Supporting Information

Experimental:

Metarials

Dimanganesedecacarbonyl (98%, Sigma-Aldrich), α,α′-dibromo-*p*-xylene (97%, Sigma-Aldrich), diphenyliodonium hexafluorophosphate (≥98%, Sigma-Aldrich), anisole (≥99 %, Sigma-Aldrich), 1,4-dimethoxybenzene (99%, Sigma-Aldrich), propylene carbonate (99%, Sigma-Aldrich).

Characterization

Gel permeation chromatography (GPC) analyses were performed by a TOSOH EcoSEC GPC system including an autosampler system, a column oven, temperature-controlled pump, a degasser unit, TSKgel superhZ2000 4.6 mm ID × 15 cm × 2 cm column and a refractive index detector. As eluent, tetrahydrofuran (THF) was used with flow rate of 1.0 mL min^{-1} at 40 °C. Refractive index detector had calibrated with polystyrene standards which have narrow molecular-weight distribution. Eco-SEC Analysis software was used to analyze data coming from SEC (size- exclusion chromatography). UV−vis analyses were recorded with Shimadzu UV-1601 double-beam spectrometer equipped with deuterium lamp and a 50 W halogen lamp that can emit light between 190 nm and 1100 nm. Fluorescence spectra were recorded via PerkinElmer LS55 spectrometer which can work between 200 nm and 900 nm wavelengths with a slit width of 10 nm. ^{1}H NMR spectra were recorded in deuterated chloroform ($CDCl_3$ with an internal standard tetramethylsilane) with 500 MHz Agilent VNMRS 500 spectrometer.

Fourier-transform infrared (FT-IR) spectra were taken via PerkinElmer Spectrum One spectrometer with ATR accessory and a mercury cadmium telluride (MCT) detector.

Polymerization Procedure

Dimanganesedecacarbonyl ($Mn_2(CO)_{10}$) (110 mg, 0.28 mmol), α,α′-dibromo-*p*-xylene (DBX) (75 mg, 0.28 mmol), diphenyliodonium hexafluorophosphate (240mg 0.56 mmol) and corresponding nucleophile (0.28 mmol) was dissolved in propylene carbonate (1 mL) in a Schlenk tube under nitrogen atmosphere. The reaction medium was irradiated for 12 hours via photoreactor containing 12 fluorescent lamps that emit visible light (λ = 400-500 nm). The

resulting polymer was precipitated in methanol, filtered-off and dried under vacuum at 50 ^{o}C. Conversions were determined gravimetrically.

Electrospinning

In order to achieve the beadless electrospun microfibers, P(DMPMPM)-*b*-PMMA polymer (375 mg) was dissolved directly with THF (2 mL) vigorously magnetic stirrer until homogeneity. Thus prepared solution was loaded in a plastic syringe equipped with a 21-gauge metal needle on a syringe pump (NE-500, New Era Pump Systems Inc., Turkey). Typical electrospinning process was applied by using high voltage power supply (Elektrosis, PW1010, Turkey) on glass slides sticked on mobile aluminium collector in a transparent chamber (NE-100, Inovenso, Turkey) and process parameters were adjust as; applied voltage = 15 kV, tip-to-collector distance = 10 cm and the solution flow rate = 2 ml/h. Laboratory temperature and relative humidity were kept constant at 24.5 °C and %40 throughout the electrospinning, respectively.