Macromolecules

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Hyperbranched Polymers by Visible Light Induced Self-Condensing Vinyl Polymerization and Their Modifications

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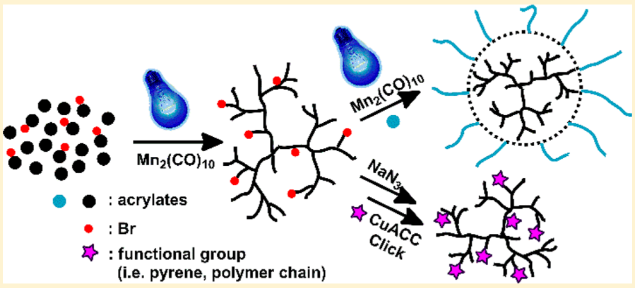
Supporting Information

ABSTRACT: Visible light induced self-condensing vinyl polymerization is explored using 2-bromoethyl methacrylate (2-BEMA) and methyl methacrylate (MMA) as inimer and comonomer, respectively, in the presence of dimanganese decacarbonyl ($Mn_2(CO)_{10}$) for the preparation of hyperbranched polymers. Upon photoexcitation in the visible range, $Mn_2(CO)_{10}$ undergoes irreversible decomposition leading to the formation of initiating radicals through bromine abstraction from 2-BEMA. Depending on the concentrations of 2-BEMA and $Mn_2(CO)_{10}$ and irradiation time, hyperbranched polymers with different branching density and cross-linked polymers were formed. The resulting polymers possess unreacted bromide groups in the structure which allow postfunctionalization through visible light photopolymerization and Cu(I)-catalyzed click reactions.



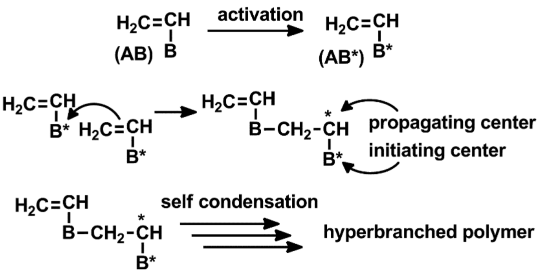
INTRODUCTION

In recent years, hyperbranched polymers have become an attractive field of research not only due to their inherent characteristics such as increased solubility, reduced solution viscosity[1,2] and a higher level of terminal functionality[3,4] but also relatively easier preparation methods compared to the other dendritic polymers.[5,6] Based on these properties, these materials hold considerable future promises in different applications particularly as drug delivery systems, bioimaging agents, gene carriers, viscosity modifiers, and catalyst supports.[7−10]

Synthesis of hyperbranched polymers can be rationalized into three main strategies: (i) step-growth polycondensation of AB_x monomers, (ii) self-condensing vinyl polymerization (SCVP) of AB monomers, and (iii) ring-opening polymerization of latent AB_x monomers.[11−14] A stylish mode of such techniques, SCVP, was first developed by Fréchet et al.[15] to produce polymers possessing both highly branched structures and several functional groups. This approach proceeds via polymerization of "inimers", a special kind of vinyl monomer containing a pendant group that can be converted into an initiating moiety. Inimers are formulized as AB*, where A stands for a double bond and B* represents an initiating group. First, the initiating group is activated and then reacted with a double bond to form a covalent bond and a new active side on the second carbon of the double bond as shown in Scheme 1.

Depending on inimer structure, SCVP has been successfully adapted to a wide variety of controlled polymerization systems including living ionic polymerization, atom transfer radical polymerization,[14] reversible addition−fragmentation chain transfer polymerization,[16] nitroxide-mediated polymerization,[17] and group-transfer and ring-opening polymerization.[18,19]

Scheme 1. Schematic Representation of Self-Condensing Vinyl Polymerization (SCVP)



In a related work from this laboratory, we have recently reported a modified version of SCVP for the synthesis of hyperbranched and cross-linked polymers using propargyl acrylate containing two polymerizable groups, namely acrylate and propargyl groups, with different reactivities toward photochemically generated free radicals.[20]

Photoinitiated polymerization has many advantages over other polymerization processes including that it is fast, uses little energy, readily occurs at room temperature, and is low cost.[21,22] The majority of industrial applications of photoinitiated polymerizations for various techniques deal with free

