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Supporting Information

Visible Light-Induced Free Radical Promoted Cationic Polymerization Using Organotellurium Compounds

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1. Experimental Section

1.1 Materials

EMPTeMe and PMMATeMe were prepared as reported.¹⁻² All the monomers were purified by conventional drying and distillation procedures. Diphenyliodonium hexafluorophosphate (DPI) 98% was purchased from Sigma-Aldrich and was used as received without further purification. Dichloromethane solvent was dried using PureSolv MD5 solvent purification system.

1.2 Characterization

¹H-NMR and ¹³C-NMR spectra were recorded in deuterated chloroform (CDCl₃) with tetramethylsilane as an internal standard at 500 MHz and 125MHz, respectively on an Agilent VNMRS 500 spectrometer at 25°C. Fourier-transform infrared (FTIR) spectra were recorded on Perkin–Elmer Spectrum One spectrometer with an ATR Accessory (ZnSe, PikeMiracle Accessory) and mercury cadmium telluride (MCT) detector. 64 scans were averaged. UV-visible spectra were recorded with a Shimadzu UV-1601 double-beam spectrometer equipped with a 50W halogen lamp and a deuterium lamp which can operate between 190nm-1100nm. Gel permeation chromatography (GPC) measurements were performed on a TOSOH EcoSEC GPC system equipped with an auto sampler system, a temperature controlled pump, a column oven, a refractive index (RI) detector, a purge and degasser unit and TSKgel superhZ2000, 4. 6mm ID x 15 cm x 2cm column. Tetrahydrofuran was used as an eluent at flow rate of 1.0 mL/min at 40 °C. Refractive index detector was calibrated with poly(methyl methacrylate) standard having narrow molecular-weight distributions. (1.05-1.10) GPC data were analyzed using Eco-SEC Analysis software. The photo-differential scanning calorimetry (Photo-DSC) measurement was carried out by means of a modified PerkinElmer Diamond DSC equipped with a high pressure

mercury arc lamp emitting polychromatic light at 320–500 nm. A uniform UV light intensity is delivered across the DSC cell to the sample and reference pans. The intensity of the light was measured as 60 mW/cm² by a UV radiometer capable of broad UV range coverage. The mass of the sample was 1 mg (1 μ L) and the measurements were carried out in an isothermal mode at 30°C under a nitrogen flow of 10 mL/min. The reaction heat liberated in the polymerization is directly proportional to the number of divinyl ether groups reacted in the system. By integrating the area under the exothermic peak, the conversion of the divinyl ether groups (C) or the extent of the reaction was determined according to eqn (1):

$$C = \Delta H_t / \Delta H_0$$
 theory (1)

Where ΔH_t is the reaction heat evolved at time t and ΔH_0 theory is the theoretical heat for complete conversion. ΔH_0 theory = 60 kJ mol⁻¹ for divinyl ether.³

1.3 Photopolymerization

Photoinitiators (0.050 mmol), monomer (5.0 mmol) in CH_2Cl_2 (0.50 mL) and diphenyliodonium hexafluorophosphate (DPI) (0.050 mmol) were put into a Pyrex tube that was heated in vacuo with a heat gun and flushed with dry nitrogen. Homogenous mixture was irradiated at room temperature in a photoreactor (Rayonet) equipped with 6 lamps emitting light at 400-500nm (λ_{max} = 450nm). The resulted polymers were precipitated in methanol and then dried under reduced pressure at 40°C for 24h. Conversion of monomer was determined gravimetrically. Molecular weights and polydispersities of the polymers were determined by gel permeation chromatography (GPC) calibrated with poly (methylmethacrylate) standards.



Figure S1. Photo showing the elemental tellurium precipitation after sunlight irradiation.

2. Structural Characterization of EMPTeMe and EMPTeMe-DPI mixture before and after irradiation



Figure S2. ¹H-NMR spectrum of EMPTeMe (500MHz in CDCl₃).



Figure S3. ¹³C-NMR spectrum of EMPTeMe (125MHz in CDCl₃).



Figure S4. ¹H-NMR spectrum of EMPTeMe-DPI mixture (10:1) after 10 min irradiation (500MHz in CDCl₃).



Figure S5. ¹³C-NMR spectrum of EMPTeMe-DPI (10:1) mixture after 10 min irradiation (125MHz in CDCl₃).



Figure S6. ¹H-NMR spectrum of EMPTeMe-DPI-CHO (10:1:10) mixture after 30 min irradiation (500MHz in CDCl₃).



Figure S7. ¹³C-NMR spectrum of EMPTeMe-DPI-CHO (10:1:10) mixture after 30 min irradiation (500MHz in CDCl₃).



Figure S8. GPC Chromatogram of PMMATeMe and PMMA-*b*-PIBVE.



Figure S9. ¹³C-NMR spectrum of PMMA-*b*-PIBVE. (125MHz in CDCl₃).



Figure S10. Infrared spectrum of PMMA-*b*-PIBVE.

References

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