6098 *Macromolecules* **2009**, *42*, 6098–6106
DOI: 10.1021/ma901162y

Macromolecules
ARTICLE

Synthesis and Characterization of One-Component Polymeric Photoinitiator by Simultaneous Double Click Reactions and Its Use in Photoinduced Free Radical Polymerization

Gokhan Temel,[†] Binnur Aydogan,[‡] Nergis Arsu,*[,†] and Yusuf Yagci*[,‡]

[†]*Department of Chemistry, Yildiz Technical University, Davutpasa, Istanbul 34210, Turkey, and*
[‡]*Department of Chemistry, Istanbul Technical University, Maslak, Istanbul 34469, Turkey*

Received March 14, 2009; Revised Manuscript Received July 3, 2009

ABSTRACT: A polystyrene copolymer (PS-B-DMAB) possessing both benzophenone and dimethylamino moieties in the side chain was synthesized by a combination of nitroxide-mediated radical polymerization (NMRP) and simultaneous double "click" reactions. First, a random copolymer of styrene (S) and chloromethylstyrene (CMS) with 32 mol % CMS content was prepared by NMRP process. Then, chloromethyl groups were converted to azide groups by reacting with NaN_3 in DMF. The other two click components, namely, propargyl benzophenone (Pr-B) and propargyl 4-(dimethylamino)benzoate (Pr-DMAB), were prepared independently by the etherification and esterification reactions, respectively. Then, in the final stage, the obtained alkyne functional chromophoric (Pr-B) and hydrogen-donating (Pr-DMAB) molecules were anchored to azide-modified polystyrene (PS-N_3) in one-step by "click chemistry". The final polymer (PS-B-DMAB) and the intermediates were characterized in detail by spectral analysis and laser flash photolysis studies. The resulting polymer possesses absorption characteristics similar to bare bezophenone. The one-component photoinitiating nature of PS-B-DMAB was demonstrated by photopolymerization of mono- and multifunctional monomers, namely, methyl methacrylate (MMA) and trimethylolpropane triacrylate (TMPTA), respectively.

Introduction

Photopolymerization processes receive continuous interest because of their wide application in UV-curable coatings, printing inks, photoresists, and microelectronics. These processes are based on the photoinitiator system that absorbs the light to produce species capable of initiating polymerization. Although, in recent years, interest has been expanding to the application of photoinitiated cationic polymerization, the free radical mode is still the most widely employed process.[1−5] Free radical photoinitiators can be classed as α-cleavage (type I) and H-abstraction (type II) initiators. Typical type II photoinitiators include aromatic carbonyls such as benzophenone and derivatives,[6−8] thioxanthone (TX),[9] benzil,[7] quinones,[7] and organic dyes,[10] whereas alcohols, ethers, amines, and thiols are used as hydrogen donors. The free radical generation process is the H-abstraction reaction of triplet photoinitiator from hydrogen donors such as amines and alcohols. The radical derived from the donor can initiate the polymerization, whereas ketyl radicals stemming from aromatic carbonyl compound are usually not reactive toward vinyl monomers because of bulkiness, the delocalization of the unpaired electrons, or both. The overall process is depicted in the example of benzophenone in Scheme 1.

The importance of polymeric photoinitiators lies in their capability of combining the properties of polymers with those of low-molecular-weight photoinitiators.[1,11−14] Solubility and miscibility problems, often observed with coatings containing low-molecular-weight photoinitiators, do not occur with the polymeric ones because polymers are easily miscible with the resin to be cured as well as with the final cured film. Moreover, the low volatility of the large molecules prevents odor and toxicity problems perceived with the conventional photoinitiators. The low migration tendency of polymeric photoinitiators and photoproducts means that cured coatings are less prone to yellowing.[2−5] Most of the polymeric photoinitiators are based on benzophenone and thioxanthone structures because of their easy synthesis, excellent absorption characteristics, and reduced yellowing properties. Recently, side-chain and in-chain thioxanthone/benzophenone macrophotoinitiators have been synthesized via several procedures, such as, condensation[15] and addition[16,17] polymerizations, dendrimer functionalization,[18] click chemistry,[19] organic functionalization reactions,[20,21] and transfer agent reactions.[22]

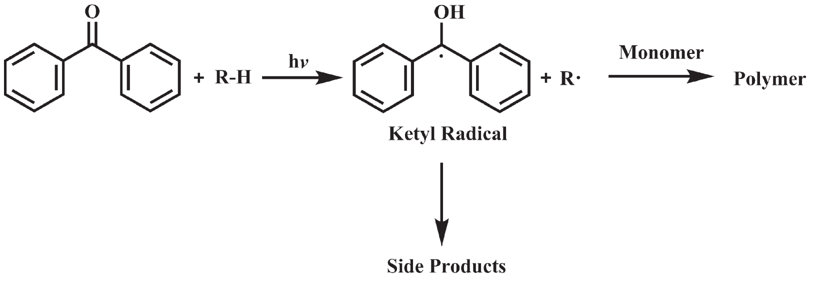
Copper-catalyzed Huisgen 1,3-dipolar cycloaddition reactions[23] between an azide and an alkyne, known as "click" reaction, have attracted much attention because of their important features including high yields, short reaction times, high tolerance of functional groups, and selectivity.[24−26] The Diels–Alder cycloaddition reaction[27] and thiol-ene chemistry[28] have recently been introduced as alternative click routes for providing new materials. Click reactions have been extensively used in the synthesis of polymers with different composition and topology, ranging from linear (telechelic,[29] macromonomer,[30] and block copolymer[31]) to nonlinear macromolecular structures (graft,[32] star,[33] miktoarm star,[34] H-type,[35] dendrimer,[36] dendronized linear polymer,[37] macrocyclic polymer,[38] self-curable polymers,[39] and network system[40]). The development and application of click chemistry in polymer and material science have recently been extensively reviewed.[41]

In this work, we report the one-pot synthesis of a novel one-component polymeric photoinitiator containing side-chain benzophenone and dimethylaminophenyl moieties via double click reactions. The resulting polymeric photoinitiator has been characterized

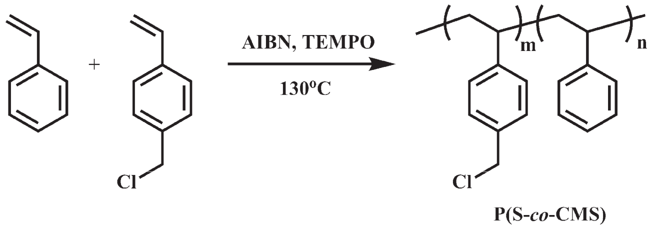
---

*Corresponding authors. (Y.Y.) E-mail: yusuf@itu.edu.tr. Fax: +90-212-2856386. Tel: +90-212-2853241. (N.A.) E-mail: narsu@yildiz.edu.tr. Fax: +90-212-3834134. Tel: +90-212-3834186.

Scheme 1. Photoinitiated Free Radical Polymerization by Using Benzophenone



Scheme 2. Nitroxide-Mediated Radical Copolymerization of Styrene and Chloromethylstyrene



by ^{1}H NMR, FT-IR, and UV spectroscopic measurements, and its photophysical properties has been determined by laser flash photolysis.

Experimental Section

Materials. Styrene (S, 99%, Aldrich) and 4-vinylbenzyl chloride (choloromethyl styrene, CMS, 90%, Acros) were distilled under reduced pressure before use. 2,2′-Azobis(isobutyronitrile) (AIBN, 98%, Aldrich) was recrystallized from ethanol. 2,2,6,6-Tetramethyl-1-piperidinyloxy (TEMPO, 99%, Aldrich) and 2,2′-bipyridine (bpy, 99+%, Acros) were used as received. Tetrahydrofuran (THF, 99.8%, J.T. Baker) was dried and distilled over benzophenone-Na. Other solvents were purified by conventional procedures. Dimethylformamide (DMF, +99%, Aldrich), *N*,*N*-dimethylaniline (DMA, ≥ 99.5%, Fluka), ethyl 4-dimethylaminobenzoate (EDAB, 99%, Alfa Aesar), 4-hydroxybenzophenone (≥98%, Merck), 4-(dimethylamino)benzoyl chloride (97%, Fluka), propargyl bromide solution (~80% in toluene, Fluka), propargyl alcohol (99%, Aldrich), and trimethylolpropane triacrylate (TMPTA, 95%, Aldrich) were used as received.

