethyl acetate and 500 mL of water. The organic layer was dried over $MgSO_4$ and filtered. The solvent was removed by a rotary evaporator and the crude product was purified by silica gel column chromatography with *n*-hexane:ethyl acetate (6:1) to afford the colorless oil. (39 g, 74 % yield). ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 6.17 (s, 1H), 5.62 (s, 1H), 4.46 (t, 2H), 3.56 (t, 2H), 2.00 – 1.92 (m, 3H).

Synthesis of 2-(4-fluorophenoxy)ethyl methacrylate (FMA)

4-fluorophenol (5.8 g, 51.8 mmol) and potassium carbonate (K_2CO_3) (21.48 g, 155.41 mmol) were dissolved in 100mL of DMF and stirred. Then, 2-bromoethyl methacrylate (2) (10.0 g, 51.8 mmol) was added and the mixture was stirred at 50 °C for 24 h. After cooling, the mixture was filtered and washed with 200 mL of ethyl acetate and 200 mL of water. The organic layer was dried over $MgSO_4$ and filtered. The solvent was removed by a rotary evaporator and the crude product was purified by silica gel column chromatography with *n*-hexane:ethyl acetate (6:1) to afford the colorless oil. (6.62 g, 57 % yield). ^{1}H NMR (400 MHz,

$CDCl_3$), δ (ppm): 7.02 – 6.93 (m, 2H), 6.88 – 6.84 (m, 2H), 6.14 (s, 1H), 5.59 (s, 1H), 4.51 – 4.44 (m, 2H), 4.22 – 4.15 (m, 2H), 1.95 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 167.45, 158.83, 156.46, 154.84, 136.12, 126.21, 116.14, 116.00, 115.93, 115.91, 66.85, 63.20, 63.17, 18.42. HRMS (ESI, *m/z*): $[M+Na]^+$ calcd for $C_{12}H_{13}FO_3Na$, 247.0743; found 247.0746

RAFT polymerization of 2-(4-(methylsulfonyl)phenoxy)ethyl methacrylate (PSMA)

The polymerizations proceeded as free-radical polymerization and using CDP as RAFT agent. 2-(4-(methylsulfonyl)phenoxy)ethyl methacrylate (SMA) (2.5 g, 8.79 mmol) and AIBN (0.004 g, 0.025 mmol) and CDP (0.025 g, 0.063 mmol) were used, and 1,4-dioxane was used as a solvent, and the experiment was conducted under the same conditions as above to obtain a product. (2.05 g, 81 % yield). ^1H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.81 (br, 2H), 7.00 (br, 2H), 4.17 (br, 4H), 2.02 – 1.79 (br, 2H), 1.00 – 0.83 (br, 3H). Number-average molecular weight (GPC, eluent: MC): Mn = 14.50 kDa, PDI = 1.21.

RAFT polymerization of 2-(4-fluorophenoxy)ethyl methacrylate (PFMA)

The polymerizations proceeded as free-radical polymerization and using CPD as RAFT agent. 2-(4-fluorophenoxy)ethyl methacrylate (FMA) (3.0 g, 13.38 mmol) and AIBN (0.005 g, 0.03 mmol) and CPD (0.017 g, 0.075 mmol) were used, and 1,4-dioxane was used as a solvent, and the experiment was conducted under the same conditions as above to obtain a product. (2.17 g, 72 % yield). ^1H NMR (400 MHz, $CDCl_3$), δ (ppm): 6.92 – 6.79 (br, 4H), 4.21 – 4.02 (br, 4H), 1.92 – 1.32 (br, 2H), 1.04 – 0.91 (br, 3H). Number-average molecular weight (GPC, eluent: MC): Mn = 18.16 kDa, PDI = 1.17.

Computational Details

The structures of the monomer repeat unit were geometrically optimized by the DFT method on the B3LYP-D3 theory level with 6–31G** as the basis set, performed using Jaguar [Ref.1] implemented in Schrodinger Materials Science Suite 2024-3. The quantum chemical simulation also calculated the polarizability via Schrodinger Materials Science Suite 2024-3. The optimization and polarizability options were B3LYP/6-31G** and B3LYP/DEF2-SVPD, respectively. The equilibration temperature was 300 K. All molecular dynamics (MD) simulations were performed using Desmond with the OPLS4 force field [Ref. 2] implemented Schrodinger Materials Science Suite 2024-3. 25 Polyacrylate chains containing 27 repeat units were packed into a periodic box for the amorphous cell construction with an initial density of 0.50 g/cm^3. (**Fig. S1**) The permittivity ensemble, production time, and time step were NVE (microcanonical), 100 ns, and 2.0 fs, respectively.

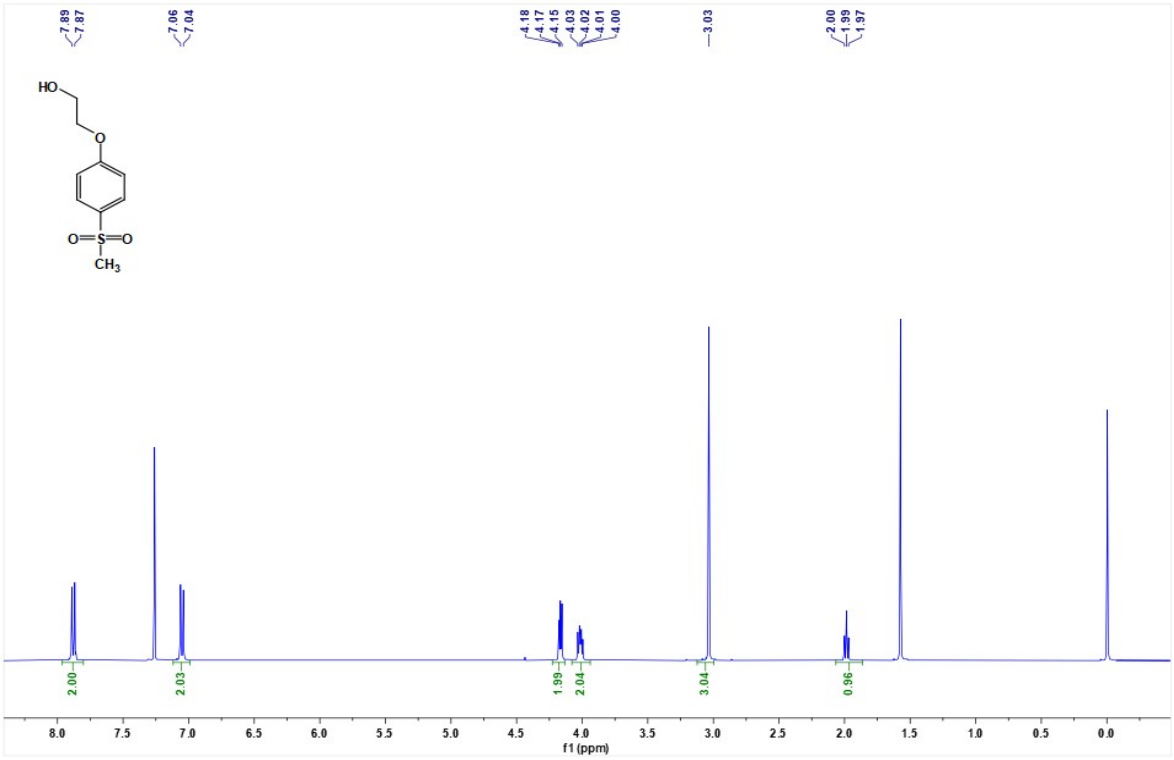


Fig. S1. ^{1}H NMR spectrum of 2-(4-(methylsulfonyl)phenoxy)ethanol (1) in $CDCl_3$.

