# Ambient Temperature Synthesis of Triblock Copolymers via Orthogonal Photochemically and Thermally Induced Modular Conjugation

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Ⓢ *Supporting Information*

ABSTRACT: A strategy for the modular ambient temperature synthesis of ABA and ABC triblock copolymers via a combination of photoinduced Diels–Alder reactions with thermal Diels–Alder reactions and azide–alkyne click chemistry is reported. Polystyrene (PS) and PMMA (PMMA) with α-2,5-dimethylbenzophenone and ω-cyclopentadienyl or ω-azide end-functionality were prepared via atom transfer radical polymerization (ATRP) and subsequent transformation of the bromine end-group. The phototriggered conjugation reaction proceeds via an *in situ* formation of highly reactive *o*-quinodimethanes. Maleimide-capped poly(*tert*-butyl acrylate) obtained via ATRP was employed as dienophile. Alkyne and maleimide functionalized poly(ethylene glycol) (PEG) were synthesized by esterification of monomethoxy PEG. P*t*BA-*b*-PMMA-*b*-P*t*BA and P*t*BA-*b*-PS-*b*-P*t*BA were successfully prepared in a one-pot reaction at ambient temperature combining photoinduced and thermal Diels–Alder reactions. ABC triblock copolymers (P*t*BA-*b*-PS-*b*-PEG) with narrow polydispersities were obtained via the combination of photoinduced Diels–Alder reactions with thermal Diels–Alder reactions as well as CuAAc chemistry. The polymers were characterized by size exclusion chromatography and ^{1}H NMR spectroscopy.
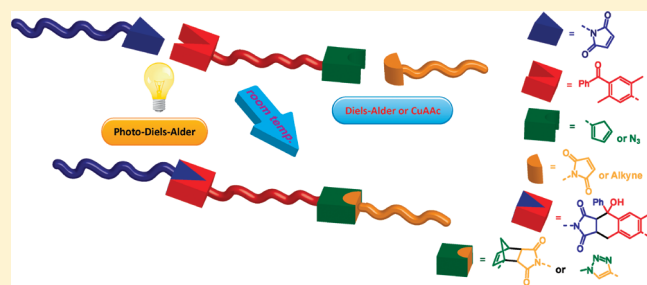
■ INTRODUCTION

Block copolymers consisting of two or more thermodynamically incompatible segments have attracted increasing interest due to their ability to form various nanostructures in bulk and solution.[1−4] The classical approach for the synthesis of block copolymers is controlled/living polymerization—including powerful anionic processes—with sequential addition of monomers. In recent years an enormous progress in this field was achieved by the utilization of controlled/living radical polymerization techniques such as nitroxide-mediated polymerization (NMP),[5] reversible addition–fragmentation chain transfer (RAFT) polymerization,[6,7] and atom transfer radical polymerization (ATRP).[8,9] The extension of the concept of "click chemistry" introduced by Sharpless and colleagues in 2001[10] to polymer synthesis provided a powerful novel approach for the construction of macromolecular architectures from polymer building blocks by effectively separating the polymerization process from the architectural buildup step.[11−13] The *click* approach allows the formation of complex macromolecular architectures from otherwise incompatible polymerization protocols. *Click* reactions for polymer–polymer conjugation should reach a very high yield using equimolar amounts of the building blocks.[14] An established method that fulfills this criteria is the copper(I)-catalyzed azide–alkyne cycloaddition (CuAAc).[15−17] Other efficient strategies include (hetero-) Diels–Alder reactions

which have been applied for the construction of various macromolecular architectures including block copolymers,[18−20] multi- and miktoarm stars,[21−24] graft copolymers,[25] and cyclic polymers[26,27] as well as for surface modification.[28,29] Tunca and co-workers utilized *in situ* CuAAc and Diels–Alder reactions for the one-pot synthesis of ABC triblock copolymers.[30] The construction of linear tetrablock polymers via CuAAc, Diels–Alder, and nitroxide radical coupling was recently reported by the same group.[31]

An alternative approach to gain a high orthogonality to other coupling methods is the use of photoinduced reactions. However, only a few *click* protocols have been developed so far that may be regarded as photoinduced. Thiol–ene[32] and thiol–yne[33] reactions employing radical photoinitiators are the most frequently used photocontrolled systems. However, the lack of spatial resolution is the major drawback of these three-component systems. Bowman and co-workers recently reported an azide–alkyne cycloaddition by photoinitiated reduction of Cu-(II).[34] The photoinduced *in situ* formation of nitrile imines from tetrazoles and subsequent 1,3-dipolar cycloaddition with alkenes was employed for protein modification by Lin and colleagues.[35,36] Our group recently reported a rapid polymer–polymer

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conjugation at ambient temperature via an UV-light triggered Diels−Alder reaction.[37] The reaction proceeds via photoinduced *in situ* formation of a highly reactive diene from a 2,5-dimethylbenzophenone precursor and subsequent cycloaddition to a maleimide functional polymer.

Here, we report the one-pot synthesis of ABA triblock copolymers via the combination of the aforementioned photoinduced conjugation with an orthogonal thermally induced Diels−Alder reaction at ambient temperature. α-2,5-Dimethylbenzophenone-ω-cyclopentadienyl functional polystyrene and poly(methyl methacrylate) and maleimide-capped poly(*tert*-butyl acrylate) are employed as building blocks within this context. The synthesis of ABC triblock copolymers through sequential phototriggered and thermally induced Diels−Alder reactions as well as CuAAc click chemistry further demonstrates the orthogonality of the photoinduced Diels−Alder conjugation protocol. We purposefully employ relatively low molecular weight material to ensure that the ATRP prepared macromolecules are of the highest possible end-group fidelity and nondormant polymeric species are minimal.