Synthesis of Propargyl Benzophenone (Pr-B). A solution of 4-hydroxybenzophenone (1 g, 5 mmol) and anhydrous potassium carbonate (1.38 g, 10 mmol) in 30 mL of acetone was stirred for 6 h. After that, propargyl bromide (0.9 g, 7.5 mmol) was added, and the mixture was refluxed for 24 h. Acetone was removed on the rotary evaporator, and the residue was diluted with dichloromethane and washed with water, followed by brine. Then, it was dried over Na_2SO_4. After the rotary evaporation, the crude product was recrystallized from *n*-hexane (yield 85%). mp 72−74 °C. FT-IR (ATR) ν (cm^{-1}): 3233, 3059, 2112, 1635, 1600, 1572, 1307, 1264. ^{1}H NMR ($CDCl_3$ 250 MHz, δ): 7.7 (d, 2H), 7.3 (m, 5H), 7.0 (d, 2H), 4.7 (s, 2H), 2.5 (s, 1H). GC−MS (EI, 70 eV): 236 (M$^+$), 159, 131, 105, 131, 77.

Synthesis of Propargyl 4-(Dimethylamino)benzoate (Pr-DMAB). A solution of 4-(dimethylamino)benzoyl chloride (2.5 g, 13.4 mmol) and propargyl alcohol (0.5 g, 8.9 mmol) in DMF (20 mL) was stirred at 80 °C overnight. After that, the mixture was poured into water, and the crude product was precipitated and filtered. The obtained solid product was dissolved in dichloromethane and extracted with saturated aqueous solution of $NaHCO_3$ (100 mL × 2) and distilled water. The organic layers were dried over anhydrous Na_2SO_4 and filtered, and the solvent was evaporated (yield: 70%). mp 113−117 °C. FT-IR (ATR) ν (cm^{-1}): 3234, 3050, 2119, 1700, 1610, 1316, 1180, 1095. ^{1}H NMR ($CDCl_3$ 250 MHz, δ): 7.8 (d, 2H), 6.5 (d, 2H), 4.8 (s, 2H), 3.0 (s, 6H), 2.5 (s, 1H). GC−MS (EI, 70 eV): 203 (M$^+$), 158, 148, 121, 77.

Synthesis of Poly(styrene-*co*-chloromethylstyrene) P(S-*co*-CMS). P(S-*co*-CMS) was prepared by NMRP of S and CMS in the presence of TEMPO and AIBN. To a Schlenk tube equipped with a magnetic stirring bar, S (1.8968 mL, 16.5 mmol), CMS (2.325 mL, 16.5 mmol), TEMPO (0.12891 g, 0.825 mmol), and AIBN (0.0542 g, 0.33 mmol) were added in that order. The tube was degassed by three freeze−pump−thaw cycles, left in vacuo, and placed in a thermostatted oil bath at 125 °C for 16 h. Subsequently, the polymerization mixture was diluted with THF and precipitated in excess methanol. The polymer was dried for 24 h in a vacuum oven at 25 °C ($M_{n,GPC}$ = 7080, M_w/M_n = 1.16). FT-IR (ATR) ν (cm^{-1}): 3050, 2924, 1602, 1493, 1452, 762, 695, 676. ^{1}H NMR ($CDCl_3$ 250 MHz, δ): 7.5−6.2 (m, 9H), 4.5 (s, 2H), 2.1−1.2 (m, 6H).

Synthesis of Polystyrene−Azide (PS-N_3). P(S-*co*-CMS) (2 g, 0.28 mmol) was dissolved in 4 mL of DMF, and NaN_3 (3.5 g, 54 mmol) was added. The resulting solution was allowed to stir at 25 °C overnight and precipitated in excess methanol. After filtration, the polymer was dried for 24 h in a vacuum oven at 25 °C ($M_{n,GPC}$ = 7180, M_w/M_n = 1.14). FT-IR (ATR) ν (cm^{-1}): 3060, 2925, 2096, 1602, 1493, 1452, 761, 698. ^{1}H NMR ($CDCl_3$ 250 MHz, δ): 7.40−6.20 (m, 9H), 4.25 (s, 2H), 2.1−1.2 (m, 6H).

Synthesis of One-Component Polymeric Initiator (PS-B-DMAB) via Click Reaction. PS-N_3 (0.5 g, 0.070 mmol), Pr-B (0.1 g, 0.43 mmol), and Pr-DMAB (0.26 g, 1.29 mmol) were dissolved in DMF (4 mL) in a Schlenk tube and purged with nitrogen. CuBr (0.25 g, 1.7 mmol) and bpy (0.54 g, 3.4 mmol) were added, and the reaction mixture was degassed by three freeze−pump−thaw cycles and left under nitrogen and stirred at room temperature for 24 h. At the end of this period, the polymer solution was precipitated into methanol and then dissolved in THF and passed through an alumina column to remove copper salt. Finally, it was dried in a vacuum oven at 25 °C (yield: 0.60 g; $M_{n,GPC}$ = 10 100; M_w/M_n = 1.22). FT-IR (ATR) ν (cm^{-1}): 3050, 2925, 2090, 1701, 1605, 1275, 1182, 1097, 769. ^{1}H NMR ($CDCl_3$ 250 MHz, δ): 7.8−6.2 (m, 32H), 5.3−5.1 (m, 8H), 4.25 (s, 2H), 2.9 (s, 6H), 2.1−1.2 (m, 12H).

Instrumentation. ^{1}H NMR measurements were recorded in $CDCl_3$ with $Si(CH_3)_4$ as internal standard using a Bruker AC250 (250.133 MHz) instrument. 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 a Perkin-Elmer Diamond DSC. Molecular weights were determined by a gel permeation chromatography (GPC) instrument, Viscotek GPCmax Autosampler system, consisting of a pump, three ViscoGEL GPC columns (G2000H_{HR}, G3000H_{HR}, and G4000H_{HR}), a Viscotek UV detector, and a Viscotek differential refractive index (RI) detector with a THF 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. Laser flash photolysis experiments employed the pulses from an Applied Photophysics with YAG laser (355 nm, pulse, 5 ns) and a computer-controlled system.

