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Graft Copolymers by the Combination of ATRP and Photochemical Acylation Process by Using Benzodioxinones

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ABSTRACT: Synthesis of graft copolymers by combination of atom transfer radical polymerization (ATRP) and photoinduced reaction of benzodioxinone was reported. First, statistical copolymers of methyl methacrylate (MMA) and 2-hydroxyethyl methacrylate (HEMA) were prepared by ATRP process. Then, the other component, namely benzodioxinone functional polystyrene (PS-B) was prepared independently by the etherification reaction of hydroxyl benzodioxinone (HDPD) with polystyrene (PS-Br) obtained by ATRP by using K_2CO_3 in acetone. Photolysis of poly(hydroxyethyl methacrylate-*co*-methyl methacrylate) (P(HEMA-*co*-MMA)) and (PS-B) prepolymers in CH_2Cl_2 at $\lambda_{inc} > 300$ nm yielded graft copolymers. The graft copolymers and the intermediates were characterized in detail by using ^{1}H NMR, GPC, UV, FT-IR, DSC, and AFM measurements.

Introduction

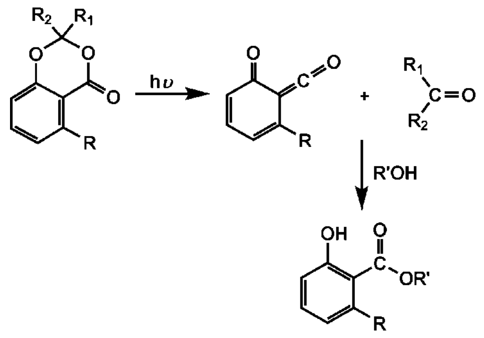
In recent years, the main scientific and applied interest in polymeric materials is focused on the development of novel synthetic methods that allow control over the composition, functionality, molecular structure, and molecular weight. During the past decade the controlled/living radical polymerization[1−4] became an established synthetic method to prepare new complex architectures of polymers such as block,[5] graft,[6] star[7] and functional polymers with well-defined structures. Nitroxide mediated polymerization (NMP)[8,9] or stable radical mediated free radical polymerization (SFRP), atom transfer radical polymerization (ATRP)[2,3,10−13] and reversible addition−fragmentation chain transfer (RAFT)[14,15] processes received interest and were successfully used for the preparation of such macromolecular structures. Among them, ATRP is appeared to be the most extensively used method because of its easy manipulation, ability to control molecular weight and structure, and applicability to a wide range of monomers.

Soltani et al. reported[16] that functionalized salicylate esters can be readily prepared by a photochemical acylation process by using benzodioxinones[17] in the presence of alcohols and phenols. Upon irradiation of benzodioxinones, ketene and the corresponding ketone are formed concomitantly. The intermediate ketene readily reacts with the alcohol present in the solution to yield salicylate ester (Scheme 1).

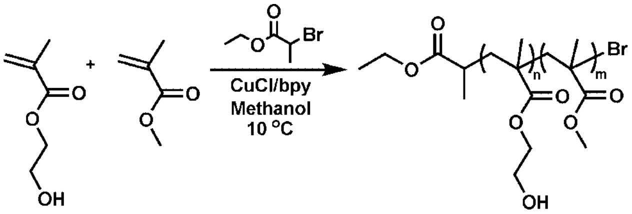
We have recently shown that this process can also be used for the preparation of oligoesters[18] when benzodioxinones are equipped with aliphatic hydroxyl groups (Scheme 2).

Moreover, we also showed that, when suitably structured, aromatic ketones, i.e., benzophenone, formed concomitantly can absorb light and act as hydrogen abstraction type photoinitiators in the presence of donors.[19] Quite recently, very useful application of this photochemistry in photoinitiated cationic polymerization was demonstrated by the generation of photoacid by stepwise two-photon absorption.[20] In this process, benzodioxinone acted as caged sensitizer for diphenyliodonium salt to generate acids for initiation of cationic polymerization. The first photon absorbed uncages the sensitizer which absorbs the second photon to reduce the iodonium salt yielding in protonic acids for the initiation of cationic polymerization.

Scheme 1. Salicylate Esters by Photoinduced Acylation



Scheme 2. Synthesis of Poly(hydroxyethyl methacrylate-*co*-methyl methacrylate) (P(HEMA-*co*-MMA)) by ATRP



Recently, the Cu(I)-catalyzed 1,3-dipolar cycloaddition reactions between an azide and an alkyne, known as "click reactions"[21] have gained a great deal of attention due to their high specificity and nearly quantitative yields in the presence of many functional groups. Click reactions have been widely used in macromolecular engineering and as a versatile method for synthesis of functional monomers and polymers,[22] bioconjugated polymers,[23,24] block[25] and graft copolymers,[24,26−28] dendrimers,[29] cyclic polymers,[30] star[31] and brush copolymers,[32] and networks.[33] The Diels−Alder cyclo addition[34] and thiol−ene reactions[35] were also treated as alternative click reactions. Despite the many potential applications, the existing click reactions have several drawbacks. For example, the removal of the copper catalyst, and thermal and shock sensitivity of the azide groups are the major concerns in the 1,3-dipolar cycloaddition reactions. On the other hand, the Diels−Alder click reactions suffer from the thermal instability caused by the retro

