

# Well-Defined Polymers from Biosourced Monomers: The Case of 2-(Methacryloyloxy)ethyl Tiglate

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ABSTRACT: Tiglic acid esters are naturally derived olefins of pleasant odor but incapable of undergoing free-radical polymerization due to the steric hindrances conferred by the  $\beta$ -methyl group. In an effort to incorporate these green olefins in well-defined (co)polymers, we first established that methyl tiglate, the simplest tiglic acid ester, could not be polymerized using controlled polymerization techniques either, and we then introduced it in a methacrylate monomer, 2-(methacryloyloxy)ethyl tiglate (MAET), which could smoothly undergo group transfer polymerization (GTP) to yield linear polymers of narrow molecular weight distributions. Subsequently, amphiphilic and double-hydrophobic block copolymers, as well as a star polymer of MAET were obtained by its sequential GTP with 2-(dimethylamino)ethyl methacrylate, methyl methacrylate, respectively. Finally, polyMAET was selectively oxidized.

#### Introduction

The imminent (within one to two generations) dwindling of oil reserves and the accompanying increase in their prices have created a strong awareness for sustainability and the necessity for the gradual replacement of petrochemicals by raw materials derived from renewable resources.<sup>1</sup> Monomers are no exception to this trend, and there is now a major effort to prepare polymers from naturally derived monomers, including sugars (e.g., alditols and aldonic and aldaric acids) and their derivatives (e.g., furan and lactic acid), terpenes (e.g., pinenes, carene, limonene, and myrcene), rosin (e.g., abietic and plaustric acids), and vegetable oils (e.g., oleic and linoleic acids).<sup>2</sup>

Tiglic acid (trans-2-methylbut-2-enoic acid) is a hemiterpene, derived from croton oil.<sup>3</sup> Its cis-isomer, angelic acid, is also derived from croton oil and is less stable than tiglic acid as it slowly isomerizes to the latter.<sup>4</sup> Crowding and possible electronic effects do not allow the polymerization of these two disubstituted acrylic acids and their derivatives.<sup>5</sup> In fact, esters of tiglic acid are encountered in fragrances because of their pleasant odor<sup>6</sup> and resistance to spontaneous polymerization. To the best of our knowledge, only two compounds with structure similar to that of tiglate esters have been polymerized to date in a controlled manner: methyl 3-methylcyclobutene-1-carboxylate<sup>7</sup> and methyl 1-cyclobutenecarboxylate.<sup>8,9</sup> The former has been polymerized by anionic polymerization, whereas the latter has been polymerized both by atom transfer radical polymerization (ATRP)<sup>8</sup> and anionic polymerization.<sup>9</sup> In these monomers, the ring stress apparently counterbalances any steric or electronic effects acting against the polymerization of the olefinic group.

The aim in this investigation is the controlled (co)polymerization of tiglic acid esters. First, the direct polymerization of the simplest ester of tiglic acid, methyl tiglate (MT), is attempted using various controlled polymerization methods: group transfer polymerization (GTP),<sup>10,11</sup> ATRP,<sup>12</sup> and reversible addition–fragmentation chain transfer (RAFT) polymerization.<sup>13</sup> Then, a tiglate-bearing methacrylate monomer,

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2-(methacryloyloxy)ethyl tiglate (MAET), is prepared and polymerized in a controlled fashion using GTP. Furthermore, that monomer is block copolymerized with a hydrophilic methacrylate, a hydrophobic methacrylate, and a dimethacrylate to obtain, respectively, amphiphilic, double-hydrophobic, and star polymers of that tiglate ester which are characterized appropriately. Finally, the property of tiglate units for selective oxidation by singlet oxygen is demonstrated by successfully subjecting one of the tiglate ester-containing polymers to porphyrin-catalyzed oxidation.

