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Design of Semi-Crystalline Elastomeric Glassy Triblock Copolymers from Oligoamide-based RAFT Agents

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This paper is dedicated to the memory of our dear colleague and friend, Prof. Jean-Pierre Pascault, who recently passed away.

ABSTRACT:

Semi-crystalline-elastomeric-glassy ABC triblock copolymers, consisting of precisely-defined blocks based on oligoamide 11 (OPA11), poly(lauryl methacrylate) (PLMA), and poly(methyl methacrylate) (PMMA) have been designed via the combination of melt polycondensation and reversible-addition fragmentation-transfer (RAFT) polymerization techniques. Semi-crystalline OPA11 prepared via melt polycondensation was equipped with a RAFT agent at the ω -position. The resulting functionalized oligomers were further used to mediate the radical polymerization of methacrylate monomers (LMA and MMA) and generate well-defined OPA11-*b*-PLMA-*b*-PMMA triblock copolymers. AFM observations of the triblock copolymer in bulk revealed a microphase separation consisting in the formation of PMMA domains surrounded by the PLMA matrix, and the presence of additional spherical nanodomains embedded into the PLMA matrix possibly corresponding to OPA11 semi-crystalline regions. The triblocks were finally dissolved into a reactive epoxy-based mixture which was subsequently cured to generate a well-defined nanostructured epoxy-amine network by freezing the ABC triblock reaction-induced phase separation. Thus, the morphology appears as a homogeneous dispersion of nanometric spherical micelles (≈ 20 nm diameter) constituted of an elastomeric core of PLMA, an outer shell of PMMA and OPA11 in between. The described synthetic strategy and the proposed block copolymer structures may contribute to future efforts aiming at developing new hierarchically organized polymeric materials, which can be implemented in polymer physics and material science.

KEYWORDS: Thermoplastic elastomers, Crystalline-elastomeric-glassy triblock copolymers, RAFT polymerization, Nanostructured epoxy networks

INTRODUCTION

Thermoplastic elastomers (TPE)^{1,2} are multifunctional polymer materials that possess both the melt-processability of the thermoplastics and elastic properties of rubber. Typically, TPEs are linear,³⁻⁵ star⁶ or brush-shaped⁷ block copolymers (BCPs) that microphase separate into “hard” glassy or/and crystalline domains embedded in a “soft” rubbery matrix. The TPE family includes some examples of linear ABC triblock copolymers^{8,9} made of crystalline, elastomeric, and glassy blocks prepared by anionic polymerizations,^{7,10-13} ring-opening metathesis polymerization (ROMP),¹⁴ or by combination of ring-opening polymerization (ROP) with atom transfer radical polymerization (ATRP).¹⁵ Because crystalline-rubbery-glassy ABC triblocks combine the specific attributes of each phase,^{16,17} they constitute promising macromolecular tools to develop high performance materials.^{5,16,18-20}

Advances in synthetic polymer chemistry during the past two decades, especially reversible-deactivation radical polymerization techniques (RDRP such as ATRP and RAFT) techniques, have significantly broaden the range of monomer structures that can be incorporated into BCPs. Merging step growth processes and RDRP techniques²¹⁻²³ is particularly appealing to develop advanced polymer materials as it affords the production of a number of interesting BCPs with vinylic and polycondensate segments (polystyrenes, polyacrylates, polymethacrylates vs. polyesters, polysulfones, polyurethane, polyethers...) for diverse purposes, *i.e.*, surface patterning or toughening brittle highly crosslinked polymers as pioneered by Bates in the late 90's.³ This last topic has been the subject of much research,^{16,17,24-28} due to the variety of nanostructures that can be built and of mechanical behaviors that can be encountered. Different macromolecular architectures have been used as additives for epoxy resins in order to form nanoscale dispersed structures, such as spherical micelles, worm-like micelles, vesicles or octopus-like nanostructures in epoxy matrix.^{29,30} The nanostructural heterogeneities were considered to determine the physical properties of epoxy thermosets, which were continually used in a variety of

applications such as coatings, adhesives, and structural composites.³¹ However, to the best of our knowledge, incorporating *crystalline-rubbery-glassy* triblock copolymers that consist of “epoxy-philic” and “epoxy-phobic” blocks into an epoxy matrix has remained unexplored so far.

In this work, we explore a straightforward strategy to design well-defined *crystalline-rubbery-glassy* ABC triblock copolymers and investigate their self-assembly in bulk and in reactive epoxy systems. The approach developed herein relies on the facile one-step synthesis of oligomeric of polyamide 11 (OPA11) via melt polycondensation and the consecutive ligation of a relevant dithiobenzoate group on the oligoamide chain ends to generate the oligomeric RAFT agents (**Figure 1**). The propensity of the resulting oligoRAFT agents to efficiently mediate the radical polymerization of methacrylates has been subsequently studied in order to grow ABC triblock copolymers. More precisely, we have designed an ABC block copolymer where the blocks A and B, respectively constituted of semi-crystalline OPA11 and rubbery PLMA are expected to act in concert to toughen the epoxy materials while the glassy block C (PMMA) is necessary to overcome macrophase separation between the block copolymer and the epoxy-amine system. The capability of obtained OPA11-*b*-PLMA-*b*-PMMA triblock copolymers to self-organize in bulk has been investigated by atomic force microscope (AFM). Furthermore, the idea beneath this synthesis is to blend and self-organize such triblock polymer on a nanometer scale into epoxy precursors solutions, and to subsequently cure the reactive medium to generate nanostructured epoxy-amine networks by freezing the organization during the formation of the network. Taking advantage of the miscibility of the PMMA block in epoxy-amine systems such as DGEBA/MCDEA before and in the course of the network formation, the ability of semi-*crystalline-rubbery-glassy* ABC triblock to self-organize at the nanometer scale into an epoxy-amine matrix has been finally explored.