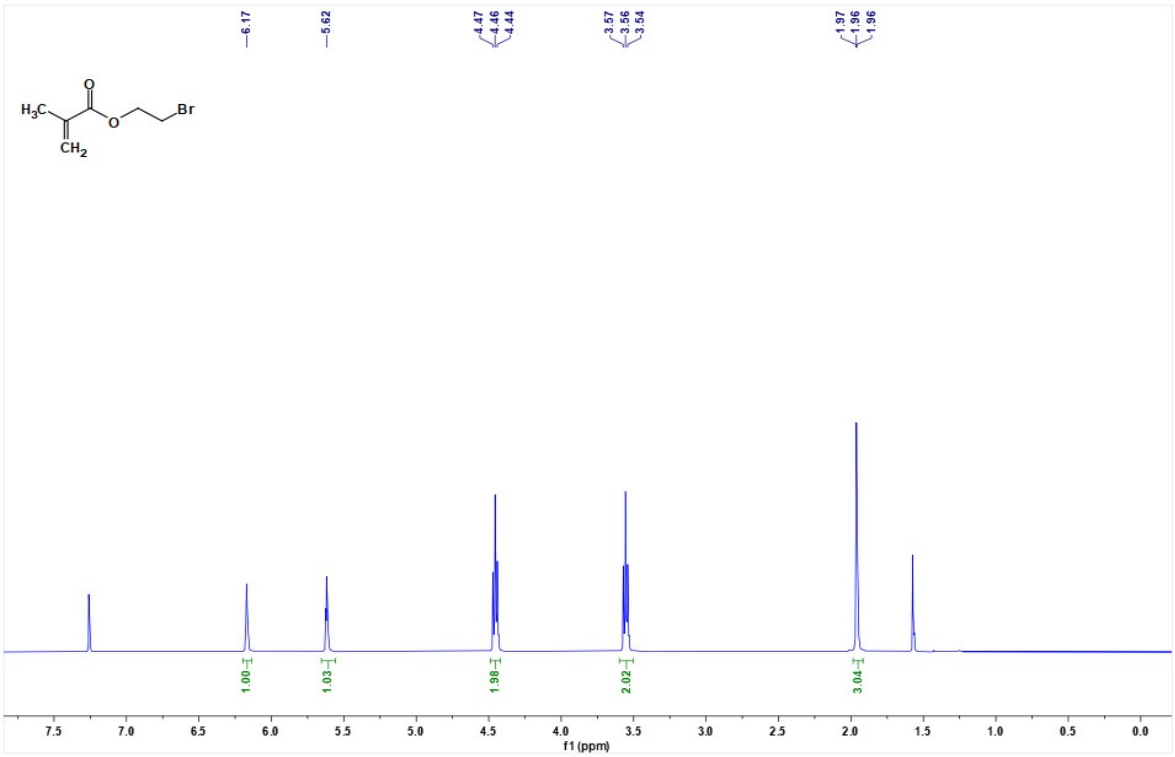


Fig. S2. ^{1}H NMR spectrum of 2-bromoethyl methacrylate (2) in $CDCl_3$.

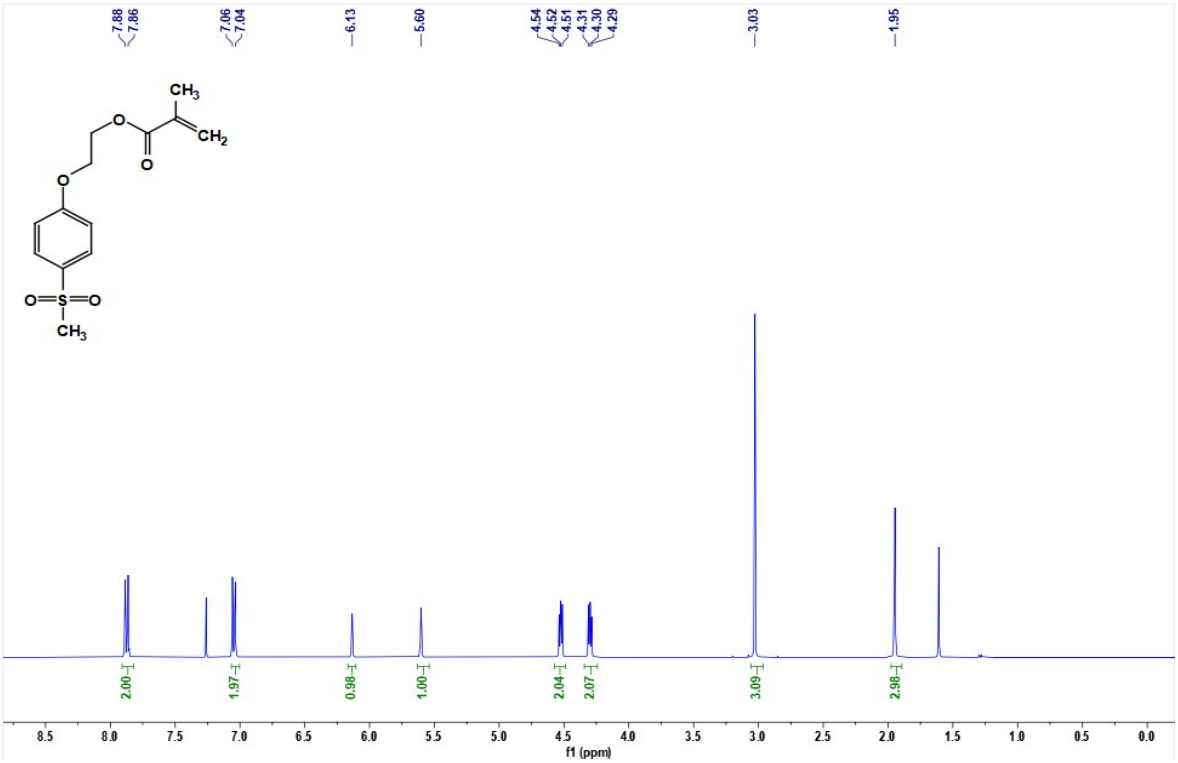


Fig. S3. ^{1}H NMR spectrum 2-(4-(methylsulfonyl)phenoxy)ethyl methacrylate (**SMA**) in $CDCl_3$.

