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

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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 α-anthracene-ω-hydroxy-polymethylene by polyhomologation using tri (9-anthracene-methyl propyl ether) borane as initiator, b) synthesis of furan-protected-maleimide-terminated poly (ε-caprolactone) or polyethylene glycol and c). Diels-Alder reaction between the anthracene and maleimide-terminated polymers. In the case of triblock terpolymers the α-anthracene-ω-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 (ε-caprolactone) or polyethylene glycol to give the triblock terpolymers. All intermediate and final products were characterized by SEC, ^{1}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.[1-2] Recently, due to its broad practicability and orthogonality, DA reaction became an important linking method in polymer chemistry too.[3-4] 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 [5-6], combs [7-8], cyclic [9], dendritic [10], etc.[11-12]

On the other hand, alkylborane-initiated polymerization of dimethyl sulfoxonium methylide recently developed by Shea, [13-15] 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(ε-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.[16-32]

Experimental

Materials

Sodium hydride (60% dispersion in mineral oil, Acros) was washed with petroleum ether (40‒60ºC) 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), ε-caprolactone (99%, Alfa Aesar), allyl bromide (97%, Aldrich), and ethanol amine (99.5%, Aldrich) were distilled from CaH$_2$. D, L-lactide (99%, Across); exo-3,6-epoxy-1,2,3,6-tetrahydrophathalic anhydride (99%, Aldrish) was purified by crystallization in toluene. 9-anthracenemethanol (97%, Alfa Aesar) was purified by crystallization in ethyl acetate. Calcium hydride (CaH$_2$) (95%, Aldrich), trimethylsulfoxonium iodide (98%, Alfa Aesar), t-BuP$_2$ (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 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 μm MIXED-B columns using 1,2,4-trichloro benzene as eluent at a flow rate of 0.8 mL/min at 150 ºC. ^{1}H NMR spectra were recorded on a Bruker AVANCE III-600 spectrometer. SEC chromatograms at 35 ºC were recorded on a Viscotek TDA 305 instrument with a column of PLgel 10 μm MIXED-C (only used for PS$_3$B) or two columns of Styragel HR2 THF (7.8×300 mm) and Styragel HR4 THF (7.8×300 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 dimethylsulfoxiunim methylide and α-furan-protected-maleimide-ε-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.[33,34] The DP_n of PEG (Aldrich, nominal DP_n=91) checked by ^{1}H 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.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 0ºC. 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, 0.3mmol/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). ^{1}H NMR (600 MHz, toluene-d_8, 80°C) values included 8.40 ppm (s, 1H, Ar*H* of anthracene), 8.18 ppm (d, 2H, Ar*H* of anthracene), 7.77 ppm (d, 2 H, Ar*H* of anthracene), 7.35–7.28 ppm (m, Ar*H* of anthracene), 5.34 ppm (s, 2H, O-CH_2-anthracene), 3.56 ppm (t, 2H, CH_2-O-CH2-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_{100} and PM_{100}-*b*-PCL_{50} copolymers

ant-PM_{100}-OH (0.1 g, 0.062 mmol, $M_{n,NMR}$=1600 g/mol, 1 equiv.) and PEG_{100}-MI (0.18 g, 0.041 mmol, $M_{n,NMR}$=4500g/mol, 1.5 equiv.) were dissolved in 25 mL of toluene under Ar. The mixture was refluxed at 110ºC 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 40ºC overnight (yield=0.24 g, 70%, $M_{n,NMR}$=5600 g/mol, M_w/M_n=1.14). ^{1}H 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_{100}-OH and MI-PCL_{50} targeting PM_{100}-*b*-PCL_{50} (subscript: degree of polymerization) was performed similarly to that described for the synthesis of PM_{100}-*b*-PEG_{100}. The toluene was evaporated until dryness; the product was dissolved in THF, precipitated in methanol, and dried in a vacuum oven at 40ºC overnight (yield = 0.20, 50%, $M_{n,NMR}$=6900 g/mol, M_w/M_n= 1.51). ^{1}H 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_{100}-*b*-PLA_{20})