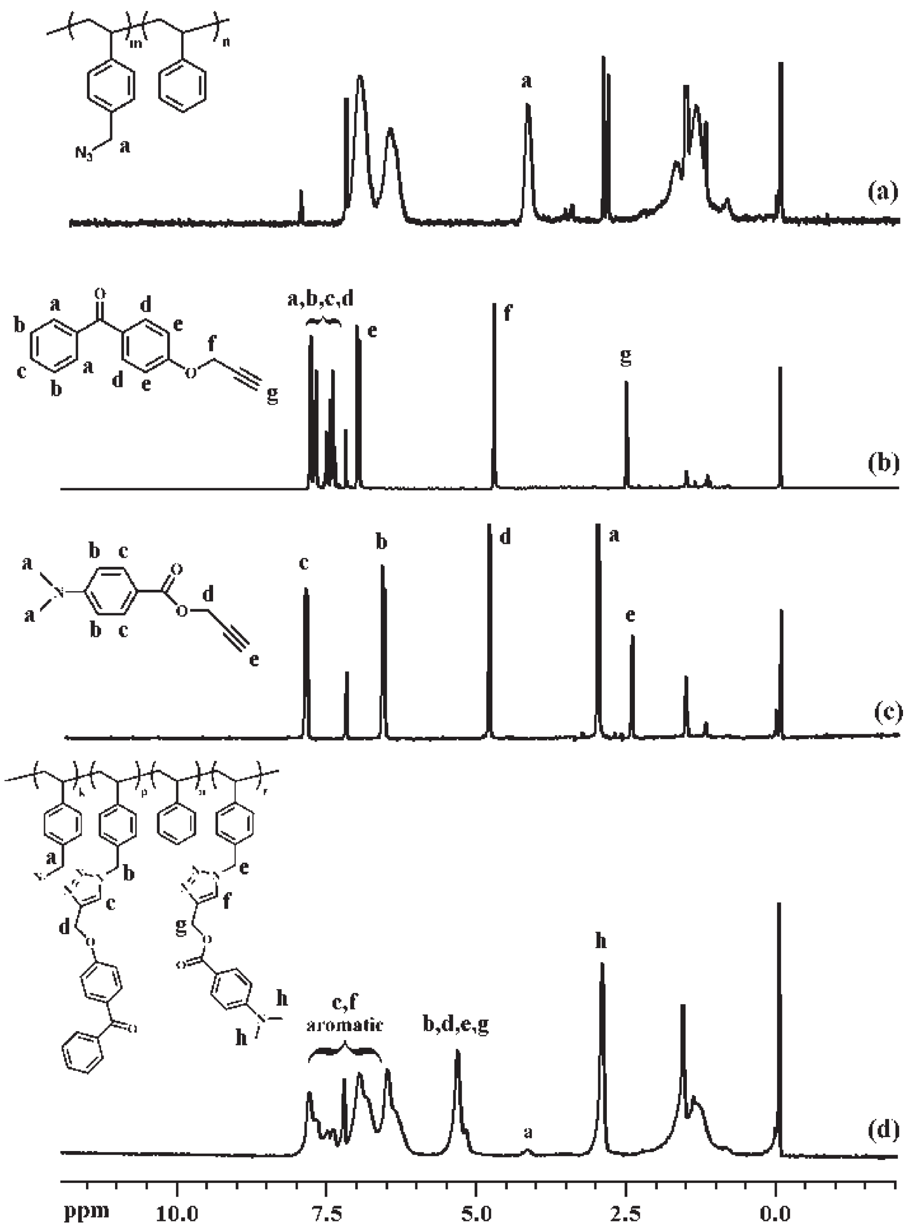


Figure 1. ^{1}H NMR spectra of (a) PS-N_3, (b) Pr-B, (c) Pr-DMAB, and (d) PS-B-DMAB in $CDCl_3$.

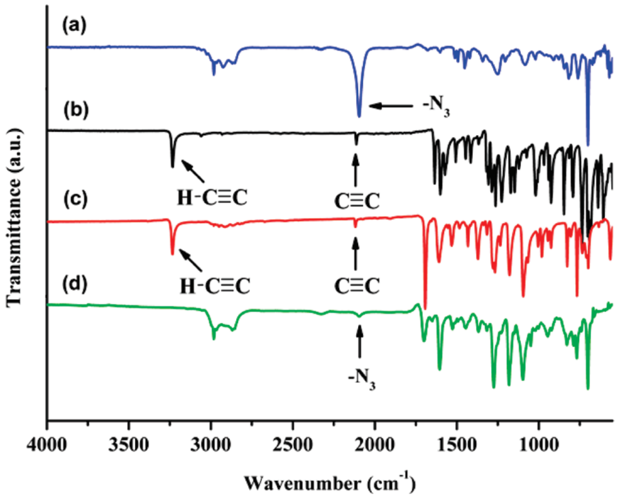


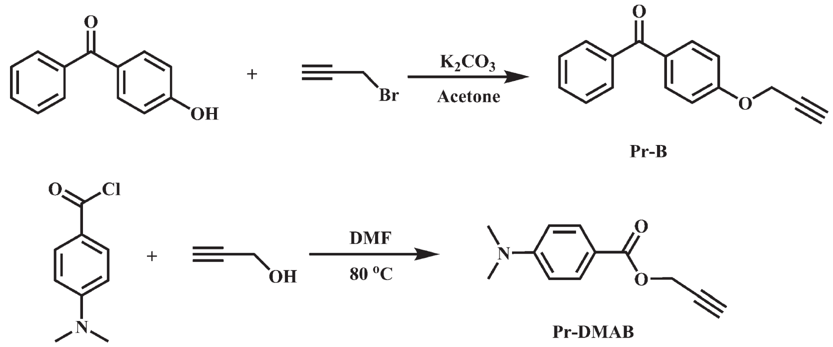
Figure 2. FT-IR spectra of (a) PS-N_3, (b) Pr-B, (c) Pr-DMAB, and (d) PS-B-DMAB.

Gas chromatography−mass spectroscopy (GC−MS) was performed using an Agilent 6890/5973 inert gas chromatograph/mass selective detector system in electrospray ionization mode (70 eV) through an HP-5MS capillary column using helium as the carrier gas at a flow rate of 1.6 mL min^{-1}.

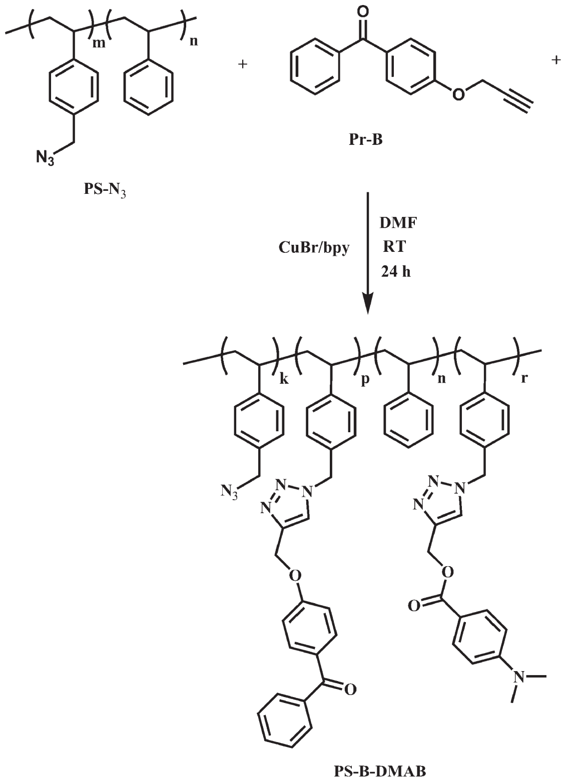
Photocalorimetry (Photo-DSC). The photodifferential scanning calorimetry (photo-DSC) measurements were carried out by means of a modified Perkin-Elmer Diamond DSC equipped with a high-pressure mercury arc lamp (320−500 nm). A uniform UV light intensity is delivered across the DSC cell to the sample and reference pans. The intensity of the light was measured to be 53 mW cm^{-2} by a UV radiometer capable of broad UV range coverage. The mass of the sample was 8 mg, and the measurements were carried out in an isothermal mode at 30 °C under a nitrogen flow of 20 mL min^{-1}. The reaction heat liberated in the polymerization was directly proportional to the number of acrylate groups reacted in the system. By integrating the area under the exothermic peak, the conversion of the acrylate groups (*C*) or the extent of the reaction was determined according to eq 1

$$C = \Delta H_t / \Delta H_0^{\text{theory}} \qquad (1)$$

Scheme 3. Propargylation of Benzophenone and Dimethylaminophenyl Derivatives



Scheme 4. Synthesis of One-Component Polymeric Photoinitiator by Simultaneous Double Click Reaction



where $\triangle H_t$ is the reaction heat evolved at time t and $\triangle H_0^{\text{theory}}$ is the theoretical heat for complete conversion. $\triangle H_0^{\text{theory}}$ = 86 kJ mol^{-1} for an acrylic double bond.[42] The rate of polymerization (R_p) is directly related to the heat flow (dH/dt) by eq 2

$$R_p = dC/dt = (dH/dt)/\Delta H_0^{\text{theory}} \qquad (2)$$

Results and Discussion

A one-component polymeric photoinitiator (PS-B-DMAB) possessing benzophenone (type II photoinitiator) and dimethylaminobenzoic acid derivative (hydrogen donor) as side-chain moieties was synthesized according to click chemistry strategy in a one-pot reaction. First, poly(styrene-*co*-chloromethylstyrene) P(S-*co*-CMS) containing 32 mol % of CMS units, as determined using ^{1}H NMR spectroscopy, was prepared via nitroxide-mediated radical copolymerization (NMRP) (Scheme 2).

