

Highly stable gel electrolytes for dye solar cells based on chemically engineered polymethacrylic hosts

Gian Luca De Gregorio, Rita Agosta, Roberto Giannuzzi, Francesca Martina, Luisa De Marco Michele Manca* and Giuseppe Gigli

Materials and methods. Methylmethacrylate (MMA), 2,2,2-trifluoroethylmethacrylate (TFEMA), 4-vinylpyridine (4VPy), 1-vinylimidazole (VI), α,α' -azobisisobutyronitrile (AIBN), iodine and iodomethane were furnished by Sigma Aldrich and used as received. 1,2-dimethyl-3-propylimidazolium iodide (DMPII) was purchased from IoLiTec and stored under vacuum before use. 3-methoxypropionitrile (MPN) and 3-methyl-2-oxazolidinone (NMO) were purchased from Sigma-Aldrich and stored in nitrogen atmosphere before use.

A typical copolymerization was performed in a three necked flask immersed in a thermostatic oil bath, connected with an Allihn reflux condenser refrigerated with cooling liquid. Temperature was maintained at 70°C and controlled by a thermocouple trough all reaction period. A feed of monomers in toluene was added to the reactor and purged with nitrogen for 20 min. AIBN was dissolved in a small portion of solvent and injected by a syringe pump. The solution was purged under nitrogen for an additional 20 min and then the temperature was increased to 70°C. Reactions were carried out for 48 hours under nitrogen blanket and stirring. Polymerizations were stopped by cooling down the temperature to room temperature and polymers were recovered by precipitation in diisopropyl ether to remove unreacted monomers and low molecular weight oligomers. Polymeric latexes were then collected, washed twice with diisopropyl ether and dried in oven at 60°C for two days.

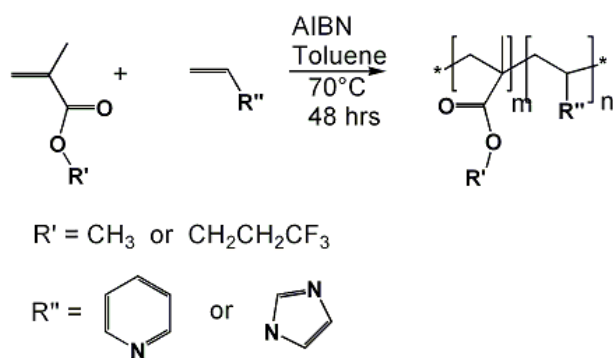


Figure S1: schematic representation of the co-polymerization reactions

Characterization of polymers. Effective macromolecular compositions were confirmed by Fourier transformed infrared spectroscopy (FTIR) and nuclear magnetic resonance (NMR) spectroscopy. FT-IR spectra of polymers were recorded on a Jasco FT/IR-6300 spectrophotometer from film casted samples over ZnSe trough plate. NMR spectra were recorded on a Bruker 400 MHz spectrophotometer, from polymeric solutions in CDCl_3 . Molecular weight and PDI for the synthesized polymers were obtained using an Agilent 1200 gel permeation chromatography (GPC) system equipped with Agilent PLgel 7.5 mm ID column (500 Å), G1312A binary HPLC pump, and G1362 refractive index detector. The mobile phase employed was tetrahydrofuran at 1 ml min⁻¹ flow rate. The system was calibrated with six PMMA standards (Sigma-Aldrich) with peak molecular weights ranging from 800 to 23500 Da and PDI from 1.03 to 1.13. Thermogravimetric

analyses were performed on a Mettler-Toledo TGA STAR^e system under nitrogen flow and heating rate 5°C/min.

Infrared spectra of synthesized polymers are reported in Fig. S2. Carbonyl stretching vibration at 1724 cm⁻¹ of methylmethacrylate unities and at 1745 cm⁻¹ of 2,2,2-trifluoroethylmethacrylate unities are clearly observed in the respective polymers. Aromatic C=N vibrations of pyridine ring are observed at 1598 cm⁻¹ and 1557 cm⁻¹, finally, C=N stretching of imidazole ring is observed at 1651 cm⁻¹.