#### **Experimental Section**

Materials and Methods. Tiglic acid (98%), ethylene glycol (99.8%), methacryloyl chloride (97%), methyl methacrylate (MMA, 99%), 2-(dimethylamino)ethyl methacrylate (DMAEMA, 98%), ethylene glycol dimethacrylate (EGDMA, 98%), 1-methoxy-1-trimethylsiloxy-2-methyl propene (MTS, 95%), methyl 2-methylbutyrate (99%), n-butyllithium (nominal concentration 2.5 M in hexanes, actual concentration of 1.9 M after titration with diphenylacetic acid), diphenylacetic acid (99%), diisopropylamine (redistilled), ethyl 2-bromoisobutyrate (98%), tetrabutylammonium hydroxide (40% w/w in water), benzoic acid (99.5%), copper(I) bromide (99.999%), copper(II) bromide (99%), 2,2'-bipyridine (99%), sulfuric acid (98%), sodium hydrogencarbonate (NaHCO<sub>3</sub>, 99%), 2,2-diphenyl-1-picrylhydrazyl hydrate (DPPH, 95%), calcium hydride (CaH<sub>2</sub>, 90-95%), and potassium metal (99%) were purchased from Aldrich, Germany. Tetrahydrofuran (THF, 99.8%) was purchased from Labscan, Ireland, and was used as the mobile phase in chromatography (HPLC grade) and as a solvent (reagent grade) for the polymerizations. Trimethylsilyl chloride (99%), methanol (99.9%), carbon tetrachloride (99.8%), ethyl acetate (99.5%), N,N-dimethylformamide (DMF), meso-tetraphenylporphyrin (99.8%), and sodium chloride (99%) were from Merck. Synthesis grade triethylamine ( $Et_3N$ ) and diethyl ether, benzene (extra pure), and *n*-hexane (96%) were obtained from Scharlau, Spain. Finally, sodium metal (98%) was from Fluka, whereas anhydrous magnesium sulfate (MgSO<sub>4</sub>) was from Himedia, India. The chain transfer agent (CTA) for RAFT polymerization, 2-(2-carboxyethylsulfanylthiocarbonylsulfanyl)propionic

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acid, was kindly provided by our colleague Professor A. B. Lowe of the University of Southern Mississippi (now at the University of New South Wales, in Sydney, Australia).

THF was dried by being refluxed over a potassium-sodium alloy for three days and was freshly distilled prior to use. Benzene and N,N-dimethylformamide were distilled from CaH<sub>2</sub>. Tetrabutylammonium bibenzoate (TBABB, GTP catalyst) was synthesized by the reaction of tetrabutylammonium hydroxide and benzoic acid in water, following the procedure of Dicker et al.,<sup>11</sup> and was kept under vacuum until use. DMAE-MA, MMA, and EGDMA were passed through basic alumina columns to remove the polymerization inhibitors and any other acidic impurities. These reagents as well as MT and MAET were subsequently stirred over CaH<sub>2</sub> (to remove the last traces of moisture and protic impurities) in the presence of added DPPH free-radical inhibitor and stored in the refrigerator at about 5 °C. Finally, they were freshly distilled under vacuum just before their use and kept under a dry nitrogen atmosphere. The GTP initiators were distilled once prior to the polymerization, but they were neither contacted with CaH2 nor passed through basic alumina columns because of the risk of hydrolysis. All glassware were dried overnight at 120 °C and assembled hot under dynamic vacuum prior to use.