The macroinitiator ant-PM_{100}-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 90ºC 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 90ºC. After 21h, the solvent was evaporated; the polymer was precipitated/washed with methanol several times, and dried overnight at 40ºC in vacuum oven. (yield = 0.68 g, 89%, $M_{n,NMR}$ = 4500 g/mol, M_w/M_n= 1.56). ^{1}H NMR results of PM_{100}-*b*-PLA_{20} (600 MHz, toluene-d_8, 80°C) include 8.40 ppm (s, 1H, Ar*H* of anthracene), 8.18 ppm (d, 2H, Ar*H* of anthracene), 7.77 ppm (d, 2H, Ar*H* of anthracene), 7.35–7.28 ppm (m, Ar*H* of anthracene), 5.34 ppm (s, 2H, O-CH_2-anthracene), 5.11 ppm (m, 2 *CH*C=O of LA), 3.56 ppm (t, 2H, CH_2-O-CH2-anthracene), 3.40 ppm (m, 2*CH3*CHC=O of LA), and 1.42 ppm (m, *CH2* of PM).

Synthesis of PLA_{20}-*b*-PM_{100}-*b*-PEG_{100} and PLA_{20}-*b*-PM_{100}-*b*-PCL_{50} terpolymers via the Diels-Alder reaction

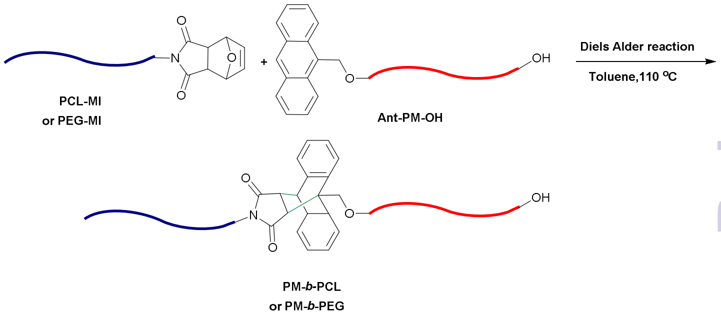
ant-PM_{100}-*b*-PLA_{20} (0.2 g, 0.044 mmol, $M_{n,NMR}$=4500 g/mol, 1 equiv) and PEG_{100}-MI (0.13g, 0.029 mmol, $M_{n,NMR}$=4500g/mol, 1.5 equiv.) were dissolved in 25 mL of toluene under Ar. The mixture was refluxed at 110ºC and stored in the dark for 48 h. The solvent was then evaporated until dryness, the product was dissolved in THF, precipitated in hexane, and dried in vacuum oven at 40ºC overnight (yield = 0.26 g, 72%, $M_{n,NMR}$=8300, M_w/M_n=1.32). ^{1}HNMR (600 MHz, toluene-d_8, 80ºC) values include 5.17 ppm (m, 2 *CH*C=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_{100}-PLA_{20} and PCL_{50}-MI targeting PLA_{20}-*b*-PM_{100}-*b*-PCL_{50} was performed similarly to the procedure described for the synthesis of PLA_{20}-*b*-PM_{100}-*b*-PEG_{100}. The solvent was evaporated until dryness, the product was dissolved in THF, precipitated in methanol, and dried in vacuum oven at 40ºC overnight (yield=0.25, 60%, $M_{n,NMR}$=9500 g/mol, M_w/M_n=1.64). ^{1}H NMR (600 MHz, toluene-d_8, 80°C) values include 5.17 ppm (m, 2 *CH*C=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, *CH2* of PM).

Results and Discussion

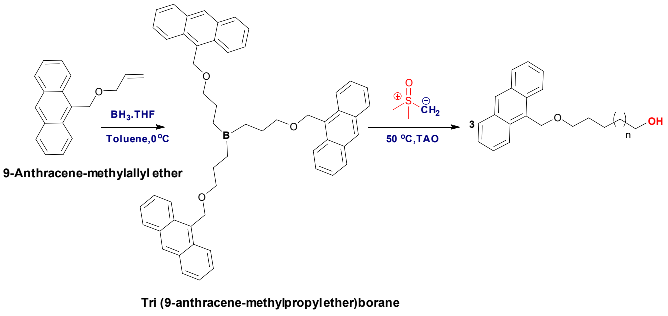
Polymethylene (PM)-based diblock copolymers.