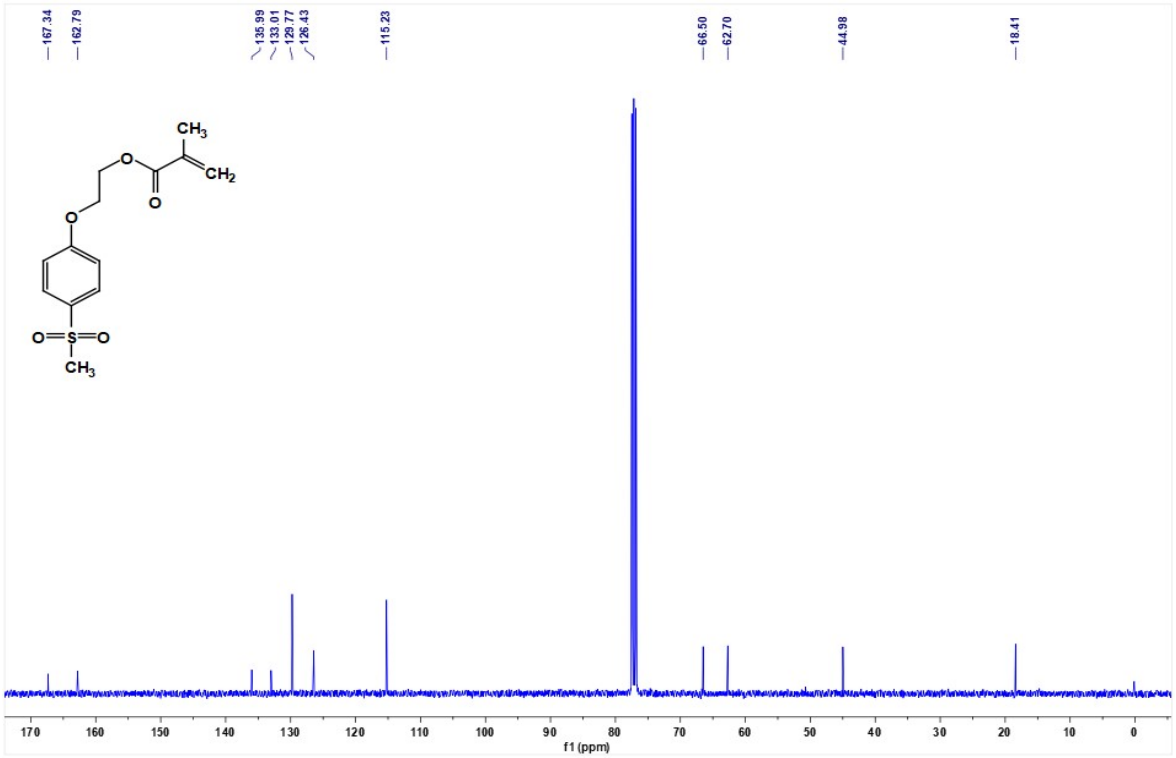


Fig. S4. ^{13}C NMR spectrum 2-(4-(methylsulfonyl)phenoxy)ethyl methacrylate (**SMA**) in $CDCl_3$.

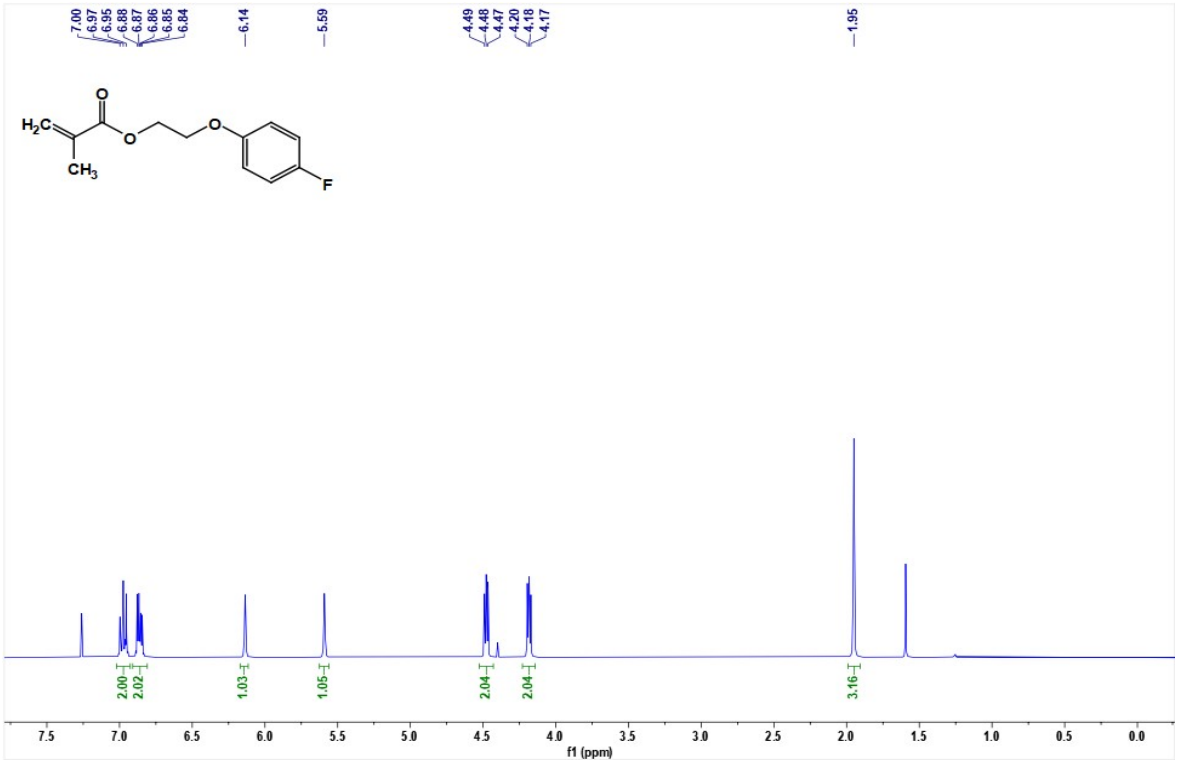


Fig. S5. ^{1}H NMR spectrum 2-(4-fluorophenoxy)ethyl methacrylate (**FMA**) in $CDCl_3$.

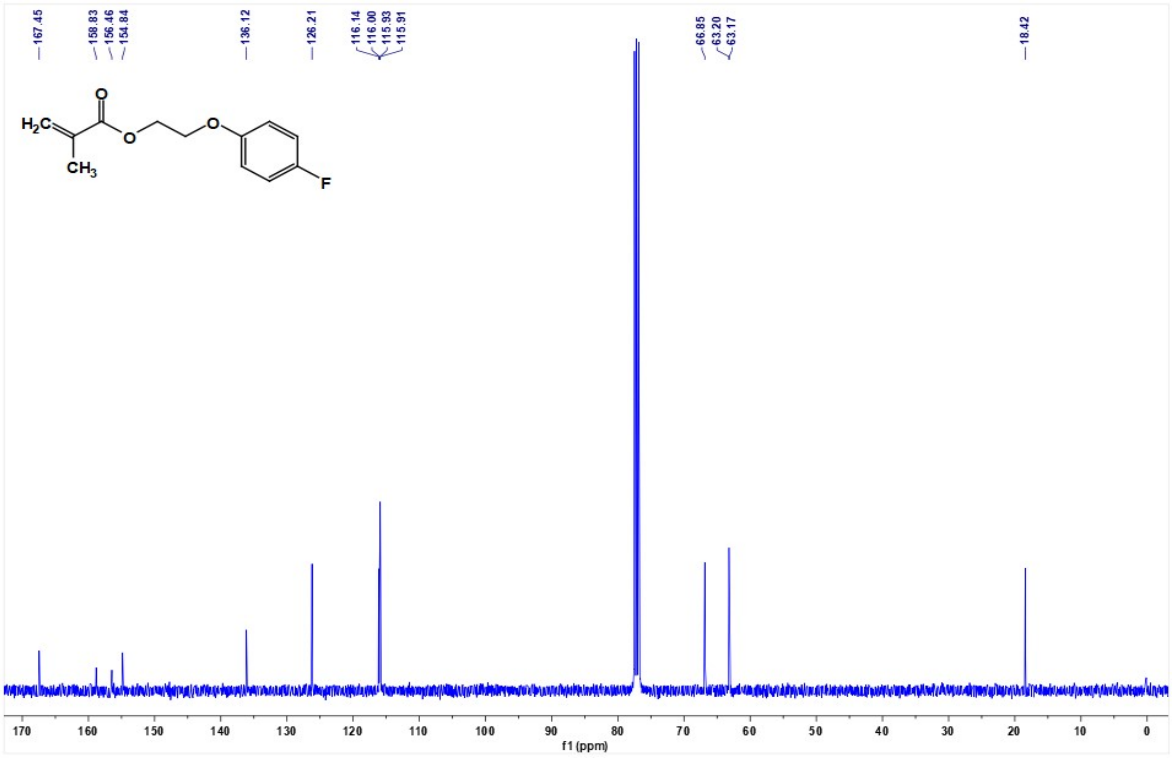


Fig. S6. ^{13}C NMR spectrum 2-(4-fluorophenoxy)ethyl methacrylate (**FMA**) in $CDCl_3$.

