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Anthracene−Maleimide-Based Diels−Alder "Click Chemistry" as a Novel Route to Graft Copolymers

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ABSTRACT: Using the Diels−Alder (DA) "click chemistry" strategy between anthracene and maleimide functional groups, two series of well-defined polystyrene-*g*-poly(ethylene glycol) (PS-*g*-PEG) and polystyrene-*g*-poly(methyl methacrylate) (PS-*g*-PMMA) copolymers were successfully prepared. The whole process was divided into two stages: (i) preparation of anthracene and maleimide functional polymers and (ii) the use of Diels−Alder reaction of these groups. First, random copolymers of styrene (S) and chloromethylstyrene (CMS) with various CMS contents were prepared by the nitroxide-mediated radical polymerization (NMP) process. Then, the choromethyl groups were converted to anthryl groups via the etherifaction with 9-anthracenemethanol. The other component of the click reaction, namely protected maleimide functional polymers, were prepared independently by the modification of commercially available poly(ethylene glycol) (PEG) and poly(methyl methacrylate) (PMMA) obtained by atom transfer radical polymerization (ATRP) using the corresponding functional initiator. Then, in the final stage PEG and PMMA prepolymers were deprotected by retro-Diels−Alder in situ reaction by heating at 110 °C in toluene. The recovered maleimide groups and added anthryl functional polystyrene undergo Diels−Alder reaction to form the respective (PS-*g*-PEG) and (PS-*g*-PMMA) copolymers. The graft copolymers and the intermediates were characterized in detail by using ^{1}H NMR, GPC, UV, fluorescence, DSC, and AFM measurements.

Introduction

Nowadays there is a considerable interest not only in the synthesis of new types of polymeric materials but also in the modification of existing polymers in order to alter their properties to meet requirements for new applications.[1] One of the methods for modification is the grafting reaction, which provides an opportunity to vary physical and chemical properties of polymers. Graft copolymers can be obtained with three general methods: (i) grafting-onto, in which side chains are preformed and then attached to the backbone; (ii) grafting-from, in which the monomer is grafted from the backbone; and (iii) grafting-through, in which the macromonomers are copolymerized.[2,3]

The Diels−Alder reaction (DA), [4 + 2] system, generally consists of a coupling of a diene and a dienophile by intra- or intermolecular reaction.[4] Recently, DA reaction based on the macromolecular chemistry has attracted much attention, particularly for providing new materials.[5−14] As an alternative route, recently, 1,3-dipolar cycloadditions, such as reactions between azides and alkynes or nitriles, named "click reaction",[15,16] have been applied to macromolecular chemistry, offering molecules ranging from the block copolymers[17] to the complexed macromolecular structures.[18−25] Both DA and 1,3-dipolar cycloaddition reactions enabled the C−C bond formation in a quantitative yield without side reaction and requirement for an additional purification step.

The study presented in this paper is aimed at describing the anthracene−maleimide-based DA "click reaction" as a novel route to prepare well-defined graft copolymers. Scheme 1 outlines our synthetic strategy to this various phases of this work, viz., (i) preparing random copolymers of styrene (St) and 4-chloromethylstyrene (CMS) (which is a functionalizable monomer); (ii) attachment of anthracene functionality to the preformed copolymer by the *o*-etherification procedure; (iii) by using efficient DA "click chemistry", maleimide-functionalized poly(methyl methacrylate) (PMMA−MI) via ATRP of MMA or poly(ethylene glycol) (PEG−MI) via modification of commercial PEG was introduced into copolymers bearing pendant anthryl moieties. The details of these procedure and the results obtained are discussed below.

Experimental Section

Materials. Styrene (St, 99%, Aldrich) and 4-chloromethylstyrene (CMS, ca. 60/40 meta/para isomer mixture, 97%, Aldrich) were distilled under reduced pressure before use. 2,2′-Azobis(isobutyronitrile) (AIBN, 98%, Aldrich) was recrystallized from ethanol. *N*,*N*′-Dicyclohexylcarbodiimide (DCC, 99%, Aldrich), 2,6-di-*tert*-butyl-4-methylphenol (BHT, 99%, Aldrich), 4-(dimethylamino)-pyrridine (DMAP, 99%, Aldrich), and 2,2,6,6-tetramethylpiperidine-*N*-oxyl free radical (TEMPO, 99%, Aldrich) were used as received. *N*,*N*,*N*′,*N*″,*N*″-Pentamethyldiethylenetriamine (PMDETA, Aldrich) was distilled over NaOH prior to use. Poly(ethylene glycol) methyl ether (Me-PEG, Acros) was dried over anhydrous toluene by azeotropic distillation. Tetrahydrofuran (THF, 99.8%, J.T. Baker) was dried and distilled over benzophenone−Na. Other solvents were purified by conventional procedures. All other reagents were purchased from Aldrich and used as received. 4-(Dimethylamino)-pyridinium 4-toluenesulfonate (DPTS) was obtained according to a published procedure.[26]