■ EXPERIMENTAL SECTION

Materials. 2-Bromo-2-methylpropionic acid 2-(3,5-dioxo-10-oxa-4-azatricyclo[5.2.1.0²,⁶]-dec-8-en-4-yl)ethyl ester (**1**),[38] 4-(2-{[(3-acetyl-7-oxabicyclo[2.2.1]hept-5-en-2-yl)carbonyl]amino}ethoxy)-4-oxobutanoic acid (**2**),[39] and (4-(2-hydroxyethoxy)-2,5-dimethylphenyl)phenylmethanone (**3**)[37] were synthesized according to the literature. Methyl methacrylate (MMA, Acros), *tert*-butyl acrylate (*t*BA, 99%, Aldrich), and styrene (Merck) were passed through a short column of basic alumina to remove inhibitor. Copper(I) bromide (Fluka) was purified by sequential washing with sulfurous acid, acetic acid, and ethanol, followed by drying under reduced pressure. Poly(ethylene glycol) monomethyl ether (MeO-PEG, M_n = 550 g mol^{-1}, abcr), poly(ethylene glycol) monomethyl ether (MeO-PEG, M_n = 2000 g mol^{-1}, Fluka), 4-(dimethylamino)pyridine (DMAP, abcr), N,N'-dicyclohexylcarbodiimide (DCC, Acros), 2-bromo-2-methylpropionyl bromide (98%, Aldrich), THF (extra dry, over molecular sieves, Acros), 2,2'-bipyridyl (bpy, ≥99%, Sigma-Aldrich), N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDETA, Merck), copper(II) bromide (≥99%, Fluka), nickelocene (NiCp₂, 99%, Strem Chemicals), sodium iodide (≥99%, Fluka), and triphenylphosphine (Merck) were used as received.

Characterization. ¹H NMR spectroscopy was performed using a Bruker AM 400 spectrometer at 400 MHz for hydrogen nuclei. All samples were dissolved in CDCl₃. The δ-scale is referenced to tetramethylsilane as internal standard.

Size Exclusion Chromatography. For the determination of molecular weight distributions (MWD), an SEC system (Polymer Laboratories PL-GPC 50 Plus) comprising an autoinjector and a guard column (PLgel Mixed C, 50 × 7.5 mm) followed by three linear columns (PLgel Mixed C, 300 × 7.5 mm, 5 μm bead size) and a differential refractive index detector was employed. THF was used as the eluent at 40 °C with a flow rate of 1 mL min^{-1}. The SEC system was calibrated using linear polystyrene standards ranging from 160 to 6 × 10⁶ g mol^{-1} and linear poly(methyl methacrylate) standards ranging from 700 to 2 × 10⁶ g mol^{-1}. The resulting molecular weight distributions were determined by universal calibration using Mark−Houwink parameters for PS (K = 14.1 × 10^{-5} dL g^{-1}, α = 0.70),[40] PMMA (K = 12.8 × 10^{-5} dL g^{-1}, α = 0.69),[41] and P*t*BA (K = 19.7 × 10^{-5} dL g^{-1}, α = 0.66).[42]

SEC/ESI-MS spectra were recorded on an LXQ mass spectrometer (ThermoFisher Scientific, San Jose, CA) equipped with an atmospheric pressure ionization source operating in the nebulizer-assisted electrospray mode. The instrument was calibrated in the m/z range 195−1822 using a standard containing caffeine, Met-Arg-Phe-Ala acetate (MRFA), and a mixture of fluorinated phosphazenes (Ultramark 1621) (all from Aldrich). A constant spray voltage of 4.5 kV, a dimensionless sweep gas flow rate of 2, and a dimensionless sheath gas flow rate of 12 were applied. The capillary voltage, the tube lens offset voltage, and the capillary temperature were set to 60 V, 110 V, and 275 °C, respectively. The LXQ was coupled to a Series 1200 HPLC-system (Agilent, Santa Clara, CA) consisting of a solvent degasser (G1322A), a binary pump (G1312A), and a high-performance autosampler (G1367B), followed by a thermostated column compartment (G1316A). Separation was performed on two mixed bed size exclusion chromatography columns (Polymer Laboratories, Mesopore 250 × 4.6 mm, particle diameter 3 μm) with precolumn (Mesopore 50 × 4.6 mm) operating at 30 °C. THF at a flow rate of 0.30 mL min^{-1} was used as eluent. The mass spectrometer was coupled to the column in parallel to an RI-detector (G1362A with SS420x A/D) in a setup described previously.[43] 0.27 mL min^{-1} of the eluent was directed through the RI detector, and 30 μL min^{-1} was infused into the electrospray source after postcolumn addition of a 100 μM solution of sodium iodide in methanol at 20 μL min^{-1} by a microflow HPLC syringe pump (Teledyne ISCO, Model 100DM). 20 μL of a polymer solution with a concentration of ~3 mg mL^{-1} was injected onto the HPLC system.

Synthesis of Maleimide-Functionalized Poly(*tert*-butyl acrylate) (P*t*BA-Mal). *tert*-Butyl acrylate (*t*BA), initiator (**1**), copper(I) bromide (CuBr), and PMDETA were added to a round-bottom flask in the ratio 100/1/1/1. Nitrogen was then percolated through the mixture for 30 min to remove residual oxygen. The mixture was subsequently sealed under nitrogen and placed in a thermostated oil bath set to 40 °C. After 6 h, the polymerization was stopped by cooling the mixture in an ice bath and exposure to oxygen. The mixture was then diluted with THF and passed through a short column of neutral alumina to remove the copper catalyst. Subsequently, the solvent and residual monomer were removed under reduced pressure. The polymer was redissolved in toluene and refluxed for 6 h. The toluene was removed under reduced pressure, and the polymer was dried under high vacuum. GPC (THF): M_n = 1800 g mol^{-1}, PDI = 1.23. ¹H NMR (400 MHz, CDCl₃, δ/ppm): 6.71 (s, vinylic), 4.20−4.07 (m, NCH₂*CH₂*OC=O), 3.78−3.70 (m, NC*H₂*CH₂OC=O), 2.25−1.00 (m, P*t*BA).

Synthesis of Maleimide-Functionalized Poly(ethylene glycol) (PEG-Mal). A solution of DCC (562 mg, 2.72 mmol) in 3 mL of CH₂Cl₂ was added to a solution of MeO-PEG (M_n = 550 g mol^{-1}) (1.00 g, 1.81 mmol), DMAP (221 mg, 1.81 mmol), and **2** (842 mg, 2.72 mmol) in 5 mL of CH₂Cl₂. The reaction mixture was stirred overnight at ambient temperature. The mixture was filtered, washed with saturated NaHCO₃-solution, dried over MgSO₄, and the solvent was removed under reduced pressure. The residue was dissolved in toluene, filtered, and refluxed for 6 h. The toluene was removed under reduced pressure and the polymer was dried under high vacuum. ¹H NMR (400 MHz, CDCl₃, δ/ppm): 6.71 (s, vinylic), 4.24−4.20 (m, NCH₂*CH₂*OC=O), 3.78−3.51 (m, PEG backbone), 3.36 (s, PEG−OC*H₃*), 2.61−2.56 (C=OC*H₂*-*CH₂*C=O).