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Table 1. Conditions[a] and Results for the Synthesis of Poly(hydroxyethyl methacrylate-*co*-methyl methacrylate) (P(HEMA-*co*-MMA))

code	time (h)	convn[b] (%)	$F_{\mathrm{HEMA/MMA}}$[c] (mol %)	M_{nGPC}[d] (g/mol)	M_w/M_n[d]	N_{OH}[e]
P(HEMA-*co*-MMA)-1	15	66	19.6	8610	1.26	12.9
P(HEMA-*co*-MMA)-2	5	30	19.0	4290	1.30	6.3

[a] Feed ratio of HEMA/MMA: 2 mL/7.22 mL (20/80 mol %) in methanol, [M]/[I]/[CuCl]/[bpy]: 90/1/1/2.5, Ethyl-2-bromopropionate was used as an initiator, temperature: 10 °C. [b] Determined by gravimetrically. [c] Calculated by using ^{1}H NMR spectra. [d] Determined from GPC measurements based on polystyrene standard. M_n: The number average molecular weight, M_w: The weight average molecular weight. [e] Number of HEMA unit in copolymer was calculated by using ^{1}H NMR spectra and GPC results.

reactions. Although thiol−ene addition does not require inorganic catalyst and was proved to be a reaction with very high conversion under mild conditions, the simultaneous reactions of the photochemically formed primary radicals with enes reduce the click efficiency. Thus, a key challenge still remains to improve the existing three methods and to develop new and efficient click reactions, and their application to polymer synthesis. In this connection it is worth to mention recent work of Matyjaszewski and co-workers who reported[27] the much safer and very efficient introduction of azide groups in copolymers prepared by the ATRP of the relatively easy to handle, stable, and commercially available monomer glycidyl methacrylate (GMA) via opening of the oxirane rings in the presence of sodium azide.

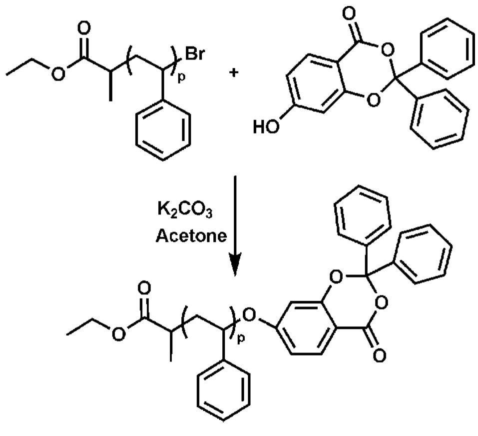
Photoinduced processes have the advantage of being applicable at low temperatures, especially at room temperature. Moreover, because of selective absorptions of certain groups (chromophores), it is possible to produce reactive sites at definite positions. However, most of the photochemical methods applied for the synthesis of graft copolymer[36] involve either free radical or cationic initiation through the reactive sites generated photochemically on the backbone and usually accompanied with homopolymer formation.

As part of our ongoing research efforts in the design and development of photoinitiating systems for the preparation of complex macromolecular architectures, we report herein an efficient synthetic methodology for the preparation of graft copolymers. Our approach toward the preparation of graft copolymers is unique in the way that the process can be performed at room temperature in the absence of any catalyst. As will be shown below, although low molar mass ketones are also formed as byproduct in the process, most of the click reaction prerequisites such as simplicity, selectivity and efficiency are accomplished.

Experimental Section

Materials. Styrene (S, 99%, Aldrich) and methyl metacrylate (MMA, 99%, Aldrich) and 2-hydroxylethyl metacrylate (HEMA, 99%, Aldrich) were passed through basic alumina column to remove the inhibitor. *N*,*N*,*N*′,*N*″,*N*″-Pentamethyldiethylenetriamine (PMDETA, 99%, Aldrich), as a ligand, was distilled before use. Ethyl-2-bromopropionate (99%, Aldrich), CuBr (98%, Acros), CuCl (≥99%, Acros), 2,2-dipyridine (bpy, 99% Acros) and dried methanol (99.8%, BDH), 2,6-dihydroxybenzoic acid (97%, Acros), ethylene glycol dimethyl ether (99.5%, Fluka), thionyl chloride (99.5% Acros), *N*4,*N*4-dimethylpyridin-4-amine (DMAP, 99%, Acros), benzophenone (≥99%, Aldrich), potassium carbonate anhydrous (99.9%, Aldrich), sodium sulfate anhydrous (≥99.0%, Aldrich), and silicagel 60 (Merck, 0.040−0.063 mm) were used as received. All solvents were of HPLC or ACS grade. Solvents used for moisture sensitive operations were distilled from drying reagents under a nitrogen atmosphere: Et_2O and THF from sodium benzophenone ketyl, benzene and toluene from sodium, CH_2Cl_2 from CaH_2, and acetone over 4 Å molecular sieves.