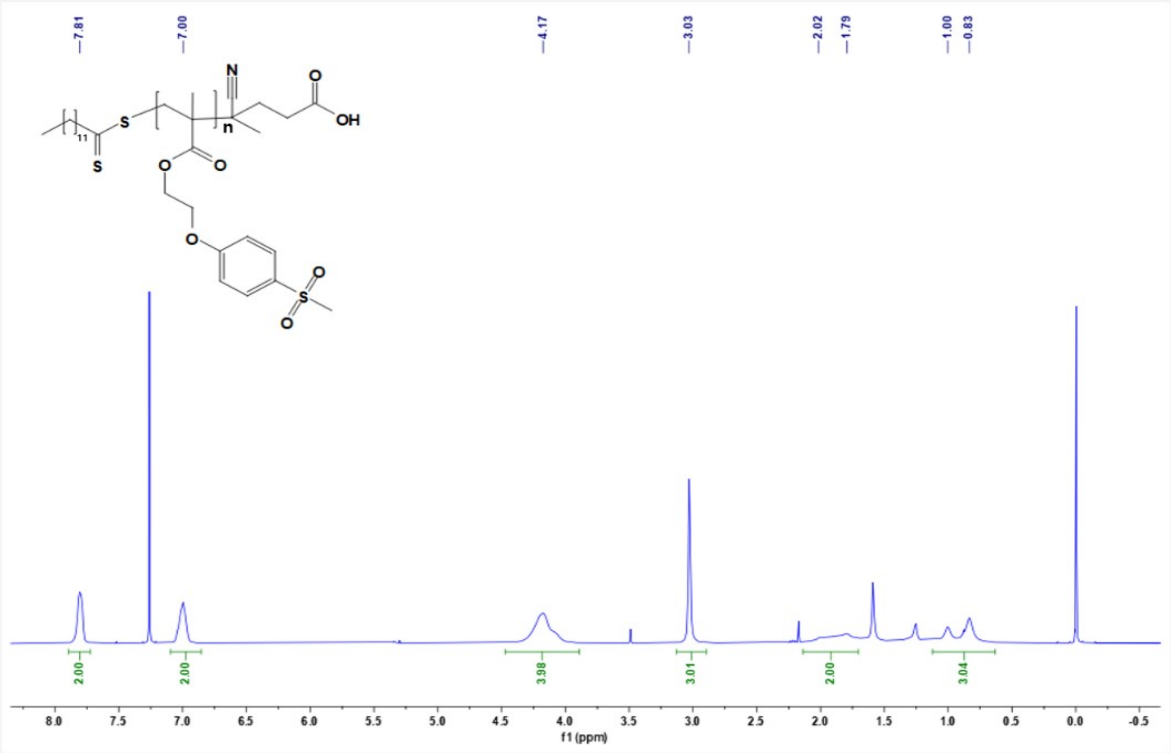


Fig. S7. ^{1}H NMR spectrum of **PSMA** in $CDCl_3$.

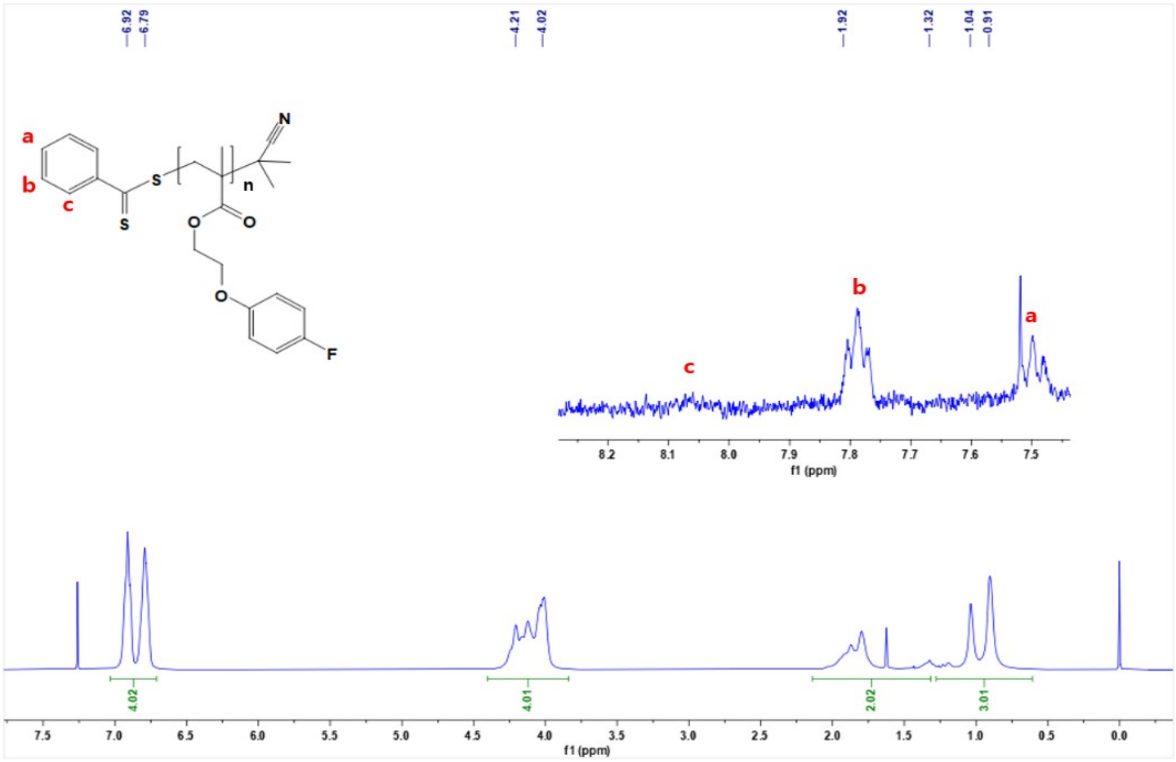


Fig. S8. ^{1}H NMR spectrum of **PFMA** in $CDCl_3$.