Synthesis of Alkyne-Functionalized Poly(ethylene glycol) (PEG-Alkyne). MeO-PEG (M_n = 2000 g mol^{-1}) (2.00 g, 1.00 mmol), 4-pentynoic acid (294 mg, 3.00 mmol), and DMAP (24.4 mg, 0.20 mmol) were dissolved in 15 mL of CH₂Cl₂. The resulting mixture was cooled to 0 °C, and a solution of DCC (619 mg, 3.00 mmol) 5 mL of CH₂Cl₂ was added dropwise. After the addition, the stirred mixture was allowed to warm to ambient temperature and allowed to continue stirring at this temperature for 20 h. The formed precipitate was removed by filtration, and the polymer was recovered from the filtrate by 2-fold precipitation in cold diethyl ether.

Synthesis of 2-(4-Benzoyl-2,5-dimethylphenoxy)ethyl 2-Bromo-2-methylpropanoate (4). Compound **3** (0.800 mmol, 216 mg) and triethylamine (1.1 equiv, 0.880 mmol, 89.0 mg) were dissolved in dry THF (5 mL) and cooled to 0 °C. 2-Bromo-2-methylpropionyl

Scheme 1. Synthesis of α-2,5-Dimethylbenzophenone-ω-cyclopentadienyl Functional Polystyrene and Poly(methyl methacrylate)
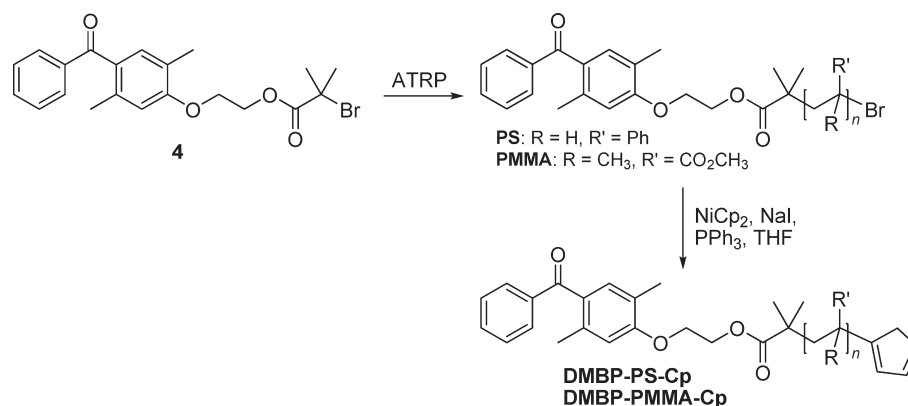
bromide (1.04 eq, 0.832 mmol, 191 mg), dissolved in THF (3 mL), was added slowly dropwise to the solution under stirring. The suspension was stirred at 0 °C for 3 h and then allowed to reach ambient temperature overnight. The formed salt was removed by filtration, and the solvent was removed under reduced pressure. The residue was dissolved in DCM (5 mL), washed three times with 10% KOH (10 mL) solution, and subsequently filtered by passing through a column filled to 5 cm with silica (hexane:ethyl acetate, 2:1). The organic phase was dried over Na_2SO_4 and evaporated at reduced pressure to give the pure product as a pale yellow solid (98% yield). ^1H NMR (CDCl$_3$, 250 MHz) δ/ppm: 1.66 (bs, 1H, OH), 2.13 (s, 3H, CH$_3$), 2.30 (s, 3H, CH$_3$), 3.94 (t, J = 4.14 Hz, 2H, CH$_2$), 4.10 (t, J = 4.20 Hz, 2H, CH$_2$), 6.66 (s, 1H, ArH), 7.10 (s, 1H, ArH), 7.35–7.41 (m, 2H, ArH), 7.46–7.53 (m, 1H, ArH), 7.68–7.72 (m, 2H, ArH).

Synthesis of 2,5-Dimethylbenzophenone-Functionalized Polystyrene (DMBP-PS-Br). In a 25 mL Schlenk tube a mixture of styrene, initiator (**4**), copper(I) bromide (CuBr), copper(II) bromide (CuBr$_2$), and PMDETA in the ratio 200/1/1.02/0.21/1.22 was deoxygenated by three consecutive freeze–pump–thaw cycles and left under nitrogen. The Schlenk tube was placed in a thermostatted oil bath held at 80 °C. After a predetermined time the polymerization was stopped by cooling the mixture in an ice bath and exposure to oxygen. After dilution with THF, the mixture was passed through a short column of neutral alumina to remove the copper catalyst. Poly(styrene) was isolated by 2-fold precipitation in cold methanol. DMBP-PS(A)-Br: polymerization time 2.5 h, M_n(THF-SEC) = 2400 g mol^{-1}, PDI = 1.06. DMBP-PS(B)-Br: polymerization time 3 h, M_n(THF-SEC) = 3200 g mol^{-1}, PDI = 1.06.

Synthesis of 2,5-Dimethylbenzophenone-Functionalized Poly(methyl methacrylate) (DMBP-PMMA-Br). Methyl methacrylate (MMA), initiator (**4**), copper(I) bromide (CuBr), copper(II) bromide (CuBr$_2$), and 2,2′-bipyridine (bpy) were added to a round-bottom flask in the ratio 100/1/0.105/0.01250/0.25. Acetone was subsequently added such that the resulting mixture contained 50 vol % acetone. Nitrogen was subsequently percolated through the mixture for 30 min to remove residual oxygen. The mixture was subsequently sealed under nitrogen and placed in a thermostated oil bath set to 50 °C. After 2.5 h, the polymerization was stopped by cooling the mixture in an ice bath and exposure to oxygen. The mixture was then passed through a short column of neutral alumina to remove the copper catalyst. PMMA was isolated by 2-fold precipitation in cold n-hexane and dried under high vacuum. GPC (THF): M_n = 3200 g mol^{-1}, PDI = 1.14.