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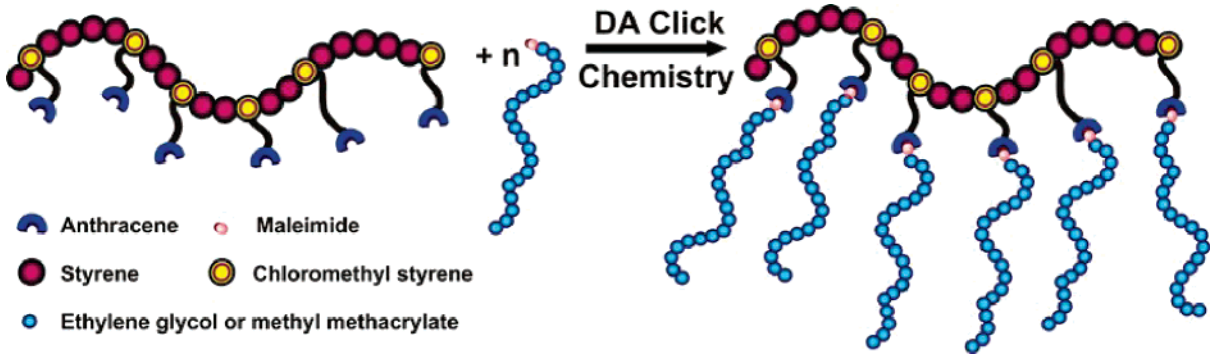
Scheme 1. General Presentation of Grafting Process by Diels−Alder "Click Chemistry"



Instrumentation. The ^{1}H and ^{13}C NMR spectra of the samples were recorded by using a Bruker NMR spectrophotometer (250 MHz for proton and 62.89 MHz for carbon) in $CDCl_3$. Molecular weights were determined using a gel permeation chromatography (GPC) instrument equipped with a Waters Styragel column (HR series 2, 3, 5E) with THF as eluent at a flow rate of 0.3 mL/min, and a Waters 410 differential refractometer was used as detector. Differential scanning calorimetry (DSC) was performed on Perkin-Elmer Diamond DSC with a heating rate of 10 °C/min under nitrogen flow. UV spectra were recorded on a Shimadzu UV-1601 spectrophotometer. Fluorescence spectra were obtained by using a Perkin-Elmer LS 50 luminescence spectrophotometer. NT-MDT Solver P47 atomic force microscopy (AFM) was used in tapping mode for morphological characterization. Ultrasharp Si cantilevers having force constant of 48 N/m were used.

Syntheses and Polymerizations. 3-Acetyl-*N*-(2-hydroxyethyl)-7-oxabicyclo[2.2.1]hept-5-ene-2-carboxamide (**1**) and 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 (**2**) were synthesized as described in the literature.[27]

Synthesis of 4-(2-{[(3-Acetyl-7-oxabicyclo[2.2.1]hept-5-en-2-yl)carbonyl]amino}ethoxy)-4-oxobutanoic Acid (3). For synthesis of compound **3**, the above-obtained compound, 5.0 g of compound **1** (23.9 mmol) was dissolved in 150 mL of 1,4-dioxane. To this solution Et_3N (16.58 mL, 119.6 mmol) and DMAP (4.4 g, 35.8 mmol) were added. Then, 9.6 g of succinic anhydride (95.6 mmol) was added to this reaction mixture and stirred overnight at 40 °C. The resulting solution was poured into ice-cold water and extracted with CH_2Cl_2. The organic phase was washed with 1 M HCl and was dried over Na_2SO_4 and then concentrated. The crude product was crystallized from ethanol, and white crystalline product was obtained (5.9 g, yield 80%); mp = 122−123 °C (DSC). ^{1}H NMR ($CDCl_3$, δ): 6.50 (s, 2H, C*H*═C*H*, as bridge protons), 5.25 (s, 2H, −C*H*O, bridgehead protons), 4.25 (t, J = 5.2 Hz, 2H, NCH_2CH_2OC═O), 3.74 (t, J = 5.2 Hz, 2H, NCH_2CH_2OC═O), 2.87 (s, 2H, C*H*−C*H*, as bridge protons), 2.66−2.53 (m, 4H, C═OCH_2CH_2C═OOH).

Preparation of PEG−Maleimide (PEG−MI). Me−PEG (M_{na} = 550) (2.0 g, 3.63 mmol) was dissolved in 20 mL of CH_2Cl_2. To the reaction mixture compound **3** (3.4 g, 11 mmol) and DPTS (1.2 g, 3.63 mmol) were added successively. After stirring 5 min at room temperature, a solution of DCC (2.3 g, 11 mmol) in 10 mL of CH_2Cl_2 was added to it. The reaction mixture was stirred overnight at room temperature. After filtration of the salt, the solution was concentrated and the viscous brown color product was purified by column chromatography over silica gel eluting with a CH_2Cl_2/ethyl acetate mixture (1:1, vol/vol) and then with CH_2Cl_2/MeOH (0.95:0.05) to obtain compound **4** as a viscous yellow oil (yield: 2.7 g, 88%). $M_{n,theo}$ = 840; $M_{n,NMR}$ = 850; $M_{n,GPC}$ = 1300; M_w/M_n = 1.01. ^{1}H NMR ($CDCl_3$, δ): 6.50 (s, 2H, C*H*═C*H*), 5.25 (s, 2H, C*H* as bridgehead protons), 4.23 (m, 4H, CH_2OC═O), 3.75−3.51 (m, OCH_2CH_2 repeating unit of PEG, C═ONCH_2, and CH_2−PEG repeating unit), 3.36 (s, 3H, PEG−OCH_3), 2.87 (s, C*H*−C*H*, as bridge protons) 2.61−2.56 (m, 4H, C═OCH_2CH_2C═O).