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 α-anthracene-ω-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 α-anthracene ω-hydroxy polymethylene.

The structure of ant-PM-OH was confirmed by ^{1}H NMR and UV-VIS spectroscopy. As shown in Figure 1 all hydrogen of the ant-PM-OH are present in the ^{1}H NMR spectrum, except that of the –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}H NMR spectrum by comparing the integrated peak of polymethylene (-CH_2 -) at 1.40 ppm to the peak of the end-CH_2-OH group at δ= 3.40 ppm, $M_{n,NMR}$ = [100 (DP_n of PM) X [14 g/mol (M_W of CH_2)] + 248 g/mol (M_W of anthracene end-group)] = 1600 g/mol close to the theoretical value (Table 1).

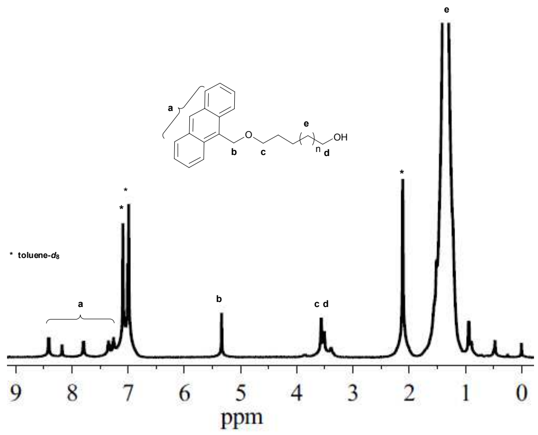


Figure 1. ^{1}H NMR spectrum of α-anthracene-ω-hydroxy polymethylene in toluene-d_8 at 80ºC (600 MHz).

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_{100}-OH was reacted with furan-protected-maleimide-terminated PCL or PEG to afford PM_{100}-*b*-PEG_{100} and PM_{100}-*b*-PCL_{50} 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_{100}-*b*-PEG_{100} (Figure 3(C)) and PM_{100}-*b*-PCL_{50} 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}HNMR spectra of PM_{100}-*b*-PEG_{100} (Figure 4) and PM_{100}-*b*-PCL_{50} copolymers (Figure S3†) are clear proofs of the target structures of diblock copolymers, demonstrating the successful performance of the Diels-Alder reaction.

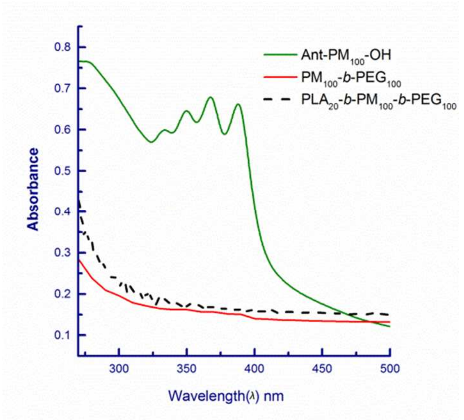


Figure 2. UV-VIS spectra of ant-PM_{100}-OH (C_0= 6.2X10^{-5}M), PM_{100}-*b*-PEG_{100} (C= 1.5 X10^{-5}M), PLA_{20}-*b*-PM_{100}-*b*-PEG_{100} (C=1.11 X 10^{-5} M) in 1, 2-dichloroethane at 80°C.

