

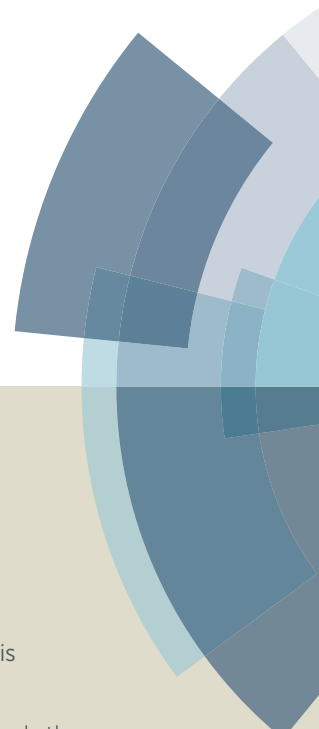


## Well-defined Polymethylene-Based Co/ Terpolymers by Combining Anthracene/Maleimide Diels-Alder Reaction with Polyhomologation

|                |  |
|----------------|--|
| Item Type      | Article  |
| Authors        | Hadjichristidis, Nikos;Alkayal, Nazeeha  |
| Citation       | Well-defined Polymethylene-Based Co/Terpolymers by Combining Anthracene/Maleimide Diels-Alder Reaction with Polyhomologation 2015 Polym. Chem. |
| Eprint version | Post-print   |
| DOI            | <a href="https://doi.org/10.1039/C5PY00601E">10.1039/C5PY00601E</a>  |
| Publisher      | Royal Society of Chemistry (RSC)   |
| Journal        | Polymer Chemistry  |
| Rights         | Archived with thanks to Polym. Chem.   |
| Download date  | 2023-12-05 13:06:56  |
| Link to Item   | <a href="http://hdl.handle.net/10754/556095">http://hdl.handle.net/10754/556095</a>  |

# Polymer Chemistry

Accepted Manuscript



This article can be cited before page numbers have been issued, to do this please use: N. Hadjichristidis and N. Alkayal, *Polym. Chem.*, 2015, DOI: 10.1039/C5PY00601E.



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

*Accepted Manuscripts* are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

## ARTICLE

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,

Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

# Well-defined Polymethylene-Based Block Co/Terpolymers by Combining Anthracene/Maleimide Diels-Alder Reaction with Polyhomologation†

Nazeeha Alkayal and Nikos Hadjichristidis\*

A novel strategy towards well-defined polymethylene-based co/terpolymers, by combining anthracene/maleimide Diels-Alder reaction with polyhomologation, is presented. For the synthesis of diblock copolymers the following approach was applied: a) synthesis of  $\alpha$ -anthracene- $\omega$ -hydroxy-polymethylene by polyhomologation using tri (9-anthracene-methyl propyl ether) borane as initiator, b) synthesis of furan-protected-maleimide-terminated poly ( $\epsilon$ -caprolactone) or polyethylene glycol and c). Diels-Alder reaction between the anthracene and maleimide-terminated polymers. In the case of triblock terpolymers the  $\alpha$ -anthracene- $\omega$ -hydroxy-polymethylene was used as macroinitiator for the ring-opening polymerization of D, L-lactide to afford an anthracene-terminated PM-*b*-PLA copolymer, followed by Diels-Alder reaction with furan-protected maleimide-terminated poly ( $\epsilon$ -caprolactone) or polyethylene glycol to give the triblock terpolymers. All intermediate and final products were characterized by SEC,  $^1\text{H}$  NMR, UV-VIS spectroscopy and DSC.

## Introduction

The Diels-Alder (DA) reaction is still one of the most useful and important reactions in modern organic chemistry.<sup>1,2</sup> Recently, due to its broad practicability and orthogonality, DA reaction became an important linking method in polymer chemistry too.<sup>3-4</sup> Indeed, the Diels-Alder reactions fulfill most of the requirements for the “click” chemistry concept. It has been successfully applied for the synthesis of polymers, mainly styrenic and (meth) acrylic, with different macromolecular architectures, e.g. homo- and miktoarm stars<sup>5-6</sup>, combs<sup>7-8</sup>, cyclic<sup>9</sup>, dendritic<sup>10</sup>, etc.<sup>11-12</sup>

On the other hand, alkylborane-initiated polymerization of dimethyl sulfoxonium methylide recently developed by Shea,<sup>13-15</sup> leads to perfectly linear polymethylene, PM (or polyethylene, PE). The general reaction scheme involves the formation of an organo boron zwitterionic complex between the dimethylsulfoxonium methylide and the trialkylborane which breaks down by intramolecular 1, 2-migration. As a consequence, the methylene group is randomly inserted one by one (C1 polymerization or polyhomologation) into the three branches of the trialkylborane leading to a 3-arm star having boron as junction point. The resulting star is subsequently oxidized/hydrolysed to give OH-end-capped linear PMs.

By combining polyhomologation and anthracene/furan-protected maleimide Diels-Alder reaction we were able to synthesize well-defined PM-based diblock copolymers of PM with poly( $\epsilon$ -caprolactone) (PCL) or polyethylene glycol (PEG) as well as triblock terpolymers of polylactide with PM and either PCL or PEG. This method is a general one opening new horizons for the synthesis of well-defined PE-based polymeric materials with different macromolecular architectures. Due to their amphiphilic nature these copolymers are perfect candidates for many industrial applications in compatibilization, dyeing, printing, adhesion, etc.<sup>16-32</sup>