P(S-*co*-CMS) copolymer with the molecular weight of M_n = 7080 and polydispersity M_w/M_n = 1.16 was modified by azidation procedure using NaN_3 as described in the Experimental Section to obtain copolymers with azide groups. Primarily, the extent of substitution in the azidation was determined by ^{1}H NMR and FT-IR. From the ^{1}H NMR spectrum of $PS-N_3$ (shown in Figure 1a), it was observed that whereas the signal at 4.5 ppm corresponding to CH_2-Cl protons of the precursor P(S-*co*-CMS) completely disappeared, a new signal appeared at 4.25 ppm because of CH_2 linked to azide groups. The structure of polystyrene-azide ($PS-N_3$) was further supported by the observation from the IR spectrum of the azide stretching band at 2094 cm^{-1} (Figure 2a).

In our study, we selected propargyl groups as the reactive click components because they can easily be prepared from cheap and commercially available compounds by simple etherification and esterification reactions. Additionally, the ether and ester linkages provide sufficient flexibility for the ultimate photoexcitation and hydrogen abstraction reactions of benzophenone and amino groups. Therefore, propargyl functionality was introduced independently into hydroxyl functional benzophenone and acid chloride of dimethylaminobenzoic acid (Scheme 3).

Propargyl functional benzophenone (Pr-B) and dimethylaminobenzoate (Pr-DMAB) were characterized by ^{1}H NMR and FT-IR spectroscopy. As can be seen from Figures 1 and 2, both

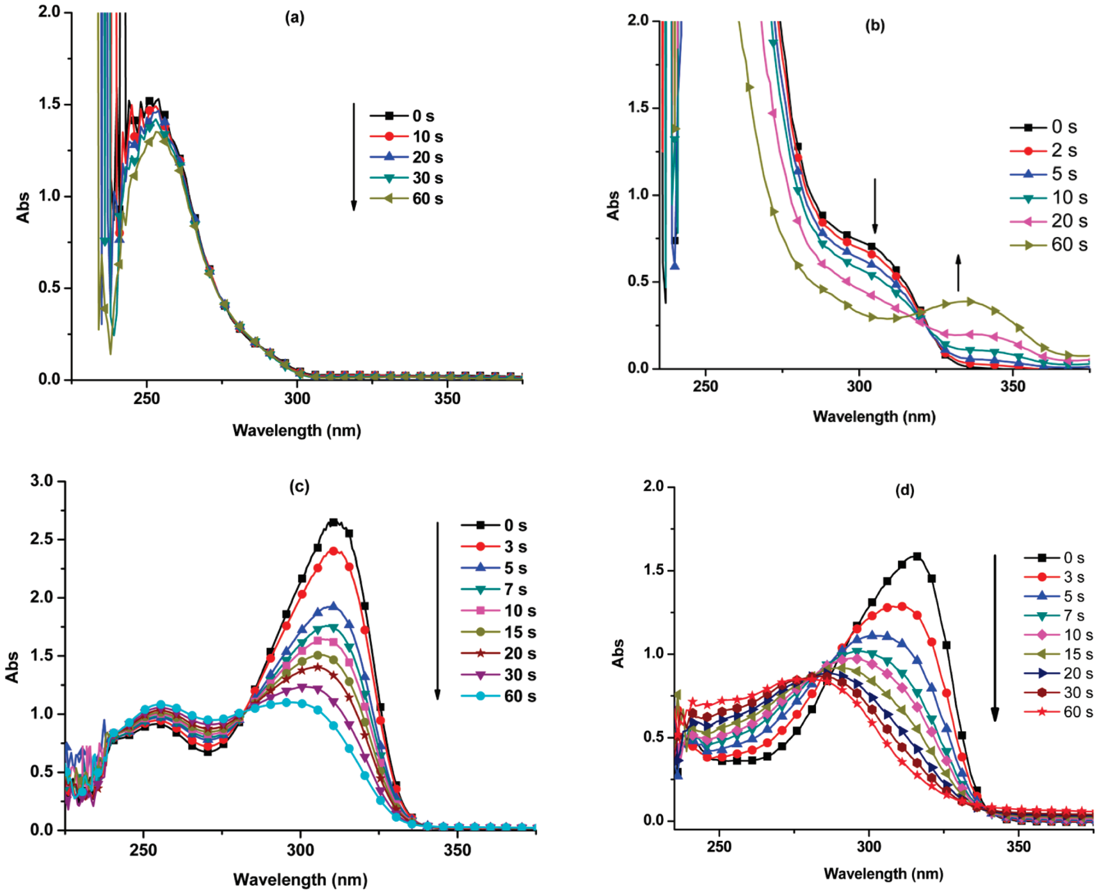


Figure 3. Absorption spectra of (a) B (2.5×10^{-5} mol L^{-1}), (b) B (2.5×10^{-5} mol L^{-1})/DMA (7.5×10^{-5} mol L^{-1}), (c) B (2.5×10^{-5} mol L^{-1})/EDAB (7.5×10^{-5} mol L^{-1}), and (d) PS-B-DMAB (1.3×10^{-5} mol L^{-1}, in terms of benzophenone moieties) in $CHCl_3$.

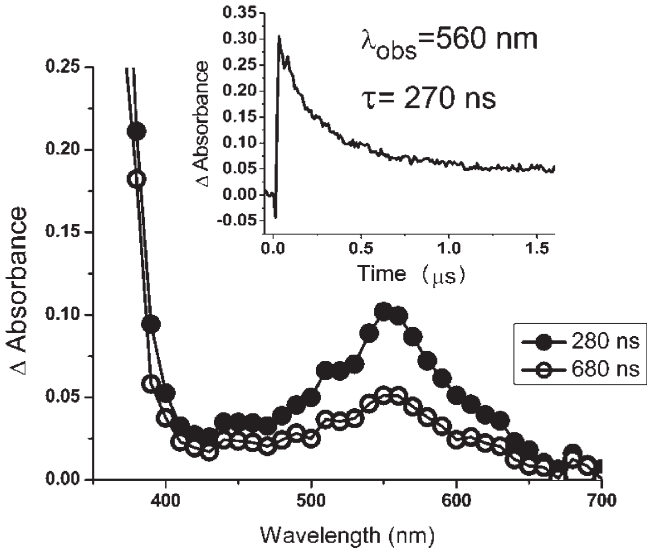


Figure 4. Transient optical absorption spectra recorded at 280 and 680 ns following laser excitation (355 nm, 5 ns) in nitrogen-saturated $CHCl_3$ solution of PS-B-DMAB (concentration = 2×10^{-3} mol L^{-1} in terms of benzophenone moieties).

compounds exhibit characteristic protons and signals emerging from the acetylene and corresponding ether or ester and aromatic groups in their ^1H NMR and IR spectra.

Then, a standard "click" protocol has been performed. The PS-N_3 was dissolved in DMF and reacted with Pr-B and Pr-DMAB in the presence of a catalytic amount of CuBr and bipyridine at room temperature. The simultaneous two click reactions afforded the desired product, PS-B-DMAB (Scheme 4). After we removed the catalyst, the polymeric photoinitiator possessing both light-absorbing and hydrogen-donating sites in the structure was precipitated and dried under vacuum.

In this connection, it should be noted that the amount of Pr-DMAB compared with Pr-B in the click reaction was deliberately kept in excess so as to obtain polymeric photoinitiator with more hydrogen-donating sites in the structure. In fact, in curing applications involving type II photoinitiation, formulations usually contain amine at high concentrations. As far as the ultimate use of the resulting polymer (PS-B-DMAB) as the initiator in photopolymerizations is concerned, two points were important: the extent of conversion of the side azido moieties and the effect of click reaction on the stability of the benzophenone chromophore. We monitored the former issue by ^1H NMR by observing the disappearance of the methylene protons adjacent to the azido group (N_3-CH_2Ph) at 4.2 ppm and the appearance of the new methylene protons adjacent to the triazole ring at 5.3 ppm (triazole-CH_2Ph) (Figure 1). Moreover, the band corresponding to the $-N_3$ group at 2094 cm^{-1} almost completely disappeared (Figure 2). Therefore, the side-group click reaction was efficient, as evidenced by near-quantitative functionalization. In accordance with the molar feed ratios of propargyl compounds in the click reaction, the amino groups were found to be about three times more than benzophenone units, as determined by ^1H NMR analysis.