Figure 1. General strategy to prepare *semi-crystalline-rubbery-glassy* ABC triblock copolymers: OPA11-*b*-PLMA-*b*-PMMA.

EXPERIMENTAL SECTION

Materials. All starting materials, including benzyl amine, 11-aminoundecanoic acid, 4-cyano-4-(phenylcarbonothioylthio) pentanoic acid (CPADB), N-hydroxysuccinimide (NHS), dicyclohexylcarbodiimide (DCC), lauryl methylacrylate (LMA), methyl methacrylate (MMA), 2, 2'-azobis(isobutyronitrile) (AIBN), diglycidyl ether of bisphenol A (DGEBA, DER332, $M_w = 346 \text{ g}\cdot\text{mol}^{-1}$), 4, 4'-methylene bis-[3-chloro 2, 6-diethylaniline] (MCDEA), were purchased from Aldrich or Fluka. The solvents were ordered from Carlo Erba. LMA was diluted with cyclohexane, then washed with 5% NaOH solution (3×50 mL) and distilled water (3×50 mL). The organic phase was filtered prior to passing through a column of basic aluminium oxide to remove the inhibitor. At last the cyclohexane was removed in a rotavapor under reduced pressure and at low temperature ($\leq 30 \text{ }^\circ\text{C}$). MMA was filtered prior to passing through a column of basic aluminium oxide to remove inhibitors. AIBN was recrystallized twice from ethanol. Unless otherwise indicated the other chemicals were used without further purification.

Characterization Methods. ^1H and ^{13}C NMR spectra were recorded on a Bruker AVANCE250 (250 MHz) or AVANCE400 (400 MHz) spectrometer using CDCl_3 , mixture of CDCl_3 with trifluoroacetic anhydride (TFAA) or 1, 1, 1, 3, 3, 3-hexafluoro-2-propanol (HFIP). All the obtained polymers were analyzed by SEC with an apparatus running in THF at $25 \text{ }^\circ\text{C}$ (flow rate: $1 \text{ mL}\cdot\text{min}^{-1}$) and equipped with a Viscotek VE 1121 automatic injector, three Waters HR1 (effective molar mass range 100-5000 g/mol, employed for OPA11 analysis) or HR5E (effective molar mass range 2000-4000000 g/mol, employed for OPA11-*b*-PLMA and OPA11-*b*-PLMA-*b*-PMMA analysis) columns and a differential refractive index detector (Viscotek VE3580). The average molar masses of OPA11, OPA11-*b*-PLMA and OPA11-*b*-PLMA-*b*-PMMA were derived from a calibration curve based on PS and PMMA standards, respectively.

Differential scanning calorimetry (DSC) analyses were carried out on a TA Q20 calorimeter. DSC capsules containing about 5-15 mg of polymers were heated from -100 to 250 °C at a heating rate of 10 °C/min. The glass transition temperatures (T_g) were taken as the midpoint of the heat capacity change during the second heating cycle.

To perform atomic force microscopy (AFM) measurements, silicon substrates (approximately $1 \times 1 \text{ cm}^2$) were cleaned by ozonolysis treatment. Samples were prepared by spin-coating from dichloromethane (DCM) solution (2g/L, 2800 rpm, 30 s), and then annealed at 180 °C under vacuum for 3 days. AFM images were acquired in air at room temperature using a Nanoscope IIIa Multimode (Digital Instruments/VEECO, CA). Intermittent contact imaging (*i.e.*, tapping mode) was performed at a scan rate of 1 Hz. Uncoated silicon probes with a resonant frequency between 280 and 405 kHz, a spring constant 20 and 80 N/m, length of 115-135 μm , width of 30-40 μm , and nominal tip radius of curvature less than 10 nm were used. Images were displayed and analyzed using the Nanoscope 6.14R1 software.

Transmission electron microscopy (TEM) analysis was performed on Philips CM120 transmission electron microscope with an accelerating voltage of 80 kV. Epoxy samples were trimmed using an ultra-microtome and the slices (60-70 nm in thickness) were placed in 300 mesh copper grids for observation. The grids were subsequently exposed to RuO_4 vapors (2% wt of Ruthenium III chloride in 50/50 water/sodium hypochlorite solution) for 25 min to stain.

Synthesis of OPA11. A series of oligoamides 11 (OPA11) ($DP_n = 6, 10, 15$) were synthesised by a solventless melt polycondensation reaction between benzyl amine and 11-aminoundecanoic acid. Typically, the 11-aminoundecanoic acid (25.0g, 124.18mmol) was mixed with appropriate quantity of benzyl amine (adjusted to tune the DP_n of the oligomers) in a 500 mL glass flask equipped with a mechanical stirrer, then heated to 260 °C for 2h under argon flow. After cooling down, the obtained OPA11 were conveniently purified by precipitation in methanol to remove residual benzyl amine,