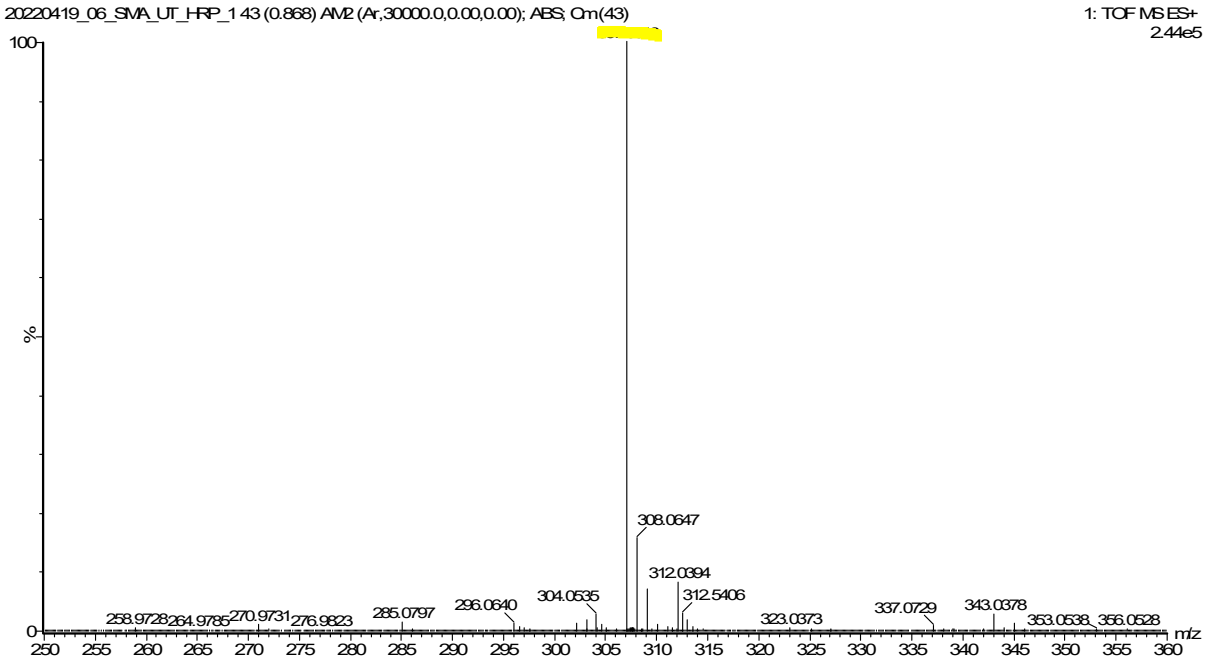


Fig. S9. Mass spectrum of **SMA** (ESI).

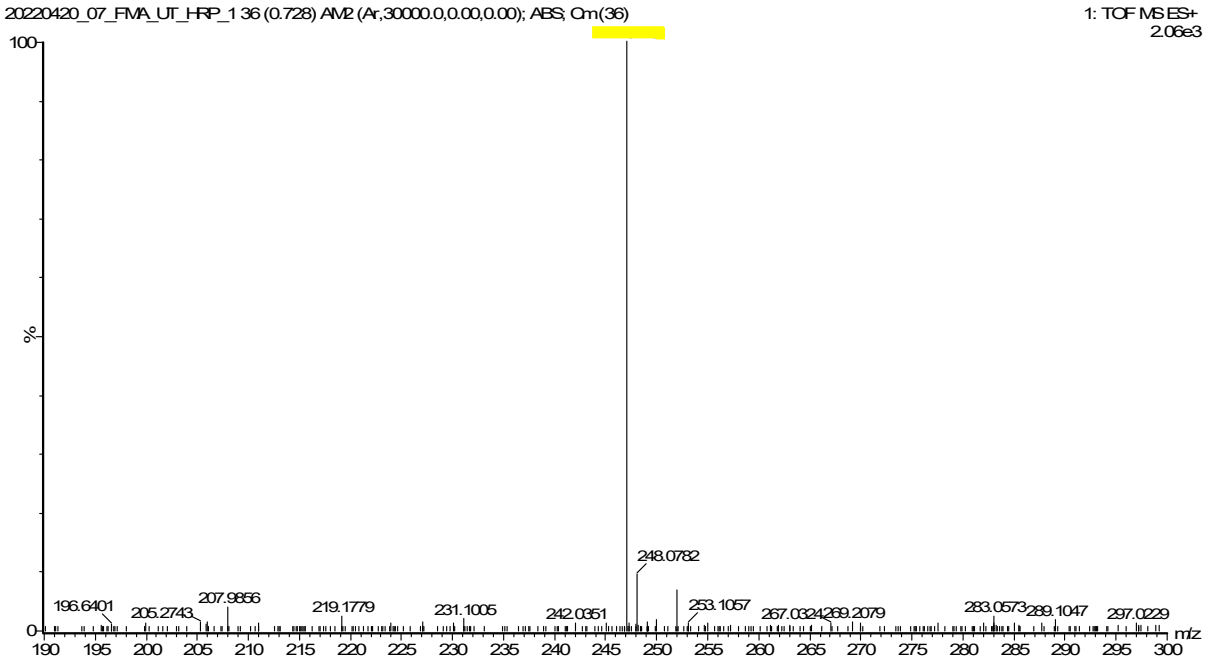


Fig. S10. Mass spectrum of **FMA** (ESI).

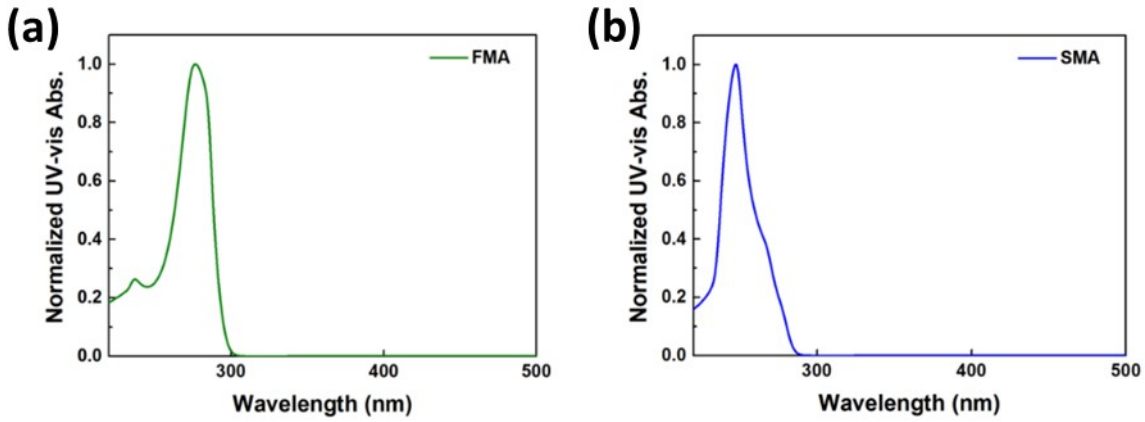


Fig. S11. Normalized UV-vis absorption spectra of (a) **FMA** and (b) **SMA** in Chloroform solution.

Table S1. Summary of optical properties of monomers.