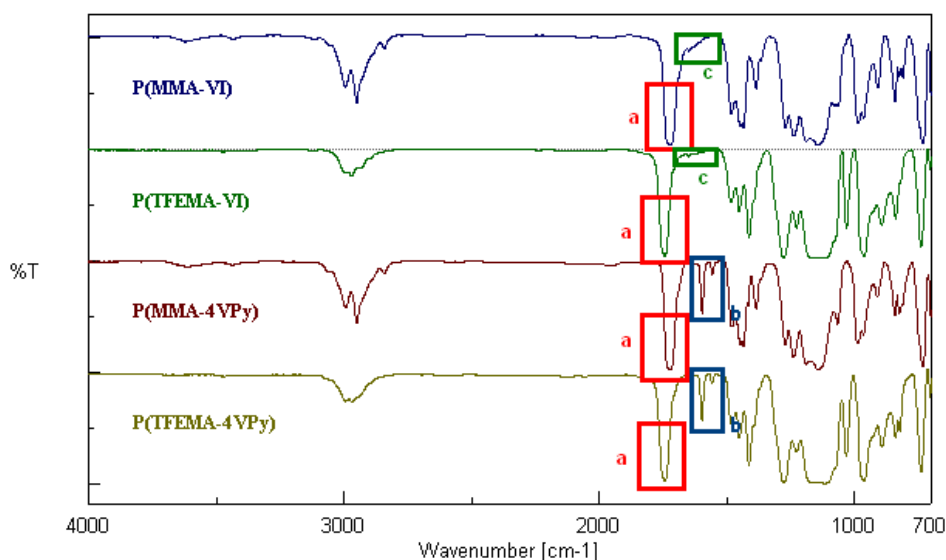


Figure S2: FTIR transmittance spectra of synthesized polymers *P(MMA-VI)*, *P(TFEMA-VI)*, *P(MMA-4VPy)*, *P(TFEMA-4VPy)*: a (red marker): C-O stretching 1724 or 1745 cm⁻¹ b (blue marker): pyridine aromatic C=N vibration 1598 cm⁻¹ and 1557 cm⁻¹ c (green marker): imidazole C=N stretching 1651 cm⁻¹

Effective macromolecular composition was determined comparing integrals' intensities of etheroaromatic and methacrylic moieties. Spectra of synthesized copolymers are reported in Fig S3. Peaks at δ (ppm)= 8.38-8.48 and δ = 6.90-7.00 are ascribed to meta- and ortho- protons of pyridine ring. Peaks at δ = 3.53 ppm and δ = 4.27 ppm are respectively ascribed to methyl- and 2,2,2-trifluoroethyl- protons of methacrylic esters. Peaks at 7.12 ppm, 6.94 ppm and 6.69 ppm are respectively ascribed to 2H, 4H and 5H protons of imidazole ring.

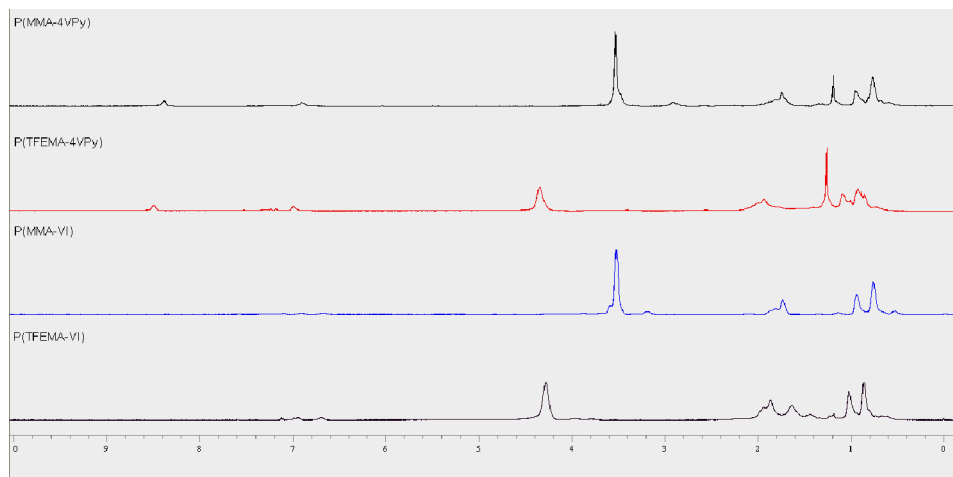


Figure S3: ¹H-NMR spectra of synthesized polymers

Magnification of GPC chromatograms in the elution range 5.5 - 7 minutes of synthesized polymers and the corresponding calculated values of molecular weights (M_w and M_n) are reported in Fig. S4. Detected peaks are positioned in a relatively short retention time interval, meaning that the molecular weights of polymers are quite similar. Intensities of peaks are strictly related to the refractive index of analyzed substance and consequently, to the chemical composition.