The incorporation of benzophenone and amino groups into the polymer was also evidenced by UV absorption and laser flash photolysis measurements. Figure 3 shows the UV spectral changes of benzophenone in the absence and presence of two

Table 1. Photoinitiated Free Radical Polymerization of MMA at λ_{max} = 350 nm[a]

run	photoinitiator (mol L^{-1})[b]	solvent	$R_p \times 10^5$ (mol L^{-1} s^{-1})	M_n (g mol^{-1})[c]
1	B (1×10^{-2})	$CHCl_3$		
2[d]	B (1×10^{-2})	$CHCl_3$	13.63	17 350
3	PS-B-DMAB (1×10^{-2})	$CHCl_3$	4.99	50 900
4	PS-B-DMAB (1×10^{-2})	$CHCl_3$[e]	7.14	111 300
5	PS-B-DMAB (2×10^{-3})	THF	5.52	45 790
6	PS-B-DMAB (2×10^{-3})	DMF	7.14	90 500

[a] [MMA] = 4.68 mol L^{-1}, time = 2 h. [b] Photoinitiator concentration is given in terms of benzophenone moieties. [c] Determined by GPC according to linear polystyrene standards. [d] Benzophenone/*N*,*N*-dimethylaniline: 1/3 is used as the photoinitiating system. [e] Carried out under a nitrogen atmosphere.

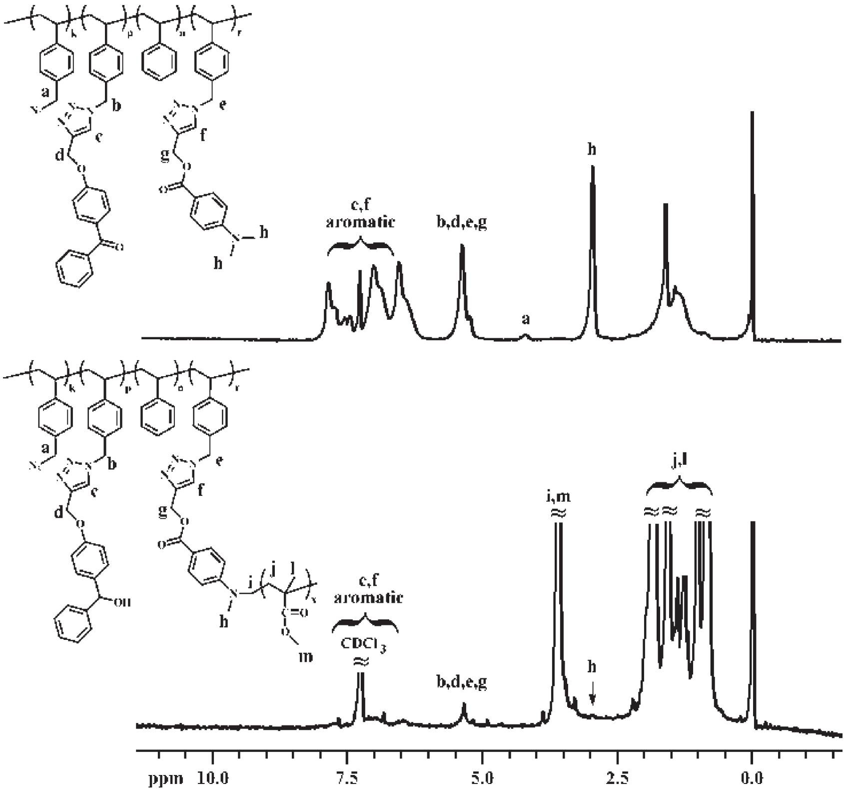


Figure 5. ^{1}H NMR spectra of PS-B-DMAB and poly(styrene-*graft*-methyl methacrylate) (P(S-*g*-MMA), obtained after photolysis in the presence of MMA).

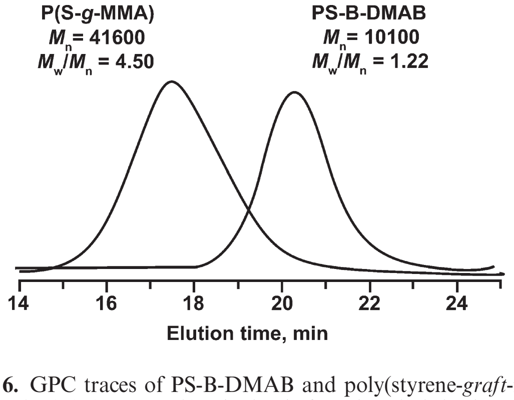


Figure 6. GPC traces of PS-B-DMAB and poly(styrene-*graft*-methyl methacrylate) (P(S-*g*-MMA), obtained after photolysis in the presence of MMA).

different amines, namely, *N*,*N*-dimethyl aniline (DMA) and ethyl 4-dimethylaminobenzoate (EDAB), and PS-B-DMAB upon irradiation at >300 nm. Initially, all spectra contain the characteristic absorption of benzophenone chromophore. Notably, whereas benzophenone is photobleached only in the presence of an added hydrogen donor, the polymeric photoinitiator rapidly decompose itself upon irradiation because it contains hydrogen-donating amino groups in the structure. Interestingly, EDAB is structurally (and regarding yellowing properties) closer to the polymer-bound amine than DMA. In this case, no new absorption developed at the higher wavelengths during photobleaching (Figure 3c).

Laser flash photolysis of a highly diluted solution of PS-B-DMAB in $CHCl_3$ affords a readily detectable transient absorption spectrum, which decayed in a first-order kinetic regime (Figure 4). The maximum absorption is at 560 nm, which is similar to the triplet–triplet absorption of parent B.[43] Therefore, we concluded that the transient absorption corresponds to the triplet–triplet absorption of side-chain benzophenone moieties. However, the transient decay kinetic is much faster with a lifetime of τ = 270 ns indicating dominant intra- and intermolecular hydrogen abstraction by side-chain amino groups.

PS-B-DMAB was used as a photoinitiator for the polymerization of methyl methacrylate (MMA) in the presence and absence of air. A comparison of the obtained results is listed in Table 1. Here photopolymerizations by using either benzophenone itself or a benzophenone/DMA combination are also included. As can be seen, benzophenone is not an efficient photoinitiator in the absence of a coinitiator. The presence of an amine such as DMA is important for effective photoreduction and photopolymerization. PS-B-DMAB initiates the polymerization in the absence of added coinitiator. The relatively lower reactivity compared with the B/DMA combination may be

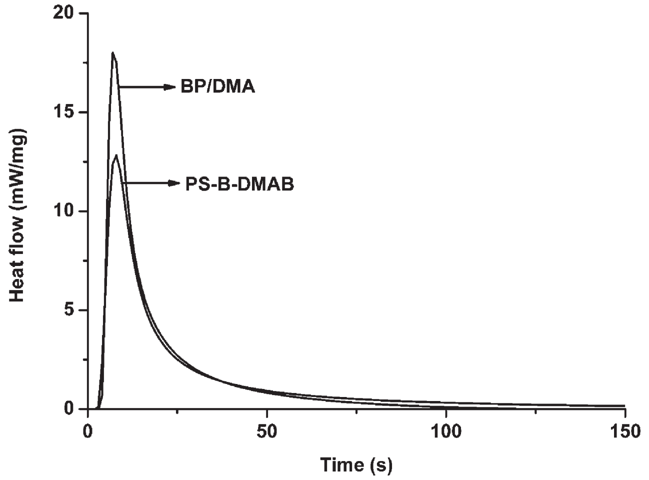


Figure 7. Heat flow versus time for the polymerization of TMPTA initiated by PS-B-DMAB and BP/DMA systems cured at 30 °C by UV light with an intensity of 53 mW cm^{-2}. (The photoinitiator concentration is 0.0015 M in terms of BP moieties.)