Received: July 22, 2013
Revised: August 14, 2013

dx.doi.org/10.1021/ma401534w | *Macromolecules* XXXX, XXX, XXX−XXX

radical systems. Many free radical photoinitiators acting at broad wavelength range are known, and their photochemistry has been studied in detail.[23−25] Among them, the dimanganese decacarbonyl ($Mn_2(CO)_{10}$)-based initiating system is particularly important due to its solubility in most of the monomers and solvents and efficiency in generating radical species upon photolysis at visible range. Although the dinuclear complex itself is stable and inactive in the dark, in conjunction with halogen containing compounds it has the ability of to generate radicals capable of initiating free radical polymerization under visible light. Moreover, because alkyl halides are also used as co-initiators to generate initiating radicals, the system provides molecular design flexibility in macromolecular synthesis.[26−29] Previously, we reported that this process can be employed for the promotion of cationic polymerization,[30] mechanism transformations involving different polymerization modes,[31] and preparation of telechelic polymers.[32]

This study further expands metal−carbonyl assisted free radical generation process to investigate the possibility of the fabrication of hyperbranched polymers. Herein, we report the synthesis and characterization of hyperbranched poly(methyl methacrylate) (PMMA) via visible light self-condensing vinyl copolymerization (VL-SCVP) of methyl methacrylate (MMA) and 2-bromoethyl methacrylate (2-BEMA) using $Mn_2(CO)_{10}$.

■ EXPERIMENTAL SECTION

Materials. Methyl methacrylate (MMA, Aldrich, 99%) and 2-hydroxyethyl methacrylate (HEMA, 99%, Aldrich) were passed through a column of basic alumina to remove the inhibitor. 2-Bromoethyl methacrylate (2-BEMA) was kindly donated by Bicak research group.[33] Dimanganese decacarbonyl ($Mn_2(CO)_{10}$, 99%, Aldrich) was purified by sublimation and stored in a refrigerator in the dark. 1-Pyrenemethanol (98%, Sigma-Aldrich), sodium azide (NaN_3, 97%, Sigma-Aldrich), copper(I) bromide (Cu(I)Br, 98%, Acros), *N,N′*-dicyclohexylcarbodiimide (DCC, 99%, Aldrich), 4-(dimethylamino)pyridine (DMAP, 99%, Aldrich), 4-pentynoic acid (98%, Alfa Aesar), poly(ethylene glycol) methyl ether (Me-PEG, $M_n \sim 2000$ g mol^{-1}, Aldrich), *n*-hexane (95%, Aldrich), tetrahydrofuran (THF, 99.8%, J.T. Baker), anhydrous *N,N*-dimethylformamide (DMF, 99.8%, Aldrich), and dichloromethane (CH_2Cl_2, J.T. Baker) were used as received. *N,N,N′,N″,N″*-Pentamethyldiethylenetriamine (PMDETA, 99%, Aldrich), used as a ligand, was distilled before use. Methanol (technical) was used for the precipitation of polymers without further purification.

Analysis. All ^{1}H NMR spectra were recorded on an Agilent NMR System VNMRS 500 spectrometer at room temperature in $CDCl_3$ with $Si(CH_3)_4$ as an internal standard.

FT-IR analyses were performed on a PerkinElmer FT-IR Spectrum One B spectrometer.

In order to determine branching frequency, both apparent and absolute molecular weights were measured from a Viscotek GPCmax Autosampler system consisting of a pump module (GPCmax, Viscotek Corp., Houston, TX), a combined light-scattering (Model 270 dual detector, Viscotek Corp.), and a refractive index (RI) detector (VE 3580, Viscotek Corp.). The lightscattering detector (λ_0 = 670 nm) included two scattering angles: 7° and 90°. The RI detector was calibrated with polystyrene standards having narrow molecular weight distribution, and so the quoted molecular weights of the polymers are expressed in terms of polystyrene equivalents. Two columns 7.8 × 300 mm, (LT5000L, Mixed, Medium Org and LT3000L, Mixed, Ultra-Low Org) with a guard column 4.6 × 10 mm (Viscotek, TGuard) were used for the chloroform eluent at 35 °C (flow rate: 1 mL min^{-1}). Data were analyzed using Viscotek OmniSEC Omni-01 software.

The ratio between $M_{n,GPC\text{-}RI}$ and $M_{n,GPC\text{-}LS}$ ($R_M = M_{n,GPC\text{-}RI}/M_{n,GPC\text{-}LS}$) gives qualitative information about the branching density of the polymers since branched structures are more compact than linear polymers for a given molecular weight.[34] As can be seen in the table, the normalized R_M value significantly differs as polymer architecture moves from linear (R_M = 1.00) to highly branched architectures (R_M = 0.19). This parameter thus indicates a trend of branching density of the synthesized polymers.