Synthesis of α-2,5-Dimethylbenzophenone-ω-cyclopentadienyl Functional Polymers (DMBP-PS-Cp and DMBP-PMMA-Cp). A solution of bromine-terminated polymer (DMBP-Ps-Br or DMBP-PMMA-Br) (0.18 mmol), triphenylphosphine (0.36 mmol, 2 equiv), and sodium iodide (1.08 mmol, 6 equiv) in anhydrous THF

(2.0 mL) was prepared under a nitrogen atmosphere. Separately, a stock solution of NiCp$_2$ in anhydrous THF (0.18 mol L^{-1}) was prepared under a nitrogen atmosphere. The NiCp$_2$ solution (2.0 mL, 4 equiv) was then added to the polymer solution and allowed to stir overnight at ambient temperature. At the end of the reaction, the mixture was passed through a short column of alumina to remove the precipitated nickel(II) bromide, and the polymer was recovered by 2-fold precipitation in cold methanol (for PS) or n-hexane (for PMMA) and dried under high vacuum.

Synthesis of α-2,5-Dimethylbenzophenone-ω-azide Functional Polystyrene (DMBP-PS-N$_3$). DMBP-PS(B)-Br (0.06 mmol, 200 mg) and NaN$_3$ (0.56 mmol, 36 mg) were dissolved in DMF (10 mL) and stirred overnight at ambient temperature. DMBP-PS-N$_3$ was isolated by 2-fold precipitation in methanol.

One-Pot Synthesis of ABA Triblock Copolymers (PtBA-b-PS-b-PtBA and PtBA-b-PMMA-b-PtBA). α-DMBP-ω-Cp functionalized polymer (10 μmol) and PtBA-Mal (20 μmol) were weighted in a vial (Pyrex, diameter 20 mm), crimped airtight, and flushed with nitrogen. Degassed DCM (2 mL) was injected and the reaction mixture stirred for 12 h. The solution was subsequently irradiated for 2 h by revolving around a 36 W compact low-pressure UV-A fluorescent lamp (Arimed B6, Cosmedico GmbH, Stuttgart, Germany; see Supporting Information for a schematic drawing) emitting at 320 nm (±30 nm) at a distance of 40–50 mm in a custom-built photoreactor. The triblock copolymers were precipitated in methanol (PS middle block) or n-hexane (PMMA middle block).

Synthesis of PEG-b-PS-PtBA via Consecutive Thermal and Photoinduced Diels–Alder Reactions. A solution of DMBP-PS-Cp (10 μmol) and PEG-Mal (11 μmol) in CH$_2$Cl$_2$ (2 mL) was stirred in the dark overnight, and the resulting block copolymer was precipitated in methanol. The photoinduced formation of PEG-b-PS-b-PtBA was performed in the same way described for the ABA triblock copolymers using 1 equiv of PtBA-Mal.

Synthesis of PEG-b-PS-b-PtBA via Consecutive CuAAc and Photoinduced Diels–Alder Reactions. DMBP-PS-N$_3$ (10 μmol), PEG-Alkyne (10 μmol), and CuBr (11 μmol) were added to a Schlenk tube which was then sealed with a septum, evacuated, and backfilled with nitrogen. In another Schlenk tube a mixture of DMF (3 mL) and PMDETA (11 μmol) was deoxygenated by three freeze–pump–thaw cycles and subsequently transferred to the Schlenk tube containing the polymers and CuBr via cannula. The reaction mixture was stirred overnight at ambient temperature. The solution was passed through a short column of neutral alumina to remove the copper catalyst and the DMF was removed under reduced pressure. The residue was dissolved in CH$_2$Cl$_2$ and precipitated in n-hexane. The resulting PEG-b-PS was reacted with 1 equiv of PtBA in the photoreactor as described above.
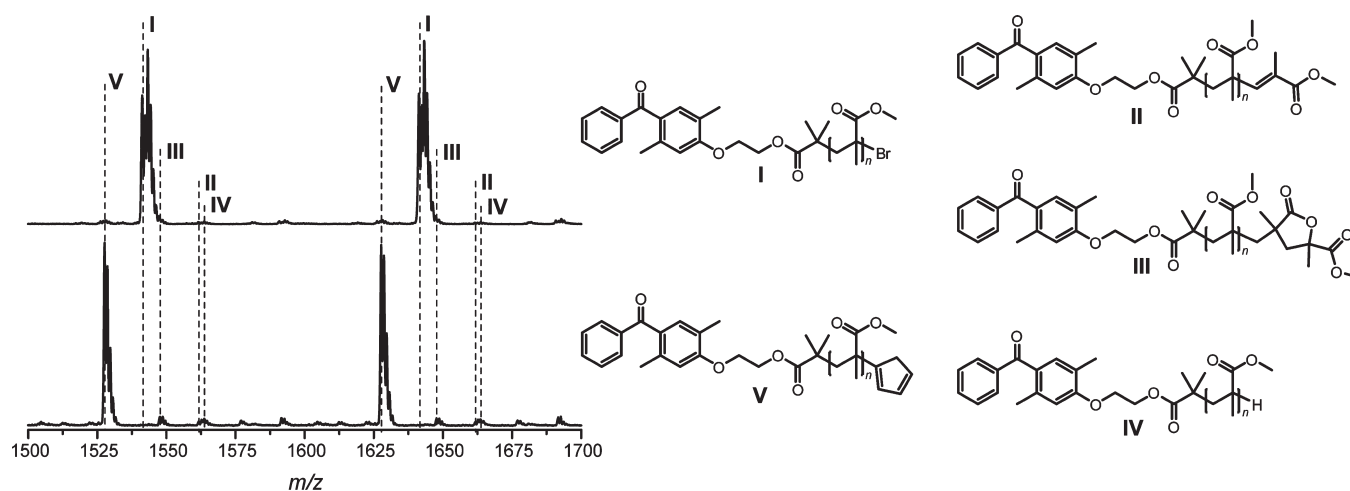
Figure 1. Expanded region of a typical repeat unit in the SEC/ESI-MS spectra of DMBP-PMMA-Br precursor (top) and the resulting DMBP-PMMA-Cp (bottom).

Table 1. Theoretical and Measured Mass-to-Charge Ratios of the Main Species Involved in the Synthesis of DMBP-PMMA-Cp

| structure | $[M + Na]^+$ | | |
	m/z_{theo}	m/z_{meas}	$\Delta m/z$
I	1541.64	1541.33	0.31
II	1561.77	1561.75	0.02
III	1547.76	1547.67	0.09
IV	1563.79	1563.67	0.12
V	1527.77	1527.67	0.10

■ RESULTS AND DISCUSSION

To enable the synthesis of various 2,5-dimethylbenzophenone functional polymers, the hydroxyl functional precursor **3**, which was used as ROP initiator in a previous study,[37] was reacted with 2-bromo-2-methylpropionyl bromide to give the ATRP initiator **4**. Highly functional α-2,5-dimethylbenzophenone-ω-bromine PS (DMBP-PS-Br) and PMMA (DMBP-PMMA-Br) were synthesized via ATRP utilizing **4** as initiator as depicted in Scheme 1.