## Experimental

### Materials

Sodium hydride (60% dispersion in mineral oil, Acros) was washed with petroleum ether (40–60°C) before use. Methanol (99%, Fisher), acetonitrile (99%, Fisher), diethyl ether (99%, Aldrich), dichloromethane (>99%, Fisher), and hexane (99%, Fisher) were used as received. Tetrahydrofuran (99%, Fisher) and toluene (99.7%, Fluka) were freshly distilled over sodium and benzophenone. 1,8 diazabicyclo[5.4.0]undec-7-ene (DBU) (99%, Fluka),  $\epsilon$ -caprolactone (99%, Alfa Aesar), allyl bromide (97%, Aldrich), and ethanol amine (99.5%, Aldrich) were distilled from  $\text{CaH}_2$ . D, L-lactide (99%, Across); exo-3,6-epoxy-1,2,3,6-tetrahydrophthalic anhydride (99%, Aldrich) was purified by crystallization in toluene. 9-anthracenemethanol (97%, Alfa Aesar) was purified by crystallization in ethyl acetate. Calcium hydride ( $\text{CaH}_2$ ) (95%, Aldrich), trimethylsulfoxonium iodide (98%, Alfa Aesar), *t*-BuP<sub>2</sub> (2.0 M in THF, Aldrich), benzyltri-*n*-butylammonium chloride (98%, Alfa Aesar), trimethylamine N-oxide dihydrate (TAO) (>99%, Fluka), succinic anhydride (99%, Aldrich), 4-(dimethyl amino) pyridine (DMAP) (99%, Aldrich), *N*, *N'*-dicyclohexylcarbodiimide (DCC) (99%, Aldrich), polyethylene glycol methyl ether (PEG) ( $M_n=4000$  g/mol,  $DP_n=91$ , Aldrich), and  $\text{BH}_3$ .THF (1M in THF, Aldrich) were used as received.

### Instrumentation

High-temperature-size exclusion chromatography (HT-SEC) measurements were performed on a Viscotek HT-SEC module 350 with two PL gel 10  $\mu\text{m}$  MIXED-B columns using 1,2,4-trichloro benzene as eluent at a flow rate of 0.8 mL/min at 150 °C.  $^1\text{H}$  NMR spectra were recorded on a Bruker AVANCE III-600 spectrometer. SEC chromatograms at 35 °C were recorded on a Viscotek TDA 305 instrument with a column of PLgel 10  $\mu\text{m}$  MIXED-C (only used for PS<sub>3</sub>B) or two columns of Styragel HR2 THF (7.8 $\times$ 300 mm) and Styragel HR4 THF (7.8 $\times$ 300 mm). THF was the eluent at a flow rate

of 1 mL/min. The system was calibrated by PS standards. Differential scanning calorimetry (DSC) characterization was performed on a Mettler Toledo DSC1/TC100 system in an inert nitrogen atmosphere. The second heating curve was used to determine the melting temperature ( $T_m$ ), glass transition temperature ( $T_g$ ), and degree of crystallinity. UV-VIS measurements were performed on an Evolution 600 instrument with a manual temperature controller.

### Synthesis of the PM-based diblock copolymers and triblock terpolymers

The synthesis of dimethylsulfoxonium methylide and  $\alpha$ -furan-protected-maleimide- $\epsilon$ -polycaprolactone (PCL-MI) are given in the Supporting Information. 9-Anthracenemethyl allyl ether and furan-protected-maleimide-terminated polyethylene glycol (PEG-MI) were prepared according to published procedure.<sup>33,34</sup> The  $DP_n$  of PEG (Aldrich, nominal  $DP_n=91$ ) checked by  $^1H$  NMR (Figure S2†) found to be 100. This more accurate  $DP_n$  was used to calculate the molecular weight of diblock copolymers and triblock terpolymers.

### Synthesis of the initiator tri (9-anthracene-methyl propyl ether)borane

1.5 mL (1.5 mmol) of a THF solution of  $BH_3 \cdot THF$  (1.0 M) was added over 5 min to a toluene solution (3.5 mL, 1.5 g, 6.04 mmol) of 9-anthracene-methyl allyl ether at 0°C. The reaction was allowed to reach room temperature over 2 h. The final concentration of the initiator solution in toluene was 0.3 mmol/mL.

### Synthesis of anthracene-terminated polymethylene(ant-PM-OH)

(0.95 mL, 0.3 mmol/mL, 0.29 mmol) of the initiator tri(9-anthracenemethyl propyl ether)borane was added to the methylide solution (80 mL, 0.75 mmol/mL, 60 mmol) at 50°C. After consumption of methylide, 0.29 g of TAO was added to the solution. Then, the solution was stirred for 2 h and precipitated in methanol. Finally, the purified polymer was dried in vacuum oven at 50°C (yield = 0.9 g, 100%,  $M_{n,NMR}=1600$  g/mol,  $M_w/M_n=1.20$ ).  $^1H$  NMR (600 MHz, toluene- $d_8$ , 80°C) values included 8.40 ppm (s, 1H, ArH of anthracene), 8.18 ppm (d, 2H, ArH of anthracene), 7.77 ppm (d, 2H, ArH of anthracene), 7.35–7.28 ppm (m, ArH of anthracene), 5.34 ppm (s, 2H, O- $CH_2$ -anthracene), 3.56 ppm (t, 2H,  $CH_2$ -O- $CH_2$ -anthracene), 1.36 ppm (m,  $-CH_2-$  of PM), and 3.38 ppm (m, 2H,  $CH_2$ -OH, end-group of PM).

### Synthesis of $PM_{100}$ - $b$ -PEG<sub>100</sub> and $PM_{100}$ - $b$ -PCL<sub>50</sub> copolymers

ant-PM<sub>100</sub>-OH (0.1 g, 0.062 mmol,  $M_{n,NMR}=1600$  g/mol, 1 equiv.) and PEG<sub>100</sub>-MI (0.18 g, 0.041 mmol,  $M_{n,NMR}=4500$  g/mol, 1.5 equiv.) were dissolved in 25 mL of toluene under Ar. The mixture was refluxed at 110°C and kept in the dark for 48 h. The solvent was then evaporated until dryness, the product was dissolved in THF, precipitated in hexane, and dried in vacuum oven at 40°C overnight (yield=0.24 g, 70%,  $M_{n,NMR}=5600$  g/mol,  $M_w/M_n=1.14$ ).  $^1H$  NMR (600 MHz, toluene- $d_8$ , 80°C) values included 3.54 ppm (m, 4H,  $CH_2CH_2O$  of PEG), 1.40 ppm (m,  $-CH_2-$  of PM).

