Supplementary Information

Nano-structured Poly(3-hexyl thiophene) Grafted on Poly(vinylidene fluoride) via Poly(glycidyl methacrylate)

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- ***Preparation of PGMA homopolymer***

To a nitrogen-purged tube (8 × 2.5 cm) containing Aliquat®336 (0.05 g), CuCl (0.005 g) was added and the tube was closed with a rubber septum. GMA (1 mL), anisole (0.3 mL) (both previously purged with nitrogen) and N,N,N',N',N-pentamethyldiethylenetriamine (PMDETA, 0.011 mL) were next introduced into the tube. The mixture was stirred magnetically to make a homogeneous solution and EBiB (0.008 mL) was injected. The tube was kept in an oil bath placed over a magnetic stirrer and maintained at 38 ^{0}C. After 24 h, the content of the tube was diluted with 1mL anisole and precipitated into pet ether (60-80 ^{0}C). The polymer was isolated by filtration, dried and washed several times to remove copper followed by drying in vacuum at 40 ^{0}C.

Preparation of P3HT homopolymer

Anhydrous $FeCl_3$ (1.8 g) and $CHCl_3$ (10 mL) were placed in a round-bottom flask, filled with nitrogen and 3-hexylthiophene (0.5 ml) was added via a syringe to the suspension. The mixture was stirred under a flow of nitrogen. After 24 hrs the mixture was poured into methanol containing 10% aqueous HCl. The precipitate was collected by filtration and washed with methanol in a Soxhlet for 24 hrs. The solid residue was extracted with $CHCl_3$ in the same apparatus, and the solvent was evaporated to give the product.

Sample Preparation: The PVDF and PG films were prepared by solvent casting technique from 5% (w/v) DMF solution. In case of P3HT and PGMA, the films are prepared from THF solution. The pre-casting films or pellets (for PGHT samples) are melt-quenched in a Mettler FP82HT hot stage for 15 min at 230 ^{0}C (160 ^{0}C for P3HT) under nitrogen atmosphere and used for further characterization. To compare the properties of the sample under similar morphology and structure we have made the

samples melt-quenched. This technique also makes the films nonporous which is required for the conductivity measurement.

Characterization:

Gel Permeation Chromatography

The gel permeation chromatography (GPC) experiments were performed using a Waters instrument with a μ-Styragel column and the signal was detected using a refractive index detector. DMF and THF solvents were used for PG samples and P3HT, respectively. The sample was eluted with a solvent flow rate of 0.5 mL/min.

Spectral Characterization

DMSO-d^6 has been used to carry out the ^{1}H NMR and ^{19}F NMR study for all the samples in a 500 MHZ Bruker instrument except P3HT. For ^{1}H NMR spectra of P3HT $CDCl_3$ has been used. The head tail regioregularity of P3HT was measured from the ^{1}H NMR spectra following the method of Amou et al.[1] The ^{19}F NMR spectra of PG samples were recorded without proton decoupling[2,3] and analyzed with a seven-carbon sequence[4,5] and the head to head (H-H) defects were calculated by the method of Wilson and Santee.[6]

The UV-visible diffuse reflectance spectra of P3HT and PGHT samples were recorded on a Shimadzu UV 2401PC with an integrating sphere attachment. BaSO4 was used as background standard. The photoluminescence (PL) spectra of the samples were performed in a Fluoromax-3 instrument (Horiva Jovin Yvon). The photoexcitation was made at a 60° angle using 500 nm radiation, and the emission was detected at a right angle with respect to the excitation beam direction using a slit width of 5 nm. The Fourier-transform infrared (FT-IR) spectra of the melt-quenched samples were recorded using a Shimadzu FT-IR instrument.

X-ray Scattering

The X-ray data were recorded using a Bruker AXS diffractometer (model D8 Advance) equipped with a Lynx Eye detector. The instrument was operated at 40 kV voltage and 40 mA current. The sample was scanned in the range $2\theta = 2 - 35^0$ at a scan rate of 0.5 s. step^{-1} with a step width of 0.02^0. For small-angle X-ray scattering (SAXS) measurements the samples on an Al holder are scanned from $2\theta = 0.2 - 5^0$ in the step-scan mode (step size 0.02^0).