revealing approximately quantitative yields, subsequently analysed by NMR in the mixture of CDCl_3 and TFAA at 25 °C. ^1H NMR ($\text{CDCl}_3/\text{TFAA}$, 3/1, v/v, δ , ppm, n = number of repeating units in OPA11 backbone): 1.22 (br, $-\text{CO}-(\text{CH}_2)_2-(\text{CH}_2)_6-(\text{CH}_2)_2-\text{N}(\text{COCF}_3)-$, 12nH), 1.52 (br, $-\text{CO}-\text{CH}_2-\text{CH}_2-(\text{CH}_2)_6-\text{CH}_2-\text{CH}_2-\text{N}(\text{COCF}_3)-$, 4nH), 2.70 (t, $-\text{CO}-\text{CH}_2-(\text{CH}_2)_9-\text{N}(\text{COCF}_3)-$, 2nH), 3.30 (q, $-\text{CO}-(\text{CH}_2)_9-\text{CH}_2-\text{NH}-\text{COCF}_3$, 2H), 3.62 (t, $-\text{CO}-(\text{CH}_2)_9-\text{CH}_2-\text{N}(\text{COCF}_3)-$, 2nH), 4.91 (s, $\text{Ph}-\text{CH}_2-\text{N}(\text{COCF}_3)-$, 2H), 6.69 (s, $-\text{CO}-(\text{CH}_2)_{10}-\text{NH}-\text{COCF}_3$, 1H), 7.08 (d, 2,6-PhH, 2H), 7.22 (t, 3,4,5-PhH, 3H), 11.02 (s, CF_3COOH , 1H).

Synthesis of NHS-CPADB. The activated ester NHS-CPADB was synthesized with slight modifications according to the method developed by Charreyre and others.³² 4-Cyano-4-(phenylcarbonothioylthio)pentanoic acid (CPADB) (2g, 7.2mmol), N-hydroxysuccinimide (NHS) (0.98g, 8.5mmol, 1.2 eq), and dicyclohexylcarbodiimide (DCC) (2.22g, 8.5mmol, 1.2 eq) were mixed together in anhydrous CHCl_3 at room temperature and reacted for 12h. The solvent was then evaporated and ethyl acetate was added to the residue. The obtained suspension was filtered. The filtrate was recovered and the solvent was evaporated resulting in red solid NHS-CPADB, which was dried under vacuum and used for the functionalization of OPA11 without further purification.

Synthesis of OPA11-CPADB. Freshly synthesized OPA11 (100mg) and NHS-CPADB (5 eq) were mixed together in 1mL of phenol/methanol (7/3, wt %), then stirred at 60 °C for 40 h. The reaction solution was subsequently precipitated in methanol. The pink precipitate (OPA11-CPADB) was collected and dried under vacuum, then characterized by NMR in a mixture of CDCl_3 and TFAA or HFIP at 25 °C. ^1H NMR ($\text{CDCl}_3/\text{TFAA}$, 3/1, v/v, δ , ppm, n = number of repeating units in OPA11 backbone, m = functionality of OPA11 with CPADB): 1.32 (br, $-\text{CO}-(\text{CH}_2)_2-(\text{CH}_2)_6-(\text{CH}_2)_2-\text{N}(\text{COCF}_3)-$, 12nH), 1.64 (br, $-\text{CO}-\text{CH}_2-\text{CH}_2-(\text{CH}_2)_6-\text{CH}_2-\text{CH}_2-\text{N}(\text{COCF}_3)-$, 4nH), 1.95 (s, $\text{CH}_3-\text{C}(-\text{CN})(-\text{S}-)-\text{CH}_2-$, 3mH), 2.70 (t, $-\text{CO}-\text{CH}_2-(\text{CH}_2)_9-\text{N}(\text{COCF}_3)-$ & $-\text{C}(=\text{O})-\text{CH}_2-\text{CH}_2-\text{C}(-\text{CN})(-\text{CH}_3)-\text{S}-$, 2nH+4mH), 3.61 (t, $-\text{CO}-(\text{CH}_2)_9-\text{CH}_2-\text{N}(\text{COCF}_3)-$ 2nH), 4.90 (s, $\text{Ph}-\text{CH}_2-\text{N}(\text{COCF}_3)-$, 2H), 7.09 (d, 2,6-PhH- CH_2- , 2H), 7.21

(t, 3,4,5-PhH-CH₂-, 3H), 7.34 (t, 3,5-PhH-C(=S)-S-, 2mH), 7.58 (t, 4-PhH-C(=S)-S-, mH), 7.90 (d, 2,6-PhH-C(=S)-S-, 2mH), 10.32 (s, CF₃COOH, 1H). ¹³C NMR (CDCl₃+HFIP, δ, ppm): 24.82, 26.21, 26.42, 26.56, 27.07, 27.15, 27.35, 29.36, 29.45, 32.23, 34.13, 37.16, 40.60, 43.57, 44.56, 118.67, 126.25, 128.08, 129.44, 134.02, 137.24, 173.15, 177.12, 224.02.

General procedure for solution polymerization of LMA. Solution polymerization of LMA was performed using AIBN as initiator and OPA11-CPADB ($DP_n = 6, 10, 15$) as chain transfer agent. Typically, the polymerization of LMA (5.26 mL, 18 mmol) was carried out using AIBN (0.36 mg, 2.2×10^{-6} mol), OPA11-CPADB ($DP_n = 6, 10, 15$) (4.5×10^{-5} mol), hexafluoro-isopropanol (HFIP) (2.6 mL), toluene (2.6 mL) and trioxane (243 mg, 2.7×10^{-3} mol) as an internal reference for the measurement of LMA consumption via ¹H NMR. A stock solution was transferred into Schlenk tubes which were thoroughly deoxygenated by five consecutive freeze-pump-thaw runs. The tubes were subsequently placed in an oil bath thermostated at 60 °C. The reaction was stopped by plunging the tubes into liquid nitrogen. The polymer was subsequently precipitated twice into methanol in order to eliminate residual monomer, AIBN and trioxane. Further investigations of the conditions allowing for purifying the OPA11-*b*-PLMA diblock copolymers from traces of unfunctionalized OPA11, and unreacted OPA11-CPADB, in this view, HFIP was proven to selectively precipitate the BCP (appears as a pink sticky gel) providing that the molecular weight of the PLMA block is higher than 30000 g/mol.