The bromine end-group was subsequently converted to a cyclopentadienyl (Cp) functionality employing the previously reported nickelocene method,[44] yielding α-2,5-dimethylbenzophenone-ω-cyclopentadienyl telechelic polymers. Monitoring of the transformation by size exclusion chromatography/electrospray ionization-mass spectrometry (SEC/ESI-MS) (see Figure 1) shows that DMBP-PMMA-Cp is obtained with high functionality and only small amounts of impurities which can be assigned to inescapable side products of the ATRP process.[45]

The theoretical and measured mass-to-charge ratios of the involved species collated in Table 1 are in excellent agreement within experimental error.

In the case of PS the success of the reaction sequence is confirmed by ^{1}H NMR spectroscopy (see Figure S1 in the Supporting Information). We have shown in a previous study[37] that 2,5-dimethylbenzophenone functional polymers undergo a rapid Diels−Alder reaction with maleimide functional polymers via the UV-light induced *in situ* formation of *o*-quinodimethanes. These species act as highly reactive dienes in the [4 + 2]
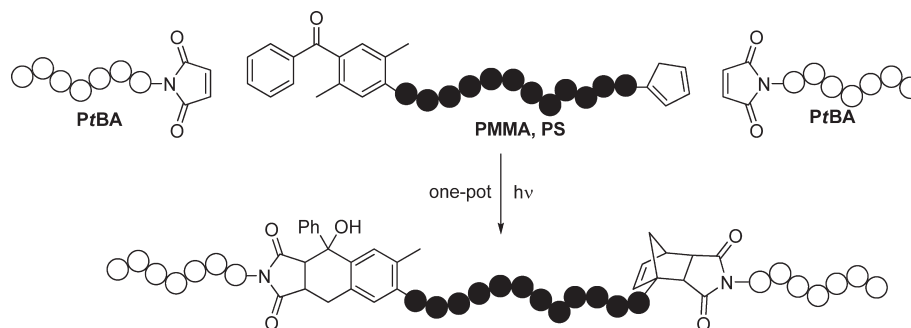
cycloaddition. It is known that maleimides undergo a fast Diels−Alder reaction with cyclopentadiene at ambient temperature.[46] Thus, the combination of photoinduced and thermal Diels−Alder reactions permits an efficient one-pot synthesis of ABA triblock copolymers at ambient temperature as displayed in Scheme 2.

Maleimide-capped P*t*BA (P*t*BA-Mal) (see Scheme 3 for the exact structure) was synthesized by ATRP employing a furan protected maleimide functional initiator (**1**) and subsequent deprotection in refluxing toluene. Maleimide functional PEG (PEG-Mal) (see Scheme 3 for the exact structure) was obtained from commercially available MeO-PEG via esterification with the carboxylic acid functional protected maleimide derivative (**2**), followed by deprotection as described for P*t*BA.
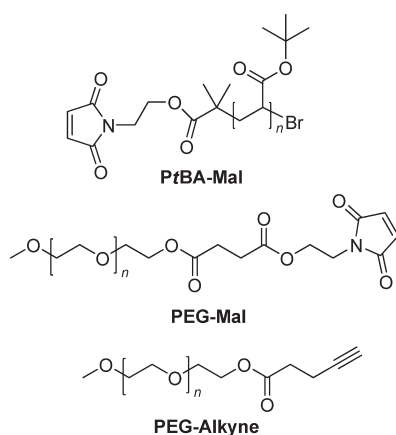
The one-pot synthesis of P*t*BA-*b*-PS-*b*-P*t*BA and P*t*BA-*b*-PMMA-*b*-P*t*BA was performed by stirring a deoxygenated solution of α-DMBP-ω-Cp functional polymer and 2 equiv of P*t*BA-Mal in CH$_2$Cl$_2$ for 12 h at ambient temperature. After this time, a sample for SEC analysis was taken and subsequent irradiation for 2 h with a 36 W compact fluorescent lamp (λ_{max} = 320 nm) was performed, followed by precipitation of the resulting triblock copolymer in methanol (for PS middle block) or *n*-hexane (for PMMA middle block). It was shown in our previous study that 2 h irradiation time is sufficient to achieve complete polymer−polymer conjugation. Figure 2 shows the SEC traces of the macromolecular building blocks, the resulting triblock copolymers, and the samples taken before irradiation.

Inspection of Figure 2a shows a clear shift to lower retention times after reaction at ambient temperature and a further shift to lower retention times after irradiation with UV-light indicating the formation of ABA triblock copolymer (thus the SEC traces are showing the expected double shift). The shoulder at higher retention times in the SEC trace before irradiation is due to the remaining second equivalent of P*t*BA. The same observations can be made when PS is acting as middle block (see Figure 2b). Close inspection of the sample taken before irradiation in the case of PS reveals a shoulder at lower retention times that can be explained by ambient-light-induced formation of P*t*BA-*b*-PS-*b*-P*t*BA. The observation that the Diels−Alder reaction between 2,5-dimethylbenzophenone precursors and maleimides can be triggered by ambient light was already

Scheme 2. One-Pot Synthesis of ABA Triblock Copolymers via Photoinduced and Thermal Diels–Alder Reactions

Scheme 3. Alkyne and Maleimide Functional Polymers Used in the Present Work

Figure 2. Overlay of SEC traces showing the one-pot formation of triblock copolymers (a) P*t*BA-*b*-PMMA-*b*-P*t*BA from P*t*BA-maleimide and DMBP-PMMA-Cp and (b) P*t*BA-*b*-PS-*b*-P*t*BA from P*t*BA-maleimide and DMBP-PS-Cp. Efficient block formation was achieved after 2 h irradiation time.

described in our previous publication.[37] Number-average molecular weights and polydispersities of the macromolecular building blocks and the final ABA triblock copolymers are collated in Table 2. The number-average molecular weights of the triblock copolymers should, however, be treated with care as they are based on a linear PMMA and PS calibration and are thus only apparent values.