Preparation of PMMA−Maleimide (PMMA−MI). PMMA−MI was prepared by ATRP of MMA. In a 50 mL Schlenk tube, MMA (10 mL, 93.5 mmol), toluene (10 mL), PMDETA (0.4 mL, 1.87 mmol), CuCl (0.19 g, 1.87 mmol), and **2** (0.67 g, 1.87 mmol) were added, and the reaction mixture was degassed by three freeze−pump−thaw cycles and left in a vacuum. The tube was then placed in an oil bath at 40 °C for 3 h. Afterward, the resulting polymerization mixture was diluted with THF, passed through a basic alumina column to remove the catalyst, and then precipitated into hexane. The polymer obtained was dried for 24 h in a vacuum oven at 30 °C. $[M]_0/[I]_0$ = 50; $[I]_0$:[CuCl]:[PMDETA] = 1:1:1; conversion (%) = 18; $M_{n,theo}$ = 1250; $M_{n,NMR}$ = 2350; $M_{n,GPC}$ = 2100; M_w/M_n = 1.2.

General Procedure for Etherification of Chloromethyl Moieties (8, 30, and 50%) of Poly(styrene-*co*-chloromethylstyrene), P(S-*co*-CMS). P(S-*co*-CMS) copolymers containing various amounts of CMS moieties were prepared via nitroxide-mediated radical polymerization (NMP) of St and CMS at 125 °C.

To a solution of 9-anthracenemethanol (1.1 equiv) in dry 20 mL of THF was added to sodium hydride (60 wt % dispersion in oil) (1.1 equiv), and the reaction mixture was stirred at room temperature under nitrogen for 30 min. A solution of random copolymer (1.0 CMS equiv) in dry THF was then added to this mixture, and the reaction mixture was refluxed for 12 h in the dark. It was then cooled to room temperature, evaporated to half of its volume, and then precipitated into methanol. The light yellow product, P(S-*co*-CMS) with anthryl pendant groups, was dried for 24 h in a vacuum oven at 30 °C.

General Procedure for Preparation of Graft Copolymer via DA Reaction of PMMA−MI and PS with Anthryl Pendant Groups (PS−Anth). A solution of PMMA−MI (1.1 equiv) in 10 mL of toluene was added to a 10 mL solution of random copolymer (1.0 anthracene equiv) in toluene. A catalytic amount of BHT as a radical inhibitor was added. The mixture was bubbled with nitrogen for 30 min and refluxed for 48 h at 110 °C in the dark. The reaction mixture was evaporated under high vacuum. The crude product obtained was then dissolved in 5 mL of THF and poured into methanol. The white product formed was dried for 24 h in a vacuum oven at 30 °C.

General Procedure for Preparation of Graft Copolymer via DA Reaction of PEG−MI and PS−Anth. A solution of PEG−MI (1.1 equiv) in 10 mL of toluene was added to a 10 mL solution of random copolymer (1.0 anthracene equiv) in toluene. A catalytic amount of BHT as a radical inhibitor was added. The mixture was bubbled with nitrogen for 30 min and refluxed for 48 h at 110 °C in the dark. The reaction mixture was evaporated under high vacuum. The crude product obtained was then dissolved in 5 mL of THF and poured into methanol. The pale yellow product was dried for 24 h in a vacuum oven at 30 °C.

Preparation of Samples for AFM. Solutions of graft copolymers were prepared in toluene at a concentration of 8 mg/mL. Films were spin-coated at 2000 rpm for 1 min from these solutions on oxidized silicon substrates. Spin-coated films were kept in a vacuum oven at low temperatures for solvent evaporation.

Scheme 2. Incorporation of Anthryl Moieties by Etherification Process

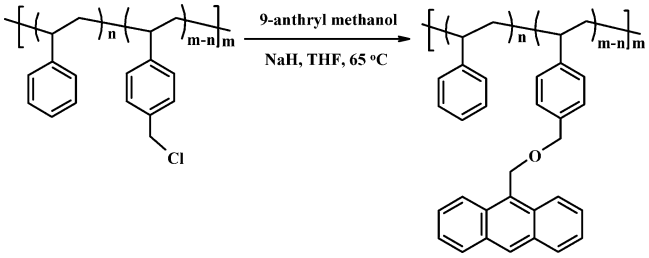


Table 1. Molecular Weights and Functionalities of the Polymers at Various Stages

			functionality (mol %)[b]	
polymers	M_n[a]	M_w/M_n[a]	CMS	Anth
P(S-*co*-CMS) (8%)	3700	1.38	8.5	
PS−Anth (8%)	4000	1.51		
PS-*g*-PEG (8%)	4400	1.42		
PS-*g*-PMMA (8%)	12100	1.26		
P(S-*co*-CMS) (30%)	4100	1.33	30.0	
PS−Anth (30%)	4400	1.36		30.0
PS-*g*-PEG (30%)	5700	1.47		
PS-*g*-PMMA (30%)	18000	1.24		
P(S-*co*-CMS) (50%)	4200	1.39	50.6	
PS−Anth (50%)	4800	1.31		50.6
PS-*g*-PEG (50%)	7100	1.40		
PS-*g*-PMMA(50%)	27000	1.20		