Scheme 3. Preparation of Benzodioxinone Functional Polystyrene (PS-B)



Synthesis of 7-Hydroxy-2,2-diphenyl-4*H*-benzo[*d*][1,3]dioxin-4-one (HDPD). The precursor compound was synthesized according to the literature procedure.[37] Thus, to an ice-cold suspension of 2,4-dihydroxybenzoic acid (2.5 g, 16.23 mmol) in trifluoroacetic acid (13 mL) were added trifluoroacetic anhydride (14 mL) and benzophenone (4.43 g, 24.37 mmol). The mixture was warmed slowly to room temperature and then stirred for 24 h. The mixture was then concentrated on the rotary evaporator, poured into a saturated solution of aqueous $NaHCO_3$, and extracted with three portions of diethyl ether. Collected extracts were washed with water and brine, dried (MgSO4), and concentrated to leave yellow solids. Chromatography over silica using EtOAc/Hex (30/70) as the eluent afforded 0.9 g (17%) of HDPD as yellow solid. Mp: 63−65 °C. ^{1}H NMR ($CDCl_3$): $\delta = 10.43$ (s, 1H, OH), 7.60−7.54 (dd, $J = 7.4$, $J = 1.4$, 4H, Ar), 7.35−7.31 (m, 6H, Ar), 7.71 (d, $J = 8.7$, 1H, Ar), 6.63 (s, 1H, Ar), 6.52 (d, $J = 8.6$, 1H, Ar). FT-IR: 3230, 2975, 1687, 1612, 1594, 1491, 1447, 1240, 1121, 960, 750 cm^{-1}. UV (CH_2Cl_2): $\lambda_{\max}$., nm (ε, l mol^{-1} cm^{-1}); 303 (8932), 263(18470), 229 (21869). MS (EI) *m*/*z* (%): 318(60), 273(7), 241(8), 183(80), 136(100), 105(67), 77(47), 71(42), 43(27).

Preparation of Polystyrene by ATRP (PS-Br). CuBr (0.25 g, 1.72 mmol), PMDETA (361 μL 1.72 mmol), ethyl-2-bromopropionate as an initiator (225 μL, 1.72 mmol), and styrene (20 mL, 172 mmol) were introduced in a Schlenk tube, and the reaction mixture was degassed by three freeze−pump−thaw cycles and left in vacuo. The tube was heated at 90 °C in an oil bath and stirred for 46 min. Then the mixture was diluted with THF, and passed through an alumina column to remove the complex salts. Precipita-

Table 2. Conditions[a] and Results for the Synthesis of P(HEMA-*co*-MMA)-*g*-PS Graft Copolymers

						thermal properties[f]	
code	initial polymer	yield[b] (%)	M_{nGPC}[c] (g/mol)	M_w/M_n[c]	X_{grafting}[e] (%)	$T_{\mathrm{g(HEMA}\text{-}co\text{-}\mathrm{MMA)}}$	T_{ggraft}
G1	P(HEMA-*co*-MMA)-1	52	19600	1.33	58	79.0	86.4
G2	P(HEMA-*co*-MMA)-2	40	11480	1.30	45	76.5	*g*

[a] Polymerization carried out in CH_2Cl_2 at 300 nm for 20 h at room temperature with [PS-B]/[OH]: 1.2/1 mol ratio. $M_{n\mathrm{GPC,PS\text{-}B}}$: 4130. M_w/M_n: 1.07. [b] Yield was determined gravimetrically after purification. [c] Determined from GPC measurements based on polystyrene standard. M_n: the number average molecular weight. M_w: the weight average molecular weight. [e] Grafting efficiency was calculated from ^{1}H NMR spectra by using eq 1. [f] The glass transition temperature (T_g) of polymers were determined by using DSC. T_g of PS-B was determined as 92.0 °C. [g] The glass transition temperature (T_g) of graft copolymer G2 was not determined.