Microscopy

The morphology of the melt-quenched PG films was studied using a field emission scanning electron microscope (FESEM; JEOL, JSM-6700F). The samples were platinum-coated prior to observation. For TEM study, a drop of THF dispersion of PGHT samples was taken on a carbon coated copper grid (200 mesh) followed by drying and then melt-quenched as stated earlier. The micrographs were taken through a high-resolution transmission electron microscope (JEOL, 2010 EX). The instrument was operated at an acceleration voltage of 200 kV without staining. A CCD camera was used to record the pictures. The diameter of the P3HT nano-spheres was measured using photoshop software and taking average over 50 particles from different spots.

Thermal Study

The melting point and enthalpy of fusion data of the samples were measured by a Perkin-Elmer differential scanning calorimeter (DSC) (Diamond DSC-7) working under nitrogen atmosphere. It was calibrated with indium before each set of experiment. Weighed samples (~5 mg) were crimped by a universal crimpier. They were heated from 0 to 230 °C at 10 °C/min (0-175 ^{0}C for P3HT).

The thermal stability of the samples was measured using a TGA/DTA instrument (model SDT Q600, TA instrument) under nitrogen atmosphere at a heating rate of 10 °C/min.

dc Conductivity Measurement

The dc conductivity of the melt-quenched PGHT samples (iodine doped and undoped) were measured by a two-probe method using an electrometer (Keithley model - 617). The thickness of the film is measured by using screw gauze, and the film is then gold coated by the vacuum deposition technique. The samples were connected to the electrometer through a copper wire using silver paste. The resistance is measured, and the conductivity (σ) is calculated from the equation

$$\sigma = (1/R) \times (l/A)$$

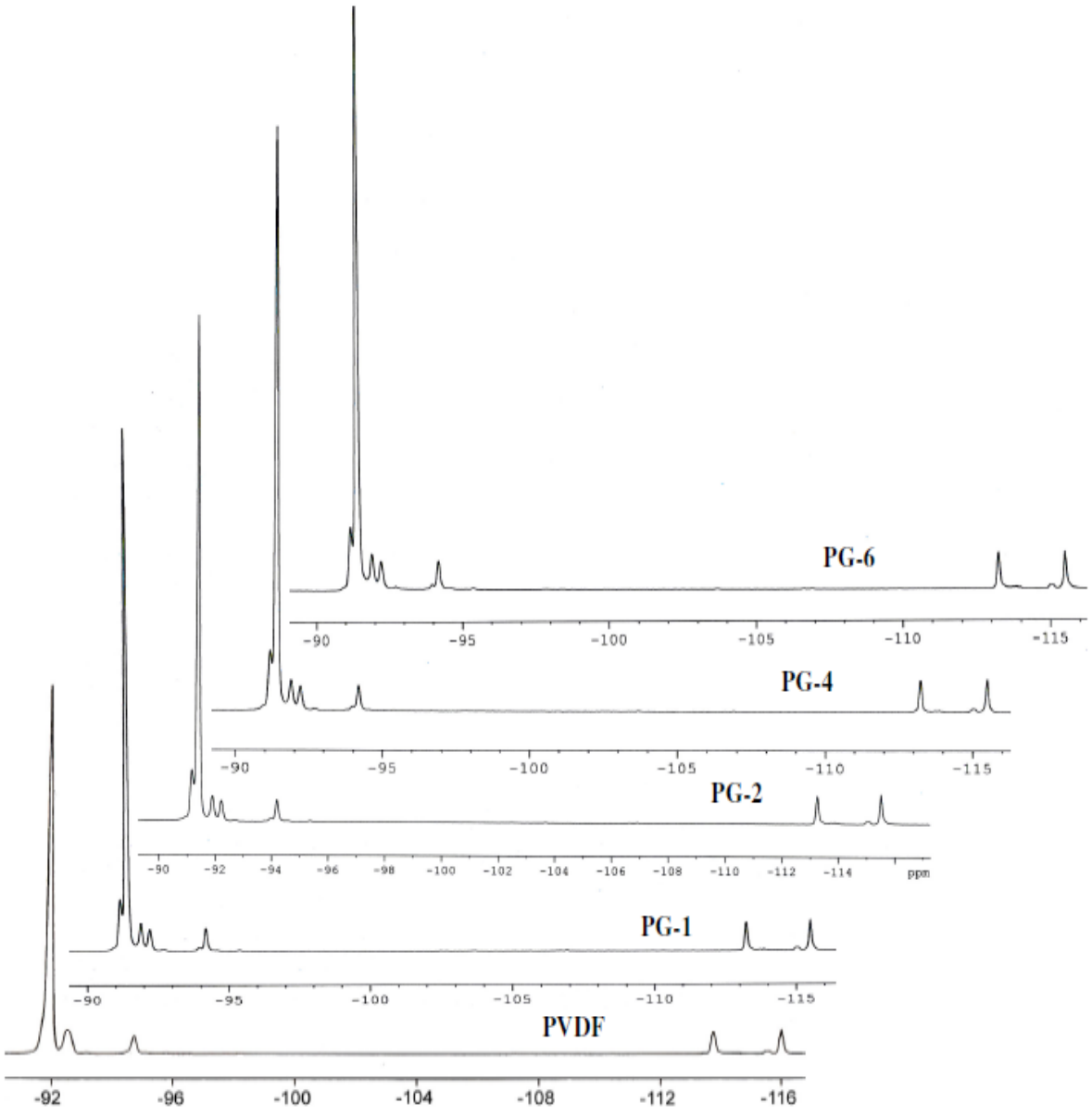
where "l" is the thickness and "A" is the area of the sample.