[a] Determined by GPC according to linear polystyrene standards. [b] Determined from ^{1}H NMR spectra of the corresponding polymers (see text).

Results and Discussion

P(S-*co*-CMS) copolymers containing 8, 30, and 50% CMS units were prepared via NMP of St and CMS at 125 °C. 9-Anthrylmethanol was successfully introduced into the preformed P(S-*co*-CMS) copolymer backbone via etherification reaction through nucleophilic substitution of CMS units (Scheme 2).

Copolymer compositions of polymers were determined using ^{1}H NMR spectroscopy. The mole fractions of CMS and St were calculated from the ratio of the peak areas around 4.4 ppm, corresponding to two side-chain methylene protons of CMS to the total area between 6.3 and 7.4 ppm, which was attributed to the total aromatic protons. A similar method was applied for all random copolymers to calculate the mole fractions of CMS and St. The molar compositions of copolymers and number-average molecular weights of P(S-*co*-CMS) determined by GPC are presented in Table 1.

P(S-*co*-CMS) (8, 30, and 50%) copolymers were modified by the etherification procedure as described in the Experimental Section to obtain copolymers with anthryl pendant groups (PS−Anth). Primarily, the extent of substitution in the etherification was determined. The FTIR and ^{1}H NMR spectra confirmed the structure. In the NMR spectrum of a typical example, the new signals corresponding to methylene protons CH_2 adjacent to the anthracene ring at 5.3 ppm and aromatic protons of the anthryl group between 7.3 and 8.5 ppm were detected (Figure 1). Moreover, the integrals of methylene protons CH_2 adjacent to the anthryl and phenyl ring on the modified random copolymer were in the ratio of 1:1, indicating complete etherification for each PS−Anth copolymer. The FTIR spectra support this result, showing no absorption around 1265 cm^{-1}, proving disappearance of the CH_2Cl moiety.

Independently, a maleimide functionality was introduced into PEG via esterification reaction of monohydroxyl end-functionalized PEG and **3**. The number-average molecular weight ($M_{n,NMR}$) of PEG−MI was calculated using NMR signals by comparison of the integrals of the vinyl end-group signals (6.5 ppm) and that of the $-CH_2CH_2O$ signal of PEG (3.64 ppm), respectively. $M_{n,theo}$ and $M_{n,NMR}$ values for PEG-MI are 840 and 850, respectively. In fact, the direct incorporation of maleimide end functionality by ATRP of MMA using maleimide functional initiator can be considered. However, this possibility is disregarded because of the participation of the maleimide double bond during the free radical process. Therefore, ATRP of MMA using the maleimide-protected initiator **2** was performed to yield polymers with the corresponding functionality. The polymerization temperature was deliberately kept low, i.e., 40 °C, so as to prevent possible deprotection during the polymerization. The intermediates used for maleimide functionalization of both PEG and PMMA are presented in Scheme 3. The theoretical MW of PMMA−MI was calculated by using the following equation: $M_{n,theo} = ([M]_0/[I]_0) \times$ conversion % $\times$ MW of monomer + MW of **2**. In addition, $M_{n,NMR}$ of PMMA−MI was determined from the ratio of integrated signals at 3.58 ppm (OCH_3 protons of MMA) to 6.5 ppm (vinyl end protons). $M_{n,theo}$ and $M_{n,NMR}$ values of PMMA−MI were calculated as 1250 and 2350, respectively.