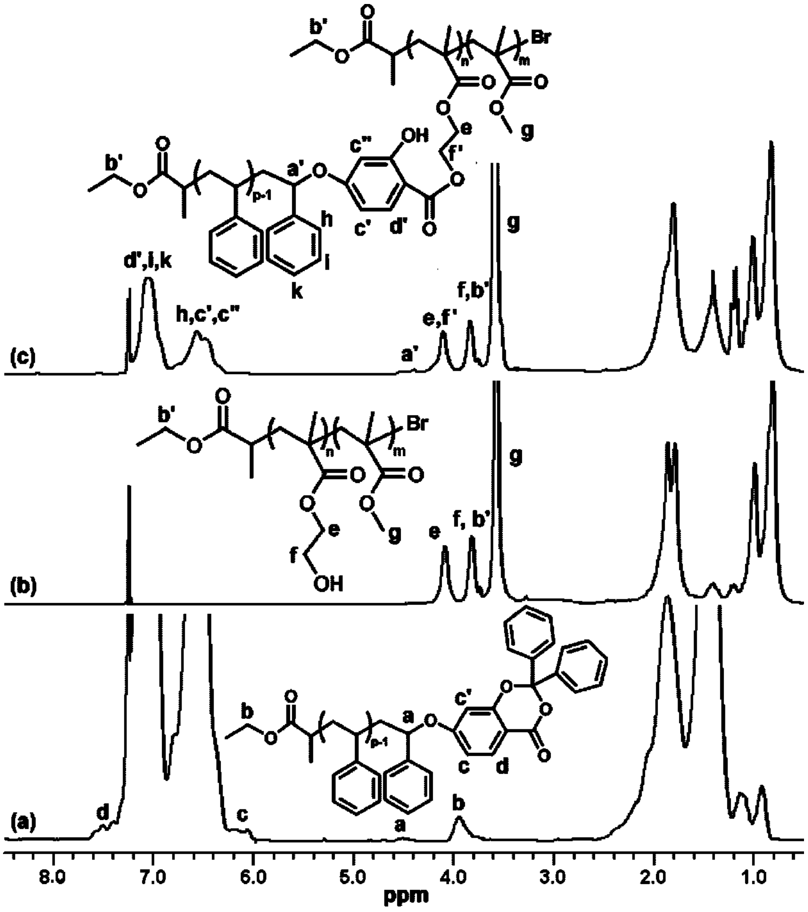


Figure 1. ^{1}H NMR spectra of benzodioxinone terminated polystyrene (PS-B) (a), poly(hydroxyethyl methacrylate-*co*-methyl methacrylate) (P(HEMA-*co*-MMA)-1) (b), and P(HEMA-*co*-MMA)-*g*-PS graft copolymer (G1) (c) in $CDCl_3$.

tion of the polymer was performed in a 10-fold volume of methanol. The solid was then collected after filtration. (Conversion %: 32. $M_{n,th}$: 3500. $M_{n,NMR}$: 3630. $M_{n,GPC}$: 3470. M_w/M_n: 1.08.)

Copolymerization of HEMA and MMA by ATRP (P(HEMA-*co*-MMA)). CuCl (0.09 g, 0.91 mmol), bpy (0.357 g 2.28 mmol), ethyl-2-bromopropionate (118 μL, 0.91 mmol) as an initiator HEMA (2 mL, 16.4 mmol), MMA (7.22 mL 67.5 mmol) and 6 mL dried methanol were introduced in a Schlenk tube, and the reaction mixture was degassed by three freeze−pump−thaw cycles and left in vacuo. The tube was stirred at 10 °C for certain time. Then the mixture was diluted with THF, and passed through a silica column to remove the complex salts. The resulting copolymers was precipitated in hexane and collected by filtration. Conditions and results are summarized in Table 1.^{1}H NMR ($CDCl_3$): δ = 4.08 (br s, 2H, CO−O−*CH$_2$*−), 3.81 (br s, 4H, −*CH$_2$*−OH, CH$_3$−*CH$_2$*−O−CO), 3.57 (br s, 3H, CO−O−*CH$_3$*), 1.86−0.81 (m, 17H, *CH$_2$*−C*CH$_3$*, *CH$_3$*−CH$_2$−O−CO, CO−*CH*−*CH$_3$*). FT-IR: 3513, 3002, 2950, 2843, 1727, 1484, 1449, 1387, 1271, 1243, 1148, 1069, 988, 750 cm^{-1}.

Preparation of Benzodioxinone Terminated Polystyrene (PS-B). A solution of HDPD (0.19 g, 0.6 mmol) and anhydrous potassium carbonate (1.24 g, 9 mmol) in acetone (25 mL) were stirred for 3 h. After that time, PS-Br (0.83 g, 0.24 mmol) was added and the mixture was heated at reflux temperature for 16 h. The reaction mixture was filtered to remove the salt. Then, the mixture was concentrated on the rotary evaporator and precipitated in methanol. The functional polymer was collected by filtration. (0.8 g; yield: 96%).^{1}H NMR ($CDCl_3$): δ = 7.51 (s, 1H, Ar), 7.25−6.51 (m, 15H, Ar), 6.20−6.05 (m, 2H, Ar), 4.50 (s, 1H, Ph−*CH*−O), 3.94 (m, 2H, CH$_3$−*CH$_2$*−O−CO), 1.85−0.92 (m, 10H, *CH$_2$*−*CH*Ph, *CH$_3$*-CH$_2$−O−CO, CO−*CH*−*CH$_3$*).^{13}C NMR ($CDCl_3$): δ = 176.7, 176.6, 162.8, 161.6, 146.0, 145.7, 145.3, 145.3, 129.7−127.4, 115.4, 107.1, 96.5, 59.9, 46.4, 45.9, 43.8, 40.4, 37.3, 37.2. FT-IR: 3513, 3026, 2981, 2912, 1731, 1680, 1601, 1492, 1452, 1370, 1181, 1072, 1028, 908, 756 cm^{-1}.