References:

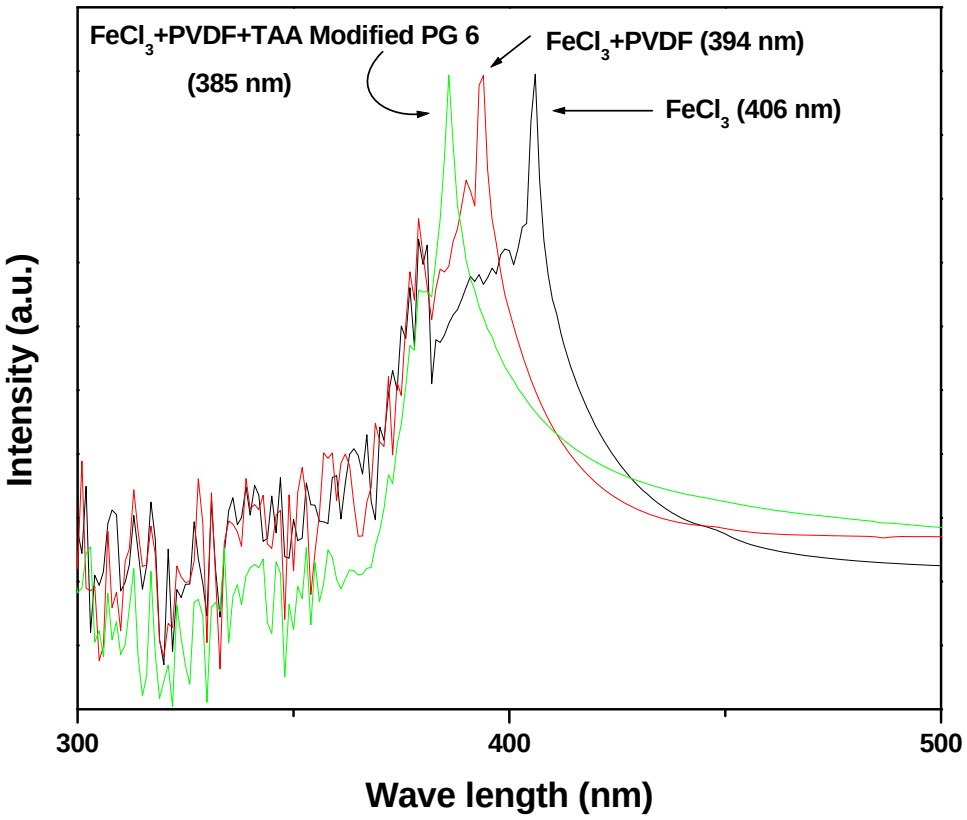
1. S. Amou, O. Haba, K. Shiroto, T. Hayakawa, M. Ueda, K. Takeuchi, M. Asai, *J. Polym. Sci., Part A: Polym. Chem.,* 1999, **37**, 1943-1948.
2. A. K. Nandi, L. Mandelkern, *J. Polym. Sci., Part B: Polym. Phys.,* 1991, **29**, 1287-1297.
3. A. K. Dikshit, A. K. Nandi, *J. Polym. Sci., Part B: Polym. Phys.,* 2000, **38**, 297-308.
4. R. C. Ferguson, E. G. Brame, Jr. *J. Phys. Chem.,* 1979, **83**, 1397-1401.
5. R. E. Cais, N. J. A. Solane, *Polymer,* 1983, **24**, 179-187.
6. C. W. III. Wilson, E. R., Jr. Santee, *J Polym Sci: Part C,* 1965, **8**, 97.