The incorporation of the OPA11 sequence was assessed by ¹H NMR analysis with the appearance of the characteristic methylene peaks of the benzyl end group at 4.90 ppm and methylene peaks next to -NH- and -(=O)- groups at 3.60 and 2.69 ppm, respectively. The molar masses of OPA11-*b*-PLMA were finally evaluated by ¹H NMR (CDCl₃/TFAA, 10/1, v/v) from relative integration of the PLMA backbone (-O-CH₂-C₁₁H₂₃, 2nH, δ = 3.86 ppm, with n being the degree of polymerization) and of methylene protons of benzyl end group in OPA11 (Ph-CH₂-, 2H, δ = 4.90 ppm).

General procedure for solution polymerization of MMA. Solution polymerization of MMA was performed using AIBN as initiator and OPA11-*b*-PLMA ($DP_n = 15$) as macro-CTA. Typically, the polymerization of MMA (2 mL, 1.8×10^{-2} mol) was carried out using AIBN (0.27 mg, 1.65×10^{-6} mol), OPA11-*b*-PLMA (1.16g, 3.3×10^{-5} mol), HFIP (2 mL), toluene (2 mL) and trioxane (243 mg, 2.7×10^{-3} mol) as an internal reference for the measurement of monomers consumption via ^1H NMR. A stock solution was transferred into Schlenk tubes which were thoroughly deoxygenated by five consecutive freeze-pump-thaw runs. The tubes were subsequently placed in an oil bath thermostated at 60 °C. The reaction was stopped by plunging the tubes into liquid nitrogen. The polymer was subsequently precipitated twice into methanol in order to eliminate residual monomer and trioxane. The polymer, slight pink powder, was dried under vacuum and characterized by ^1H NMR and SEC. The molar masses of the PMMA block was finally evaluated by ^1H NMR ($\text{CDCl}_3/\text{TFAA}$, 10/1, v/v) from relative integration of the PLMA backbone ($-\text{O}-\text{CH}_2-\text{C}_{11}\text{H}_{23}$, 2nH, $\delta = 3.86$ ppm, with n being the degree of polymerization), of methylene protons of benzyl end group in OPA11 ($\text{Ph}-\text{CH}_2-$, 2H, $\delta = 4.90$ ppm) and of characteristic protons of PMMA ($\text{CH}_3-\text{O}-$, 3mH, $\delta = 3.54$ ppm, with m being the degree of polymerization).

Preparation of nanostructured epoxy-amine networks. The networks were prepared as previously described.³³⁻³⁵ Blends containing different amounts (5, 10 and 20 parts per hundred epoxy resin-phr) and diglycidyl ether of bisphenol A (DGEBA, DER332, $M_w = 346 \text{ g}\cdot\text{mol}^{-1}$) were prepared by mechanical stirring in a glass reactor at 180 °C for 30 min leading to a homogeneous premix. The diamine comonomer, 4,4'-methylene bis-[3-chloro 2,6-diethylaniline] (MCDEA, stoichiometric ratio of amine to epoxy functions), was then added over 5 min, the mixture was then casted in 50 mm×50 mm×1.5 mm PTFE mold and polymerized for one day at 80 °C, one day at 135 °C and post-reacted for one day at 180 °C.

RESULTS AND DISCUSSION

Design of oligoamide functionalized RAFT agents. The marriage of *low-(synthesis)-cost* yet robust OPA11 with versatile and tolerant RAFT process facilitates the preparation of BCPs with crystallization abilities. To this end, the original oligoRAFT agents OPA11-CPADB have been designed (**Figure 1**).

Syntheses of OPA11. In a preliminary step, three OPA11 exhibiting degrees of polymerization ranging from 6 to 15 ($DP_n = 6, 10, 15$) were synthesized through the melt polycondensation under argon flow to prevent oxidation reactions occurring at high temperature and to extract the formed water. Aiming at controlling the DP_n of the oligoamides and generating oligomers bearing a benzyl group at α -position and a reactive amine group at ω -position, the polymerization of 11-aminoundecanoic acid was carried out in the presence of various amounts of benzyl amine as chain stopper, leading to nearly quantitative yields of OPA11.

The resulting oligomers exhibit very poor solubility in common organic solvents with the exception of HFIP and phenol/methanol mixtures (7/3, w/w). The obtained OPA11 were thus conveniently purified by precipitation in methanol to remove residual monomers. Fractions of OPA11 were subsequently reacted with TFAA to allow for ^1H NMR and SEC characterizations. The conditions of polymerization and the main characteristics of the generated OPA11 are respectively given in **Table 1**.

Table 1: Characteristics of the OPA11.

DP_n^a of OPA11	n^b	M_n^c g/mol	M_n^a NMR g/mol	M_n^d Titration g/mol	M_n^e SEC g/mol	D^e	T_m^f °C	X_c^f %
6	4	1000	1300	1400	900	1.68	152	36
10	8	1600	1700	1600	1300	1.73	163	34
15	13	2500	2900	3000	2000	2.01	171	33