Monomer Synthesis. Methyl Tiglate (MT). Tiglic acid (7.0 g, 0.070 mol), methanol (200 mL, 182 g, 5.70 mol), and sulfuric acid catalyst (1 mL) were transferred to a 250-mL round-bottom flask fitted with a condenser. The mixture was stirred at 65 °C for 2 days. Subsequently, the mixture was diluted with 200 mL of diethyl ether, washed three times with 150 mL of 5% NaHCO<sub>3</sub>, three times with 150 mL water, and finally with 50 mL of a saturated NaCl aqueous solution. The organic layer was dried with anhydrous MgSO<sub>4</sub>, and the solvent was evaporated off under reduced pressure to give 3.97 g (0.035 mol) of pure methyl tiglate in 49.7% yield. This was characterized using <sup>1</sup>H and <sup>13</sup>C NMR spectroscopies. <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ ): 1.75 ppm (1s+1d,  $CH_3CH=CCH_3$ , 6 H), 3.68 ppm (s,  $OCH_3$ , 3 H), and 6.8 ppm (m,  $CH_3CH=CCH_3$ , 1 H cis to  $CO_2CH_3$ ). <sup>13</sup>C NMR (CDCl<sub>3</sub>,  $\delta$ ): 11.79 ppm (s, CH<sub>3</sub>CH=CCH<sub>3</sub>, 1 C), 14.07 ppm (s, H<sub>3</sub>CCH= CH<sub>3</sub>, 1 C), 51.39 ppm (s, -OCH<sub>3</sub>, 1 C), 128.32 ppm (s, H<sub>3</sub>CCH= CCH<sub>3</sub>, 1 C), 136.96 ppm (s, H<sub>3</sub>CCH=CCH<sub>3</sub>, 1 C), and 168.37 ppm (s, -COOCH<sub>3</sub>, 1 C).

2-Hydroxyethyl Tiglate. Tiglic acid (10 g, 0.1 mol), ethylene glycol (28 mL, 0.5 mol), and sulfuric acid catalyst (1 mL) were transferred to a 100-mL round-bottom flask with a condenser. The mixture was stirred at 65 °C for 17 h. After evaporation of ethylene glycol, the product was purified by column chromatography (silica gel/hexane/ethyl acetate = 50:50 v/v) at a final yield of 59%. The purity of 2-hydroxyethyl tiglate was confirmed using <sup>1</sup>H and <sup>13</sup>C NMR spectroscopies. <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ ): 1.75 ppm (1s+1d, CH<sub>3</sub>CH=CCH<sub>3</sub>, 6 H), 3.84 ppm (t, OCH<sub>2</sub>CH<sub>2</sub>OH, 2 H), 4.26 ppm (t, OCH<sub>2</sub>CH<sub>2</sub>OH, 2 H), and 6.8 ppm (m, CH<sub>3</sub>CH=CCH<sub>3</sub>, 1 H cis to CO<sub>2</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>,  $\delta$ ): 11.79 ppm (s, CH<sub>3</sub>CH=CCH<sub>3</sub>, 1 C), 14.18 ppm (s, CH<sub>3</sub>CH=CCH<sub>3</sub>, 1 C), 137.86 ppm (s, CH<sub>3</sub>CH=CCH<sub>3</sub>, 1 C) and at 168.35 ppm (s, -CO<sub>2</sub>, 1 C).

2-(Methacryloyloxy)ethyl Tiglate (MAET). 2-Hydroxyethyl tiglate (8.45 g, 0.059 mol), Et<sub>3</sub>N (41.0 mL, 29.3 g, 0.29 mol), and absolute THF (100 mL) were transferred to a 100-mL roundbottom flask containing a magnetic stirring bar. The solution was stirred and cooled down to 0 °C. After stabilization of the temperature, methacryloyl chloride (7.35 mL, 7.94 g, 0.076 mol) was added dropwise using a glass syringe, and the reaction was stirred for 1 h at room temperature. Subsequently, the mixture was filtered and passed through a basic alumina column to remove the acidic impurities. Then, the solvent was evaporated off to give pure monomer in 76% yield. Finally, MAET was stirred over CaH<sub>2</sub> in the presence of DPPH to remove all of the moisture and the last traces of acidic impurities. MAET was characterized using <sup>1</sup>H NMR and <sup>13</sup>C NMR spectroscopies. <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ ): 1.75 ppm (1s+1d, CH<sub>3</sub>CH=CCH<sub>3</sub>, 6 H), 1.89 ppm (s, CH<sub>2</sub>=CCH<sub>3</sub>, 3 H), 4.33 ppm (m, OCH<sub>2</sub>CH<sub>2</sub>O, 4 H), 5.53 ppm (s, olefinic methacrylate H trans to CO<sub>2</sub>, 1 H), 6.07 ppm (s, olefinic methacrylate H cis to CO<sub>2</sub>, 1 H), and 6.8 ppm (m, olefinic tiglate H cis to CO<sub>2</sub>, 1 H). <sup>13</sup>C NMR (CDCl<sub>3</sub>,  $\delta$ ): 11.91 ppm (s, CH<sub>3</sub>CH=CCH<sub>3</sub>, 1 C), 14.32 ppm (s, CH<sub>3</sub>CH=CCH<sub>3</sub>, 1 C), 18.19 ppm (s, CH<sub>2</sub>=CCH<sub>3</sub>, 1 C), 62.03 and 62.20 ppm (2s, OCH<sub>2</sub>CH<sub>2</sub>O, 2 C), 125.88 ppm (s, CH<sub>2</sub>=CCH<sub>3</sub>, 1 C), 128.19 ppm (s, CH<sub>3</sub>CH=CCH<sub>3</sub>, 1 C), 135.94 ppm (s, CH<sub>2</sub>=CCH<sub>3</sub>, 1 C), 137.78 ppm (s, CH<sub>3</sub>CH=CCH<sub>3</sub>, 1 C), and 167.07 and 167.70 ppm (2s, CO<sub>2</sub>, 2 C).