Graft Copolymerization by Photoinduced Click Chemistry Process. A solution of PS-B (1.2 equiv) P(HEMA-*co*-MMA) copolymers (1 hydroxyl equiv) in 2 mL of CH_2Cl_2 were introduced in a quartz tube and irradiated at 300 nm for 20 h. After this time, graft copolymer first precipitated in hexane then reprecipitated in diethyl ether for the removing of excess polystyrene. Conversion determined by gravimetrically. Conditions and results are summarized in Table 2.^{1}H NMR ($CDCl_3$): δ = 7.55 (br s, 1H, Ar), 7.25−6.51 (m, 5H, Ar), 6.08 (m, 2H, Ar), 4.52 (s, 1H, Ph−*CH*−O), 4.10 (s, 4H, Ph−CO−O−*CH$_2$*, CO−O−*CH$_2$*), 3.83 (s, 4H, *CH$_2$*−OH, CH$_3$−*CH$_2$*−O−CO), 3.58 (s, 3H, CO−O−*CH$_3$*), 1.85−0.82 (m, 24H, *CH$_2$*−C*CH$_3$*, *CH$_2$*−C*CH$_3$*, *CH$_3$*−CH$_2$−O−CO, CO−*CH*−*CH$_3$*). FT-IR: 3513, 3026, 2982, 2880, 1725, 1660, 1625, 1484, 1451, 1382, 1269, 1240, 1147, 1065, 988, 840, 756 cm^{-1}.

Characterization. ^{1}H NMR and ^{13}C NMR spectra of 5−10% (w/w) solutions in $CDCl_3$ with $Si(CH_3)_4$ as an internal standard were recorded at room temperature at 250 and 62.5 MHz, respectively, on a Bruker DPX 250 spectrometer. Gel permeation chromatography (GPC) measurements were obtained from a Viscotek GPCmax Autosampler system consisting of a pump, a Viscotek UV detector and Viscotek a differential refractive index (RI) detector. Three ViscoGEL GPC columns (G2000H$_{HR}$, G3000H$_{HR}$, and G4000H$_{HR}$), (7.8 mm internal diameter, 300 mm length) were used in series. The effective molecular weight ranges were 456−42 800, 1050−107 000, and 10 200−2 890 000, respectively. THF was used as an eluent at flow rate of 1.0 mL min^{-1} at 30 °C. Both detectors were calibrated with PS standards having narrow molecular weight distribution. Data were analyzed using Viscotek OmniSEC Omni-01 software. Molecular weights were

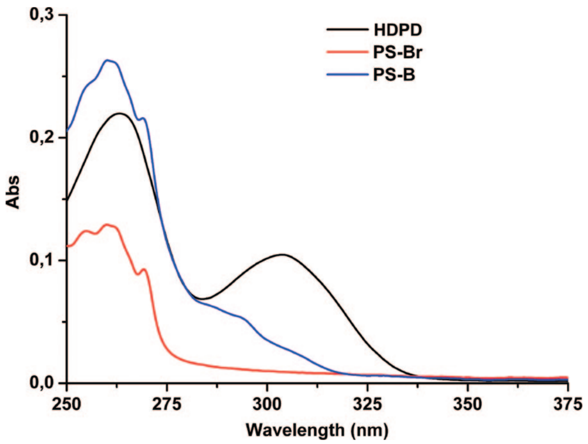
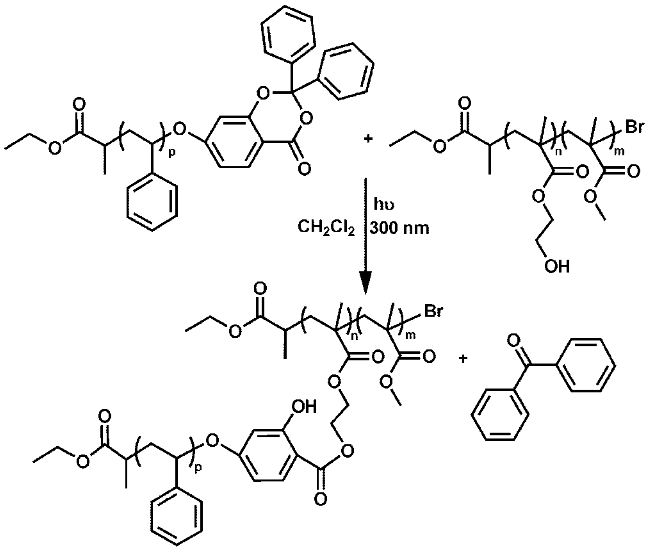


Figure 2. Optical absorption spectra of benzodioxinone (HDPD), polystyrene (PS-Br), and benzodioxinone terminated polystyrene (PS-B) at same concentration (5.3 × 10^{-5} mol L^{-1}) in CH_2Cl_2.

Scheme 4. Synthesis of Graft Copolymers by Photochemical Acylation Reaction



calculated with the aid of polystyrene standards. FT-IR spectra were recorded on a Perkin-Elmer FT-IR Spectrum One B spectrometer. UV spectra were recorded on a Shimadzu UV-1601 spectrometer. Differential scanning calorimetry (DSC) was performed on Perkin-Elmer Diamond DSC calibrated with indium. Glass transition temperatures were measured, after a first heating (from 20 to 150 °C) and cooling (from 150 to 20 °C) cycle. Thermograms were recorded during the second heating cycle at 10 °C/min under nitrogen flow. For atomic force microscopy (AFM) measurements, films were spin coated on silicon oxide substrates from 10 mg/ml solutions in $CHCl_3$. Height and phase images were taken by NT-MDT Solver P47 in tapping mode with ultra sharp Si cantilevers having a force constant of 48 N/m.