Monomer	λ_{abs} [nm] [a]
SMA	248
FMA	277

[a] Measured in the Chloroform solution

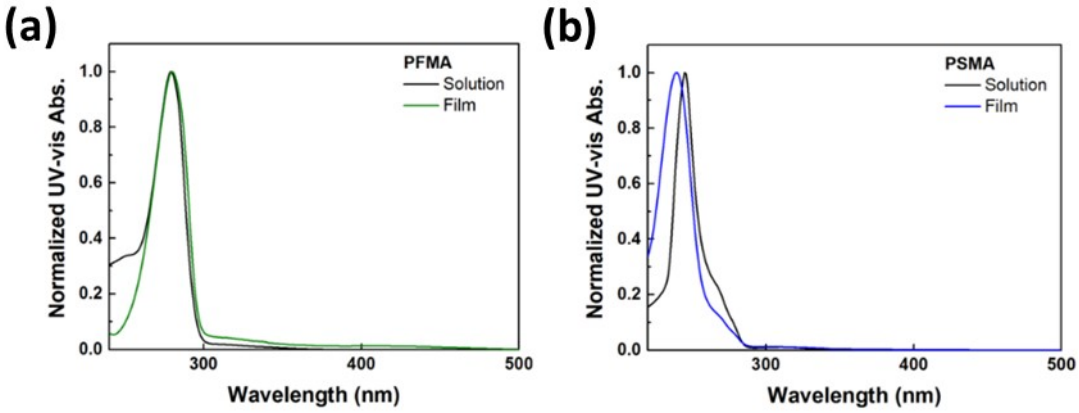


Fig. S12. Normalized UV-vis absorption spectra of (a) **PFMA**, and (b) **PSMA** in Chloroform solution and spin-coated films.

Table S2. Summary of optical properties of polymers.

Polymer	$\lambda_{abs,solution}$ [nm] [a]	$\lambda_{abs,film}$ [nm] [b]
PSMA	245	240
PFMA	279	280

[a] Measured in the Chloroform solution

[b] Measured in spin-coated neat films.

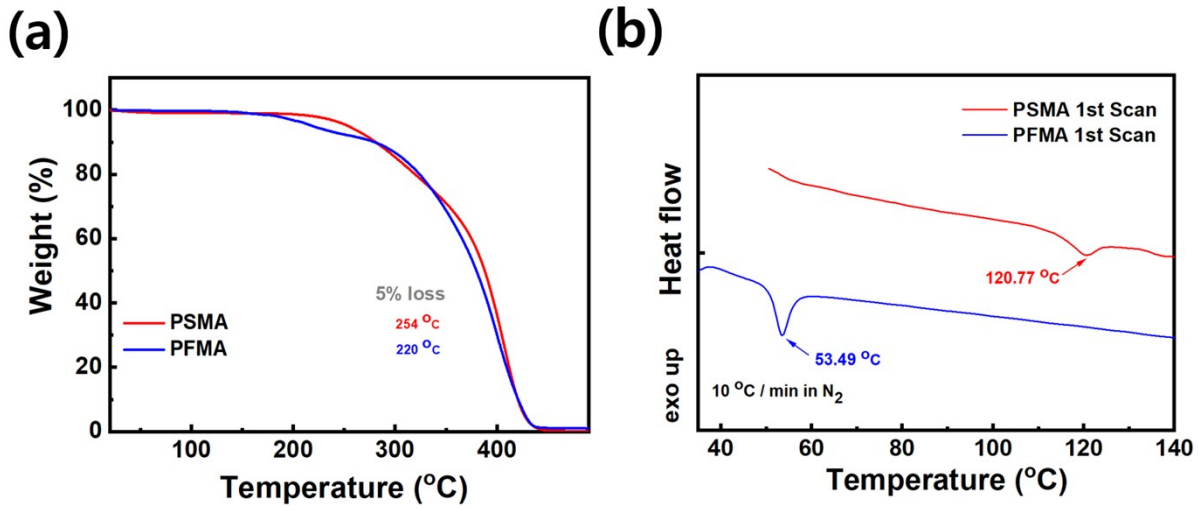


Fig. S13. Thermal properties of HEMA derivated Polymers: (a) TGA and (b) DSC curves

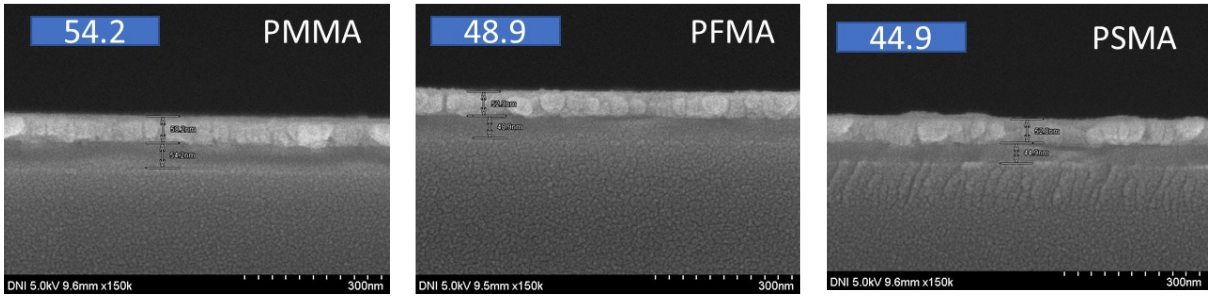


Fig. S14. Cross-section SEM image of polymeric layers.

Supplementary Note

We conducted quantum and molecular dynamics (MD) calculations to correlate the dipole moment of monomers and the dielectric properties of their polymers. They could illustrate a clear link between molecular characteristics and macroscopic behavior. This correlation also enables a more precise selection of monomers for designing polymers with targeted dielectric properties. Three monomers' calculated dipole moment values are 1.75D, 2.67D, and 5.00D for **MMA**, **FMA**, and **SMA**, respectively. Furthermore, it was found that the k value increased

as methoxy < para-F substituted phenoxy < para-methyl sulfonylated phenoxy group was substituted in the carbonyl group of monomers, and this trend was found to match well even when these monomers were polymerized. The resulting k values were observed as 4.17, 5.07, and 6.53 for **PMMA**, **PFMA**, and **PSMA**, respectively. **Table S3** shows the computational results of MD calculation using three polymers. The tendency of the simulated dielectric constants for three amorphous cells is consistent with the experimental results: 4.3567 for **PMMA**, 6.7846 for **PFMA**, and 13.781 for **PSMA**, respectively. (**Fig. S17**) These results suggest polymers may retain dielectric properties based on their monomer dipole moments. From the bottom of the view, these results could provide new insights and valuable directions for future exploration in polymer science.

Table S3. Computational results of dielectric constants (MD Calculation).

Polymers	Density ($g\ cm^{-3}$)	Polarizability ($bohr^3$)	Refractive Index	Static Dielectric Constant (k)
PMMA	1.1124	1603.3	1.445	4.3567
PFMA	1.2352	3804.6	1.539	6.7846
PSMA	1.2591	4667.2	1.301	13.781