^a: Determined by ^1H NMR in CDCl_3 at 25 °C, (OPA11 samples were trifluoroacetylated with TFAA prior to perform ^1H NMR), from relative integration of the methylene protons of the benzyl end group and OPA11 backbone peaks. ^b: n represents the initial ratio between 11-aminoundecanoic acid and

benzyl amine. ^c: calculation of theoretical molar mass assuming that all the 11-aminoundecanoic acid and benzyl amine are consumed. ^d: Amino group titration performed by potentiometry in a m-cresol solution using perchloric acid as reagent. ^e: OPA11 samples were reacted with TFAA prior to perform SEC in THF (PS calibration). ^f: Obtained from DSC analysis (2nd cycle), the crystallinity ratio (X_c) of the OPA11 was obtained according to the following definition: $X_c = \Delta H_c / \Delta H_{c\infty}$, where ΔH_c and $\Delta H_{c\infty}$ are heats of melting of measured sample and fully crystalline PA11, respectively, $\Delta H_{c\infty} = 206 \text{ J}\cdot\text{g}^{-1}$ for 100% crystalline PA11.³⁶

As illustrated by **Table 1**, incorporating benzyl amine within 11-aminoundecanoic acid constitutes a simple and efficient way of controlling the overall degree of polymerization of the oligoamides (**Figure 2A**).

Figure 2: (A) Normalized SEC traces of TFAA-modified OPA11 (THF as eluent). (B) DSC curve of the neat OPA11s (2nd cycle).

The thermal properties of the oligomers were subsequently investigated by DSC (**Figure 2B**). As expected, all the samples exhibit a crystalline character. Tuning the degree of polymerization of the OPA11 has a significant impact on the properties of the resulting materials. As seen in **Figure 2B**, the shortest OPA11s ($DP_n = 6$ and 10) display a complex thermal behavior with several successive endothermic peaks (including a major peak at respectively 152 and 163 °C) possibly corresponding to the melting of crystalline phases of different nature or to consecutive crystallization/melting processes.³⁷ In contrast, the longest oligomer (15 repeating units) exhibits a more classical behavior with one melting

temperature ($T_m = 171\text{ }^{\circ}\text{C}$ for $DP_n = 15$). No matter the considered OPA11, crystallinity ratio around 30% is measured. It is also worth mentioning that the glass transition temperatures of synthesized OPA11s (expected to be below $50\text{ }^{\circ}\text{C}$) could not be detected on DSC traces.

Synthesis of oligoamide functionalized RAFT agents (oligoRAFT). The presence of an amine group in ω -position of OPA11 was further exploited to generate original oligoRAFT agents with OPA11 being part of the “R” leaving/initiating group. Relying on a procedure reported by Charreyre and others,³² the ligation on the OPA11s of a dithiobenzoate mediating agent capable to polymerize methacrylates was achieved through amidation reaction involving CTAs bearing an (succinimidyl) activated ester group (**Figure 1**).

After purification by precipitation in methanol, the oligoamide functionalized RAFT agents were analyzed by ^1H NMR in CDCl_3 after reaction with TFAA (**Figure 3B**), and ^{13}C NMR in a mixture of CDCl_3 with minimum amount of HFIP (**Figure S1**). When compared to the OPA11 precursor (**Figure 3A**), the incorporation of the dithiobenzoate is first evidenced by the changing of color from beige to red, then proven by the appearance of typical peaks at 7.90 ppm (2H) on ^1H NMR spectrum corresponding to aromatic protons of the CPADB (**Figure 3B**) and by the presence of a characteristic C=S peak at 224.02 ppm on ^{13}C NMR spectrum (**Figure S1**). The yields of functionalization were further determined from relative integration of CPADB end group peaks at 7.90 ppm for the dithiobenzoate and of the $\text{Ph-CH}_2\text{-N-}$ protons at 4.90 ppm for the OPA11 backbone (**Figure 3B**).

Figure 3: ^1H NMR spectra of (A) TFAA-modified OPA11 ($DP_n = 6$), and (B) TFAA-modified OPA11-CPADB ($DP_n = 15$), recorded in CDCl_3 at 25 $^\circ\text{C}$. Note: the signals due to H_2O and trifluoroacetic acid (TFA) are in fast exchange, finally giving rise to the signals at 12.3 ppm (A) and 11.7 ppm (B), respectively, these peak positions are due to very high TFA/ H_2O molar ratio.³⁸

The optimized oligoamides functionalization yield with NHS-functionalized dithiobenzoate ranges from 72% for the longest OPA11 ($DP_n = 15$), to 77% for the shortest OPA11 ($DP_n = 6$) suggesting a slight negative influence of the OPA11 backbone length on the functionalization extent (**Table 2**). Although the quantitative functionalization of OPA11 via CPADB is not achieved, functionalization yields are comparable to values reported in the literature with other polymers.^{39,40}

Characterization of the resulting oligoRAFT agents by DSC revealed similar thermal properties as their amine-functionalized OPA11 precursors, the shortest ones ($DP_n = 6$ and 10) still display a complex thermal behavior with several different endothermic peaks (including the similar major peak at respectively 152 and 163 °C). In all cases, crystallinity ratios around 30% are measured (**Table 2**).

Table 2: Properties of OPA11-CPADB.

DP_n of OPA11-CPADB	Functionality ^a %	T_m ^b °C	X_c ^b %
6	77	153	32
10	73	162	34
15	72	172	31

^a: Determined by ¹H NMR in CDCl₃ at 25 °C, (samples are trifluoroacetylated with TFAA prior to perform ¹H NMR), from relative integration of methylene protons of the benzyl end group and aromatic protons of the dithiobenzoate group. ^b: Obtained from DSC analysis (2nd cycle), $\Delta H_{c\infty} = 206 \text{ J}\cdot\text{g}^{-1}$ for 100% crystalline PA11.³⁶

Synthesis of OPA11-*b*-PLMA diblock copolymers. The capability of the oligomer-functionalized RAFT agents to grow macromolecular blocks in a controlled manner was subsequently investigated. OPA11-CPADB mediated polymerizations of lauryl methacrylate were carried out at 60 °C in HFIP/toluene (1/1, v/v) in the presence of AIBN ([CTA]/[AIBN] = 20). As shown in **Figure S2**, whatever the degree of polymerization of the oligoamides, pseudo-first order kinetics are observed.