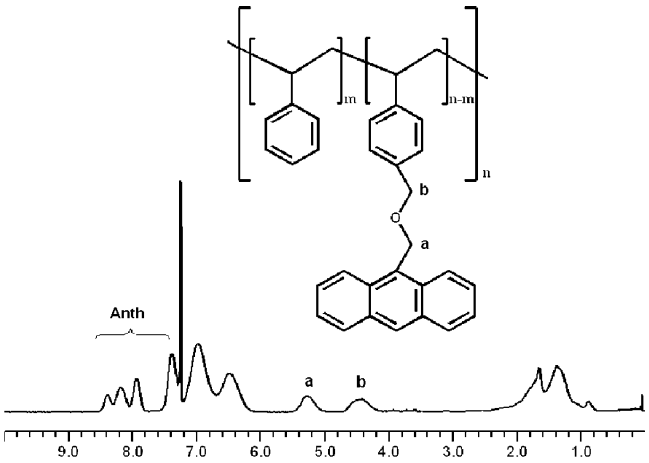
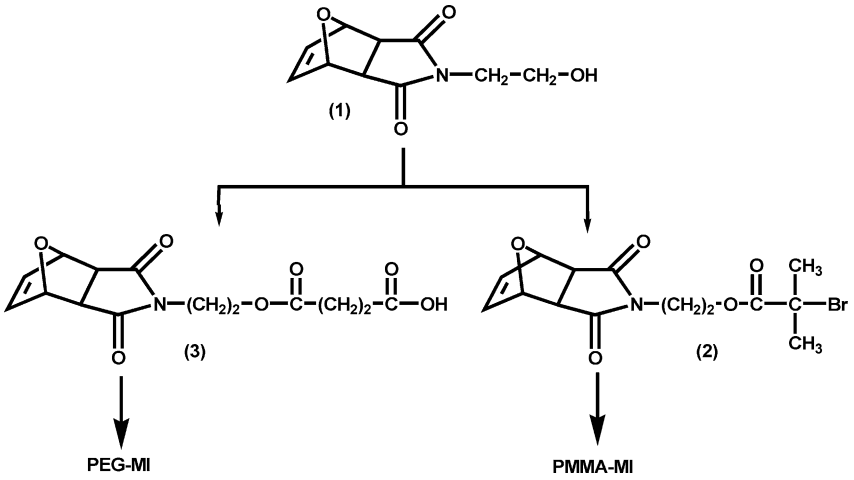


Figure 1. ^{1}H NMR spectrum of PS−Anth (30%) in $CDCl_3$.

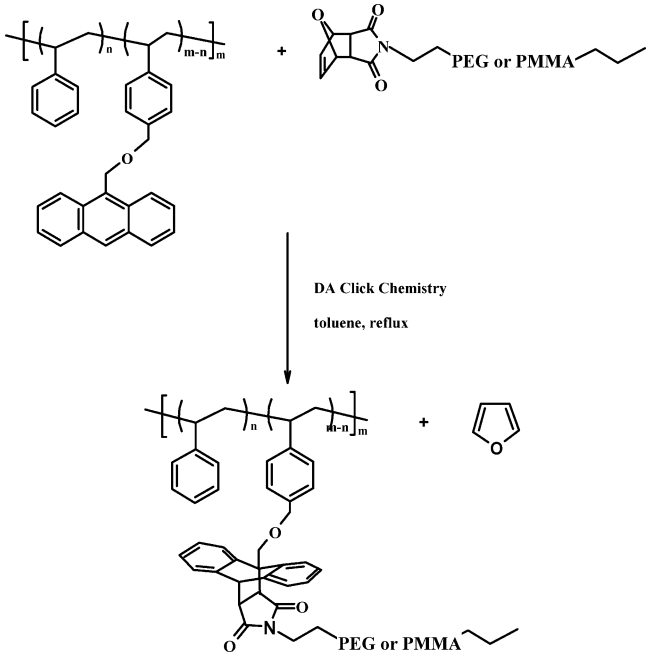
As will be described below, the combined retro-DA and "DA click reaction" utilizing polymers with antagonist functional groups leads to the formation of well-defined graft copolymers, where both main- and side-chain segments were prepared in a controlled manner. The overall process is presented in Scheme 4.

Deprotections of maleimide-functionalized polymers (retro-DA) were carried out in situ during DA "click reaction" by heating PS−Anth copolymers with PEG−MI or PMMA−MI in toluene at 110 °C. First, a retro-DA reaction of PEG−MI or PMMA−MI proceeds via releasing of furan to give the deprotected maleimide functionality at the reflux temperature of toluene. Then, at this temperature, efficient DA reaction of the recovered maleimide and copolymers with pendant anthryl units resulted in the expected well-defined graft copolymers, PS-*g*-PEG or PS-*g*-PMMA. The copolymerization reaction was completed with quantitative yields without need for an additional purification step. The byproduct, furan, and excess PEG−MI or PMMA−MI (having relatively low molecular weight) all are completely soluble in methanol, which is the precipitating solvent. Evidence for the formation of DA adduct of the resulting PS-*g*-PEG graft copolymer was observed in the ^{1}H NMR spectra (Figure 2). Also, the efficiency of DA for the grafting process was investigated by UV and fluorescence

Scheme 3. Intermadiates Used for Maleimide Functionalization



Scheme 4. Grafting by in Situ Retro-DA and DA Processes



spectroscopy (vide infra). The peaks between 7.3 and 8.5 ppm, characteristic for aromatic protons of anthracene, completely disappeared. It also revealed that the aromaticity of the central phenyl unit of anthracene disappeared as a result of DA cycloaddition, and a new bridgehead proton appeared. A broad peak at 4.7 ppm, due to the bridgehead proton of the cycloadduct CH, appeared, and it overlapped with the peaks corresponding to methylene protons of CH_2 adjacent to anthracene and phenyl ring. Moreover, a new signal corresponding to CH proton on the fused maleimide ring and OCH_3 methoxy protons of the PEG end group was observed at 3.4 ppm. The main-chain protons of PEG (OCH_2CH_2) and CH_2CH_2 protons adjacent to nitrogen atom of maleimide gave a distinct signal at 3.6 ppm. Obviously, the resulting graft copolymers are amphiphilic in nature and are expected to form aqueous micelles as demonstrated by Schubert and co-workers,[28,29] who reported the linking of PEG chains to a hydrophopic backbone via ruthenium−terpyridine complexes. Further studies in this line are in progress and will be reported elsewhere.