SI Table-1: Representative I^0_{hkl}/I^0_{110} data of PVDF present in melt-quenched PG samples obtained from Fig7a.

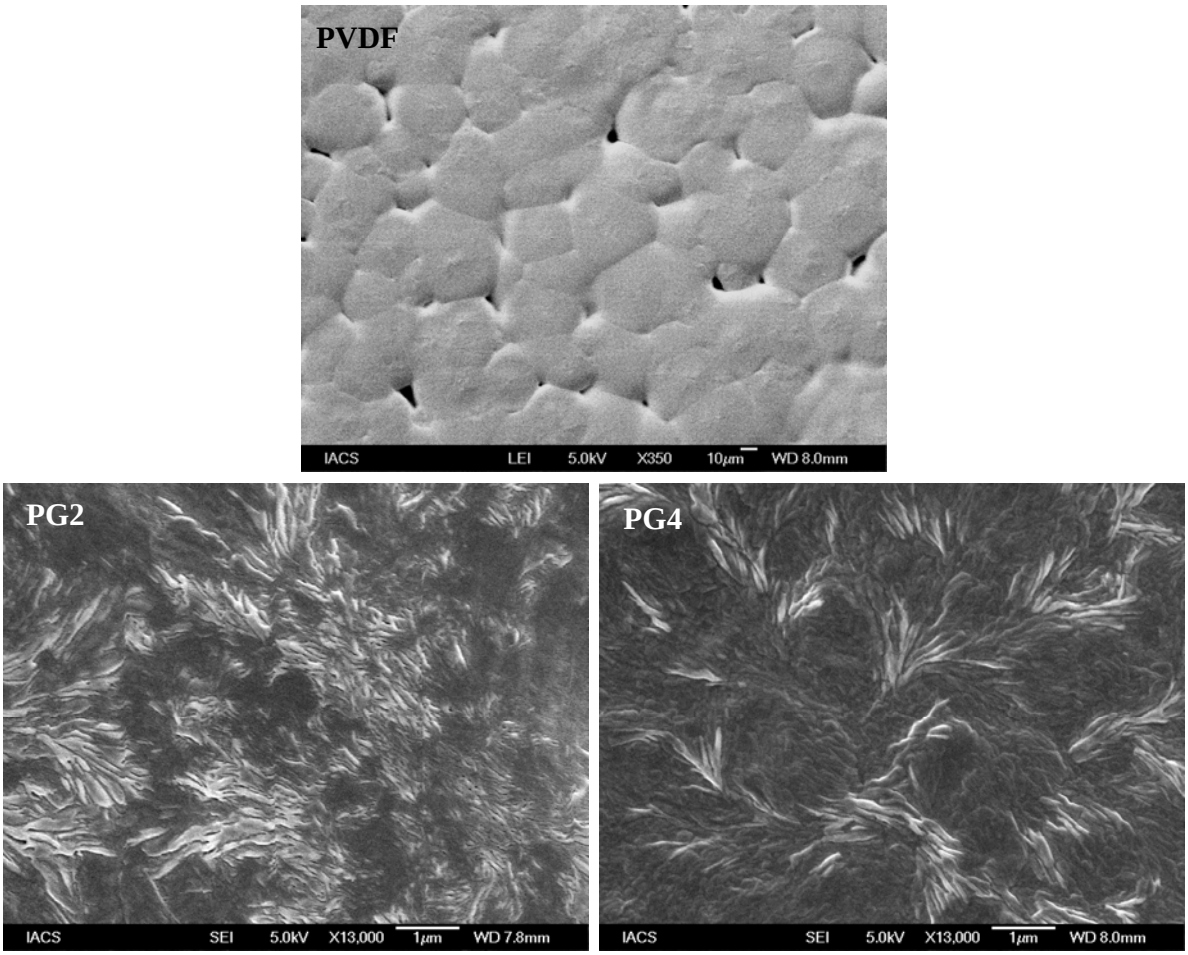
		I^0_{hkl}/I^0_{110}				
hkl	d_{hkl}^{cal}	**PVDF**	**PG 1**	**PG 2**	**PG 4**	**PG 6**
020	4.82	1.58	0.98	0.94	0.79	0.78
110	4.44	1	1	1	1	1
021 101	3.35	0.39	0.14	0.16	0.18	0.09



