

SUPPORTING INFORMATION

Synthesis of Block Copolymers by Mechanistic Transformation from Photoinitiated Cationic Polymerization to RAFT Process

Antonino Puglisi, Eljesa Murtezi, Gorkem Yilmaz, Yusuf Yagci*

Materials

4-Cyano-4-(phenylcarbonothioylthio)pentanoic acid (Sigma-Aldrich, 97%), tetrahydrothiophene (Sigma-Aldrich, 99%), diphenyliodonium hexafluorophosphate (Alfa Aesar, 98%), bisacylphosphine oxide (Ciba® IRGACURE® 819, Ciba Specialty Chemicals) were used without further purification. Tetrahydrofuran (THF, HPLC grade, Aldrich) was dried over sodium wire under reflux in the presence of traces of benzophenone until a blue color persisted and was used directly after distillation. Methyl methacrylate (MMA, Sigma-Aldrich, 99%) was passed through basic alumina prior to use.

Instrumentation

¹H NMR spectra of the intermediates and final polymers were recorded at room temperature at 500 MHz on an Agilent VNMRS 500 spectrometer. UV–vis spectra were recorded on a Shimadzu UV-1601 spectrometer. IR spectral measurements were performed on a Perkin Elmer FTIR Spectrum One B. The resolution was 4 cm⁻¹ and 128 scans were averaged with a 0.2 cm⁻¹ scan speed. Fluorescence measurements were carried out using a Hitachi F-4500 fluorescence spectrophotometer at room temperature. Gel permeation chromatography (GPC) measurements were obtained from a Viscotek GPCmax autosampler system consisting of a pump, a Viscotek UV detector, and Viscotek a differential refractive index (RI) detector. Three ViscoGEL GPC columns (G2000H HR, G3000H HR, and G4000H HR, 7.8 mm internal diameter, 300 mm length) were used in series. THF was used as an eluent at flow rate of 1.0

mL min⁻¹ at 30 °C. Both detectors were calibrated with polystyrene standards having narrowmolecular-weight distribution. Data were analyzed using Viscotek OmniSEC Omni-01 software.

Experimental part

Synthesis of the RAFT agent terminated PTHF (PTHF-CTA)

7 ml of dry THF was placed in a flask together with 73 mg BAPO and 182 mg DPI. The solution was irradiated for 30 minutes ($\lambda = 400\text{-}500$ nm). Afterwards, 70 μl of thiolane was added and the reaction was further carried out for 1 h at room temperature. Finally, a THF solution of RAFT/TEA was added (84 mg CAPADB + 50 μl TEA in 4ml THF) and kept stirring at room temperature for another hour. The polymer was dissolved in 100ml DCM and extracted (3x100ml) with NaHCO₃ sat/aq to yield 1050 mg (17%) of gluey pink polymer (PTHF-RAFT). Thus obtained polymer was further purified by solvation and precipitation from THF/methanol. The molecular weight of the polymer was calculated by ¹H NMR, by comparing the aromatic signals of the CTA end group with the main chain protons of PTHF, which appears around 3.4 ppm. By comparing the molecular weight obtained from GPC and calculated from NMR analysis, the chain-end functionalization was found to be nearly quantitative. ($M_{n,\text{NMR}}$: 15800, $M_{n,\text{GPC}}$: 17,400, M_w/M_n : 1.60)

*Synthesis of PTHF-*b*-PMMA*

105 mg of PTHF (0.0041 mmol) + 1.5mg AIBN (0.00913) + 1000 μl MMA (9.4mmol) and 1000 μl of degassed toluene were reacted together at 70 °C for 2.5 hours at inert atmosphere and then precipitated into 50 ml cold MeOH. ($M_{n,\text{GPC}}$: 29,000, M_w/M_n : 1.63)

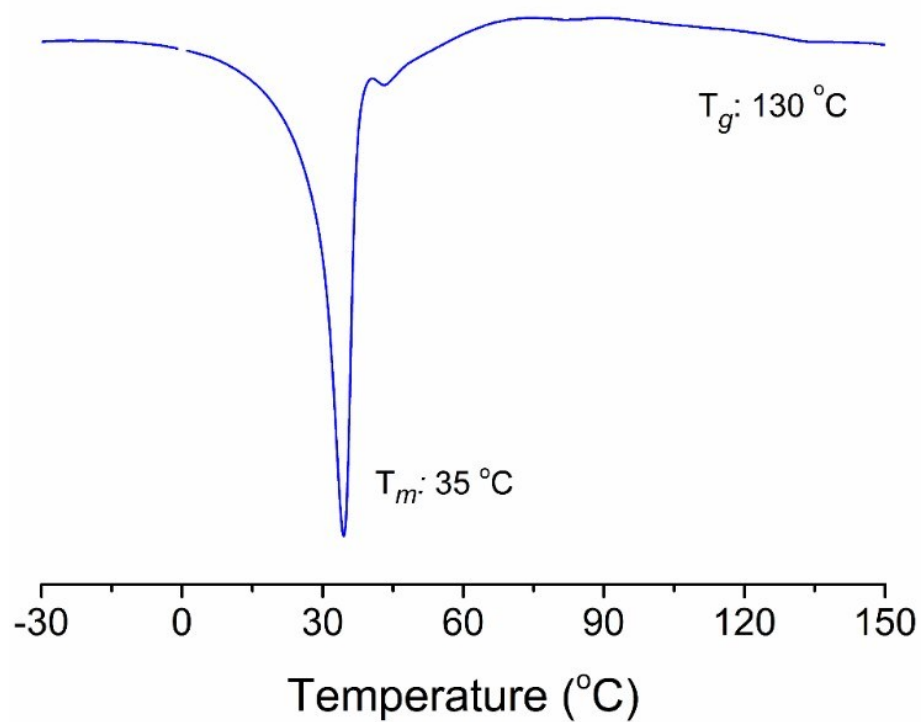


Figure S1- DSC thermogram showing an intense endotherm at 35° C and a small transition around 130°C, which correspond to the melting point of the PTHF segment and glass transition of the PMMA segment, respectively

^a Department of Chemistry, Istanbul Technical University, 34469 Maslak, Istanbul, Turkey

^b Institute of Applied Physics, Johannes Kepler University, Altenberger Straße 69, 4040 Linz, Austria.