The PS-*g*-PMMA graft copolymers, prepared by the same procedure, were characterized by ^{1}H NMR spectroscopy. These spectra revealed the corresponding DA cycloadduct. Similar chemical shifts were observed (Figure 3). The peak of OCH_3 protons of PMMA backbone and CH_2 protons adjacent to the nitrogen of the maleimide appeared at 3.6 ppm. The peaks at 3.7 ppm are attributed to the OCH_3 end group of PMMA and CH_2 protons adjacent to ester linkage. Furthermore, two CH protons of the imide ring at 3.3 ppm were also detected. Figure 4 shows the evolution of GPC traces of the PS−Anth, PS-*g*-PEG, and PS-*g*-PMMA copolymers with 30 or 50% functionality content. All GPC traces based on linear PS used as standard

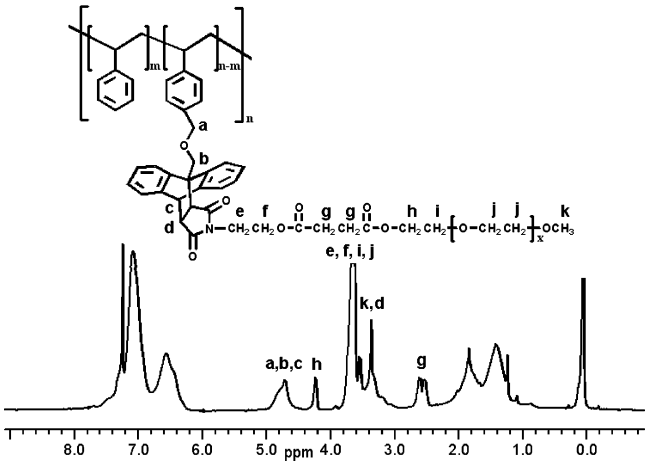


Figure 2. ^{1}H NMR spectrum of PS-*g*-PEG (30%) in $CDCl_3$.

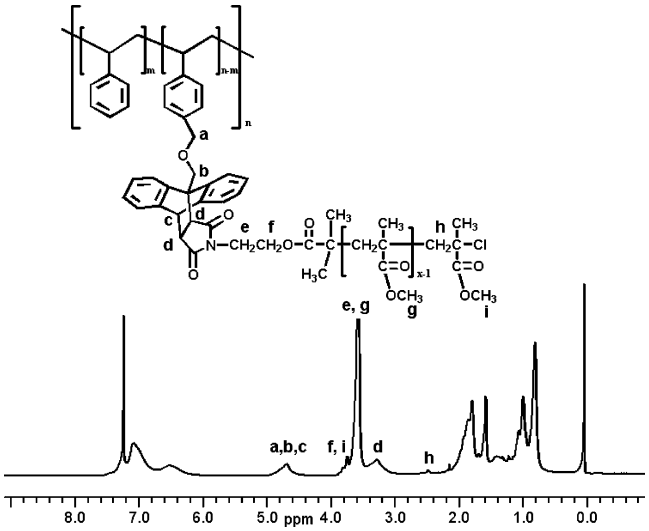


Figure 3. ^{1}H NMR spectrum of PS-*g*-PMMA (30%) in $CDCl_3$.