For each CPADB-functionalized oligoamide, molar masses grow with conversion and dispersity ranging from 1.24 to 1.37 are measured (**Table 3** and **Figure 4**). We further investigated the conditions

allowing for purifying the OPA11-*b*-PLMA diblock copolymers from traces of unfunctionalized OPA11, and unreacted OPA11-CPADB. In this view, HFIP was proven to selectively precipitate the BCP (which appears as a pink sticky gel) providing that the molar mass of the PLMA block is higher than 30000 g/mol.

Figure 4: SEC traces for the solution polymerization of LMA in HFIP/toluene (1/1, v/v) at 60 °C mediated by OPA11-CPADB using AIBN as initiator: $[M]/[CTA] = 400$, $[CTA]/[Initiator] = 20$. (A: $DP_n = 6$; B: $DP_n = 10$; C: $DP_n = 15$).

Table 3: Properties of the RAFT-made OPA11-*b*-PLMA diblock copolymers.

Sample	$[M]/[CTA]$	$Conv^a$ %	$M_{n\ th}^b$ kg/mol	$M_{n\ NMR}^c$ kg/mol	$M_{n\ SEC}^d$ kg/mol	$\bar{D}^d$	T_m^e °C	X_c^e %
(OPA11) ₆ - <i>b</i> -P(LMA) ₂₉	400	7	8.1	8.9	9.8	1.25	--	--
(OPA11) ₆ - <i>b</i> -P(LMA) ₅₇	400	16	17	15.9	18.4	1.24	--	--
(OPA11) ₆ - <i>b</i> -P(LMA) ₉₉	400	24	25.4	26.7	28.8	1.27	--	--
(OPA11) ₆ - <i>b</i> -P(LMA) ₁₁₅	400	30	31.5	30.7	34.2	1.29	152	35
(OPA11) ₁₀ - <i>b</i> -P(LMA) ₃₀	400	5	6.8	9.5	8.2	1.37	--	--
(OPA11) ₁₀ - <i>b</i> -P(LMA) ₅₇	400	13	14.8	16.3	17.5	1.30	--	--
(OPA11) ₁₀ - <i>b</i> -P(LMA) ₁₀₁	400	27	28.9	27.5	31.8	1.25	--	--
(OPA11) ₁₀ - <i>b</i> -P(LMA) ₁₆₂	400	39	41.4	42.9	40	1.29	163	30
(OPA11) ₁₅ - <i>b</i> -P(LMA) ₁₆₂	400	8	9.8	8.3	9.6	1.27	--	--
(OPA11) ₁₅ - <i>b</i> -P(LMA) ₁₀₃	400	23	26	29.3	27.9	1.26	--	--
(OPA11) ₁₅ - <i>b</i> -P(LMA) ₁₃₈	400	34	36.8	37.6	35.2	1.25	172	33
(OPA11) ₁₅ - <i>b</i> -P(LMA) ₂₀₄	400	51	54.4	56.7	52.5	1.37	--	--

^a: Conversion from ¹H NMR. ^b: Number-average molecular weight evaluated from the following equation: $M_{n\ th} = Conv \times ([M]/[CTA]) \times m_M + m_{CTA}$. ^c: Determined from relative integration of the methylene protons of the benzyl group and PLMA backbone protons. ^d: From SEC in THF (PMMA calibration, triple detection) after trifluoroacetylation of the OPA11 segment ^e: Obtained from DSC analysis (2nd cycle) with $\Delta H_{c\infty} = 206\ J\cdot g^{-1}$ for 100% crystalline PA11,³⁶ taking into account the weight fraction of OPA11 in the obtained diblock copolymers.

^1H NMR analysis gave clear evidence of the efficient purification approach. After precipitation, similar integrations are indeed observed for the characteristic peak of the two methylene protons of benzyl end group located in α position (2H at 4.90 ppm) and for the two aromatic protons of the dithiobenzoate (at 7.78 ppm), suggesting that all the residual unfunctionalized OPA11 has been extracted (**Figure 5**). Furthermore, the presence of peaks at 2.69 and 3.60 ppm corresponding to the methylene groups next to -NH- and -C(=O)- groups are consistent with the effective bonding of OPA11 to PLMA chain. The molar mass of the PLMA blocks was finally evaluated by ^1H NMR ($\text{CDCl}_3/\text{TFAA}$) from the relative integration of protons in the PLMA backbone ($-\text{O}-\text{CH}_2-\text{C}_{11}\text{H}_{23}$, $2n\text{H}$, $\delta = 3.86$ ppm, with n being the degree of polymerization) and of protons of OPA11 backbone ($-\text{NH}-\text{CH}_2-\text{CH}_2-$, $2\times 15\text{H}$, $\delta = 2.69$ ppm, with 15 being the repeat units of OPA11).

Figure 5: ^1H NMR spectra of TFAA-modified $(\text{OPA11})_{15}\text{-}b\text{-P(LMA)}_{204}$ recorded in CDCl_3 at 25 °C. Note: the signals due to H_2O and TFA are in fast exchange, finally giving rise to a signal at 6.8 ppm, the peak position is due to relative low TFA/ H_2O molar ratio.³⁸

The thermal properties of the resulting diblock copolymer were subsequently investigated by DSC. As shown in **Figure 6** and **Table 3**, the formation of the diblock copolymer is assessed by the concomitant presence of a glass transition temperature at -55 °C corresponding to the PLMA block and of melting temperatures ($152\text{-}172$ °C) attributed to the OPA11 block. Interestingly, the presence of the PLMA block does not strongly affect the crystallinity of the OPA11 segments. Even though the weakest endothermic peaks (observed at 127 °C for OPA10 and 121 and 96 °C for OPA6, see **Figure 2**) are hardly visible after chain extension, very similar T_m (for the main endothermic peak) and crystallinity ratio are obtained for OPA11-*b*-PLMA and OPA11 precursors.