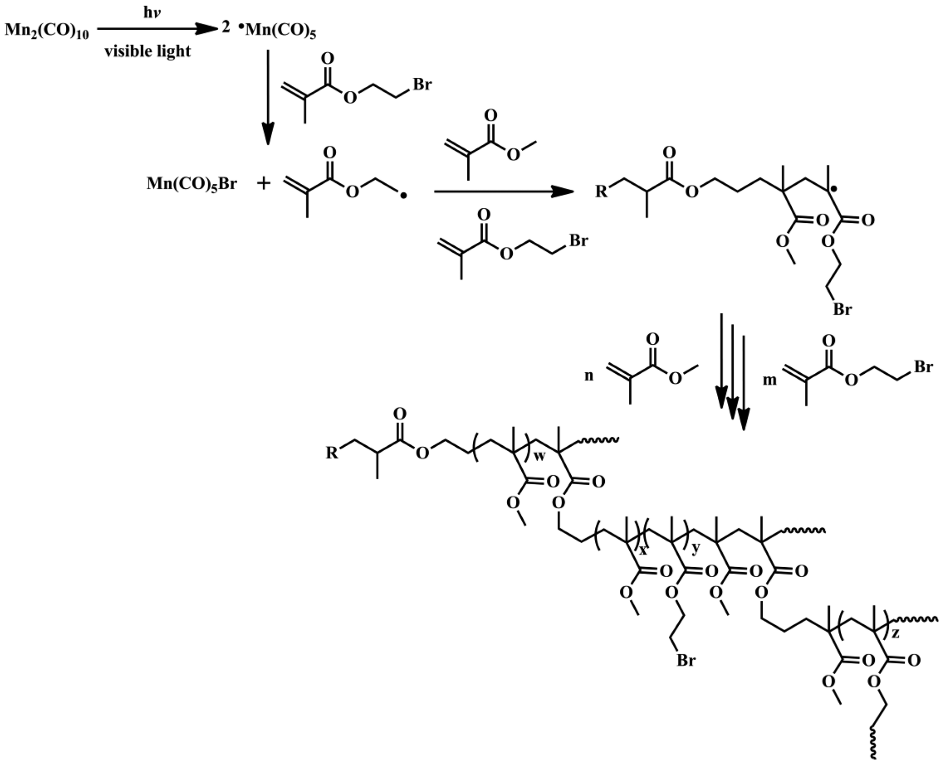
General Procedure for Synthesis of Bromo Functional Hyperbranched Poly(methyl methacrylate) (Hyperbranched PMMA−PBEMA). A representative radical photopolymerization procedure for MMA is as follows. $Mn_2(CO)_{10}$ (2.96 mg, 7.60 × 10^{-6} mol), 2-BEMA (76 μL, 7.06 × 10^{-4} mol), and 1 mL of MMA (9.38 × 10^{-3} mol) were put in a Pyrex tube and filled with dry nitrogen prior to irradiation by a Ker-Vis blue photoreactor equipped with six lamps (Philips TL-D 18 W) emitting light nominally at 400−500 nm at room temperature. The light intensity was 45 mW cm^{-2} as measured by a Delta Ohm model HD-9021 radiometer. At the end of irradiation, polymer was precipitated in excess methanol and dried in vacuum. Conversions for all samples were determined gravimetrically. All the other polymerizations were performed under identical experimental conditions. Depending on the conditions, lightly branched, highly branched, or partially cross-linked polymers were obtained. In the case of cross-linked polymer, the soluble part was extracted by THF.

General Procedure for Azidation of Bromo Functional Hyperbranched Poly(methyl methacrylate). Azidation of bromo functional hyperbranched polymers was carried out as described in the literature.[35] The resulting bromo functional hyperbranched PMMA was used as the precursor material for the "click" modification by azide functionalization through nucleophilic substitution. The bromo functional hyperbranched PMMA (100 mg) (content of bromo groups determined theoretically = 8.5 × 10^{-5} mol) was dissolved in 3 mL of DMF and was reacted with NaN_3 (11 mg, 1.7 × 10^{-4} mol). The resulting solution was left to stir at room temperature for 24 h and precipitated into 10 times excess of methanol to yield the corresponding azido-functionalized hyperbranched PMMA.

Synthesis of Acetylene Functional Poly(ethylene glycol) Methyl Ether. Synthesis of PEG-acetylene (PEG-a) was carried out as described previously.[36] Thus, Me-PEG ($M_n \sim 2000$ g mol^{-1}) (1 g, 0.5 mmol) was dissolved in 25 mL of CH_2Cl_2. 4-Pentynoic acid (0.147 g, 1.5 mmol), DMAP (0.06 g, 0.5 mmol), and DCC (0.23 g, 1.5 mmol) in 3 mL of dichloromethane were added to the solution in that order. The reaction mixture was stirred overnight at room temperature. It was filtered and evaporated, and the remaining product was purified by column chromatography over silica gel eluting first with CH_2Cl_2/ethyl acetate (1:1) and then with methanol/CH_2Cl_2 (1:10). Finally, the organic phase was evaporated to give PEG-a.