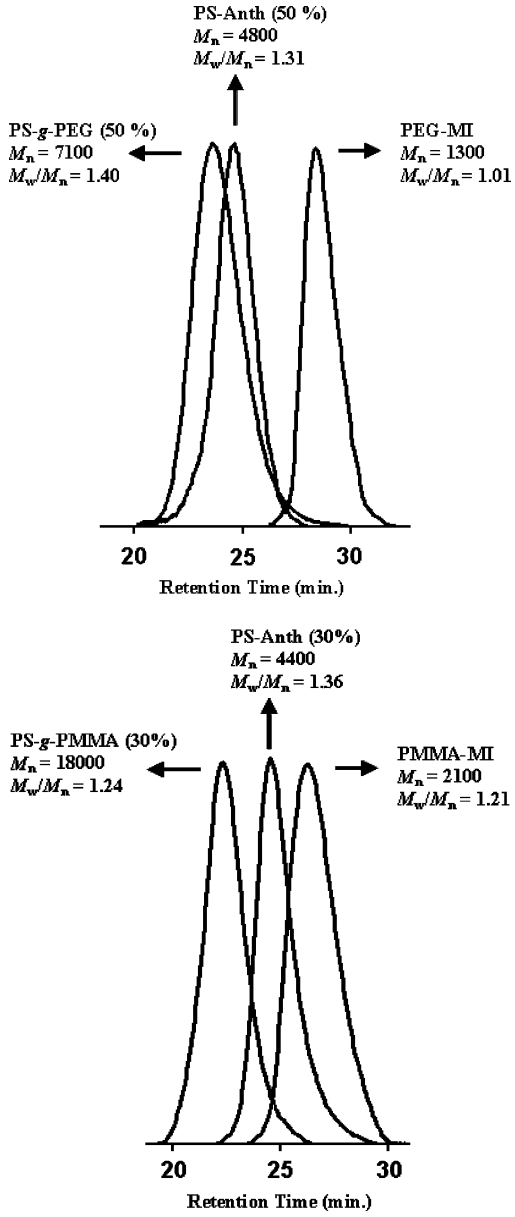


Figure 4. Evolution of GPC traces: PEG−MI PS−Anth (50%) and PS-*g*-PEG (50%) (a, top) and PMMA−MI, PS−Anth (30%), and PS-*g*-PMMA (30%) (b, bottom).

in GPC calibration were unimodal and narrow. No tailing was observed in the molecular weight of precursors. The shift of PS−Anth and PEG−MI or PMMA−MI precursors to higher molecular weight region revealed that the formation of PS-*g*-PEG or PS-*g*-PMMA by DA reaction was achieved efficiently.

DA adduct formation was also monitored by UV and fluorescence spectroscopy (Figures 5 and 6). In UV measurements, the characteristic five-finger absorbance of PS−Anth (8%) was observedfrom 300 to 400 nm, while the corresponding PS-*g*-PEG (8%) and PS-*g*-PMMA (8%) showed no absorbance in this region (Figure 5). Overall UV measurements clearly pointed out a quantitative DA reaction between anthracene and maleimide moieties.

The fluorescence spectrum of diluted solution of PS−Anth (8%) in CH_2Cl_2 excited at λ_{exc} = 390 nm showed the characteristic emission bands of the excited (singlet) anthracene at 595, 655, and 725 nm (Figure 6). In contrast, PS-*g*-PEG (8%) and PS-*g*-PMMA (8%) had no significant emission proving the disappearance of anthracene moieties after efficient DA reaction.

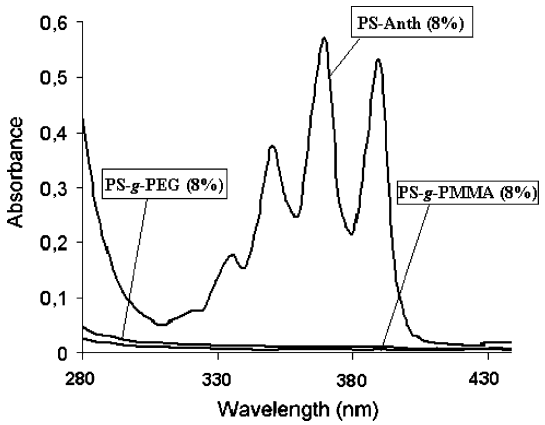


Figure 5. Absorption spectra of PS−Anth (8%), PS-*g*-PEG (8%), and PS-*g*-PMMA (8%); $c = 2 \times 10^{-5}$ M in CCl_4.

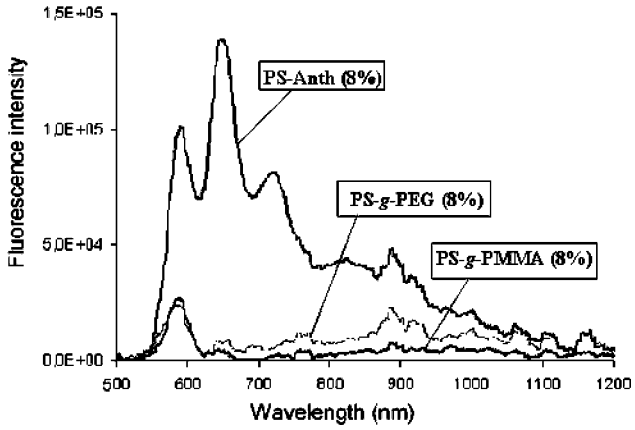


Figure 6. Emission spectra of PS−Anth (8%), PS-*g*-PEG (8%), and PS-*g*-PMMA (8%); λ_{exc} = 390 nm; $c = 2 \times 10^{-5}$ M in CCl_4.

Table 2. Glass Transition Temperatures[a] (T_g) of the Polymers at Various Stages

functionality (mol %)	T_g (°C)			
	P(S-*co*-CMS)	PS−Anth	PS-*g*-PEG	PS-*g*-PMMA
8	92	96	79	79 and 105
30	98	108	75	80 and 121
50	105	115	73	82 and 130

[a] Determined by DSC under nitrogen at a heating rate of 10 °C/min.