The Diels-Alder reaction of ant-PM<sub>100</sub>-OH and MI-PCL<sub>50</sub> targeting  $PM_{100}$ - $b$ -PCL<sub>50</sub> (subscript: degree of polymerization) was performed similarly to that described for the synthesis of  $PM_{100}$ - $b$ -PEG<sub>100</sub>. The toluene was evaporated until dryness; the product was dissolved in THF, precipitated in methanol, and dried in a vacuum oven at 40°C overnight (yield = 0.20, 50%,  $M_{n,NMR}=6900$  g/mol,  $M_w/M_n=1.51$ ).  $^1H$  NMR (600 MHz, toluene- $d_8$ , 80°C) values included 4.02 ppm (t,  $CH_2O-$  of PCL), 2.23 ppm (t,  $C=OCH_2$  of PCL), 1.61–1.26 ppm (m,  $CH_2$  of PCL), 1.40 ppm (m,  $-CH_2-$  of PM).

### Synthesis of anthracene-terminated block copolymer (ant-PM<sub>100</sub>- $b$ -PLA<sub>20</sub>)

The macroinitiator ant-PM<sub>100</sub>-OH (0.27 g, 0.173 mmol,  $M_{n,NMR}=1600$  g/mol) and D,L-lactide (0.5 g, 3.46 mmol) were dissolved in 15 mL of dry toluene at 90°C in a Schlenk flask equipped with a stirring bar under dry Ar. After the polymer was completely dissolved, the catalyst solution (0.02 mL DBU, 0.173 mmol in 1 mL toluene) was added to perform ROP under argon at 90°C. After 21h, the solvent was evaporated; the polymer was precipitated/washed with methanol several times, and dried overnight at 40°C in vacuum oven. (yield = 0.68 g, 89%,  $M_{n,NMR}=4500$  g/mol,  $M_w/M_n=1.56$ ).  $^1H$  NMR results of  $PM_{100}$ - $b$ -PLA<sub>20</sub> (600 MHz, toluene- $d_8$ , 80°C) include 8.40 ppm (s, 1H, ArH of anthracene), 8.18 ppm (d, 2H, ArH of anthracene), 7.77 ppm (d, 2H, ArH of anthracene), 7.35–7.28 ppm (m, ArH of anthracene), 5.34 ppm (s, 2H, O- $CH_2$ -anthracene), 5.11 ppm (m, 2  $CHC=O$  of LA), 3.56 ppm (t, 2H,  $CH_2$ -O- $CH_2$ -anthracene), 3.40 ppm (m, 2  $CH_3CHC=O$  of LA), and 1.42 ppm (m,  $CH_2$  of PM).

### Synthesis of PLA<sub>20</sub>- $b$ -PM<sub>100</sub>- $b$ -PEG<sub>100</sub> and PLA<sub>20</sub>- $b$ -PM<sub>100</sub>- $b$ -PCL<sub>50</sub> terpolymers via the Diels-Alder reaction

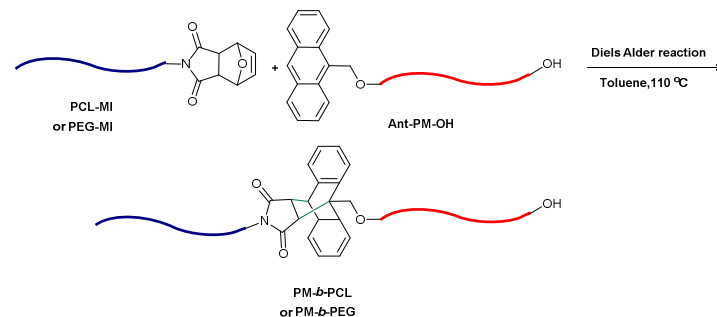
ant-PM<sub>100</sub>- $b$ -PLA<sub>20</sub> (0.2 g, 0.044 mmol,  $M_{n,NMR}=4500$  g/mol, 1 equiv) and PEG<sub>100</sub>-MI (0.13g, 0.029 mmol,  $M_{n,NMR}=4500$ g/mol, 1.5 equiv.) were dissolved in 25 mL of toluene under Ar. The mixture was refluxed at 110°C and stored in the dark for 48 h. The solvent was then evaporated until dryness, the product was dissolved in THF, precipitated in hexane, and dried in vacuum oven at 40°C overnight (yield = 0.26 g, 72%,  $M_{n,NMR}=8300$ ,  $M_w/M_n=1.32$ ).  $^1H$ NMR (600 MHz, toluene- $d_8$ , 80°C) values include 5.17 ppm (m, 2  $CHC=O$  of LA), 3.54 ppm (m, 4H,  $CH_2CH_2O$  of PEG), and 1.40 ppm (m,  $-CH_2-$  of PM).

The Diels-Alder reaction of ant-PM<sub>100</sub>-PLA<sub>20</sub> and PCL<sub>50</sub>-MI targeting PLA<sub>20</sub>- $b$ -PM<sub>100</sub>- $b$ -PCL<sub>50</sub> was performed similarly to the procedure described for the synthesis of PLA<sub>20</sub>- $b$ -PM<sub>100</sub>- $b$ -PEG<sub>100</sub>. The solvent was evaporated until dryness, the product was dissolved in THF, precipitated in methanol, and dried in vacuum oven at 40°C overnight (yield=0.25, 60%,  $M_{n,NMR}=9500$  g/mol,  $M_w/M_n=1.64$ ).  $^1H$  NMR (600 MHz, toluene- $d_8$ , 80°C) values include 5.17 ppm (m, 2  $CHC=O$  of LA), 4.09 ppm (m,  $CH_2OC=O$  of PCL), 2.23 ppm (t,  $C=OCH_2$  of PCL), and 1.42 ppm (m,  $CH_2$  of PM).