Synthesis of 1-Methoxy-1-trimethylsiloxy-2-methyl Butene (methyl-MTS, Modified GTP Initiator). Absolute THF (35 mL) and diisopropylamine (5.88 mL, 4.25 g, 42 mmol) were transferred into a three-necked 250-mL round-bottom flask containing a stirring bar and fitted with a rubber septum and a thermometer and kept under an inert nitrogen atmosphere. After cooling to 0 °C by placing the flask in an ice-bath, n-butyllithium (22 mL, 1.9 M, 42 mmol) was added dropwise using a glass syringe, and the reaction was stirred for 1.5 h at 0 °C. Then, the reaction mixture was cooled down to -78 °C, and methyl 2-methylbutyrate (5 mL, 4.42 g, 38 mmol) was added dropwise. The reaction mixture was stirred for 2 h, and trimethylsilyl chloride (7 mL, 6.2 g, 57 mmol) was added. After stirring for 2 h, the formed lithium chloride crystals were filtered away from the mixture, and the solvent was evaporated off to give the oily product in 51% yield. The product was further purified by distillation and characterized by <sup>1</sup>H and <sup>13</sup>C NMR. <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ ): 0.156 ppm (s, Si(CH<sub>3</sub>)<sub>3</sub>, 9 H), 0.873 ppm (t, CCH<sub>2</sub>CH<sub>3</sub>, 3 H), 1.53 ppm (d, C=CCH<sub>3</sub>, 3 H), 1.91 ppm (m, CCH<sub>2</sub>CH<sub>3</sub>, 2 H), and 3.48 ppm (s, OCH<sub>3</sub>, 3 H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ): 0.1 ppm (s, Si(CH<sub>3</sub>)<sub>3</sub>, 3 C), 12.43 ppm (s, CCH<sub>2</sub>CH<sub>3</sub>, 1 C), 14.05 ppm (s, C=CCH<sub>3</sub>, 1 C), 23.44 ppm (s, CCH<sub>2</sub>CH<sub>3</sub>, 1 C), 56.55 ppm (s, OCH<sub>3</sub>, 1 C), 96.76 ppm (s, -C=C(OCH<sub>3</sub>)OSi(CH<sub>3</sub>)<sub>3</sub>, 1 C)) and at 149.16 ppm (s, -C=C(OCH<sub>3</sub>)OSi(CH<sub>3</sub>)<sub>3</sub>, 1 C).

**Polymerizations.** *GTP*. A catalytic amount of TBABB (~20 mg, ~40  $\mu$ mol, ~3% mol relative to the initiator) was transferred to a 100-mL round-bottom flask containing a stirring bar. The flask was immediately sealed with a rubber septum, and it was purged with dry nitrogen. Freshly distilled THF was subsequently transferred directly into the flask via a glass syringe, followed by the addition of the MTS initiator (0.3 mL, 0.258 g, 1.48 mmol). Finally, the monomers MAET, MT, MMA, DMAEMA, and EGDMA were added in the appropriate order. The reactions were carried out at 20 °C, and the polymerization exotherm was monitored by a digital thermometer to follow the progress of the polymerization reaction. A similar procedure was followed for the polymerizations using the methyl-MTS initiator.