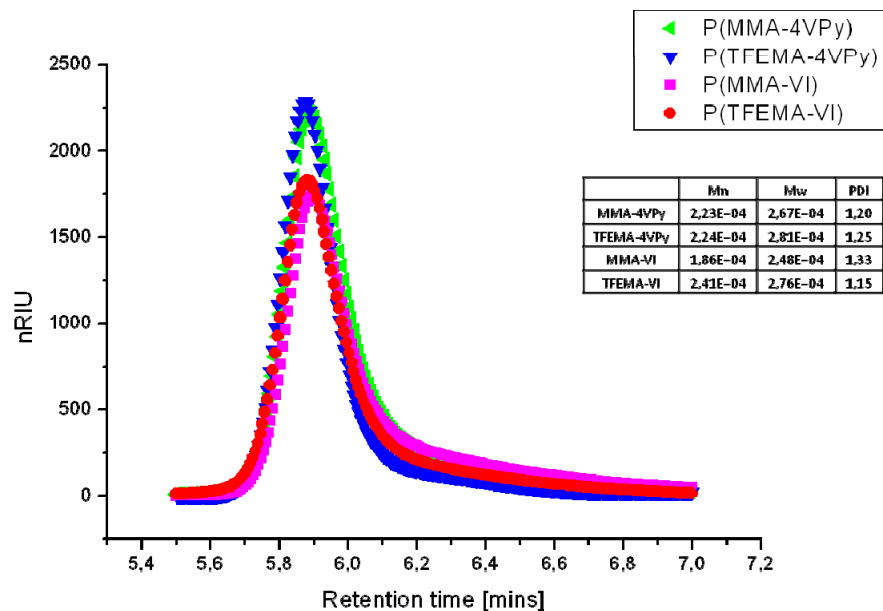


Figure S4: GPC chromatograms of synthesized polymers.

Electrochemical characterization. Electrochemical impedance spectroscopy (EIS) spectra were performed with a computer-controlled AUTOLAB PGSTAT 302N potentiostat operating in a two-electrode mode. Measurements were carried out at zero bias potential in the 100 kHz to 0.01 Hz frequency range and applying AC voltage of 10mV. The obtained spectra were fitted with Z-view software.

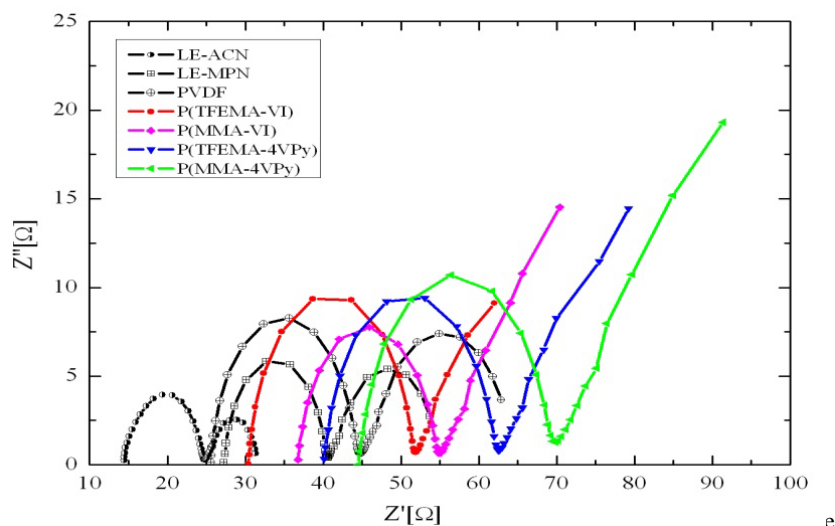


Figure S5 shows the Nyquist plots of the four proposed gel electrolytes as well as those ones obtained from the liquid electrolyte and a PVDF-co-HFP based gel electrolyte. As expected for the high frequencies, the serial resistance (R_s), including the resistance of bulk electrolyte and the platinized TCO coated glass, is dominating the impedance of the cell. Two semicircles are thus detectable: the first one (high frequencies) concerns the Pt/electrolyte interface; the second one (at lower frequencies) is referred to the contribution due to the Nernst diffusion layer into the electrolyte.