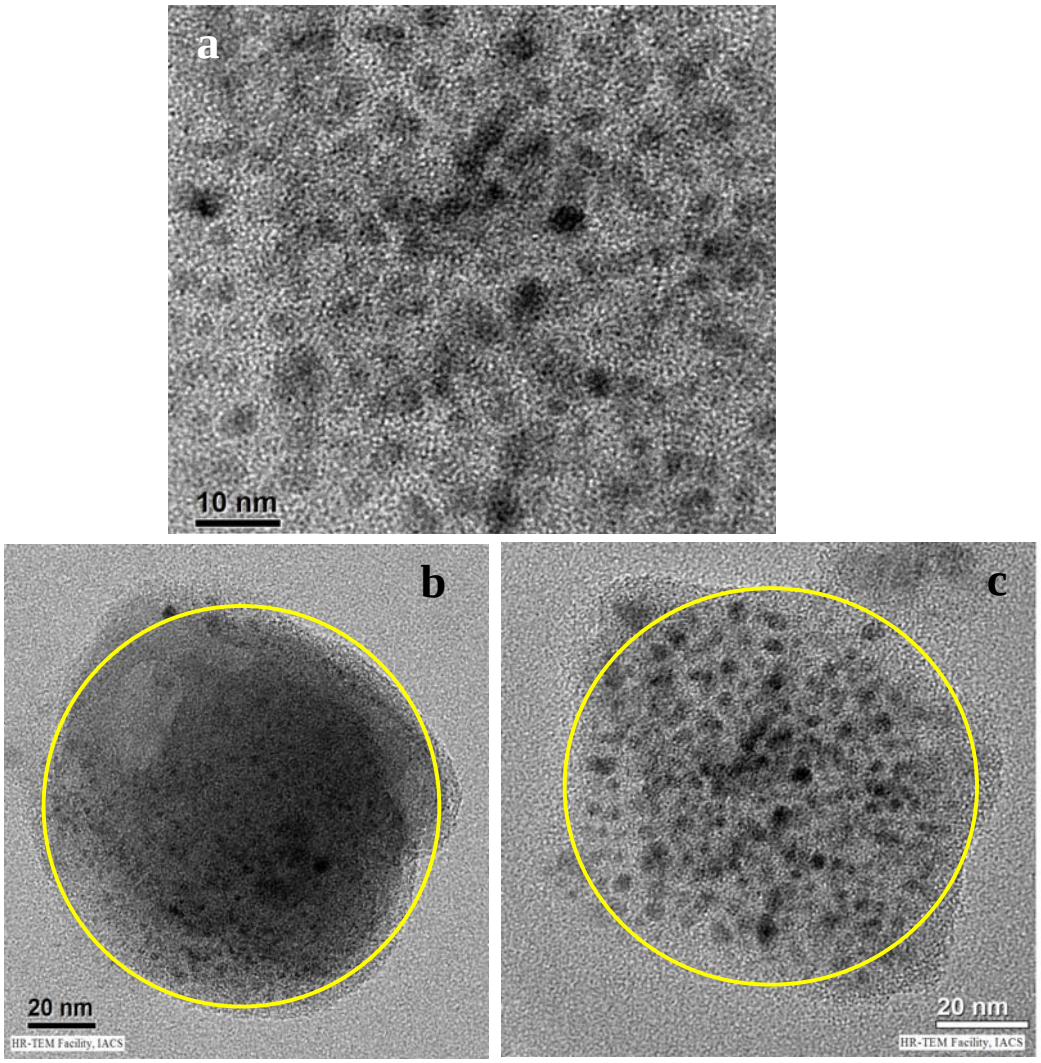
SI Fig. 1: ^{19}F NMR spectra of PVDF, PG1, PG2, PG4, and PG6 graft co-polymers.