Thus, to further confirm the structure of the ABA triblock copolymers P*t*BA-*b*-PS-*b*-P*t*BA and their individual building blocks, they were analyzed via ^{1}H NMR spectroscopy. For DMBP-PS(A)-Cp the number-average molecular weight was calculated by integration of the backbone signals relative to the signals according to the DMBP end-group (see Figure S1 in the Supporting Information), resulting in a $M_{n,NMR}$ (DMBP-PS(A)-Cp) of 3100 g mol^{-1}. Comparison of the vinylic maleimide signals with the P*t*BA backbone gives an $M_{n,NMR}$ (P*t*BA-Mal) = 1500 g mol^{-1}. Thus, the theoretical ratio of PS repeat units, n(PS), to P*t*BA repeat units, n(P*t*BA), is n(PS)/n(P*t*BA) = 1.30 for the ABA triblock copolymer. The experimental result n(PS)/n(P*t*BA) = 1.39 obtained from the ^{1}H NMR spectrum depicted in Figure 3 is very close to the theoretical value for the ABA triblock copolymer, thus underpinning the formation of P*t*BA-*b*-PS-*b*-P*t*BA.

The fact that Diels–Alder reactions of the DMBP moiety are fully suppressed when the compounds are handled in the dark can be utilized for the modular construction of ABC triblock copolymers via consecutive thermal and photoinduced Diels–Alder reactions as illustrated in Scheme 4.
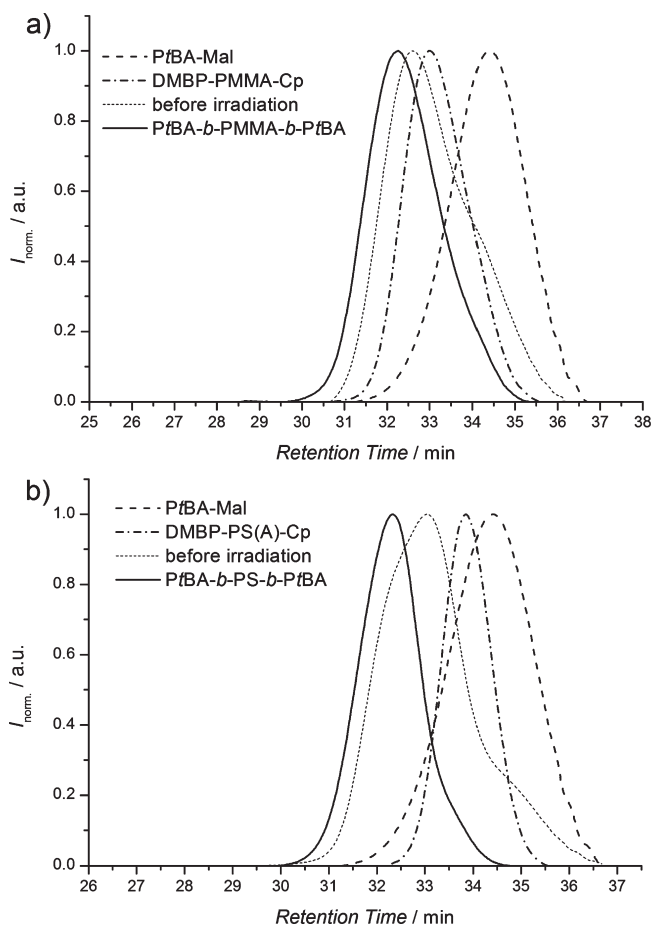
To investigate the combination of photochemically and thermally induced Diels–Alder reactions, a solution of DMBP-PS(B)-Cp and PEG-Mal in CH$_2$Cl$_2$ was initially stirred overnight in the dark, and the resulting PEG-*b*-PS was subsequently irradiated with UV-light for 2 h in the presence of an equimolar amount of P*t*BA-Mal, yielding the triblock copolymer PEG-*b*-PS-*b*-P*t*BA. SEC traces of the starting materials, the diblock copolymer PEG-*b*-PS, and the triblock copolymer PEG-*b*-PS-*b*-P*t*BA are depicted in Figure 4.

Table 2. SEC Characterization of the Macromolecular Building Blocks and the Final ABA Triblock Copolymers Prepared in a One-Pot Reaction

	$M_{n,SEC}/g\ mol^{-1}$	PDI
DMBP-PMMA-Cp[a]	3200	1.14
DMBP-PS(A)-Cp[b]	2400	1.06
PtBA-Mal[c]	1800	1.23
PtBA-b-PMMA-b-PtBA[a]	4300	1.21
PtBA-b-PS-b-PtBA[b]	4800	1.09

[a] Relative to linear PMMA standards. [b] Relative to linear PS standards. [c] Values for PtBA-Mal have been corrected by applying the Mark–Houwink parameters of PtBA provided in the Experimental Section.
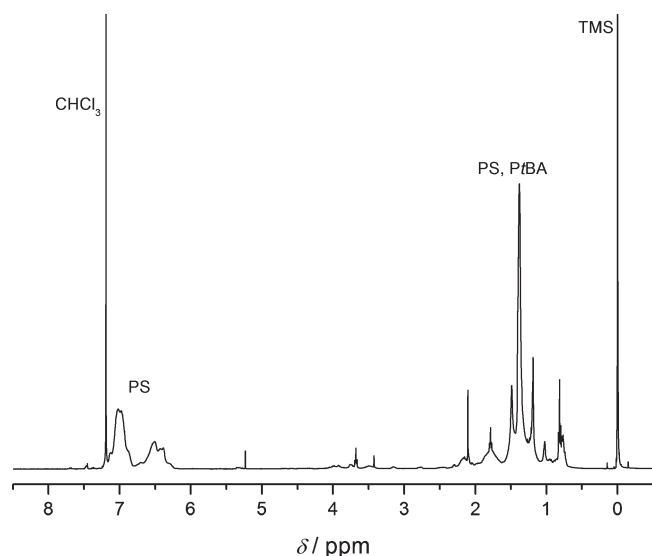
Figure 3. ^1H NMR spectrum of PtBA-b-PS-b-PtBA in CDCl₃.

The SEC chromatogram after reaction in the dark is shifted to lower retention times, indicating the formation of PEG-b-PS. The efficient formation of PEG-b-PS-b-PtBA triblock copolymer is indicated by an additional shift to lower retention times after the UV-light triggered reaction with PtBA-Mal. A unimodal and narrow molecular weight distribution results devoid of any tail assignable to the starting materials. Estimated M_n values and PDIs for the building blocks and the copolymers are given in Table 3.