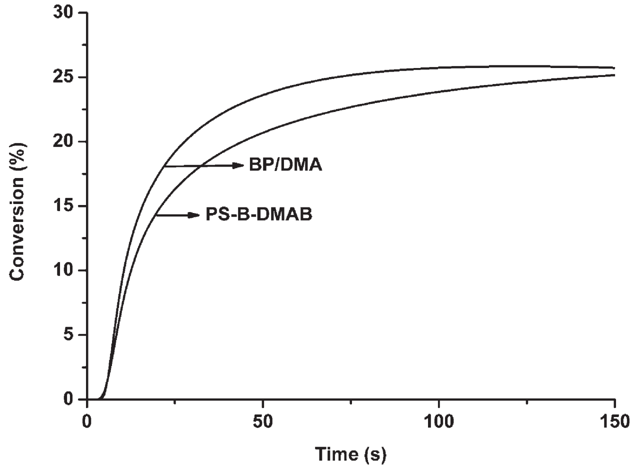
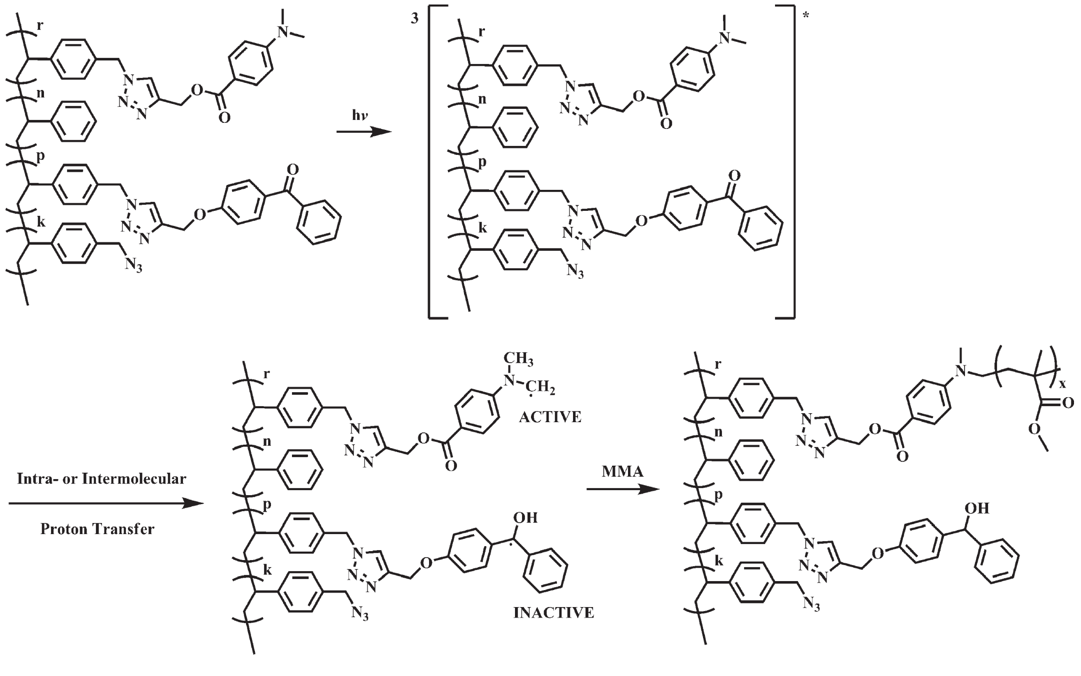


Figure 8. Conversion versus time for the polymerization of TMPTA initiated by PS-B-DMAB and BP/DMA systems cured at 30 °C by UV light with an intensity of 53 mW cm^{-2}. (The photoinitiator concentration is 0.0015 M in terms of BP moieties.)

Scheme 5. Photoinitiated Free Radical Polymerization of Methyl Methacrylate (MMA) by Using Polymeric Photoinitiator (PS-B-DMAB)



attributed to the mobility and activity of polymeric radicals. A similar polymer effect was observed with other polymeric photoinitiators.[44] Polarity and hydrogen-donating capability of the solvents also effects the polymerization. Dimethylformamide (DMF) seemed to be a quite suitable solvent for the photopolymerization initiated by PS-B-DMAB. Although radical polymerizations are not sensitive to the polarity of the solvent,[45] the triplet-state lifetime of photoinitiators involving electron transfer such as thioxanthone and benzophenone derivatives may depend on some polarity effects.[46] Tetrahydrofuran (THF) is another suitable solvent that is known[7] to be a good hydrogen-donating solvent for excited aromatic carbonyl compounds.

To gain more insight into the chemistry and reactivity of macromolecular free radicals, an independent control experiment was performed in $CHCl_3$. In this case, the monomer concentration and polymerization time were deliberately reduced ([MMA] = 2 mol L^{-1}, [PS-B-DMAB] = 1×10^{-2} mol L^{-1}, time = 1 h) so as to obtain graft copolymers with a relatively short PMMA side chain for better structural analysis. Figure 5 shows the ^{1}H NMR spectra of the PS-B-DMAB before and after photolysis in the presence of MMA. As can be seen, the intensity of $N(CH_3)$ protons appearing at 3.0 ppm significantly decreased after the photolysis, indicating that the initiation occurs through aminomethyl radicals stemming from the hydrogen abstraction by the excited benzophenone. Moreover, in the spectrum (Figure 5), characteristic protons of both main chain (PS) and side chain (PMMA) are detectable. GPC analysis of PS-B-DMAB before and after photolysis in the presence of MMA confirmed the grafting reaction by means of a clear shift toward the lower elution volume (Figure 6). On the basis of these results and the general behavior of benzophenone-based type II photoinitiating systems, a mechanism is proposed in Scheme 5.

For the possibility of using the described photoinitiator in practical applications, the efficiency of PS-B-DMAB in the photocuring of formulations containing multifunctional monomers such as trimethylolpropane triacrylate (TMPTA) was also studied. Photo-DSC plots of this experiment and its comparison with benzophenone/*N*,*N*-dimethylaniline are shown in Figure 7. Figure 8 displays a plot of the conversion versus irradiation time derived from Figure 7.

The results verify that PS-B-DMAB can efficiently be used in multifunctional UV curable systems. This initiating system has the advantage of overcoming the presence of migratables in a coating because both sensitizer and amine are incorporated into the same polymer. Apparently, BP/DMA can initiate the photopolymerization of TMPTA more efficiently than the PS-B-DMAB. This behavior may be ascribed to the limited mobility because the addition of the polymeric photoinitiator to the formulation leads to an increase in the viscosity of the formulation to a far greater extent than for its monomeric counter parts.[47]

In conclusion, in this article, we have reported the synthesis of a one-component type II macrophotoinitiator for free radical polymerization via one-pot double click reactions. The obtained photoinitiator, possessing both light absorbing and hydrogen-donating sites as side-chains in the structure, is able to polymerize mono- and multifunctional acrylate monomers without the requirement of an additional coinitiator.

Although the conventional benzophenone amine system is still the more efficient photoinitiator, it is clear that PS-B-DMAB avoids the use of large amounts of amines in the formulation. This is particularly important for curing applications because formulations containing amine at high concentrations cause a decrease in the pendulum hardness of the cured films as a result of the plasticizing effect of amines.[48] Moreover, migration problems associated with photofragments of low-molar-mass photoinitiators are overcome. These properties suggest that the polymeric photoinitiator may find use in a variety of practical applications.

Acknowledgment. Y.Y. would like to thank the Turkish Academy of Sciences for financial support.

References and Notes

(1) Davidson, R. S. *J. Photochem. Photobiol., A* **1993**, *73*, 81–96.

(2) Arsu, N.; Reetz, I.; Yagci, Y.; Mishra, M. K. Chapter 8. In *Handbook of Vinyl Polymers: Radical Polymerization, Process, and Technology*, 2nd ed.; Mishra, M. K., Yagci, Y., Eds.; CRC Press: Boca Raton, FL, 2009; pp 141−204.