## Results and Discussion

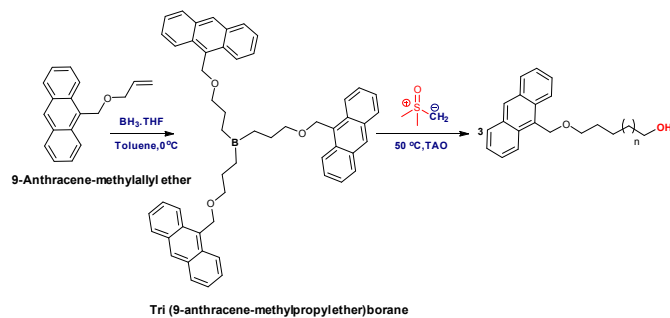
### Polymethylene (PM)-based diblock copolymers.

The basic reaction for the synthesis of diblock copolymer is given in Scheme 1.



Scheme 1. Synthesis of polymethylene-based diblock copolymers via the Diels-Alder coupling.

The  $\alpha$ -anthracene- $\omega$ -hydroxy polymethylene (ant-PM-OH) was prepared by polyhomologation of sulfoxonium methylide using tri(9-anthracenemethyl propyl ether)borane as initiator (Scheme 2) at 50°C for 1 h, followed by oxidation with TAO.



Scheme 2. Preparation of  $\alpha$ -anthracene  $\omega$ -hydroxy polymethylene.

The structure of ant-PM-OH was confirmed by  $^1\text{H}$  NMR and UV-VIS spectroscopy. As shown in Figure 1 all hydrogen of the ant-PM-OH are present in the  $^1\text{H}$  NMR spectrum, except that of the  $-\text{OH}$  group (extremely low concentration) and in Figure 2 (upper line) the characteristic five-finger absorbance (350-400 nm) of anthracene is also present. The number-average molecular weight of ant-PM-OH was estimated from the  $^1\text{H}$  NMR spectrum by comparing the integrated peak of polymethylene ( $-\text{CH}_2-$ ) at 1.40 ppm to the peak of the end- $-\text{CH}_2-\text{OH}$  group at  $\delta = 3.40$  ppm,  $M_{n,\text{NMR}} = [100 (DP_n \text{ of PM}) \times 14 \text{ g/mol} (M_w \text{ of } \text{CH}_2)] + 248 \text{ g/mol} (M_w \text{ of anthracene end-group}) = 1600 \text{ g/mol}$  close to the theoretical value (Table 1).

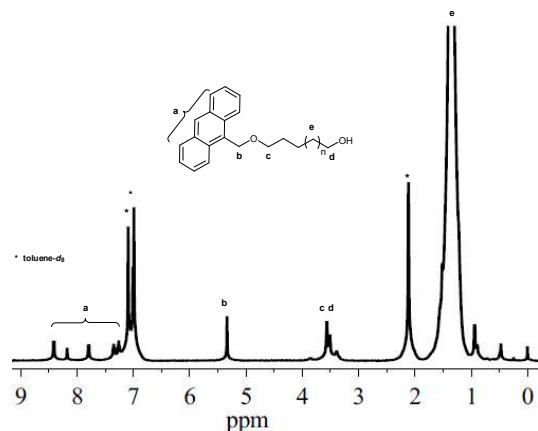


Figure 1.  $^1\text{H}$  NMR spectrum of  $\alpha$ -anthracene- $\omega$ -hydroxy polymethylene in toluene- $d_8$  at 80°C (600 MHz).

The SEC trace of ant-PM-OH [Figure 3 (A)] shows a monomodal distribution (PDI= 1.20) with no tail in the lower molecular weight region or any shoulder in the higher molecular weight region. This evidences the successful initiation of the polyhomologation of ylide using this novel borane initiator (Scheme 2).

The ant-PM<sub>100</sub>-OH was reacted with furan-protected-maleimide-terminated PCL or PEG to afford PM<sub>100</sub>-*b*-PEG<sub>100</sub> and PM<sub>100</sub>-*b*-PCL<sub>50</sub> diblock copolymers. The Diels-Alder reaction was monitored by UV-VIS spectroscopy by following the disappearance of the characteristic five-finger absorbance of anthracene (Figures 2 and S8† red line).

The HT-SEC chromatograms of PM<sub>100</sub>-*b*-PEG<sub>100</sub> (Figure 3(C)) and PM<sub>100</sub>-*b*-PCL<sub>50</sub> copolymers (Figure S4† (C)) display a monomodal distribution of polymethylene-based diblock copolymers and clearly after the Diels-Alder reaction the chromatogram is shifted to the

higher molecular weight region. Furthermore, the  $^1\text{H}$ NMR spectra of PM<sub>100</sub>-*b*-PEG<sub>100</sub> (Figure 4) and PM<sub>100</sub>-*b*-PCL<sub>50</sub> copolymers (Figure S3†) are clear proofs of the target structures of diblock copolymers, demonstrating the successful performance of the Diels-Alder reaction.

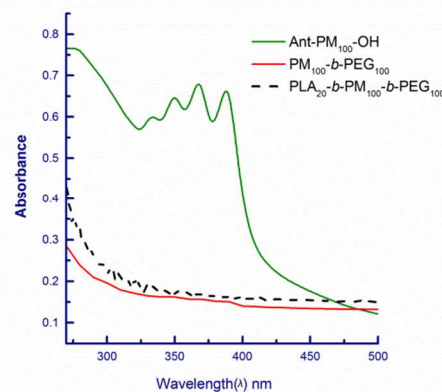


Figure 2. UV-VIS spectra of ant-PM<sub>100</sub>-OH ( $C_0 = 6.2 \times 10^{-5} \text{ M}$ ), PM<sub>100</sub>-*b*-PEG<sub>100</sub> ( $C = 1.5 \times 10^{-5} \text{ M}$ ), PLA<sub>20</sub>-*b*-PM<sub>100</sub>-*b*-PEG<sub>100</sub> ( $C = 1.11 \times 10^{-5} \text{ M}$ ) in 1,2-dichloroethane at 80°C.