Synthesis of Propargylpyrene. Synthesis of propargylpyrene was carried out as described previously.[37] To a solution of pyrene−methanol (0.5 g, 2.15 mmol) in dry 10 mL of THF was added sodium hydride (60 wt % dispersion in oil) (0.057 g, 2.37 mmol), and the reaction mixture was stirred at 0 °C under nitrogen for 30 min. A solution of propargyl bromide (0.28 g, 2.37 mmol) in toluene was added portionwise to the solution. The mixture was kept stirring at room temperature for 24 h, and then it was refluxed for 3 h in the dark. The resulting mixture was cooled to room temperature and evaporated to half of its volume. The solution was extracted with ethyl acetate, and the organic layer was dried over anhydrous $MgSO_4$. Evaporating ethyl acetate afforded light yellow product. The crude product was dissolved in toluene and was passed through a column of basic silica gel to remove unreacted pyrene methanol. Toluene was removed by evaporating and the residue was dried in a vacuum oven.

CuAAC Click Reaction of PEG−Acetylene with Azide Functional Hyperbranched Poly(methyl methacrylate). CuAAC click reaction of PEG-a with azide functional polymer was performed as described previously.[38] In a typical click reaction, branched polymer (100 mg) (content of azide groups determined theoretically = 8.5 × 10^{-5} mol), PEG-a (1.3 × 10^{-4} mol), catalyst (CuBr, 1.3 × 10^{-4} mol), ligand (PMDETA, 1.3 × 10^{-4} mol), and 3 mL of DMF were placed in a Schlenk tube. The reaction mixture was degassed by three freeze−pump−thaw cycles and stirred at 25 °C for 24 h. After click reaction, the reaction mixture passed through a column filled with neutral alumina to remove the copper salt, Scheme 2. Visible Light Induced Synthesis of Hyperbranched Polymers



precipitated into methanol, and finally dried in a vacuum at room temperature. Evidence for the occurrence of the "click" reaction is obtained from ^{1}H NMR and FTIR spectroscopy.

CuAAC Click Reaction of Propargylpyrene with Azide Functional Hyperbranched Poly(methyl methacrylate). In a typical click reaction, branched polymer (100 mg) (content of azide groups determined theoretically = 8.5 × 10^{-5} mol), propargylpyrene (1.3 × 10^{-4} mol), catalyst (CuBr, 1.3 × 10^{-4} mol), ligant (PMDETA, 1.3 × 10^{-4} mol), and 3 mL of DMF were placed in a Schlenk tube. The reaction mixture was degassed by three freeze−pump−thaw cycles and stirred at 45 °C for 48 h. After click reaction, the reaction mixture passed through a column filled with neutral alumina to remove the copper salt, precipitated into methanol, and finally dried in a vacuum at room temperature. Evidence for the occurrence of the "click" reaction is obtained from ^{1}H NMR and FTIR spectroscopy.

Syntheses of Amphiphilic Star-Hyperbranched Poly(methyl methacrylate)-*b*-poly(2-hydroxyethyl methacrylate) Copolymers. The amphiphilic star-hyperbranched copolymers were prepared by photocopolymerization of bromo functional hyperbranched PMMA macroinitiator (100 mg, 2.8 × 10^{-7} mol) with HEMA (0.5 mL, 3.8 × 10^{-3} mol) in the presence of Mn$_2$(CO)$_{10}$ (8.3 mg, 2.1 × 10^{-5} mol) under visible light irradiation. After the polymerization, the copolymer was precipitated in *n*-hexane and characterized by ^{1}H NMR and FT-IR spectroscopy.

■ RESULTS AND DISCUSSION

The synthesis of PMMA hyperbranched polymers having bromo functionalities by the VL-SCVP technique was possible. In this approach, BEMA inimer containing a vinyl function and a bromine atom was used to generate branching points and comonomer, MMA simply acted to form spacer units between branching points. The overall process involving photochemical activation by Mn$_2$(CO)$_{10}$ is outlined in Scheme 2.

