Dithioesters and Trithiocarbonates as Anchoring Groups for the 'Grafting-to' Approach

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Materials

Gold films on silicon were used for the adsorption of the CTA. Silicon wafers were primed with 5 nm of titanium followed by the deposition of 30 nm of gold by thermal evaporation under vacuum. Gold films on mica, prepared from thermal evaporation of gold, were used for the preparation of the polymer brushes. All reagents and solvents were used as received unless otherwise specified.

Synthesis

Benzyl dithiobenzoate (BDTB) was synthesized following a modification of a reported procedure [1]. A solution of phenylmagnesium bromide in ether (14 mL of 3M solution) was added dropwise to a solution of carbon disulfide (3.44 g ,0.045 mol) in dry tetrahydrofuran (30 mL) at room temperature. The mixture was warmed to 40 °C, and benzyl bromide (7.69g, 0.04

mol) was added dropwise. The reaction temperature was raised to 50 °C and maintained at that temperature overnight. Ice-cold water (100 mL) was added and the mixture was extracted twice with 150 mL of diethyl ether. The combined ethereal extracts were washed with water and brine and dried over anhydrous magnesium sulfate. The solution was condensed under vacuum and the product was purified *via* column chromatography (alumina) with chloroform/petroleum ether (1:5) as eluent, followed by a distillation under reduced pressure. The product was obtained as red oil (62%). ^{1}H-NMR ($CDCl_3$): 4.6(s, 2H, CH_2-Ph), 7.3-7.6(m, 8H, Ar*H*), 8.0(m, 2H, Ar*H*).

Dibenzyl trithiocarbonate (DBTTC) was synthesized following a reported procedure [2]. In brief, Amberlyst A-26 (OH^-) (40 g, 20±50 mesh) was added to carbon disulfide (200 mL) and stirred at room temperature for about 3 min. To this suspension was added benzyl bromide (3.42 g, 20 mmol) and the reaction mixture stirred under reflux for about 5 hours. The mixture was then filtered and washed with THF. The filtrate was dried over anhydrous magnesium sulfate and condensed under vacuum to afford dibenzyl trithiocarbonate as a yellow oil (90%).^{1}H-NMR ($CDCl_3$): 4.71(s, 4H, CH_2-Ph), 7.36-7.41(m, 10H, Ar*H*).

Polystyrene was prepared in bulk using the two types of CTA following a standard procedure [3]. Styrene was purified by filtration through alumina. Styrene and the CTA were placed in a round bottom flask which was degassed by four freeze-pump-thaw cycles, and then heated with an oil bath at 110 °C under argon for16 hours. The polystyrenes were purified twice by precipitation in methanol. Conversions were measured gravimetrically and the polymers were characterized by GPC in THF. Polymerization with BDTB: styrene (4.18 g, 40.2 mmol), BDTB (17 mg, 6.9×10^{-2} mmol), conversion: 54%, M_n:36000 g mol^{-1} (PDI: 1.14). Polymerization with

BDTTC: styrene (4.56 g, 43.8 mmol), BDTB (20 mg, 6.9×10^{-2} mmol), conversion: 43%, M_n:31000 g mol^{-1} (PDI: 1.29).

Monolayer preparation

Solutions of the chain transfer agents (BDTB and DBTTC) were prepared in dichloromethane at a concentration of 2×10^{-3}M. The gold substrates were cleaned by UV-ozone treatment, immersed 20 min in ethanol, rinsed with dichloromethane, and finally immersed in the CTA solutions for 4 hours. The samples were copiously rinsed with dichloromethane and dried with a flux of nitrogen.

PS brush preparation

Solutions of the two polystyrenes were prepared in toluene at a concentration of 2 g/L. The gold substrates were cleaned by UV-ozone treatment, immersed 20 min in ethanol, rinsed with toluene, and finally immersed in the polymer solutions for 24 hours. The samples were copiously rinsed with toluene and dried with a flux of nitrogen.

XPS analysis

XPS was performed on a SSIX probe (SSX 100/206) spectrometer from Fisons equipped with a monochromatic Al Kα X-ray source (hν = 1486.7 eV). Spectra were recorded at a take-off angle of 35° (angle between the plane of the sample surface and the entrance lens of the analyzer) with a pass energy of 150 eV. No flood-gun was used. We adjusted the acquisition time and parameters to avoid the appearance of beam-induced sulfur species and keeping an acceptable

signal to noise ratio and a good enough resolution to detect multi-components in a peak [4]. The spectra were referenced to Au($4f_{7/2}$) at 84.0 eV. The spectra of BDTB and DBTTC were recorded in exactly the same conditions. The mathematical reconstruction of the S2p spectra was performed using doublets (using a Gaussian-Lorentzian 85%-15% linear combination and a linear background) with an intensity ratio 2:1 and a splitting of 1.18 eV for the $2p_{1/2}$ and $2p_{3/2}$ components.

Brush characterization

AFM-based Force spectroscopy experiments were carried out in toluene with a PicoSPM equipped with a fluid cell (Molecular Imaging) and controlled by Nanoscope III electronics (Digital Instruments). Silicon nitride cantilevers with a spring constant of 0.05 N m^{-1} were used. In about 20% of the force curves, bridging interaction was observed, but was not investigated here. We focused our attention on the compression profiles. AFM images were obtained using a Digital Instruments Nanoscope IV scanning force microscope in tapping mode using NCH type cantilevers (Si, 48 N/m, 330 kHz, Nanosensors).

References

1 Chong, Y. K.; Krstina, J.; Le, T. P. T.; Moad, G.; Postma, A.; Rizzardo, E.; Thang, S. H. *Macromolecules* **2003**, *36*, 2256.

2 Tamami, B.; Kiasat, A. R. *J. Chem. Res.* **1998**, 454.

3 Chiefari, J.; Mayadunne, R. T. A.; Moad, C. L.; Moad, G.; Rizzardo, E.; Postma, A.; Skidmore, M. A.; Thang, S. H. *Macromolecules* **2003**, *36*, 2273

4 A.-S. Duwez *J. Electron Spectrosc. Relat. Phenom.* **2004**, *134*, 97.