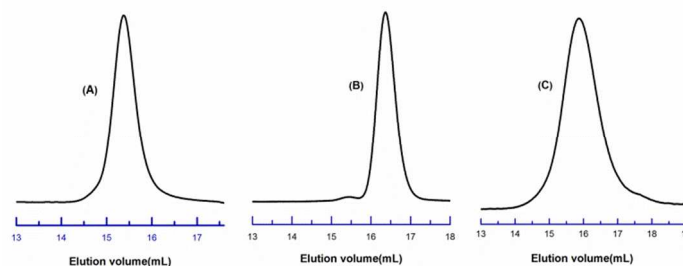


Figure 3. SEC traces of ant-PM<sub>100</sub>-OH from HT-SEC (A), PEG<sub>100</sub>-MI from THF-SEC (B), and diblock copolymer PM<sub>100</sub>-*b*-PEG<sub>100</sub> from THF-SEC (C).

Figure 4 shows the  $^1\text{H}$ NMR spectrum of PM<sub>100</sub>-*b*-PEG<sub>100</sub>, all characteristic proton signals of polyethylene glycol (4H,  $-\text{CH}_2\text{CH}_2\text{O}-$ ) and polymethylene (2H,  $-\text{CH}_2-$ ) are present. The molecular weight of the PM<sub>100</sub>-*b*-PEG<sub>100</sub> copolymer was calculated from  $^1\text{H}$  NMR (Figure 4) by comparing the integrated signal at 1.40 ppm (2H,  $-\text{CH}_2-$ ) to 3.54 ppm (4H,  $-\text{OCH}_2\text{CH}_2-$ ),  $M_{n,\text{NMR}} = [100 (DP \text{ of PEG}) \times 44 \text{ g/mol} (M_w \text{ of } \text{CH}_2\text{CH}_2\text{O})] + [86 (DP \text{ of PM}) \times 14 \text{ g/mol}] = 5600 \text{ g/mol}$ , close to the theoretical value (Table 1).

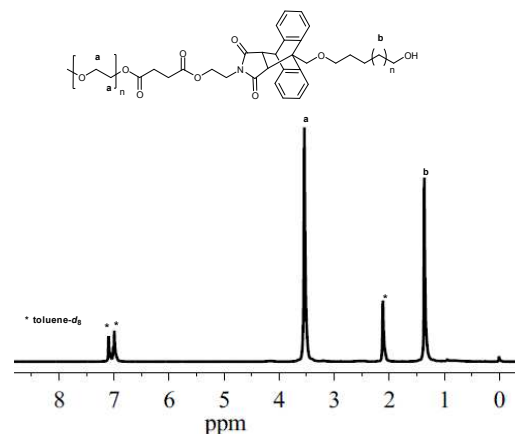
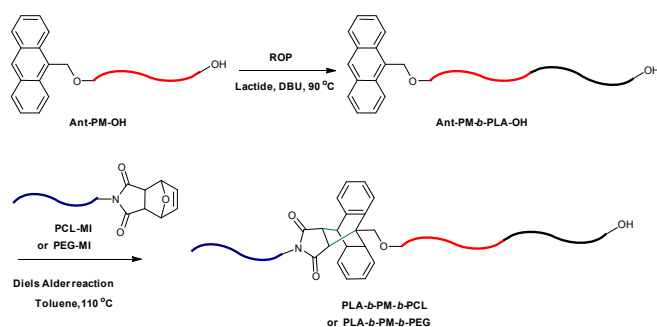


Figure 4. The  $^1\text{H}$  NMR spectrum of the diblock copolymer (PM<sub>100</sub>-*b*-PEG<sub>100</sub>) in toluene- $d_8$  at 80°C (600MHz).

The  $^1\text{H}$  NMR spectrum of the obtained  $\text{PM}_{100}\text{-}b\text{-PCL}_{50}$  copolymer (Figure S3†) shows signals at  $\delta = 1.40$  ppm (polymethylene backbone) and at  $\delta = 4.02, 3.56, 1.61\text{--}1.26$  ppm (protons of poly( $\epsilon$ -caprolactone, PCL). The  $DP_n$  of homopolymer PCL, calculated by  $^1\text{H}$  NMR (Figure S1†) from the ratio of integrated signal at 4.02 ppm (2H,  $\text{OCH}_2\text{C}=\text{O}$ ) and the integrated signal for the initiator at 6.58 ppm (2H,  $-\text{CH}=\text{CH}-$ ) was 50. The molecular weight of the  $\text{PM}_{100}\text{-}b\text{-PCL}_{50}$  copolymer was calculated from the  $^1\text{H}$  NMR spectrum (Figure S3†) by comparing the integrated signal at 1.40 ppm to 4.02 ppm  $M_{n,\text{NMR}} = [50(DP_{\text{PCL}}) \times 114.14 \text{ g/mol (MW of repeating unit)}] + (87 (DP \text{ of PMX14 g/mol}) = 6900 \text{ g/mol}$  close to the theoretical value (Table 1).

### Polymethylene (PM)-based triblock terpolymers

The basic reactions for the synthesis of PM-based triblock terpolymers are given in Scheme 3.



Scheme 3. Synthesis of polymethylene-based triblock terpolymers via the Diels-Alder coupling.