(3) Dietliker, K. In *Chemistry & Technology of UV & EB Formulation for Coatings, Inks, and Paints*; SITA Technology Ltd.: London, 1991; Vol. *III*, pp 76−78.

(4) Fouassier, J. P. In *Photoinitiation, Photopolymerization, and Photocuring: Fundamentals and Applications*; Hanser: Munich, 1995; pp 1−7.

(5) Pappas, S. P. In *UV Curing: Science and Technology*; Technology Marketing Corporation: Norwalk, CT, 1987; pp 2−13.

(6) Davidson, R. S. In *Advances in Physical Chemistry*; Bethel, D., Gold, V., Eds.; Academic Press: London, 1983; p 1.

(7) Ledwith, A.; Bosley, J. A.; Purbrick, M. D. *J. Oil Colour Chem. Assoc.* **1978**, *61*, 95–104.

(8) Ledwith, A.; Purbrick, M. D. *Polymer* **1973**, *14*, 521–522.

(9) (a) Aydin, M.; Arsu, N.; Yagci, Y. *Macromol. Rapid Commun.* **2003**, *24*, 718–723. (b) Aydin, M.; Arsu, N.; Yagci, Y.; Jockusch, S.; Turro, N. J. *Macromolecules* **2005**, *38*, 4133–4138. (c) Cokbaglan, L.; Arsu, N.; Yagci, Y.; Jockusch, S.; Turro, N. J. *Macromolecules* **2003**, *36*, 2649–2653. (d) Balta, D. K.; Arsu, N.; Yagci, Y.; Jockusch, S.; Turro, N. J. *Macromolecules* **2007**, *40*, 4138–4141. (e) Balta, D. K.; Cetiner, N.; Temel, G.; Turgut, Z.; Arsu, N. *J. Photochem. Photobiol., A* **2008**, *199*, 316–321.

(10) (a) Polykarpov, A. Y.; Hassoon, S.; Neckers, D. C. *Macromolecules* **1996**, *29*, 8274–8276. (b) Shi, J. M.; Zhang, X. P.; Neckers, D. C. *J. Org. Chem.* **1992**, *57*, 4418–4421. (c) Shi, J. M.; Zhang, X. P.; Neckers, D. C. *Tetrahedron Lett.* **1993**, *34*, 6013–6016. (d) Tanabe, T.; Torresfilho, A.; Neckers, D. C. *J. Polym. Sci., Polym. Chem. Ed.* **1995**, *33*, 1691–1703. (e) Valdesaguilera, O.; Pathak, C. P.; Shi, J.; Watson, D.; Neckers, D. C. *Macromolecules* **1992**, *25*, 541–547.

(11) Ajayaghosh, A. *Polymer* **1995**, *36*, 2049–2053.

(12) (a) Angiolini, L.; Caretti, D.; Carlini, C.; Corelli, E.; Salatelli, E. *Polymer* **1999**, *40*, 7197–7207. (b) Angiolini, L.; Caretti, D.; Corelli, E.; Carlini, C.; Rolla, P. A. *J. Appl. Polym. Sci.* **1997**, *64*, 2247–2258. (c) Angiolini, L.; Caretti, D.; Salatelli, E. *Macromol. Chem. Phys.* **2000**, *201*, 2646–2653. (d) Carlini, C.; Angiolini, L.; Caretti, D.; Corelli, E. *Polym. Adv. Technol.* **1996**, *7*, 379–384.

(13) Corrales, T.; Catalina, F.; Peinado, C.; Allen, N. S. *J. Photochem. Photobiol., A* **2003**, *159*, 103–114.

(14) (a) Degirmenci, M.; Hizal, G.; Yagci, Y. *Macromolecules* **2002**, *35*, 8265–8270. (b) Degirmenci, M.; Akbulut, M. A.; Hicri, S.; Yilmaz, H. *Polym. J.* **2008**, *40*, 729–735. (c) Degirmenci, M.; Hicri, S.; Yilmaz, H. *Eur. Polym. J.* **2008**, *44*, 3776–3781. (d) Degirmenci, M.; Taskesen, E.; Hicri, S.; Yilmaz, H. *J. Polym. Sci., Polym. Chem. Ed.* **2008**, *46*, 5404–5413. (e) Hizal, G.; Yagci, Y.; Schnabel, W. *Polymer* **1994**, *35*, 4443–4448.

(15) (a) Wei, J.; Wang, H. Y.; Jiang, X. S.; Yin, J. *Macromol. Chem. Phys.* **2006**, *207*, 1752–1763. (b) Wei, J.; Wang, H. Y.; Yin, J. *J. Polym. Sci., Polym. Chem. Ed.* **2007**, *45*, 576–587. (c) Jiang, X. S.; Yin, J. *Macromol. Rapid Commun.* **2004**, *25*, 748–752. (d) Jiang, X. S.; Yin, H. *Polymer* **2004**, *45*, 5057–5063. (e) Jiang, X. S.; Yin, J. *Macromol. Chem. Phys.* **2008**, *209*, 1593–1600. (f) Jiang, X. S.; Yin, J. *J. Appl. Polym. Sci.* **2004**, *94*, 2395–2400.

(16) Wang, H. Y.; Wei, J.; Jiang, X. S.; Yin, J. *J. Photochem. Photobiol., A* **2007**, *186*, 106–114.

(17) Rufs, A. M.; Valdebenito, A.; Rezende, M. C.; Bertolotti, S.; Previtali, C.; Encinas, M. V. *Polymer* **2008**, *49*, 3671–3676.

(18) (a) Jiang, X. S.; Xu, H. J.; Yin, J. *Polymer* **2005**, *46*, 11079–11084. (b) Jiang, X. S.; Yin, J. *Macromolecules* **2004**, *37*, 7850–7853.

(19) Gacal, B.; Akat, H.; Balta, D. K.; Arsu, N.; Yagci, Y. *Macromolecules* **2008**, *41*, 2401–2405.

(20) (a) Temel, G.; Arsu, N. *J. Photochem. Photobiol., A* **2009**, *202*, 63–66. (b) Temel, G.; Arsu, N.; Yagci, Y. *Polym. Bull.* **2006**, *57*, 51–56.

(21) Jiang, X. S.; Xu, H. J.; Yin, H. *Polymer* **2004**, *45*, 133–140.

(22) Karasu, F.; Arsu, N.; Yagci, Y. *J. Appl. Polym. Sci.* **2007**, *103*, 3766–3770.

(23) Huisgen, R. In *1,3-Dipolar Cycloaddition Chemistry*; Padwa, A., Ed.; Wiley: New York, 1984; Vol. *1*, pp 1−176.

(24) Kolb, H. C.; Finn, M. G.; Sharpless, K. B. *Angew. Chem., Int. Ed.* **2001**, *40*, 2004–2021.

(25) Rostovtsev, V. V.; Green, L. G.; Fokin, V. V.; Sharpless, K. B. *Angew. Chem., Int. Ed.* **2002**, *41*, 2596–2599.

(26) Tornøe, C. W.; Christensen, C.; Meldal, M. *J. Org. Chem.* **2002**, *67*, 3057–3064.

(27) Kwart, H.; King, K. *Chem. Rev.* **1968**, *68*, 415–447.

(28) Gress, A.; Volkel, A.; Schlaad, H. *Macromolecules* **2007**, *40*, 7928–7933.

(29) (a) Gao, H. F.; Louche, G.; Sumerlin, B. S.; Jahed, N.; Golas, P.; Matyjaszewski, K. *Macromolecules* **2005**, *38*, 8979–8982. (b) Lutz, J.-F.; Borner, H. G.; Weichenhan, K. *Macromol. Rapid Commun.* **2005**, *26*, 514–518.

(30) (a) Liu, Q. C.; Chen, Y. M. *J. Polym. Sci., Polym. Chem. Ed.* **2006**, *44*, 6103–6113. (b) Vogt, A. P.; Sumerlin, B. S. *Macromolecules* **2006**, *39*, 5286–5292.