The glass transition temperatures (T_g) of copolymers were determined by DSC under a nitrogen atmosphere. As shown in Table 2, the addition of a more rigid and bulky anthracene functionality into P(S-*co*-CMS) copolymers further increases the T_g, compared with those of the pristine polymers. T_g values for the copolymer series of PS−PEG (8, 30, and 50%) are determined as 79, 75, and 73 °C, respectively. It was obvious that T_g values gradually decreased depending on the increasing PEG content. Any T_g for the PEG segment (T_g of PEG−MI = −44 °C) was not observed because of the relatively shorter PEG−MI when compared with that of PS−Anth. The first transitions were almost identical to that of PMMA−MI segment (T_g of PMMA−MI = 78 °C), while the second transitions were increased with the increase of the grafted PMMA concentration, which affected the rigidity of PS backbone. For PS-*g*-PMMA copolymers, two T_g values were observed (see Table 2). These thermal data clearly indicated that PS backbone and grafted PMMA segments were phase separated for these studied compositions. Atomic force microscopy (AFM) investigations of the PS-*g*-PMMA (8%) showed indications of this behavior.

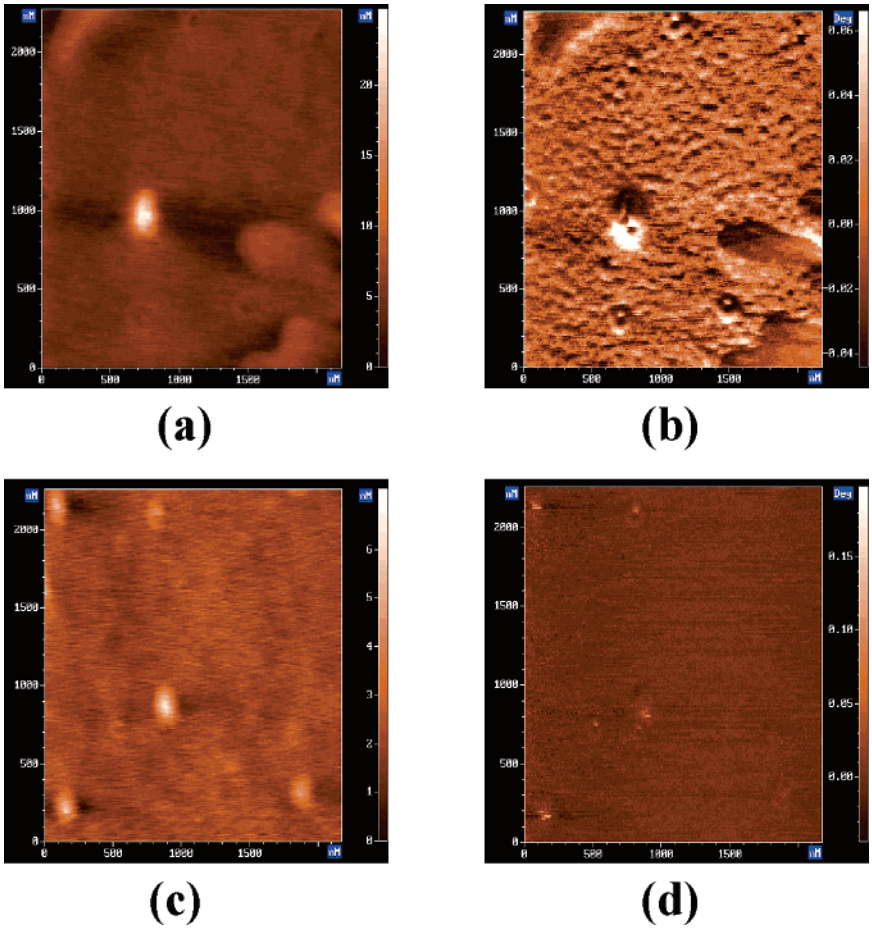


Figure 7. Atomic force microscopy pictures: height (a) and phase (b) picture of PS-*g*-PMMA (8%); height (c) and phase (d) picture of PS-*g*-PEG (8%). All pictures correspond to an area of 2 μm × 2 μm.

While the AFM height picture (Figure 7a) showed a relatively smooth surface, the corresponding AFM phase picture (Figure 7b) showed bright and dark contrast undulations, indicating polymers of different viscoelasticity in the material. The length scale of these regions is less than 100 nm. PS-*g*-PEG (8%) also showed smooth surface features (Figure 7c), but any indication of the regions of different viscoelastic materials was not observed. The AFM phase picture (Figure 7d) showed a uniform phase throughout the surface without any contrast undulations. This is due to the relatively shorter PEG chain compared to the PS main chain, in agreement with observation of only one T_g in DSC measurements for this molecule.

Conclusion

We have demonstrated a new synthetic approach for the preparation of well-defined graft copolymers on the basis of the DA "click chemistry" between copolymers bearing anthryl pendant groups and maleimide as end-functionalized polymers. The grafting processes were carried out at the reflux temperature of toluene with a quantitative yield and without need for an additional purification step. Moreover, ^{1}H NMR, GPC, UV, fluorescence, and DSC measurements of resulting graft copolymers confirmed the high efficiency of DA "click chemistry". Interestingly, two different T_g values in the ranges 79−82 and 105−130 °C were detected for PS-*g*-PMMA, while only one T_g was observed at 73−79 °C in the case of the corresponding PS-*g*-PEG. The strategy adopted in this study appears to be entirely satisfactory in terms of efficiency and simplicity.

References and Notes

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