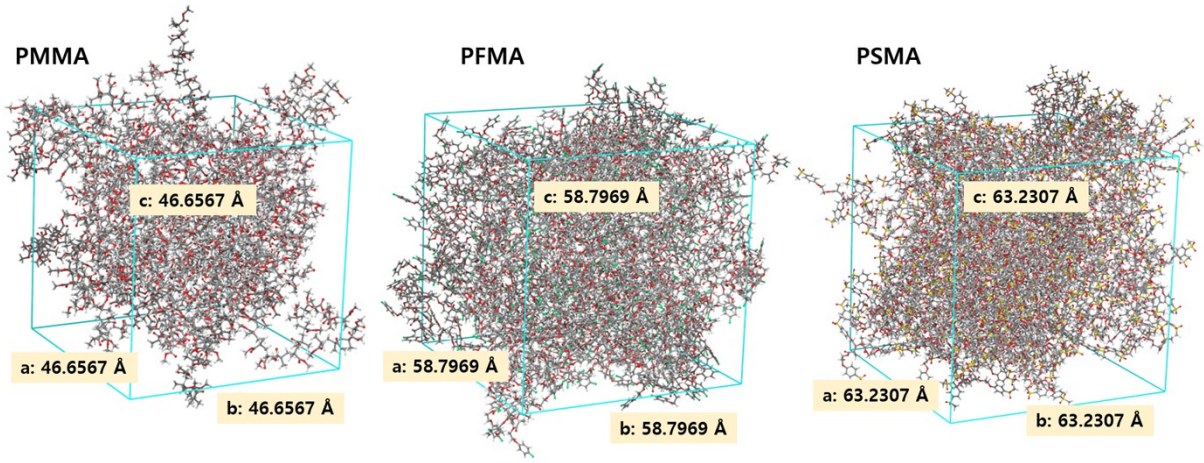


Fig. S15. Molecular dynamics (MD) amorphous cells for three polymers

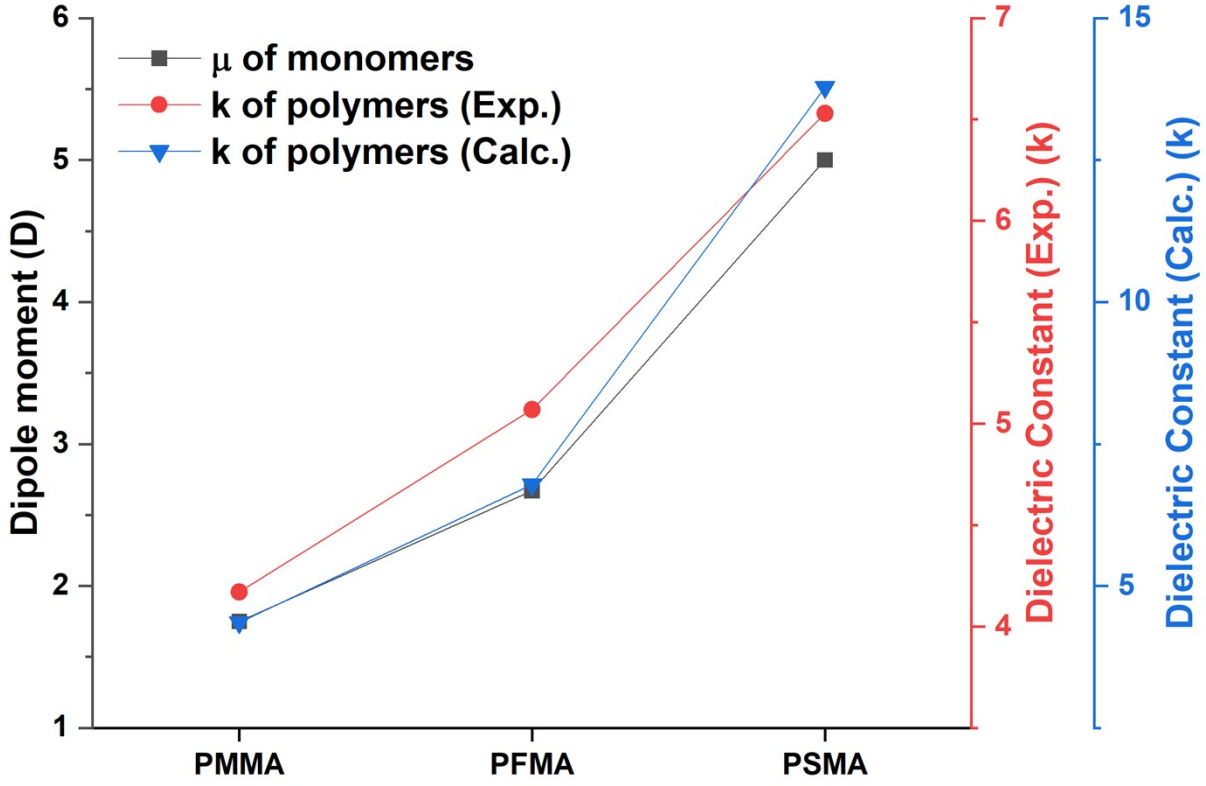


Fig. S16. Relationship between dipole moment(μ) of monomers and dielectric properties (k) of three polymers.

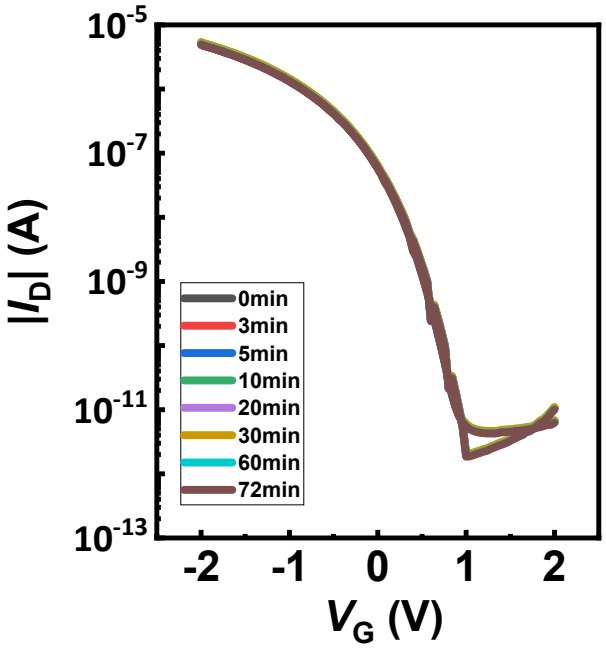


Fig. S17. PSMA OTFT transfer curves with bias-stress test.