Results and Discussion

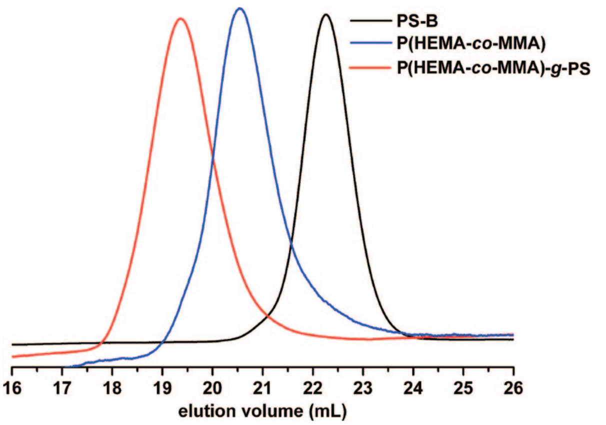


Figure 3. GPC traces of benzodioxinone terminated polystyrene (PS-B), poly(hydroxyethyl methacrylate-*co*-methyl methacrylate) (P(HEMA-*co*-MMA)-1), and P(HEMA-*co*-MMA)-*g*-PS graft copolymer (G1).

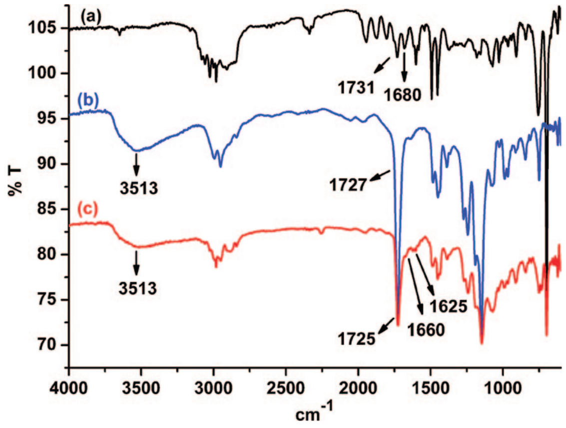


Figure 4. FT-IR spectra of benzodioxinone terminated polystyrene (PS-B) (a), poly(hydroxyethyl methacrylate-*co*-methyl methacrylate) (P(HEMA-*co*-MMA)-1) (b), and P(HEMA-*co*-MMA)-*g*-PS graft copolymer (G1) (c).

In the frame of our previous studies on the investigation of benzodioxinone photochemistry for various synthetic applications, the present paper is devoted to photoinduced grafting by taking advantage of chemoselective reactions of ketene intermediates toward hydroxyl groups. Thus, statistical linear copolymers of methyl methacrylate (MMA) and 2-hydroxyethyl methacrylate (HEMA) were prepared by ATRP at 10 °C in methanol by using ethyl-2-bromopropionate and CuCl/2,2′-bipyridine as initiator and catalyst, respectively (Scheme 2). This monomer couple and feed ratio were selected because of the absorption characteristics and solubility of the resultant polymer. HEMA acted as the side chain functional monomer possessing antagonist hydroxyl functionality. The experimental conditions and results are presented in Table 1.

Photochemically active benzodioxinone functional polystyrene (PS-B) was synthesized independently by a consecutive two-step procedure. The ATRP of styrene using the CuBr/N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDETA) catalytic system provided a precursor polymer with a terminal halide group. As the functionalized polystyrene was intended to be used in a further photoinduced reaction, the conditions of ATRP (low temperature, high concentration of initiator—0.85 M, and short reaction time—46 min) were chosen for obtainment a low molecular weight polymer, combined with a satisfactory conversion (32%) and polydispersity (M_w/M_n: 1.08). Moreover, the agreement of the theoretical molecular weight ($M_{n,th}$: 3500) with the measured one ($M_{n,GPC}$: 3470) indicate the well-defined structure of the precursor polymer. Subsequent etherification with 7-hydroxy-2,2-diphenyl-4*H*-benzo[*d*][1,3]dioxin-4-one (HDPD) in acetone by using K_2CO_3 yielded the desired polystyrene bearing terminal benzodioxinone group with 93% functionalization efficiency as determined by ^{1}H NMR analysis. The overall process is depicted in Scheme 3.

The spectral data (NMR, FT-IR, UV spectroscopy) proved the presence of benzodioxinone functional group in the structure