Figure 6: DSC traces of the obtained OPA11-*b*-PLMA diblock copolymers with different DP_n of OPA11 (2nd cycle).

Synthesis of OPA11-*b*-PLMA-*b*-PMMA triblock copolymers.

Aiming at incorporating our BCPs as nanostructuring agents for epoxy thermosets, we subsequently investigated the chain extension of (OPA11)₁₅-*b*-P(LMA)₁₃₈, $M_n \text{ NMR} = 37.6 \text{ kg}\cdot\text{mol}^{-1}$, $\bar{D} = 1.25$) with MMA whose resulting homopolymer has been previously proven to stay miscible with DGEBA/MCDEA epoxy system upon network polymerization.³³⁻³⁵ Thanks to the combined presence of miscible PMMA and immiscible PLMA and OPA blocks, we anticipated that the targeted BCP would self-organize at the nanometer scale in the final material. Therefore, a series of (OPA11)₁₅-*b*-P(LMA)₁₃₈-*b*-(MMA)_y triblock copolymers have been prepared. As can be seen in **Figure 7**, **Table 4** and **Figure S3**, the chain extension follows a typical controlled polymerization process. The molar mass increases linearly with conversion while the dispersity stays below 1.4.

Figure 7: SEC traces for the solution polymerization of MMA in HFIP/toluene (1/1, v/v) at 60 °C mediated by (OPA11)₁₅-*b*-P(LMA)₁₃₈ using AIBN as initiator: $[M]/[CTA] = 550$, $[CTA]/[Initiator] = 20$, samples were modified with TFAA.

Table 4: Properties of the obtained OPA11-*b*-PLMA-*b*-PMMA triblock copolymers.

	[M]/	$Conv^a$	$M_{n\ th}^b$	$M_{n\ NMR}^c$	$M_{n\ SEC}^d$		T_m^e	X_c^e
Sample	[CTA]	%	g/mol	g/mol	g/mol	$\bar{D}^d$	°C	%
(OPA11) ₁₅ - <i>b</i> -P(LMA) ₁₃₈ - <i>b</i> -P(MMA) ₂₆	550	15	45.9	40.2	43.1	1.29	--	--
(OPA11) ₁₅ - <i>b</i> -P(LMA) ₁₃₈ - <i>b</i> -P(MMA) ₁₂₁	550	26	52	49.7	53.5	1.33	--	--
(OPA11) ₁₅ - <i>b</i> -P(LMA) ₁₃₈ - <i>b</i> -P(MMA) ₁₅₂	550	39	59.2	52.8	57.3	1.35	--	--
(OPA11) ₁₅ - <i>b</i> -P(LMA) ₁₃₈ - <i>b</i> -P(MMA) ₂₃₇	550	48	64	60.8	62.4	1.37	171	32

^a: Conversion from ¹H NMR. ^b: Number-average molecular weight was evaluated from the following equation: $M_{n, th} = Conv \times ([M]/[CTA]) \times m_M + m_{CTA}$. ^c: Determined from relative integration of the benzyl amine peaks and polymer backbone peaks. ^d: From SEC in THF (PMMA calibration, triple detection), after modification with TFAA. ^e: Obtained from DSC analysis (2nd cycle), $\Delta H_{c\infty} = 206\text{ J}\cdot\text{g}^{-1}$ for 100% crystalline PA11,³⁶ taking into account the weight fraction of OPA11 in the obtained triblock copolymers.

Moreover, an excellent agreement is found between theoretical and experimental molar masses evaluated by SEC and ¹H NMR (from relative integration of protons in the PMMA backbone -O-CH₃, 3mH, $\delta = 3.54$ ppm, with m being the degree of polymerization and of protons of OPA11 backbone -NH-CH₂-CH₂-, 2×14H, $\delta = 2.69$ ppm, with 14 being the repeat units of OPA11) indeed consistent with a controlled process (**Figure 8**).

Figure 8: ^1H NMR spectrum of TFAA-modified $(\text{OPA11})_{15}\text{-}b\text{-P(LMA)}_{138}\text{-}b\text{-P(MMA)}_{237}$ recorded in CDCl_3 at 25°C . Note: the signals due to H_2O and TFA are in fast exchange, finally giving rise to the signal at 6.0 ppm, the peak position is due to the relative low TFA/ H_2O molar ratio.³⁸

The formation of the semi-crystalline elastomeric glassy OPA11-*b*-PLMA-*b*-PMMA triblock was assessed by DSC analysis (**Figure 9**). The glass transition temperatures of the PLMA and PMMA blocks are clearly observed respectively at -55 and 115°C respectively, as well as a melting temperature ($T_m = 171^\circ\text{C}$) confirming the ability of the OPA11 segment to crystallize. This phenomenon confirms the microphase separation occurring between OPA11 and the two other blocks. Again, the crystalline properties of OPA11 segment incorporated in the triblock (T_m , X_c) are very similar to those exhibited by neat OPA11 highlighting that the presence of the methacrylate backbone does not hinder the crystallization process.