*ATRP.* CuBr (48.4 mg, 0.347 mmol), CuBr<sub>2</sub> (2.7 mg, 0.012 mmol), 2,2'-bipyridine (0.109 mg, 0.7 mmol), MT (1.5 mL, 1.37 g, 12 mmol), and 3.17 mL of DMF were added to a Schlenk flask containing a stirring bar and kept under an inert nitrogen atmosphere. The mixture was degassed via three freeze–pump–thaw cycles. Ethyl 2-bromoisobutyrate (35.3  $\mu$ L, 46.9 mg, 0.241 mmol) was subsequently introduced, and the reaction flask was placed in an oil bath thermostatted at 70 °C for 21 h.

*RAFT Polymerization*. A solution of MT (1 mL, 0.913 g, 8 mmol), 2-(2-carboxyethylsulfanylthiocarbonylsulfanyl)propionic acid RAFT CTA (0.042 g, 0.164 mmol), and 2,2'-azobis-isobutyronitrile (0.02 g, 0.102 mmol) in benzene (2 mL) were transferred to a 100-mL round-bottom flask containing a magnetic stirring bar. The system was degassed by three freeze–pump–thaw cycles and was subsequently placed in an oil bath at 65 °C for 24 h.

**Polymer Oxidation.** Linear homopolymer MAET<sub>20</sub> (0.5 g, 2.36 meq of MAET monomer repeating units), carbon tetrachloride (70 mL, 111 g, 0.7 mol), and *meso*-tetraphenylporphyrin (30 mg, 48  $\mu$ mol) as sensitizer were transferred to a 100-mL round-bottom flask fitted with a condenser. The mixture was irradiated at -10 °C with a 500 W HX 10 xenon lamp from Perkin-Elmer with continuous flow of oxygen. The polymer oxidation reaction was followed using <sup>1</sup>H NMR spectroscopy by recording the disappearance of the  $\beta$ -CH<sub>3</sub> proton signals (about 38% conversion at 7 h). HAZARD WARNING: The oxidized polymer should be handled with extreme caution as it is a potential explosive.

**Polymer Characterization.** Gel Permeation Chromatography. The molecular weight distributions (MWDs) of all the polymers were recorded using gel permeation chromatography (GPC), from which the number-average molecular weights,  $M_n$ , the weight-average molecular weights,  $M_w$ , and the polydispersity indices (PDI =  $M_w/M_n$ ) were calculated. A single Polymer Laboratories PL-Mixed "D" column (bead size = 5  $\mu$ m; pore sizes = 100, 500, 10<sup>3</sup>, and 10<sup>4</sup> Å) was used for the sample analysis. The mobile phase was THF, delivered using a Waters 515 isocratic pump at a flow rate of 1 mL min<sup>-1</sup>. The refractive index (RI) signal was measured using a Polymer Laboratories ERC-7515A RI detector. The calibration curve was based on eight narrow MW (630, 2680, 4250, 13000, 28900, 50000, 128000, and 260000 g mol<sup>-1</sup>) linear polyMMA standards also supplied by Polymer Laboratories.

*NMR Spectroscopy*. A 300 MHz Avance Bruker spectrometer equipped with an Ultrashield magnet was used to acquire the <sup>1</sup>H NMR spectra of all the (co)polymers in CDCl<sub>3</sub> containing traces of CHCl<sub>3</sub> which was used as an internal reference. The same instrument was also used to collect the <sup>1</sup>H and <sup>13</sup>C NMR spectra of all the new low-molecular-weight compounds synthesized and also to confirm the purity of the purchased compounds.