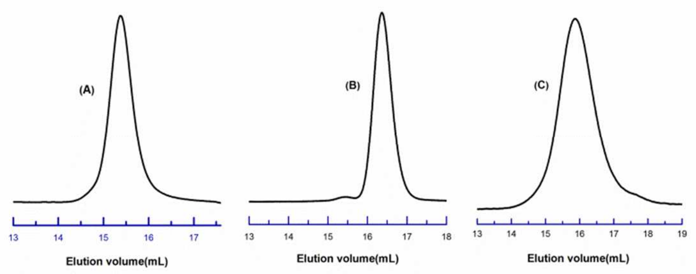


Figure 3. SEC traces of ant-PM_{100}-OH from HT-SEC **(A)**, PEG_{100}-MI from THF-SEC **(B),** and diblock copolymer PM_{100}-*b*-PEG_{100} from THF-SEC **(C).**

Figure 4 shows the ^{1}HNMR spectrum of PM_{100}-*b*-PEG_{100}, all characteristic proton signals of polyethylene glycol (4H,-CH_2CH_2O-) and polymethylene (2H, -CH_2-) are present. The molecular weight of the PM_{100}-*b*-PEG_{100} copolymer was calculated from ^{1}H NMR (Figure 4) by comparing the integrated signal at 1.40 ppm (2H,-CH_2-) to 3.54 ppm (4H, -OCH_2CH_2-), $M_{n,NMR}$= [100 (*DP* of PEG) X 44 g/mol (MW of CH_2CH_2O)] + [86 (*DP* of PM) X 14 g/mol] = 5600 g/mol, close to the theoretical value (Table 1).

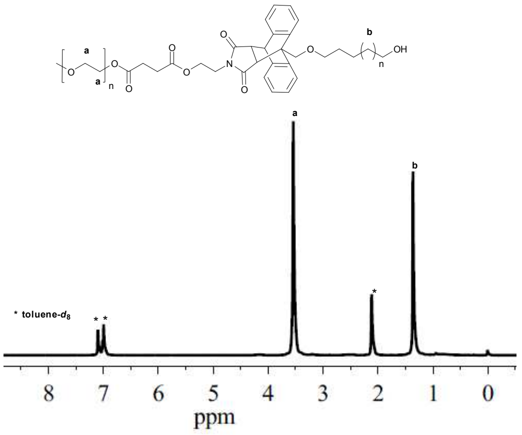
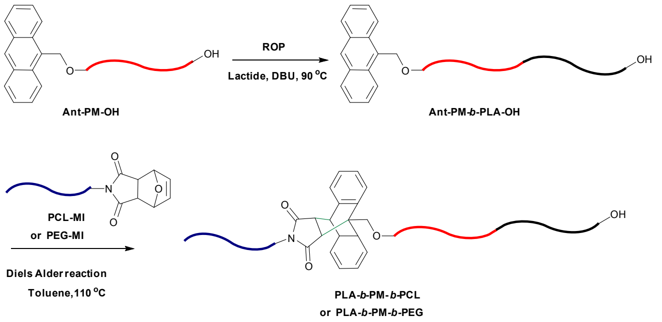


Figure 4. The ^{1}H NMR spectrum of the diblock copolymer (PM_{100}-*b*-PEG_{100}) in toluene-*d*8 at 80ºC (600MHz).

The ^{1}H NMR spectrum of the obtained PM$_{100}$-*b*-PCl$_{50}$ copolymer (Figure S3†**)** shows signals at δ = 1.40 ppm (polymethylene backbone) and at δ = 4.02, 3.56, 1.61–1.26 ppm (protons of poly (ε-caprolactone, PCL). The *DP*$_n$ of homopolymer PCL, calculated by ^{1}H NMR (Figure S1†) from the ratio of integrated signal at 4.02 ppm (2H, O*CH*$_2$C=O) and the integrated signal for the initiator at 6.58 ppm (2H,-CH=CH-) was 50. The molecular weight of the PM$_{100}$-*b*-PCL$_{50}$ copolymer was calculated from the ^{1}H NMR spectrum (Figure S3†) by comparing the integrated signal at 1.40 ppm to 4.02 ppm $M_{n,NMR}$ =[50(*DP*$_{PCL}$)X114.14 g/mol (MW of repeating unit)] + (87 (*DP* of PMX14 g/mol)=6900 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-PM$_{100}$-OH with DBU as a catalyst in toluene at 90°C to give ant-PM$_{100}$-*b*-PLA$_{20}$ copolymer. The ^{1}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}H NMR by comparing the integrated signals of the main backbone of polylactide (2H, 2 -*CH*C=O of LA) at 5.11 ppm to the signal of the macroinitiator (2H, anthracene -*CH*$_2$-O-) at 5.34 ppm, was found to be 20. Consequently, the $M_{n,NMR}$ of the ant-PM$_{100}$-*b*-PLA$_{20}$ is 4500 g/mol [20 (*DP*$_{PLA}$ from NMR)X144.11 g/mol + M_n of macroinitiator ant-PM$_{100}$-OH (1600 g/mol)]. Moreover, the SEC chromatogram (Figure 5(A)) shows a symmetrical shape meaning that the ant-PM-OH initiated system did not show any transesterification reaction.