The formation of the triblock copolymer PEG-b-PS-b-PtBA is further confirmed by the calculated number-average molecular weight (M_n = 5200 g mol^{-1}) which is close to the sum of the individual building blocks (5800 g mol^{-1}) estimated via SEC.

Utilizing CuAAc click chemistry as first conjugation method renders it unnecessary to perform the construction of the AB block copolymer in the dark. α-2,5-Dimethylbenzophenone-ω-azide-functionalized PS (DMBP-PS-N₃) was thus synthesized by nucleophilic substitution of the bromine end-group with sodium azide and employed for the modular construction of PEG-b-PS-b-PtBA triblock copolymer via consecutive CuAAc and photo-induced Diels–Alder reactions as shown in Scheme 5.

Figure 5 depicts the SEC elugrams of the macromolecular building blocks and the resulting di- and triblock copolymers. Inspection of Figure 5 shows a clear shift to lower retention times for the CuAAc product and a further shift after the UV light-triggered reaction with PtBA-Mal, indicating the formation of PEG-b-PS-b-PtBA. The SEC elugram of the di- and triblock copolymers indicates only a very small shoulder that can be assigned to PEG as remaining PS would have undergone photo-induced conjugation to PtBA forming PS-b-PtBA which is not observed in the SEC elugram of the final product. The estimated molecular weights collated in Table 4 in are in good agreement with the sum of the individual building blocks, keeping in mind that the M_n values of the block polymers are decreased by a small shoulder due to remaining PEG.

To independently confirm the molecular weight of the polymers and thus the synthetic success, PEG-b-PS-b-PtBA was

Scheme 4. Synthetic Strategy for the Modular Construction of ABC Triblock Copolymer (PEG-b-PS-b-PtBA) via Consecutive Thermally Induced and Photoinduced Diels–Alder Reactions
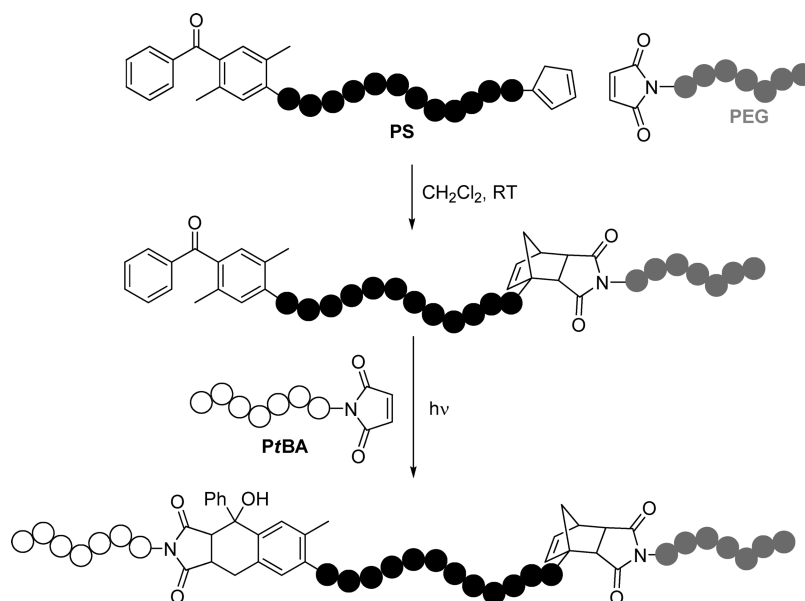
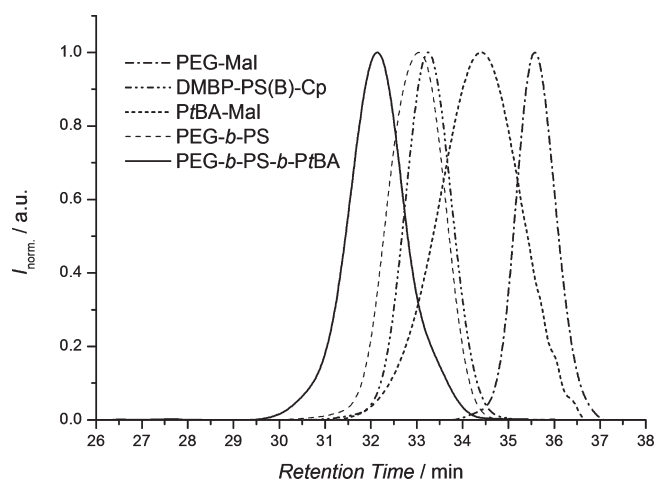**Figure 4.** Overlay of SEC traces showing the modular formation of PEG-*b*-PS and PEG-*b*-PS-*b*-P*t*BA from PEG-Mal, DMBP-PS(B)-Cp, and P*t*BA-Mal. Efficient triblock formation was achieved after 2 h irradiation time at ambient temperature.

Table 3. SEC Derived Molecular Weight Data of the Macromolecular Building Blocks and the Block Copolymers Resulting from the Modular Formation of PEG-*b*-PS and PEG-*b*-PS-*b*-P*t*BA from PEG-Mal, DMBP-PS(B)-Cp, and P*t*BA-Mal

	$M_{n,SEC}{}^a$/g mol^{-1}	PDI
PEG-Mal	800	1.09
DMBP-PS(B)-Cp	3200	1.06
P*t*BA-Mal	1800	1.23
PEG-*b*-PS	3700	1.07
PEG-*b*-PS-*b*-P*t*BA	5200	1.10

^{a} Relative to linear PS standards. Values for P*t*BA-Mal have been corrected by applying the Mark—Houwink parameters provided in the Experimental Section.

analyzed via ^{1}H NMR spectroscopy (see Figure 6). The number-average molecular weight of the triblock copolymer was calculated from the ratio of the integrated signal at 3.36 ppm (OCH$_3$ end-group of PEG) to the PEG, PS, and P*t*BA backbone signals. $M_{n,NMR}$(PEG-*b*-PS-*b*-P*t*BA) = 6300 g mol^{-1} is in excellent agreement with the sum of values of the individual segments (6800 g mol^{-1}) within experimental error.