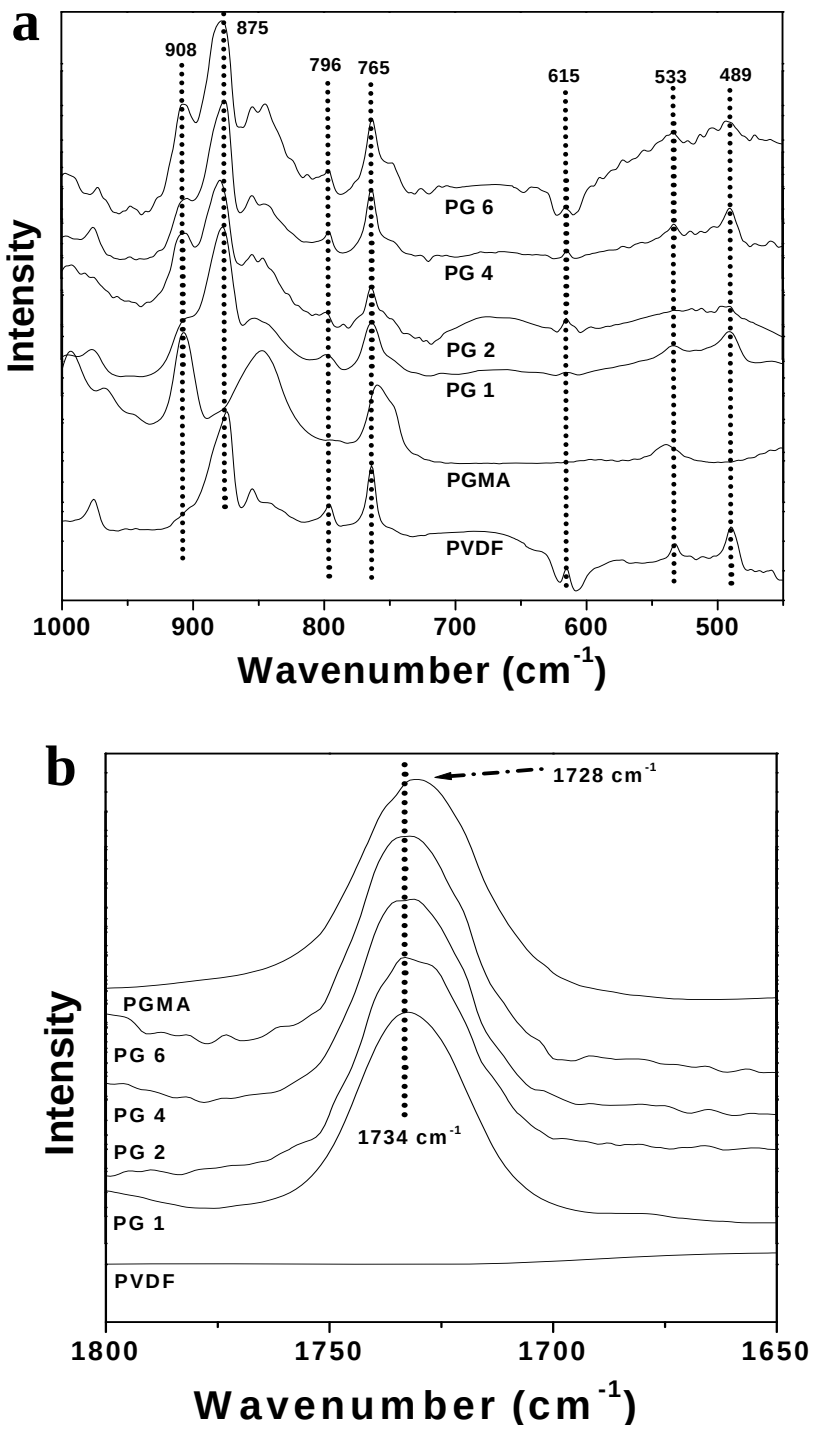
SI. Fig. 2: UV-vis absorption spectra of the indicated samples in nitromethane.