(31) (a) Durmaz, H.; Colakoclu, B.; Tunca, U.; Hizal, G. *J. Polym. Sci., Polym. Chem. Ed.* **2006**, *44*, 1667–1675. (b) Durmaz, H.; Dag, A.; Altintas, O.; Erdogan, T.; Hizal, G.; Tunca, U. *Macromolecules* **2007**, *40*, 191–198. (c) Kluger, C.; Binder, W. H. *J. Polym. Sci., Polym. Chem. Ed.* **2007**, *45*, 485–499. (d) Lutz, J.-F.; Borner, H. G.; Weichenhan, K. *Macromolecules* **2006**, *39*, 6376–6383. (e) Opsteen, J. A.; van Hest, J. C. M. *Chem. Commun.* **2005**, 57–59. (f) Quemener, D.; Davis, T. P.; Barner-Kowollik, C.; Stenzel, M. H. *Chem. Commun.* **2006**, 5051–5053.

(32) (a) Binder, W. H.; Kluger, C. *Macromolecules* **2004**, *37*, 9321–9330. (b) Ladmiral, V.; Mantovani, G.; Clarkson, G. J.; Cauet, S.; Irwin, J. L.; Haddleton, D. M. *J. Am. Chem. Soc.* **2006**, *128*, 4823–4830. (c) Li, H. M.; Cheng, F. O.; Duft, A. M.; Adronov, A. *J. Am. Chem. Soc.* **2005**, *127*, 14518–14524. (d) Luxenhofer, R.; Jordan, R. *Macromolecules* **2006**, *39*, 3509–3516. (e) Parrish, B.; Breitenkamp, R. B.; Emrick, T. *J. Am. Chem. Soc.* **2005**, *127*, 7404–7410. (f) Riva, R.; Schmeits, P.; Stoffelbach, F.; Jerome, C.; Jerome, R.; Lecomte, P. *Chem. Commun.* **2005**, 5334–5336. (g) Sumerlin, B. S.; Tsarevsky, N. V.; Louche, G.; Lee, R. Y.; Matyjaszewski, K. *Macromolecules* **2005**, *38*, 7540–7545. (h) Sun, X. L.; Stabler, C. L.; Cazalis, C. S.; Chaikof, E. L. *Bioconjugate Chem.* **2006**, *17*, 52–57. (i) Wang, X. Y.; Kimyonok, A.; Weck, M. *Chem. Commun.* **2006**, 3933–3935.

(33) (a) Altintas, O.; Yankul, B.; Hizal, G.; Tunca, U. *J. Polym. Sci., Polym. Chem. Ed.* **2006**, *44*, 6458–6465. (b) Gao, H. F.; Matyjaszewski, K. *Macromolecules* **2006**, *39*, 4960–4965. (c) Hoogenboom, R.; Moore, B. C.; Schubert, U. S. *Chem. Commun.* **2006**, 4010–4012.

(34) (a) Fu, Q.; Wang, G.; Lin, W.; Huang, J. *J. Polym. Sci., Polym. Chem. Ed.* **2009**, *47*, 986–990. (b) Gozgen, A.; Dag, A.; Durmaz, H.;

Sirkecioglu, O.; Hizal, G.; Tunca, U. *J. Polym. Sci., Polym. Chem. Ed.* **2009**, *47*, 497–504. (c) Whittaker, M. R.; Urbani, C. N.; Monteiro, M. J. *J. Am. Chem. Soc.* **2006**, *128*, 11360–11361.

(35) (a) Gungor, E.; Cote, G.; Erdogan, T.; Durmaz, H.; Demirel, A. L.; Hizal, G.; Tunca, U. *J. Polym. Sci., Polym. Chem. Ed.* **2007**, *47*, 1055–1065. (b) Gungor, E.; Durmaz, H.; Hizal, G.; Tunca, U. *J. Polym. Sci., Polym. Chem. Ed.* **2008**, *46*, 4459–4468.

(36) (a) Fernandez-Megia, E.; Correa, J.; Rodriguez-Meizoso, I.; Riguera, R. *Macromolecules* **2006**, *39*, 2113–2120. (b) Joralemon, M. J.; O'Reilly, R. K.; Matson, J. B.; Nugent, A. K.; Hawker, C. J.; Wooley, K. L. *Macromolecules* **2005**, *38*, 5436–5443. (c) Lee, J. W.; Kim, B.-K.; Kim, H. J.; Han, S. C.; Shin, W. S.; Jin, S.-H. *Macromolecules* **2006**, *39*, 2418–2422. (d) Wu, P.; Feldman, A. K.; Nugent, A. K.; Hawker, C. J.; Scheel, A.; Voit, B.; Pyun, J.; Frechet, J. M. J.; Sharpless, K. B.; Fokin, V. V. *Angew. Chem., Int. Ed.* **2004**, *43*, 3928–3932.

(37) (a) Helms, B.; Mynar, J. L.; Hawker, C. J.; Frechet, J. M. J. *J. Am. Chem. Soc.* **2005**, *126*, 15020–15021. (b) Mynar, J. L.; Choi, T.-L.; Yoshida, M.; Kim, V.; Hawker, C. J.; Frechet, J. M. J. *Chem. Commun.* **2005**, 5169–5171.

(38) (a) Ge, Z.; Zhou, Y.; Xu, J.; Liu, H.; Chen, D.; Liu, S. *J. Am. Chem. Soc.* **2009**, *131*, 1628–1629. (b) Laurent, B. A.; Grayson, S. M. *J. Am. Chem. Soc.* **2006**, *128*, 4238–4239.

(39) (a) Ergin, M.; Kiskan, B.; Gacal, B.; Yagci, Y. *Macromolecules* **2007**, *40*, 4724–4727. (b) Kiskan, B.; Demiray, G.; Yagci, Y. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 3512–3518.

(40) (a) Diaz, D. D.; Punna, S.; Holzer, P.; Mcpherson, A. K.; Sharpless, K. B.; Fokin, V. V.; Finn, M. G. *J. Polym. Sci., Polym. Chem. Ed.* **2004**, *42*, 4392–4403. (b) Johnson, J. A.; Lewis, D. R.; Diaz, D. D.; Finn, M. G.; Koberstein, J. T.; Turro, N. J. *J. Am. Chem. Soc.* **2006**, *128*, 6564–6565. (c) Malkoch, M.; Vestberg, R.; Gupta, N.; Mespouille, L.; Dubois, P.; Mason, A. F.; Hedrick, J. L.; Liao, Q.; Frank, C. W.; Kingsbury, K.; Hawker, C. J. *Chem. Commun.* **2006**, 2774–2776.

(41) (a) Binder, W. H.; Sachsenhofer, R. *Macromol. Rapid Commun.* **2007**, *28*, 15–24. (b) Lutz, J.-F. *Angew. Chem., Int. Ed.* **2007**, *46*, 1018–1025.

(42) Andrzejewska, E.; Andrzejewski, M. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 665–673.

(43) Montalti, M.; Credi, A.; Prodi, L.; Gandolfi, M. T. Chapter 3. In *Handbook of Photochemistry*, 3rd ed.; CRC Press: Boca Raton, FL, 2006; p 102.

(44) (a) Corrales, T.; Catalina, F.; Peinado, C.; Allen, N. S.; Rufs, A. M. *Polymer* **2002**, *43*, 4591–4597. (b) Corrales, T.; Catalina, F.; Peinado, C.; Allen, N. S. *J. Photochem. Photobiol., A* **2003**, *159*, 103–114.

(45) Bi, Y.; Neckers, D. C. *Macromolecules* **1994**, *27*, 3683–3693.

(46) Pouliquen, L.; Coqueret, X.; Morlet-Savary, F.; Fouassier, J.-P. *Macromolecules* **1995**, *28*, 8028–8034.

(47) Davidson, R. S. *J. Photochem. Photobiol., A* **1993**, *69*, 263–275.

(48) Paul, S. In *Surface Coating: Science & Technology*; Wiley-Intersicence: New York, 1986.