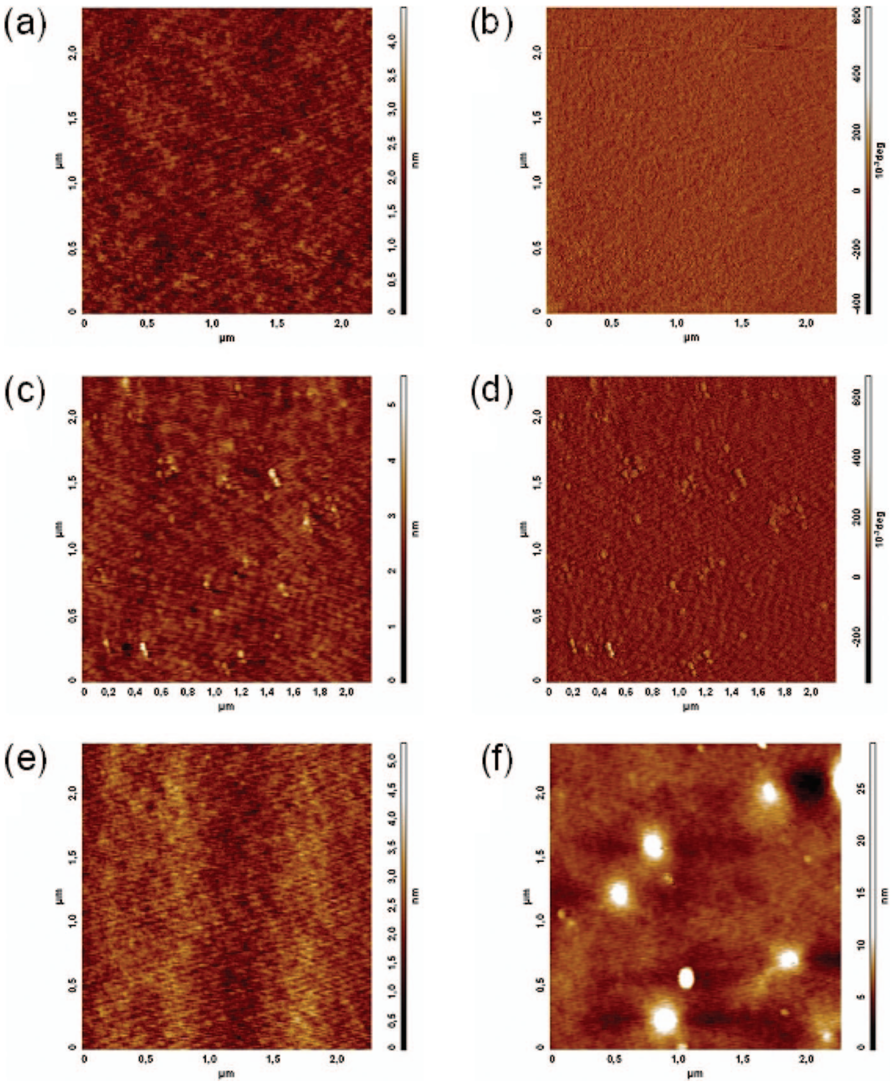


Figure 5. AFM images of the polymer films on silicon oxide substrates: (a) height and (b) phase image of poly(hydroxyethyl methacrylate-*co*-methyl methacrylate (P(HEMA-*co*-MMA)-1); (c) height and (d) phase image of P(HEMA-*co*-MMA)-*g*-PS graft copolymer (G1); (e) height image of poly(hydroxyethyl methacrylate-*co*-methyl methacrylate) (P(HEMA-*co*-MMA)-2); (f) height image of P(HEMA-*co*-MMA)-*g*-PS graft copolymer (G2).

of polymer. The presence of aromatic protons belonging benzodioxinone moiety appear very clear at 6.05 and 7.51 ppm in the ^{1}H NMR of the polymer (Figure 1a). Successful functionalization was also evidenced by UV absorption measurements. Figure 2 shows the absorption spectra of PS-B obtained, together with precursor PS-Br and HDPD. It can be seen that PS-B has spectra which is typical for benzodioxinone chromophore absorbing strongly in far UV and possessing an absorption maximum of the $n \rightarrow \pi^*$ transition around 320 nm. Thus, PS-B is suitable for use in the subsequent photolysis at above 300 nm since the polystyrene itself does not absorb strongly in this region.

As will be described below, the photoinduced esterification reaction utilizing polymers with antagonist functional groups, i.e., benzodioxinone and hydroxyl groups, leads to the formation of well-defined graft copolymers, with controlled chain lengths as both main- and side-chain segments were prepared by ATRP. The general process is presented in Scheme 4.

In this process, first photoinduced decomposition of benzodioxinone proceeds via releasing of benzophenone to give ketene functionality at room temperature. Then, efficient nucleophilic reaction of the ketene and copolymers with pendant hydroxyl units resulted in the expected well-defined graft copolymers. The, byproduct, benzophenone is soluble in hexane, which is the precipitating solvent. The results are summarized in Table 2. Overall grafting efficiency (X_{grafting}) for the graft copolymer was calculated by a following formula:

$$X_{\mathrm{grafting}} = (I_{\mathrm{aromatic}} \times 3\mathrm{DP}_{\mathrm{n,MMA}}/I_{\mathrm{aliphatic(OCH_3)}} \times 5\mathrm{DP}_{\mathrm{n,St}})/N_{\mathrm{OH}} \times 100 \quad (1)$$

where $I_{\mathrm{aliphatic}}$ and I_{aromatic} are integrated values of the sum of OCH_3 protons of P(HEMA-*co*-MMA) and the aromatic protons of PS, respectively. N_{OH} is the number of the OH groups in the backbone polymer. Additionally, calculation from the ratio of aliphatic protons of HEMA moiety after grafting to that of unreacted ones ($I_e + I_{f'}/I_e + I_{f'} + I_f + I_{b'}$) gave the same grafting efficiency.