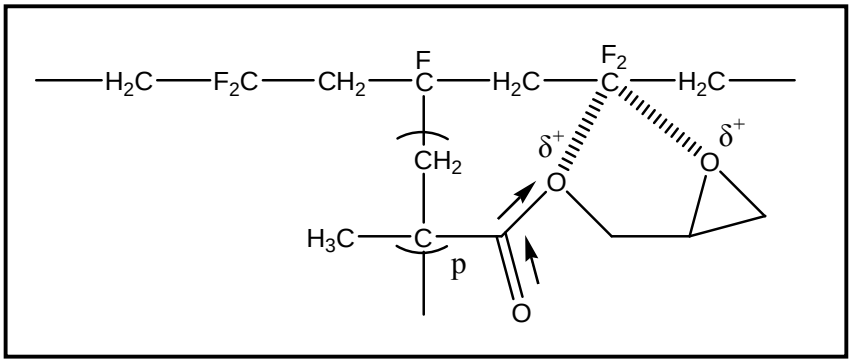
SI Fig. 3: FE-SEM micrographs of melt-quenched PVDF, PG 2 and PG 4 samples.



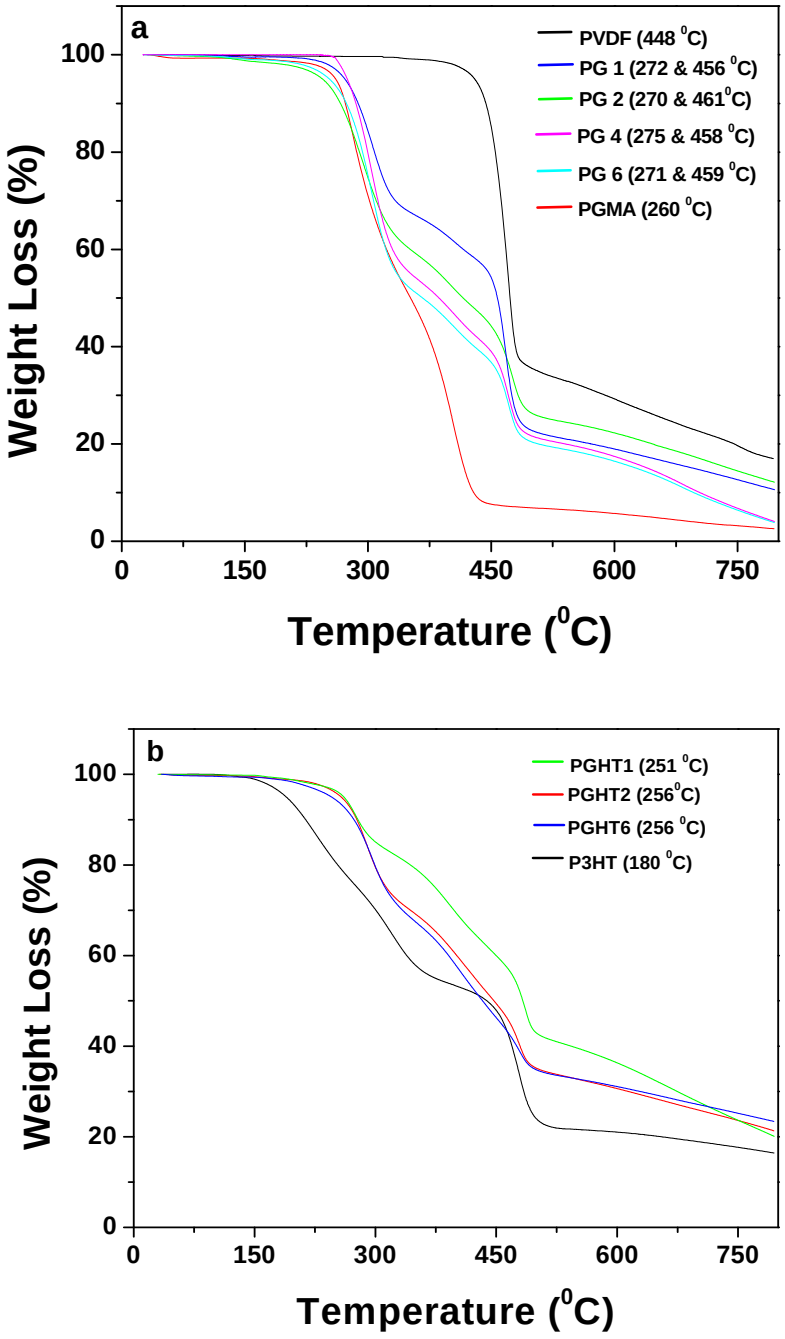
SI. Fig. 4: TEM micrograph of melt-quenched (a)PGHT2 (b) PGHT6 and (c) PGHT2 sample at lower magnification.