■ **CONCLUSIONS**

Photoinduced Diels—Alder reactions were combined with thermal Diels—Alder reactions and azide—alkyne click chemistry for the modular ambient temperature synthesis of ABA and ABC triblock copolymers. Highly functional precursors were synthesized via ATRP. The present approach demonstrates for the first time the orthogonality of the novel photo-triggered conjugation
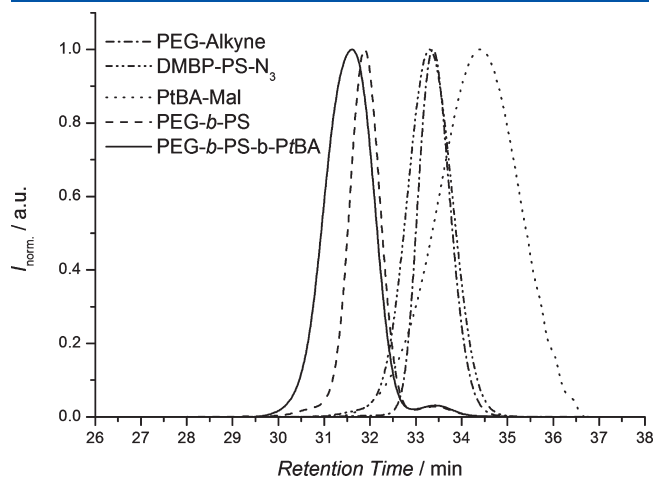

Figure 5. Overlay of SEC traces showing the modular formation of PEG-*b*-PS and PEG-*b*-PS-*b*-P*t*BA from PEG-Alkyne, DMBP-PS-N$_3$, and P*t*BA-Mal. Efficient triblock formation was achieved after 2 h irradiation time.

Scheme 5. Synthetic Strategy for the Modular Construction of ABC Triblock Copolymer (PEG-*b*-PS-*b*-P*t*BA) via Consecutive CuAAc and Photoinduced Diels—Alder Reactions
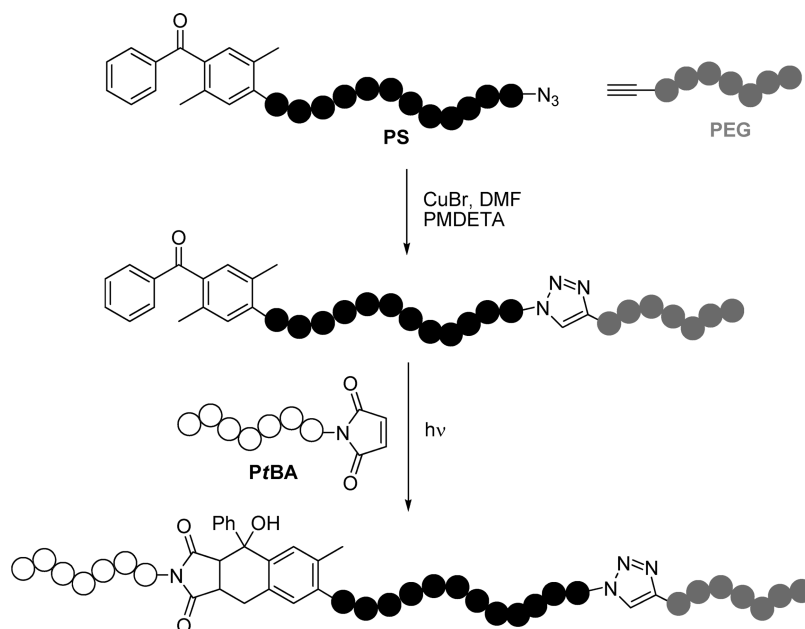
Table 4. SEC and ^{1}H NMR Characterization of the Macromolecular Building Blocks and the Resulting Block Copolymers of the Modular Formation of PEG-*b*-PS and PEG-*b*-PS-*b*-P*t*BA from PEG-Alkyne, DMBP-PS-N₃, and P*t*BA-Mal

	$M_{n,SEC}{}^{a}$/g mol^{-1}	$M_{n,NMR}$/g mol^{-1}	PDI
PEG-Alkyne	3000	2200	1.03
DMBP-PS-N₃	3200	3100	1.06
P*t*BA-Mal	1800	1500	1.23
PEG-*b*-PS	5800		1.05
PEG-*b*-PS-*b*-P*t*BA	6700	6300	1.07

[a] Relative to linear PS standards. Values for P*t*BA have been corrected by applying the Mark—Houwink parameters provided in the Experimental Section.
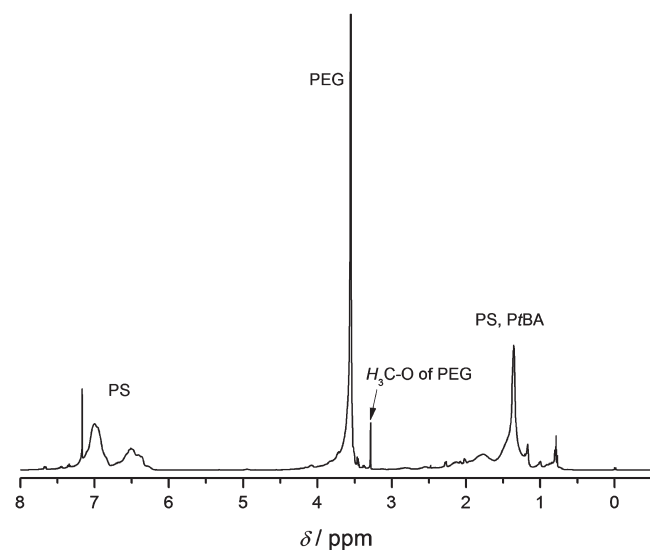

Figure 6. ^{1}H NMR spectrum of PEG-*b*-PS-*b*-P*t*BA in CDCl₃.

method[37] to other well-established click methodologies. The high photoreactivity of the employed *o*-quinodimethane-functionalized macromolecules allows efficient block formation in stoichiometric systems,[14] within 2 h reaction time at ambient temperature for the currently investigated polymers. The use of low intensity and soft UV—B irradiation from a low-cost light source or even ambient light to induce conjugation makes this protocol easy to implement in the organic laboratory.

ASSOCIATED CONTENT

Ⓢ Supporting Information. Additional ^{1}H NMR and SEC/ESI-MS spectra, an emission spectrum of the Arimed B6 compact fluorescent lamp, and a UV spectrum of (4-(2-hydroxyethoxy)-2,5-dimethylphenyl)phenylmethanone (**3**). This material is available free of charge via the Internet at http://pubs.acs.org.

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