The electrochemical cell consists of two identical platinized, FTO-coated glass substrates sealed with a parafilm, which serves as a spacer. The distance between the two electrodes is about $100\mu\text{m}$, the active area of the electrode is about 0.2cm^2 . Platinum electrodes were obtained by electron beam evaporation. The apparent diffusion coefficient (D_{app}) of triiodide was evaluated from the diffusion-limited current within the sandwiched cell by measurement of a cyclic voltammogram at a low scan rate (5 mV s^{-1}). The apparent diffusion coefficient (D_{app}) of triiodide in the electrolyte is proportional to the diffusion limited current density (i) according to the following equation: $i = 2nFCD/l$, where $n = 2$, F is the Faraday constant, C the initial concentration of I_3^- and l the thickness of the cell .

Fabrication of DSSCs. FTO glasses were cleaned in a detergent solution using an ultrasonic bath for 15 min, washed with water and ethanol. TiO_2 paste was deposited onto the conducting glass by screen-printing (screen characteristic: material, polyester; mesh count, 120 mesh/cm) and dried at 160°C for 6 minutes; this procedure was repeated several times in order to obtain the wanted film thickness ($12\mu\text{m}$). All the films were characterized by the same value of active area (0.28cm^2). The FTO-glass samples coated with the TiO_2 paste were gradually heated under an air flow at 160°C for 20 min, 350°C for 15 min, at 450°C for 15 min, and at 450°C for 20 min. After cooling to 80°C , the TiO_2 electrodes were immersed into a solution 0.5 mM of (bis(tetrabutylammonium)-*cis*-di(thiocyanato)- N,N' -bis (4 - carboxylato - 4' - carboxylic acid-2, 2 -bipyridine) ruthenium(II) (N719) in a mixture of acetonitrile and *tert*-butyl alcohol (v/v, 1:1), and kept at room temperature for 14h. Solar cells were assembled by placing a platinum-coated conducting glass (counter electrode) on the N719 dye-sensitized photoelectrode (working electrode). The two electrodes were assembled into a sandwich type cell and sealed with a Parafilm hot-melt gasket $50\mu\text{m}$ thick. Polymer electrolytes were heated at 60°C and then vacuum injected in the inner space between electrodes through the hole pre-drilled on the back of the counter electrode. The holes were sealed up using Surlyn hot-melt film and a cover glass.

Dye solar cells characterization. Photocurrent–voltage (I–V) measurements were performed using a Keithley unit (Model 2440 Source Meter). A Newport AM 1.5 Solar Simulator (Model 91160A equipped with a 300 W Xenon Arc Lamp) serves as a light source. The light intensity (or radiant power) was calibrated to 100 mW /cm² using as reference a Si solar cell.

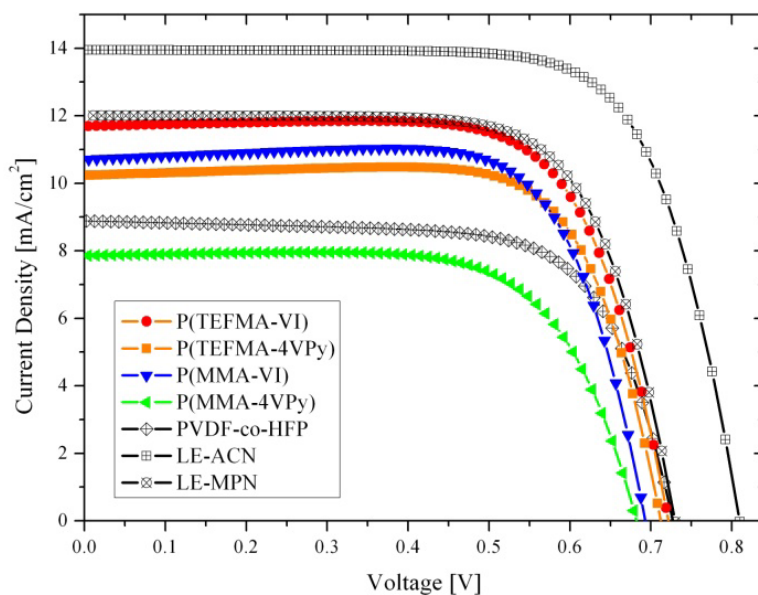


Figure S6. Current–voltage curves for DSSCs filled with our novel PGEs compared with two liquid electrolytes and a PVDF-co-HFP-based gel electrolyte as references.