The ring opening polymerization (ROP) of D,L-lactide was initiated by ant- $\text{PM}_{100}\text{-OH}$  with DBU as a catalyst in toluene at  $90^\circ\text{C}$  to give ant- $\text{PM}_{100}\text{-}b\text{-PLA}_{20}$  copolymer. The  $^1\text{H}$  NMR spectrum of this polymer shows the characteristic signals of anthracene, of polymethylene at 8.49 - 7.32 ppm, and the polylactide segments

(Figure S7†). The  $DP_n$  of the PLA, calculated from  $^1\text{H}$  NMR by comparing the integrated signals of the main backbone of polylactide (2H, 2  $-\text{CHC}=\text{O}$  of LA) at 5.11 ppm to the signal of the macroinitiator (2H, anthracene  $-\text{CH}_2\text{-O}-$ ) at 5.34 ppm, was found to be 20. Consequently, the  $M_{n,\text{NMR}}$  of the ant- $\text{PM}_{100}\text{-}b\text{-PLA}_{20}$  is 4500 g/mol [ $20 (DP_{\text{PLA}} \text{ from NMR}) \times 144.11 \text{ g/mol} + M_n$  of macroinitiator ant- $\text{PM}_{100}\text{-OH}$  (1600 g/mol)]. Moreover, the SEC chromatogram (Figure 5(A)) shows a symmetrical shape meaning that the ant- $\text{PM}\text{-OH}$  initiated system did not show any transesterification reaction.

The (ant- $\text{PM}_{100}\text{-}b\text{-PLA}_{20}\text{-OH}$ ) copolymer was reacted with the furan-protected-maleimide-terminated linear homopolymer PCL and homopolymer PEG $_{100}\text{-MI}$  to yield polymethylene-based triblock ( $\text{PLA}_{20}\text{-}b\text{-PM}_{100}\text{-}b\text{-PCL}_{50}$ ) and ( $\text{PLA}_{20}\text{-}b\text{-PM}_{100}\text{-}b\text{-PEG}_{100}$ ) terpolymers. The Diels-Alder adducts were monitored using UV-VIS spectroscopy by following the disappearance of the characteristic five-finger absorbance of the anthracene from 300 to 400 nm (Figure 2 and S8†); the Diels-Alder efficiency of terpolymers (DA eff. %) was given in Table 1.

The HT-SEC chromatograms of terpolymers ( $\text{PLA}_{20}\text{-}b\text{-PM}_{100}\text{-}b\text{-PEG}_{100}$ ) in Figure 5(C) and ( $\text{PLA}_{20}\text{-}b\text{-PM}_{100}\text{-}b\text{-PCL}_{50}$ ) in Figure S6† show monomodal distribution traces shifted to the higher molecular weight region indicating the success of the Diels Alder reaction.

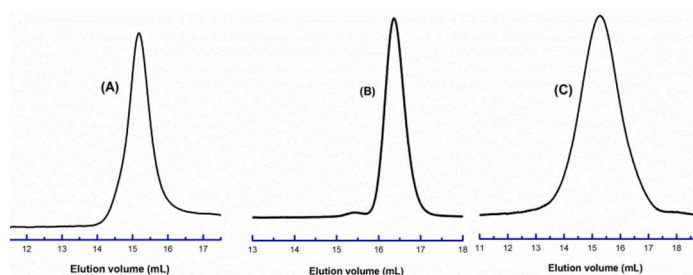


Figure 5. SEC traces of ant- $\text{PM}_{100}\text{-}b\text{-PLA}_{20}\text{-OH}$  from HT-SEC (A), PEG $_{100}\text{-MI}$  from THF-SEC (B), and the triblock terpolymer  $\text{PLA}_{20}\text{-}b\text{-PM}_{100}\text{-}b\text{-PEG}_{100}$  from THF-SEC (C).

Table 1. Characteristic Molecular Weight Data of PM-based copolymers

| Entry | Polymer  | $M_w/M_n$         | $M_{n,\text{NMR}}$<br>g/mol | $M_{n,\text{theo.}}$<br>g/mol | $DA_{\text{eff.}}^h$ |
|-------|--|-------------------|-----------------------------|-------------------------------|----------------------|
| 1     | Ant- $\text{PM}_{100}\text{-OH}$                                     | 1.20 <sup>d</sup> | 1600 <sup>b</sup>           | 1200 <sup>c</sup>             | —                    |
| 2     | $\text{PM}_{100}\text{-}b\text{-PEG}_{100}$                          | 1.14 <sup>d</sup> | 5600 <sup>f</sup>           | 6600 <sup>g</sup>             | 82%                  |
| 3     | $\text{PLA}_{20}\text{-}b\text{-PM}_{100}\text{-}b\text{-PEG}_{100}$ | 1.32 <sup>d</sup> | 8300 <sup>f</sup>           | 9500 <sup>g</sup>             | 85%                  |
| 4     | $\text{PM}_{100}\text{-}b\text{-PCL}_{50}$                           | 1.51 <sup>e</sup> | 6900 <sup>f</sup>           | 7300 <sup>g</sup>             | 75%                  |
| 5     | $\text{PLA}_{20}\text{-}b\text{-PM}_{100}\text{-}b\text{-PCL}_{50}$  | 1.64 <sup>e</sup> | 9500 <sup>f</sup>           | 10200 <sup>g</sup>            | 82%                  |

<sup>a,e</sup> High-temperature SEC, PS standards.

<sup>b</sup>  $M_{n,\text{NMR}}$  of PM homopolymer =  $14 \times DP_n$  of PM (integrated value of  $-\text{CH}_2-$  at 1.40 ppm/integrated value of  $-\text{CH}_2\text{-OH}$  at 3.40 ppm).

<sup>c</sup>  $M_{n,\text{theo.}}$  of PM homopolymer was calculated from the ratio of ylide to the initiator.

<sup>d</sup> SEC in THF, PS standards, PEG is not stable in HT-SEC.

<sup>f</sup>  $M_{n,\text{NMR}}$  of copolymers were calculated by taking into account the ratio of integrated values of PM signals to PCL or PEG signals.

<sup>g</sup>  $M_{n,\text{theo.}}$  = sum of  $M_{n,\text{NMR}}$  of homopolymers.