As can be seen from Table 2, the molecular weight of the precursor polymer (main chain) influenced the molecular weight of the resulting graft copolymer while the overall conversion and grafting efficiency did not change significantly. The moderate grafting efficiency could be attributed to the steric hindrance and the photoactivity of the benzophenone released from benzodioxinone. At the later stages of photolysis, the absorption of benzodioxinone moiety may be screened by benzophenone which absorbs the light at similar wavelengths. Attempts to prepare benzodioxinones releasing ketones either with no absorption or absorbing at different wavelengths than the initial benzodioxinone are under progress. The highest graft efficiency was about 58% in our photoinduced system. However, this value should not be underestimated as only slightly higher graft efficiencies were attained with the well-known azide–alkyne click reaction.[27,28] Evidence for the formation of ester adduct of the resulting P(HEMA-*co*-MMA)-*g*-PS graft copolymer was observed in the ^{1}H NMR spectra. In the ^{1}H NMR spectrum of the graft copolymer (Figure 1c), the resonance of terminal CH protons of polystyrene chain was observed 4.52 ppm and the presence of characteristic main chain PMMA and side-chain PS provided direct evidence for the successful coupling. The broadening and shifting of the peaks corresponding to methylene protons was also noted. The GPC traces of the starting materials and the graft copolymer are presented in Figure 3. The shift of PS-B and P(HEMA-*co*-MMA) precursors to higher molecular weight region revealed that the formation of P(HEMA-*co*-MMA)-*g*-PS by photoinduced coupling reaction was achieved efficiently.

The precursor polymers and the final graft copolymer were also analyzed by FT-IR spectroscopy and expected structures were confirmed. As can be seen from Figure 4, the carbonyl band at 1680 cm^{-1} corresponding to the dioxinone ring at the end of the polystyrene (Figure 4a) was detectable. After the photolysis, the graft copolymer exhibits new bands at 1625 and 1660 cm^{-1} attributed to intramolecular hydrogen bonded carbonyl group (Figure 4c). Additionally, broadening of the band at about 3500 cm^{-1} belonging to both phenolic and aliphatic hydroxyl groups was noted.

Glass transition temperatures (T_g) of the polymers determined by DSC measurements are tabulated in Table 2. The parent polymers P(HEMA-*co*-MMA)-1 and P(HEMA-*co*-MMA)-2 showed T_g values at 79.0 and 76.5 °C, respectively. T_g of the pristine PS-B was determined to be at 92.0 °C. The graft copolymer G1 showed a single T_g at 86.4 °C between those of P(HEMA-*co*-MMA)-1 and PS-B indicating miscibility at these low molecular weights. A control experiment with a blend of P(HEMA-*co*-MMA)-1 and PS-B confirmed the miscibility. While the first heating showed two T_g values at 74.8 and 91.0 °C, there was only a single T_g at 86.3 °C after the second heating. The lower molecular weight graft polymer G2 similarly showed miscibility of parent polymer P(HEMA-*co*-MMA)-2 and PS-B, and it was not possible to determine a clear T_g value.

Figure 5 shows the AFM images of the parent polymers P(HEMA-*co*-MMA)-1 and P(HEMA-*co*-MMA)-2 together with the graft copolymers G1 and G2. The parent polymer P(HEMA-*co*-MMA)-1 (Figure 5a) had very smooth surface topography typical of single phase amorphous polymers. Any phase contrast could not be observed (Figure 5b) which indicates the same type of material throughout the film. The surface topography of the graft polymer G1 (Figure 5c) showed 2–3 nm high, 50–60 nm wide circular regions. These regions also showed contrast in the phase images (Figure 5d) and thus can be attributed to the grafted PS side chains of the parent polymers. Although DSC measurements showed only a single glass transition in the bulk for the grafted polymer G1, the observed circular regions could be induced by the interface effects, namely the surface segregation of lower surface energy PS. The height of 2–3 nm is consistent with the molecular weight of the grafted PS chains. The PS regions persisted even after 18 h of annealing at 110 °C. The films stayed stable after such long annealing indicating the favorable interaction of the parent polymer with the silicon oxide substrate. The parent polymer P(HEMA-*co*-MMA)-2 (Figure 5e) and the corresponding graft polymer G2 (Figure 5f) also showed similar behavior.

In summary, P(HEMA-*co*-MMA)-*g*-PS graft copolymer with well-defined main and side chains was synthesized by the "grafting onto" method via combination of ATRP and photoinduced ester formation reaction of benzodioxinones. The hydroxyl group functionality of the main chain and the benzodioxinone functionality of the side chains were very high. The moderate graft efficiency in photoinduced click coupling reaction obtained may be due to the steric hindrance, as well as the photoactivity of the benzophenone produced concomitantly. The structure of target copolymer and intermediates were well characterized by ^{1}H NMR, GPC, UV, FT-IR, DSC and AFM. This work provided a new click route to prepare the graft copolymers which can be performed under mild conditions without requirement of any catalyst. The readily availability of the hydroxyl functionality in many synthetic and natural polymers makes this method particularly useful for polymer modification. Further studies on the preparation of complex macromolecular structures such as block and multi arm star copolymers, polymer brushes and dendrimers are now in progress together with the search of applying the same process to the other nucleophiles such as amines.

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