Static Light Scattering. The absolute  $M_{\rm w}$  of the MAET-EGDMA star polymer was measured using static light scattering (SLS) in a GPC configuration. To this end, a Brookhaven Molecular Weight Analyzer, BI- $M_{\rm w}A$ , equipped with a 30 mW red diode laser emitting at 673 nm and a multiangle detector, was used to determine the intensity of scattered light at 7 different angles, 35°, 50°, 75°, 90°, 105°, 130°, and 145°, whereas a PL-RI 800 RI detector was used to simultaneously measure the RI signal. A Polymer Laboratories PL-LC1120 isocratic pump was used to deliver the THF mobile phase at a flow rate of 1 mL min<sup>-1</sup> through a PL-Mixed "D" column, also supplied by Polymer Laboratories. The analysis for the calculation of the absolute  $M_{\rm w}$  was conducted using the PSS-WinGPC 7 SLS-flow software. The star polymer was dissolved in HPLC-grade THF at a 2% w/v polymer concentration and was filtered through a 0.45  $\mu$ m pore size syringe filter. The RI increment (dn/dc) of the star polymer solution in THF was determined using an ABBE refractometer and was found to be  $0.1034 \text{ mL g}^{-1}$ .

Dynamic Light Scattering (DLS). The hydrodynamic diameter of the synthesized DMAEMA-MAET amphiphilic diblock copolymer in water was measured using dynamic light scattering (DLS). A 1% w/w aqueous solution of the diblock copolymer was prepared and was filtered three times through a PTFE syringe filter with 0.45  $\mu$ m pore size diameters. The filtered solution was left to settle for about an hour so that any air bubbles could escape before the DLS measurement. A 90 Plus Brookhaven DLS spectrophotometer, equipped with a BI9000 correlator and a 30 mW red diode laser emitting at 673 nm, was used to determine the intensity of the scattered light at a 90° angle. The data were processed using multimodal size distribution (MSD) analysis based on non-negatively constrained least-squares (NNCLS).

*Hydrogen Ion Titration.* An aqueous solution of the DMAE-MAET diblock copolymer (5 g of a 1% w/w solution) was titrated in the pH range from 2 to 12 using a 0.5 M NaOH standard solution. The pH of the solution was measured using a Corning PS30 portable pH-meter. The effective pK of the DMAEMA monomer repeating units was calculated as the pH corresponding to 50% ionization. The pH at which polymer precipitation occurred during the titration was also noted.

### **Results and Discussion**

Attempted Direct Polymerizations of Methyl Tiglate (MT). Given the successful anionic polymerizations of methyl 3-methylcyclobutene-1-carboxylate<sup>7</sup> and methyl 1-cyclobutenecarboxylate,<sup>9</sup> we first attempted the group transfer polymerization  $(GTP)^{10,11}$  of the simplest ester of tiglic acid, MT. Unfortunately, no polymer was obtained under standard GTP conditions, i.e., room temperature, high monomer concentration (30% w/w), MTS initiator, and TBABB catalyst. Subsequently, the random group transfer copolymerization (GTcoP) of MT with methyl methacrylate (MMA) was pursued, again without success, as the resulting polymer product was the homopolymer of MMA. Similarly, MT resisted GTcoP when its block copolymerization off the living end of polyMMA was attempted. Essentially, the same results were obtained when a specially designed and prepared GTP initiator, methyl-MTS, bearing an extra methyl group compared to MTS which was expected to solve any tiglate structure electronic problems in its polymerization was used (since MTS is ideal for the GTP of MMA, and MT bears an extra methyl group as compared to MMA, methyl-MTS was expected to be ideal for the GTP of MT). It was found that methyl-MTS could trigger the polymerization of MMA but not of MT. Subsequently, efforts were directed toward the controlled homopolymerization of MT via ATRP<sup>12</sup> and RAFT polymerization<sup>13</sup> but, again, without any success.

**Synthesis and GTP of a Tiglate-Bearing Methacrylate.** After establishing the inability of tiglates to directly polymerize, we decided to attach tiglic acid to a methacrylate and polymerize the resulting hybrid green (biosourced) monomer. The target compound was 2-(methacryloyloxy)ethyl tiglate (MAET), differing only in one extra methyl group from the well known commercially available cross-linker EGDMA. Scheme 1 illustrates the synthetic strategy followed for the preparation of MAET and its homo- and copolymerization with conventional methacrylates.