The (ant-PM$_{100}$-*b*-PLA$_{20}$-OH) copolymer was reacted with the furan-protected-maleimide-terminated linear homopolymer PCL and homopolymer PEG$_{100}$-MI to yield polymethylene-based triblock (PLA$_{20}$-*b*-PM$_{100}$-*b*-PCL$_{50}$) and (PLA$_{20}$-*b*-PM$_{100}$-*b*-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 (PLA$_{20}$-*b*-PM$_{100}$-*b*-PEG$_{100}$) in Figure 5(C) and (PLA$_{20}$-*b*-PM$_{100}$-*b*-PCL$_{50}$) in Figure S6† show monomodal distribution traces shifted to the higher molecular weight region indicating the success of the Diels Alder reaction.

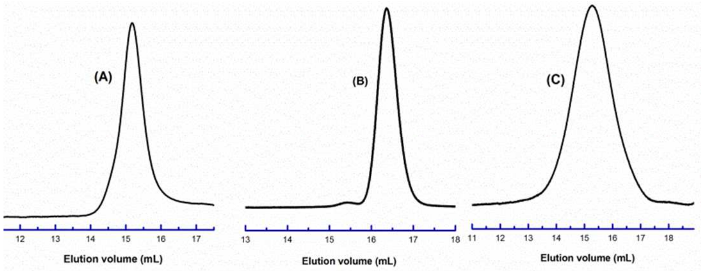


Figure 5. SEC traces of ant-PM$_{100}$-*b*-PLA$_{20}$-OH from HT-SEC **(A)**, PEG$_{100}$-MI from THF-SEC **(B),** and the triblock terpolymer PLA$_{20}$-*b*-PM$_{100}$-*b*-PEG$_{100}$ from THF-SEC **(C)**.

Table1. Characteristic Molecular Weight Data of PM-based copolymers

Entry	Polymer	M_w/M_n	$M_{n,NMR}$ g/mol	$M_{n,theo.}$ g/mol	DA $_{eff.}$ [h]
1	Ant-PM$_{100}$-OH	1.20[a]	1600[b]	1200[c]	–
2	PM$_{100}$-*b*-PEG$_{100}$	1.14[d]	5600[f]	6600[g]	82%
3	PLA$_{20}$-*b*-PM$_{100}$-*b*-PEG$_{100}$	1.32[d]	8300[f]	9500[g]	85%
4	PM$_{100}$-*b*-PCL$_{50}$	1.51[e]	6900[f]	7300[g]	75%
5	PLA$_{20}$-*b*- PM$_{100}$-*b*-PCL$_{50}$	1.64[e]	9500[f]	10200[g]	82%

[a,e] High-temperature SEC, PS standards.

[b] $M_{n,NMR}$ of PM homopolymer =14 X *DP*$_n$ of PM (integrated value of -*CH*$_2$- at1.40 ppm/ integrated value of -*CH*$_2$-OH at 3.40ppm).

[c] $M_{n,theo.}$ of PM homopolymer was calculated from the ratio of ylide to the initiator .

[d] SEC in THF, PS standards, PEG is not stable in HT-SEC.

[f] $M_{n,NMR}$ of copolymers were calculated by taking into account the ratio of integrated values of PM signals to PCL or PEG signals.

[g] $M_{n,theo.}$= sum of $M_{n,NMR}$ of homopolymers.

[h] $DA_{eff.}$%=[1-(A_t/A_0)]X100.