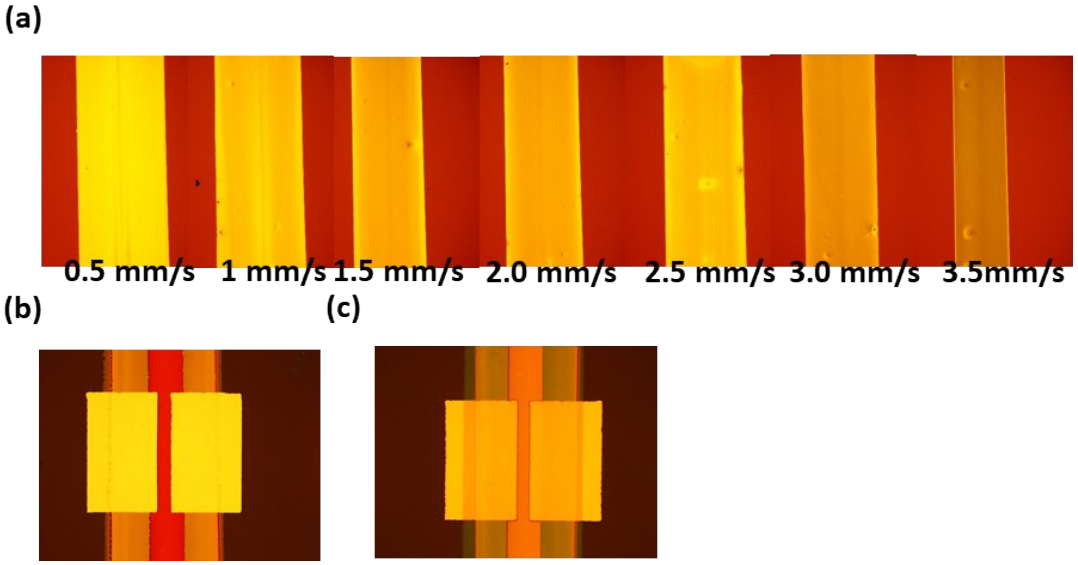
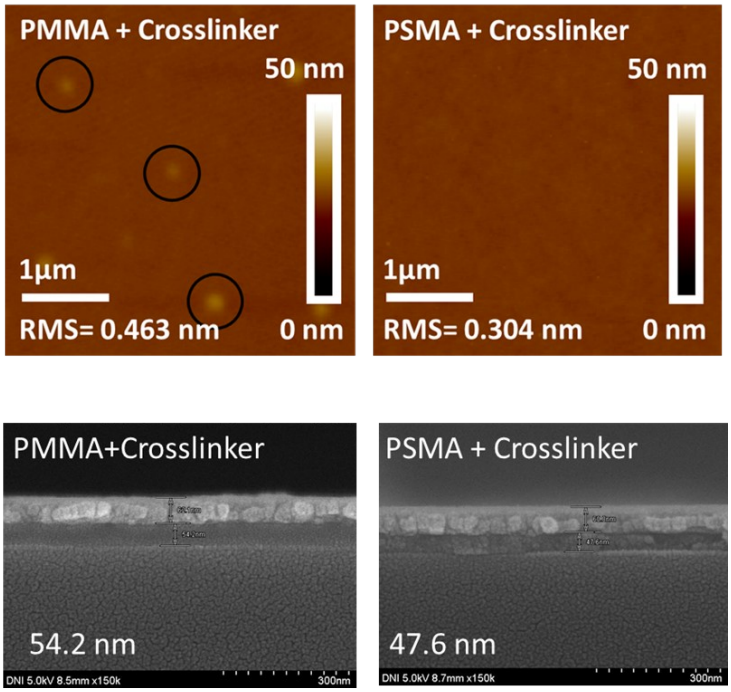


Fig. S18. OM image of electrohydrodynamic jet printed **PSMA** with photo-crosslinker, (b) p-type and (c) n-type OTFT with C_{10}-DNTT and PTCDI-C_{13} (thermally annealed).

Table S4. Comparative table of trap densities with OTFTs

Dielectrics / Semiconductors	**Trap densities** (N_{trap} / eV^{-1} cm^{-2})	**Dielectric Constant (k)**	**Reference**
AlO_x/PVP/Pentacene	2.3×10^{12}	-	[1]
TiO_x/PVP/Pentacene	5.3×10^{12}	-	[1]

TaO_x/PVP/Pentacene	4.8×10^{12}	-	[1]
pH1D6/DNTT	1.113×10^{12}	6.2	[2]
MBHCa-F-0.4	1.04×10^{12}	6.03	[3]
Crosslinked PI-MA	1.173×10^{12}	8	[4]
PFMA	1.90×10^{12}	5.07	This work
PSMA	1.152×10^{12}	6.53	This work



	Dielectric constant (k)	*Capacitance ($nF\ cm^{-2}$)*
PMMA	3.55	59.5
PSMA	6.53	123.3
PMMA+4F	3.71	62.3
PSMA+4F	7.23	121.07

Fig. S19. AFM images, cross-sectional SEM images, and a comparative table showing capacitance at 1 kHz, and dielectric constant values before and after crosslinking.

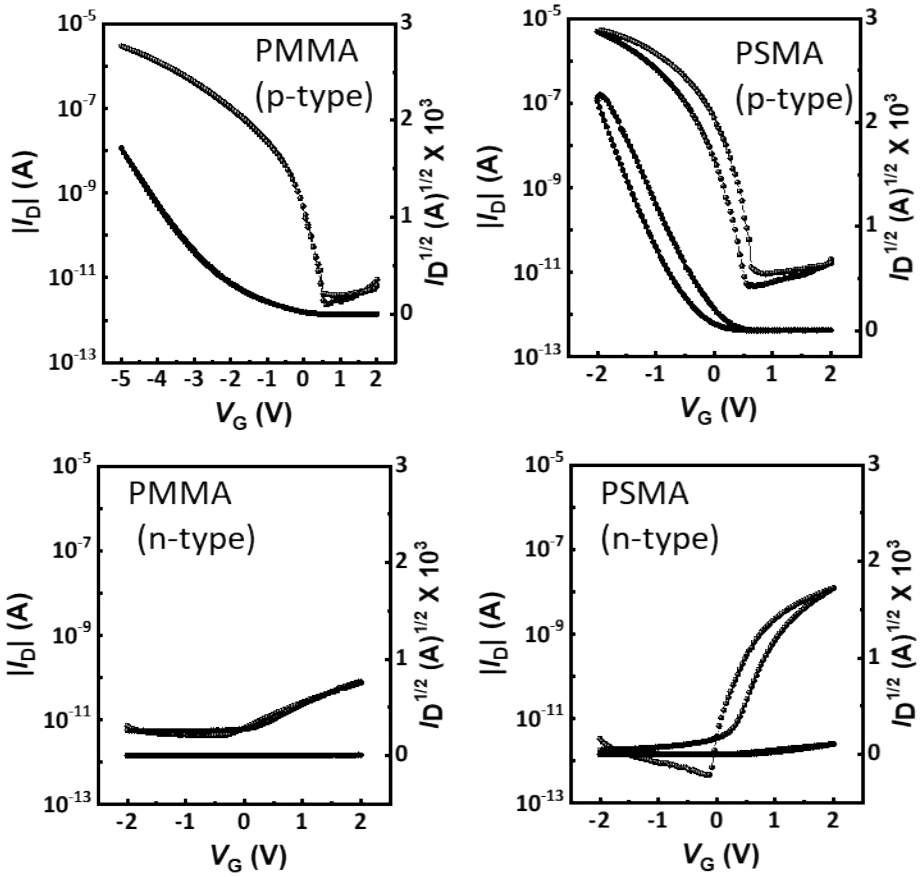


Fig. S20. unit OFETs for n-type and p-type.

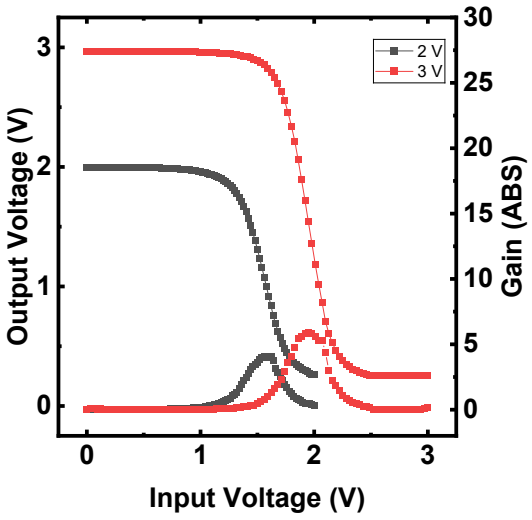


Fig. S21. VTC curve data of crosslinked PMMA based devices.

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2. J. Choi, J. Yoon, M. J. Kim, K. Pak, C. Lee, H. Lee, K. Jeong, K. Ihm, S. Yoo, B. J. Cho, H. Lee and S. G. Im, *ACS Appl. Mater. Interfaces*, 2019, **11**, 29113-29123.
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