The first two steps that ultimately led to the preparation of the polymerizable monomer were esterifications, first with excess ethylene glycol and then with methacryloyl chloride at yields (after purification) of 59% and 76%, respectively. The purified and dried MAET was readily polymerized via GTP to give homopolymers and copolymers with three common methacrylates: the hydrophobic MMA, the hydrophilic positively ionizable DMAEMA, and the EGDMA cross-linker. Table 1 lists the (co)polymers prepared, their MWs and PDIs, and compositions, as determined by GPC and <sup>1</sup>H NMR spectroscopy, respectively.

Several homopolymers of MAET were prepared at 100% yield, covering a range of MWs and relatively narrow MWDs, corresponding to PDIs lower than 1.5 in all cases. These PDI values imply lack of branching and preservation of the olefinic group of the tiglate moiety, which was also confirmed from the <sup>1</sup>H NMR spectrum of the polymer (Figure 1), and is consistent with our preliminary experiments which indicated the inability of MT to polymerize by GTP.

In addition to the homopolymers of MAET, various copolymers were synthesized using GTP to copolymerize MAET with MMA, DMAEMA, or EGDMA. Regarding MMA, three equimolar MAET-MMA copolymers with different comonomer distribution were prepared: the AB and BA diblocks as well as the statistical copolymer. The polymerization yields were 100%, the PDIs satisfactorily low, and the compositions close to those calculated from the comonomer feed ratios. The ability to successfully prepare these three copolymers suggests that the MAET-based enolate can initiate the GTP of MMA and that the

Scheme 1. Synthesis and GTP of the Tiglic Acid-Bearing Methacrylate Monomer 2-(Methacryloyloxy)ethyl Tiglate (MAET)



Table 1. Molecular Weight and Composition Characteristics of the MAET-Containing (Co)polymers Synthesized

			GPC	Results	% mol MAET	
no.	polymer structure	MW <sub>theor</sub>	$M_{\rm n}$	$M_{\rm w}/M_{\rm n}$	Theor.	<sup>1</sup> H NMR
1	MAET <sub>5</sub>	1160	2310	1.47	100	100
2a	MAET <sub>10</sub>	2220	5520	1.22	100	100
2b	MAET <sub>10</sub> -b-MMA <sub>10</sub>	3220	8270	1.55	50	52
3	MAET <sub>20</sub>	4330	11700	1.47	100	100
4a	MMA <sub>10</sub>	2501	2540	1.22	0	0
4b	MMA <sub>10</sub> -b-MAET <sub>10</sub>	3220	6920	1.30	50	47
5	MAET <sub>5</sub> -co-MMA <sub>5</sub>	1661	5032	1.42	50	49
6a	DMAEMA <sub>20</sub>	3240	3940	1.20	0	0
6b	DMAEMA <sub>20</sub> -b-MAET <sub>5</sub>	4300	4690	1.22	20	19
7a	MAET <sub>8</sub>	1800	4540	1.16	100	100
7b	MAET <sub>8</sub> - <i>b</i> -EGDMA <sub>4</sub>		67800	1.71	33	35
refractive index signal	polyMAET star 6 7		8 (min)	line	ar polyl	MAET 10
	time (min)					

Figure 1. GPC traces of the star homopolymer of MAET and the MAET-MMA block copolymer, as well as those of their linear poly-MAET precursors.

MMA-based enolate can also initiate the polymerization of MAET.