The ^{1}H NMR spectrum of (PLA$_{20}$-*b*-PM$_{100}$-*b*-PEG$_{100}$) is given in Figure 6, all characteristic proton signals of polymethylene (δ=1.40 ppm), poly ethylene glycol (δ= 3.54 ppm, and polylactide (δ=5.11 ppm) segments are present. The molecular weight of the PLA$_{20}$-PM$_{100}$-*b*-PEG$_{100}$ terpolymer was calculated from the ^{1}H NMR (Figure 6) by comparing the integrated signal at 1.40 ppm to 3.54 ppm. The $M_{n,NMR}$ of (PLA$_{20}$-*b*-PM$_{100}$-*b*-PEG$_{100}$) terpolymer = [100 (*DP*$_{PEG}$) X44 g/mol)] + [(72 (*DP*$_{PM}$) X14 g/mol) + [20 (*DP*$_{PLA}$) X144.11 g/mol)] = 8300 g/mol close to the theoretical value (Table 1).

Similarly, the ^{1}H NMR spectrum (Figure S5†) of (PLA$_{20}$-*b*-PM$_{100}$-*b*-PCL$_{50}$) clearly confirms the structure of the target triblock terpolymer by showing all characteristic signals for the three polymers PCL (δ = 4.02 ppm), PM (δ=1.40 ppm), and PLA (δ= 5.11ppm). The $M_{n,NMR}$ of the terpolymer = [50 (*DP*$_{PCL}$) X114.14

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).

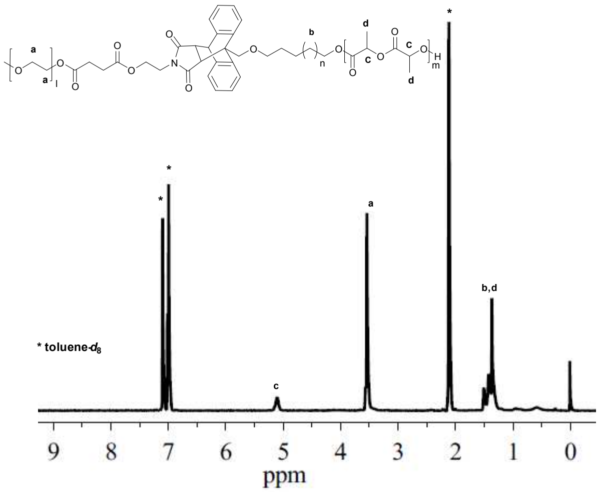


Figure.6: ^{1}H NMR spectrum of triblock terpolymer (PLA_{20}-*b*-PM_{100}-*b*-PEG_{100}) in toluene-*d8*, 80ºC, (600MHz).

As an example, the DSC traces of PLA_{20}-*b*-PM_{100}-*b*-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 ^{0}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.

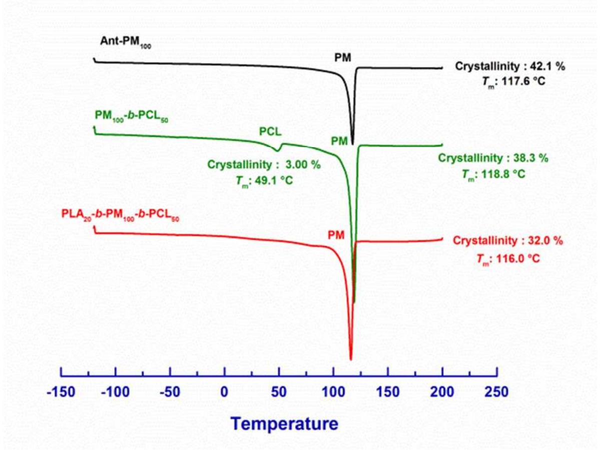


Figure 7. DSC curves of ant-PM_{100}-OH, PM_{100}-*b*-PCL_{50}, and PLA_{20}-*b*-PM_{100}-*b*-PCL_{50} (N_2 atmosphere, 10 °C/ min, second heating cycle).

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.

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Notes and references

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