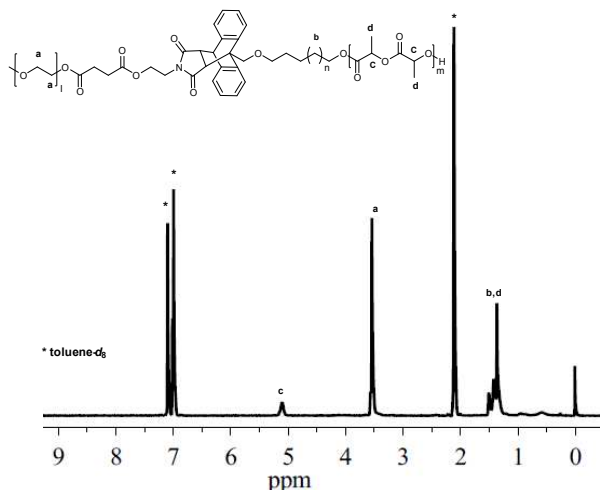
<sup>h</sup>  $DA_{\text{eff.}}\% = [1 - (A_t/A_0)] \times 100$ .

The  $^1\text{H}$  NMR spectrum of ( $\text{PLA}_{20}\text{-}b\text{-PM}_{100}\text{-}b\text{-PEG}_{100}$ ) is given in Figure 6, all characteristic proton signals of polymethylene ( $\delta = 1.40$  ppm), poly ethylene glycol ( $\delta = 3.54$  ppm), and polylactide ( $\delta = 5.11$  ppm) segments are present. The molecular weight of the  $\text{PLA}_{20}\text{-}b\text{-PM}_{100}\text{-}b\text{-PEG}_{100}$  terpolymer was calculated from the  $^1\text{H}$  NMR (Figure 6) by comparing the integrated signal at 1.40 ppm to 3.54 ppm. The  $M_{n,\text{NMR}}$  of ( $\text{PLA}_{20}\text{-}b\text{-PM}_{100}\text{-}b\text{-PEG}_{100}$ ) terpolymer = [ $100 (DP_{\text{PEG}}) \times 44 \text{ g/mol}$ ] + [ $(72 (DP_{\text{PM}}) \times 14 \text{ g/mol}) + [20 (DP_{\text{PLA}})$

$\times 144.11 \text{ g/mol}] = 8300 \text{ g/mol}$  close to the theoretical value (Table 1).

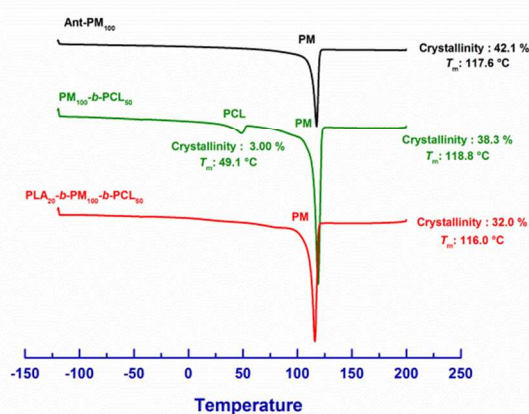
Similarly, the  $^1\text{H}$  NMR spectrum (Figure S5†) of ( $\text{PLA}_{20}\text{-}b\text{-PM}_{100}\text{-}b\text{-PCL}_{50}$ ) clearly confirms the structure of the target triblock terpolymer by showing all characteristic signals for the three polymers PCL ( $\delta = 4.02$  ppm), PM ( $\delta = 1.40$  ppm), and PLA ( $\delta = 5.11$  ppm). The  $M_{n,\text{NMR}}$  of the terpolymer = [ $50 (DP_{\text{PCL}}) \times 114.14$

g/mol] + [53 ( $DP_{PM}$ ) X14 g/mol] + [20 ( $DP_{PLA}$ ) X144.11 g/mol] = 9500 g/mol close to the theoretical value (Table 1).



**Figure 6:**  $^1\text{H}$  NMR spectrum of triblock terpolymer ( $\text{PLA}_{20}\text{-}b\text{-PM}_{100}\text{-}b\text{-PEG}_{100}$ ) in toluene- $d_8$ , 80°C, (600MHz).

As an example, the DSC traces of  $\text{PLA}_{20}\text{-}b\text{-PM}_{100}\text{-}b\text{-PCL}_{50}$  as well as the corresponding diblock and monoblock precursors are shown in Figure 7. In all cases the melting point of PM (116–118.3 °C) is present and only in the case of the diblock copolymer the PCL melting point appears. It seems that in the case of triblock copolymer the PCL trace is absent, maybe due to the triblock structure. This is in accordance with the decrease in crystallinity of PM going from the monoblock to the triblock terpolymer.



**Figure 7:** DSC curves of ant-PM<sub>100</sub>-OH, PM<sub>100</sub>-*b*-PCL<sub>50</sub>, and PLA<sub>20</sub>-*b*-PM<sub>100</sub>-*b*-PCL<sub>50</sub> ( $\text{N}_2$  atmosphere, 10 °C/ min, second heating cycle).

## Conclusions

In this work, a simple and effective method for the synthesis of polymethylene-based di/triblock co/terpolymers by combining polyhomologation and furan-protected-maleimide/anthracene Diels-Alder coupling is presented. This method is a general one opening new horizons for the synthesis of well-defined PE-based polymeric materials with complex macromolecular architectures.

## Acknowledgements

Research reported in this publication was supported by the King Abdullah University of Science and Technology. We would like to thank Haleema Alamri, Ph.D. student and Dr Hefeng Zhang for their enormous help in the synthesis of poly ( $\epsilon$ -caprolactone) (H.A.) and PM (H.Z.).

## Notes and references

Physical Sciences and Engineering Division, Catalysis Center, Polymer Synthesis Laboratory, King Abdullah University of Science and Technology (KAUST), Thuwal, 23955, Saudi Arabia.