A DMAEMA-rich amphiphilic diblock copolymer of MAET was also prepared at a 100% monomer conversion, yielding again a polymer with a low PDI and an experimental composition close to the one expected on the basis of the comonomer feed ratio. Because of its high content in the hydrophilic DMAEMA, this copolymer was watersoluble (even in pure water). Furthermore, the presence of the hydrophobic MAET units led to the aqueous solution micellization of this diblock copolymer, which was investigated using DLS. Micelles with a hydrodynamic radius of 5.3 nm were detected, which, if compared to the polymer chain contour length of about 7 nm (experimental degree of polymerization of the whole chain of about 28 and a contribution of 0.252 nm per monomer repeat unit to the contour length<sup>14</sup>), would suggest a rather stretched conformation of the constituting chains in the micelles. Hydrogen ion titration yielded an effective pK of the DMAEMA units of this copolymer of about 6.5. Quantitative precipitation of the copolymer in water at pH 7.7 and higher occurred as the degree of ionization of the DMAEMA units was lowered below 12%, thus removing the greatest part of the electrostatic repulsive stabilizing energy and allowing the hydrophobic and other attractive forces to dominate and induce macroscopic phase separation.

Finally, an arm-first star homopolymer of MAET was prepared by interconnecting the living MAET chains using the structurally related EGDMA cross-linker. The absolute  $M_w$  of this star polymer was determined using SLS and found to be 387 000 g mol<sup>-1</sup>. From this MW (after subtracting the contribution of the cross-linker) and the  $M_n$  of the arms determined by GPC, the number of arms was calculated to be 59, falling in the range of the number of arms of star polymers prepared by GTP using similar strategies.<sup>15</sup> Figure 1 plots the GPC traces of the polyMAET star polymer and its linear precursor, and also those of the MAET-MMA block copolymer and its polyMAET linear precursor.

Oxidation of the Tiglic Acid Units in the Polymers. Tiglic acid esters are known to be regioselectively oxidized by singlet oxygen, exhibiting preferential (97%) abstraction of the allylic hydrogen geminal to the ester functionality.<sup>16</sup> Thus, after the preparation of the present polymers bearing pendant tiglic acid units, the selective photooxygenation of such units was pursued for the first time in a polymer in this investigation. Figure 2 displays the <sup>1</sup>H NMR spectrum of the original polymer and that of oxidized polyMAET. The latter spectrum presents three new resonances compared to the parent material, corresponding to protons  $e_1$ ,  $e_2$ , and g in the oxidized tiglate structure. From the relative peak areas, the extent of the photooxidation reaction was estimated at 38%. The absence of any other new peaks confirms the selectivity of the reaction, directing the entering oxygen to bond to the carbon away from the carbonyl group of tiglate. It is worth mentioning that, in a control experiment, polyMMA was also subjected to the same photooxidation procedure, but the <sup>1</sup>H NMR spectrum of the processed polymer was indistinguishable from that of the starting material, confirming the inherent tendency of the tiglate units for oxidation.



**Figure 2.** <sup>1</sup>H NMR spectra of (a) polyMAET and (b) the partially photooxidized polyMAET (which is a statistical copolymer with repeating units whose structures are shown in parts a and b of this Figure). The peak indicated by the asterisk (\*) is due to an impurity in the NMR solvent (CDCl<sub>3</sub>).

#### Conclusions

In conclusion, well-defined, tiglate ester-containing homopolymers were produced by GTP via the attachment of tiglic acid to a polymerizable methacrylate (yielding the MAET green monomer), as the vinyl group of tiglate resisted GTP, ATRP, and RAFT polymerizations. Subsequently, AB and BA diblock as well as statistical copolymers of MAET with MMA were successfully prepared by GTP, demonstrating the facile cross-polymerization between the two comonomers. An amphiphilic diblock copolymer was also prepared, in which the MAET units had the role of the core-forming hydrophobes. An arm-first star polymer of MAET with EGDMA as cross-linker was synthesized too, showing in the most dramatic way that the extra methyl group of MAET, as compared to EGDMA, transforms the former compound from a dimethacrylate cross-linker to a monomethacrylate monomer. Finally, the MAET units in the polymers were selectively photooxygenated and the pendant tiglate units oxidized. The importance of this work is 2-fold. First, another green unit has been incorporated in polymers in a well-defined fashion for the first time and made available to the arsenal of the macromolecular engineer. Second, the pendant tiglate groups represent important functional units, with the properties of hydrophobicity, oxidizability, and lack of reactivity toward addition polymerization.

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