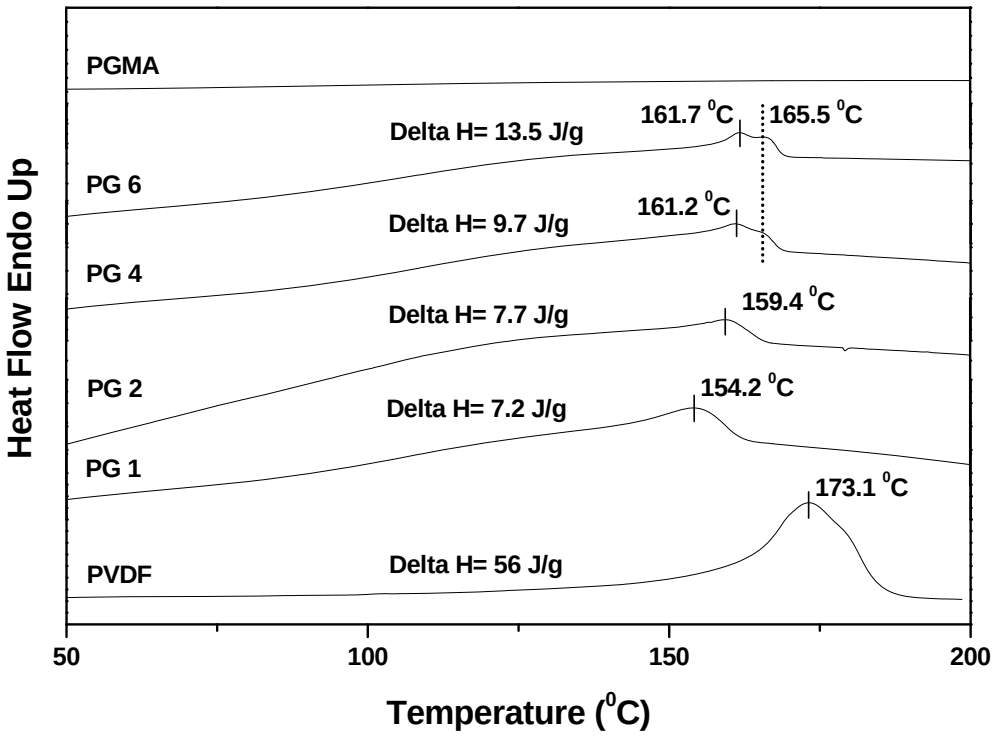
SI. Fig. 5: (a) FT-IR spectra of PVDF, PGMA & different PG samples. **(b)** Comparison of FT-IR spectral data of >C=O stretching vibration among PVDF, PGMA & different PG samples. All are melt-quenched.



SI. Fig. 6: Probable supramolecular ring structure formation in the PG samples.



SI. Fig. 7: TGA thermograms at 10 ^{0}C/min heating rate under nitrogen atmosphere **(a)** for PVDF, PGMA and different PG samples and **(b)** for P3HT and different PGHT samples.



SI. Fig. 8: DSC endotherms of PVDF, PGMA and different PG samples at 10 ^{0}C/min heating rate.