Figure 9: DSC curve of $(\text{OPA11})_{15}\text{-}b\text{-P(LMA)}_{138}\text{-}b\text{-P(MMA)}_{237}$, 2nd cycle.

Morphology of crystalline-rubbery-glassy ABC triblock copolymers as films. The morphology of $(\text{OPA11})_{15}\text{-}b\text{-P(LMA)}_{138}\text{-}b\text{-P(MMA)}_{237}$ was subsequently investigated by AFM (tapping mode). For this purpose, a copolymer/dichloromethane (DCM) solution (2 g/L) was deposited by spin-coating onto ozone-treated silicon wafers. The resulting film was further cured for 3 days at 180 °C under vacuum to promote mobility and organization of the BCP chains. AFM characterization gave clear evidence that $(\text{OPA11})_{15}\text{-}b\text{-P(LMA)}_{138}\text{-}b\text{-P(MMA)}_{237}$ phase-separates into nanostructured bulk material (**Figure 10A**). The collected pictures indicate that the triblock adopts a morphology where the glassy PMMA domains (**Figure 10B**, red arrows pointed) are surrounded by the soft PLMA matrix which also contains additional nanodomains that may be the signature of crystalline OPA11 domains (**Figure 10B**, blue arrows pointed).

Figure 10: AFM Phase images of $(\text{OPA11})_{15}\text{-}b\text{-P(LMA)}_{138}\text{-}b\text{-P(MMA)}_{237}$. Sample was prepared via spin coating, 2g/L in DCM.

Morphology of *crystalline-rubbery-glassy* ABC triblock copolymers in epoxy matrix.

We subsequently investigated the generation of $(\text{OPA11})_{15}\text{-}b\text{-P(LMA)}_{138}\text{-}b\text{-P(MMA)}_{237}$ nanostructures into a thermoset material obtained from a reactive mixture of DGEBA epoxy and MCDEA as co-monomer. In the present case, the PMMA block is known to stay miscible in DGEBA-MCDEA mixture up to the end of the network polymerization,³³⁻³⁵ while OPA11 and PLMA blocks are expected to phase-separate upon curing. First, the solubility of $(\text{OPA11})_{15}\text{-}b\text{-P(LMA)}_{138}\text{-}b\text{-P(MMA)}_{237}$ into DGEBA epoxy was checked, *i.e.*, the BCP was fully dissolved after 30 min of mechanical stirring at 180 °C and for concentrations as high as 20 phr (per hundred epoxy resin, corresponding to 11 wt%). The obtained solutions were then mixed with MCDEA over 5 min and casted on PTFE moulds, subsequently placed into an oven and polymerized for 24h at 80 °C, then 24h at 135 °C and post-reacted for 24h at 180 °C to ensure full curing of the samples.

All the cured samples are transparent assessing that no macrophase separation occurs during the reactive mixture polymerization. TEM images show the formation of nanostructured epoxy networks. As illustrated by **Figure 11** and **Figure S4**, (OPA11)₁₅-*b*-P(LMA)₁₃₈-*b*-P(MMA)₂₃₇ triblock copolymers self-assemble into spherical micelles with diameters on the order of 20 nm that are homogeneously dispersed in the epoxy matrix. These micelles are formed before the gel point of the growing network is reached (either upon dissolution in the reactive system or in the course of the polymerization) and persist upon full curing.^{33,34} We believe that the bright core of the micelles is mainly composed of PLMA while PMMA blocks form a swollen corona and remain embedded in the epoxy network.³⁵ The presence of a dark corona in between is due to the OPA11 blocks which are selectively stained by ruthenium tetroxide.⁴¹ As anticipated, higher triblock copolymer contents (varying from 5 to 20 phr, i.e. 3 to 11 wt%) result in larger amount of micelles but do not influence neither micelles size nor nanodomains organization.

Figure 11: TEM images of nanostructured epoxy networks generated from 5phr (3 wt%, A) and 20phr (11 wt%, B) of (OPA11)₁₅-*b*-P(LMA)₁₃₈-*b*-P(MMA)₂₃₇ triblock copolymers.

CONCLUSIONS

Relying on a straightforward synthetic path and benefiting from the crystallization ability of oligoamides, this paper reports on the successful synthesis of diverse *semi-crystalline-rubbery-glassy* ABC triblock copolymers. First, three OPA11s of different molar masses were successfully synthesized by melt polycondensation using a chain stopper to afford a good control over the chain length. Then CPADB-based oligoRAFT agents were generated with functionalization yields higher than 70%. All OPA11-functionalized oligoRAFT agents were proven to efficiently mediate the polymerization of laurylmethacrylate affording OPA11-*b*-PLMA diblock copolymers. Targeting the design of nanostructured epoxy-amine networks, well-defined OPA11-*b*-PLMA-*b*-PMMA *semi-crystalline-rubbery-glassy* triblock copolymers were ultimately prepared. After confirmation of their ability to self-organize as conventional BCPs by AFM, incorporation of (OPA11)₁₅-*b*-P(LMA)₁₃₈-*b*-P(MMA)₂₃₇ triblock copolymer in DGEBA/MCDEA formulations was proven to promote the formation of nanostructured epoxy-based thermosets. As shown by TEM images, the triblock copolymer forms well-dispersed spherical micelles with diameters of ~20 nm within the network. The core of the micelles is constituted of PLMA whereas PMMA forms the outer shell of the nanostructures and OPA11 is located in between. The described synthetic strategy and the proposed BCP structures may contribute to future efforts aiming at developing new nanostructured networks.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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Supporting Information

¹³C NMR of OPA11-CPAD, and first-order kinetic plots for all the solution polymerizations, supplementary TEM images of nanostructured epoxy networks (Figure S1-S4).

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