E-mail: Nikolaos.Hadjichristidis@kaust.edu.sa

[Electronic supplementary information (ESI) available: Experiments details, SEC traces and full  $^1\text{H}$  NMR spectra] See DOI: 10.1039/b000000x/

- G. Hizal, U. Tunca and A. Sanya, *J. Polym. Sci., Part A: Polym. Chem.*, 2011, **49**, 4103–4120.
- M. A. Tasdelen, *Polym. Chem.*, 2011, **2**, 2133–2145.
- S. Sinnwell, A. J. Inglis, T. P. Davis, M. H. Stenzel and C. Barner-Kowollik, *Chem. Commun.*, 2008, 2052–2054.
- A. J. Inglis, S. Sinnwell, M. H. Stenzel and C. Barner-Kowollik, *Angew. Chem. Int. Ed.*, 2009, **48**, 2411–2414.
- H. Durmaz, F. Karatas, U. Tunca, and G. Hizal, *J. Polym. Sci., Part A: Polym. Chem.*, 2006, **44**, 499–509.
- H. Durmaz, A. Dag, A. Hizal, G. Hizal and U. Tunca, *J. Polym. Sci., Part A: Polym. Chem.*, 2008, **46**, 7091–7100.
- B. Gacal, H. Durmaz, M. A. Tasdelen, G. Hizal, U. Tunca, Y. Yagci and A. L. Demirel, *Macromolecules*, 2006, **39**, 5330–5336.
- A. Dag, H. Sahin, H. Durmaz, G. Hizal, and U. Tunca, *J. Polym. Sci., Part A: Polym. Chem.*, 2011, **49**, 886–892.
- H. Durmaz, A. Dag, G. Hizal, and U. Tunca, *J. Polym. Sci., Part A: Polym. Chem.*, 2010, **48**, 5083–5091.
- M. Tonga, N. Cengiz, M. M. Kose, T. Dede, and A. Sanyal, *J. Polym. Sci., Part A: Polym. Chem.*, 2010, **48**, 410–416.
- E. Gungor, G. Hizal, and U. Tunca, *J. Polym. Sci., Part A: Polym. Chem.*, 2009, **47**, 3409–3418.
- H. Durmaz, B. Colakoglu, U. Tunca, and G. Hizal, *J. Polym. Sci., Part A: Polym. Chem.*, 2006, **44**, 1667–1675.
- B. B. Busch, Ch. L. Staiger, J. M. Stoddard, and K.J. Shea, *Macromolecules*, 2002, **35**, 8330–8337.
- K. J. Shea, J. W. Walker, H. Zhu, M. Paz, and J. Greaves, *J. Am. Chem. Soc.*, 1997, **119**, 9049–9050.
- K. J. Shea, B. B. Busch, and M. M. Paz, *Angew. Chem. Int. Ed.*, 1998, **37**, 1391–1393.
- R. P. Singh, *Prog. Polym. Sci.*, 1992, **17**, 251–281.
- T. C. Chung and J. Y. Dong, *J. Am. Chem. Soc.*, 2001, **123**, 4871–4876.
- G. Xu and T. C. Chung, *J. Am. Chem. Soc.*, 1999, **121**, 6763–6764.
- Y. Y. Lu, Y. L. Hu and T. C. Chung, *Polymer*, 2005, **46**, 10585–10591.
- N. Kashiwa, T. Matsugi, S. Kojoh, H. Kaneko, N. Kawahara, S. Matsuo, T. Nobori, J. Imuta, *J. Polym. Sci. Part A: Polym. Chem.*, 2003, **41**, 3657–3666.
- J. E. Baez, A. R. Hernandez and A. M. Fernandez, *Polym. Adv. Technol.*, 2010, **21**, 55–64.
- C. J. Han, M. S. Lee, D. J. Byun and S. Y. Kim, *Macromolecules*, 2002, **35**, 8923–8925.
- R. K. Iha, K. L. Wooley, A. M. Nystrom, D. J. Burke, M. J. Kade, and C. J. Hawker, *Chem. Rev.*, 2009, **109**, 5620–5686.

## ARTICLE

24. R. Briquel, J. Mazzolini, T. L. Bris, O. Boyron, F. Boisson, F. Delolme, F. D'Agosto, C. Boisson, and R. Spitz, *Angew. Chem. Int. Ed.*, 2008, **47**, 9311–9313.
25. T. Li, W. J. Wang, R. Liu, W. H. Liang, G. F. Zhao, Z. Y. Li, Q. Wu, and F. M. Zhu, *Macromolecules*, 2009, **42**, 3804–3810.
26. X. Z. Zhou and K. J. Shea, *Macromolecules*, 2001, **34**, 3111–3114.
27. J. Z. Chen, K. Cui, S.-Y. Zhang, P. Xie, Q.-L. Zhao, J. Huang, L.-P. Shi, G.-Y. Li, Z. Ma, *Macromol. Rapid Commun.*, 2009, **30**, 532–538.
28. K. J. Shea, C. L. Staiger, and S. Y. Lee, *Macromolecules*, 1999, **32**, 3157–3158.
29. Y. Xue, H. C. Lu, Q. L. Zhao, J. Huang, S. G. Xu, S. K. Cao and Z. Ma, *Polym. Chem.*, 2013, **4**, 307–312.
30. H. Zhang, N. Alkayal, Y. Gnanou and N. Hadjichristidis, *Chem. Commun.*, 2013, **49**, 8952–8954.
31. Q. Z. Li, G. Y. Zhang, J. Z. Chen, Q. L. Zhao, H. C. Lu, J. Huang, L. H. Wei, F. D'Agosto, C. Boisson and Z. Ma, *J. Polym. Sci., Part A: Polym. Chem.*, 2011, **49**, 511–517.
32. H. C. Lu, Y. Xue, Q. L. Zhao, J. Huang, S. G. Xu and Z. Ma, *J. Polym. Sci., Part A: Polym. Chem.*, 2012, **50**, 3641–3647.
33. E. Ciganek, *J. Org. Chem.*, 1980, **45**, 1497–1505.
34. A. Dag, H. Durmaz, G. Hizal, and U. Tunca, *J. Polym. Sci. part A: Polym. Chem.*, 2008, **46**, 302–313.