It is known that Mn$_2$(CO)$_{10}$ in the presence of alkyl halides undergoes an irreversible photolysis leading to the formation of radicals. This was further confirmed by the spectral changes of

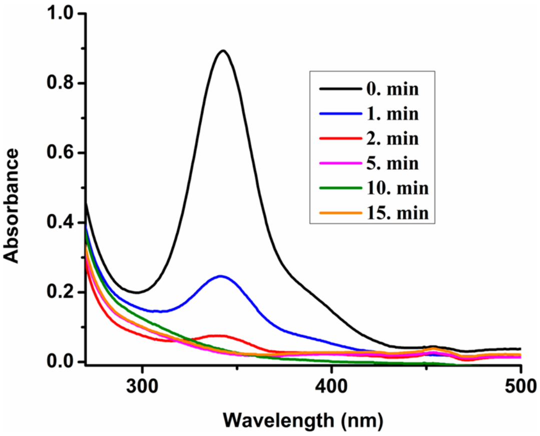


Figure 1. Photobleaching behavior of the Mn$_2$(CO)$_{10}$ (1.3 × 10^{-4} M) in CHCl$_3$.

Table 1. Effect of BEMA Concentration on Branching Density (R_M)[a]

BEMA in feed [mol %]	conv[b] [%]	BEMA cont in the polymer[c] [mol %]	soluble polym cont [%]	$M_{n,GPC-RI}$[d] [g mol^{-1}]	$M_{n,GPC-LS}$[e] [g mol^{-1}]	R_M
3	20	4.1	100	16 500	50 300	0.33
7.5	44	9.4	100	81 600	355 000	0.23
10	55	12.9	70	113 300	596 500	0.19

[a] (Co)polymerization of MMA and BEMA by irradiation (λ = 400−500 nm) of Mn$_2$(CO)$_{10}$ (0.075 mol %) at room temperature (irradiation time = 3 h). [b] Determined gravimetrically. [c] Calculated from the ^{1}H NMR. [d] With refractive index detector. [e] With light scattering detector.

Table 2. Effect of $Mn_2(CO)_{10}$ Concentration on Branching Density (R_M)[a]

$Mn_2(CO)_{10}$ [mol %]	conv[b] [%]	BEMA cont. in the polym[c] [mol %]	soluble polym cont [%]	$M_{n,GPC\text{-}RI}$[d] [g mol^{-1}]	$M_{n,GPC\text{-}LS}$[e] [g mol^{-1}]	R_M
0.038	25	8.6	100	65 400	191 000	0.34
0.075	44	9.4	100	81 600	355 000	0.23
0.150	51	12.3	100	107 100	535 000	0.20

[a](Co)polymerization of MMA (92.5% mol) and BEMA (7.5% mol) at room temperature by visible light (λ = 400−500 nm) (irradiation time = 3 h). [b]Determined gravimetrically. [c]Calculated from the ^{1}H NMR. [d]With refractive index detector. [e]With light scattering detector.

Table 3. Effect of Irradiation Time on Branching Density (R_M)[a]

time [min]	conv[b] [%]	BEMA cont in the polymer[c] [mol %]	soluble polym cont [%]	$M_{n,GPC\text{-}RI}$[c] [g mol^{-1}]	$M_{n,GPC\text{-}LS}$[d] [g mol^{-1}]	R_M
60	25	8.1	100	8 900	16 100	0.55
90	28	8.4	100	9 600	27 100	0.35
120	32	8.9	100	12 600	39 600	0.32
180	44	9.4	100	81 600	355 000	0.23

[a](Co)polymerization of MMA (92.5% mol) and BEMA (7.5% mol) by irradiation (λ = 400−500 nm) of $Mn_2(CO)_{10}$ (0.075% mol) at room temperature. [b]Determined gravimetrically. [c]Calculated from the ^{1}H NMR. [d]With refractive index detector. [e]With light scattering detector.

the model system consisting of $Mn_2(CO)_{10}$ and $CHCl_3$ (Figure 1).

The polymerizations were conducted under the same experimental conditions using different BEMA and $Mn_2(CO)_{10}$ concentrations and irradiation time. As can be seen from Tables 1−3, although higher conversions and branching densities were attained, high BEMA concentrations and prolonged irradiation times resulted in the formation of cross-linked polymers which is consisted with the proposed mechanism. The higher concentration of inimer leads to the gelation as this monomer possesses both initiating and polymerization functionalities in the structure. This effect favors radical coupling and consequently gelation.

In order to confirm that polymer chains are actually initiated by the Br-CH_2 groups of BEMA and branching occurs, several control experiments were performed. Thermal copolymerization of MMA and BEMA was performed as in literature[39] by using 2,2-azobis(isobutyronitrile) at 70 °C for 3 h yielded poly(methyl methacrylate)-*co*-poly(bromoethyl methacrylate) (PMMA-*co*-PBEMA) with 73% conversion. The number-

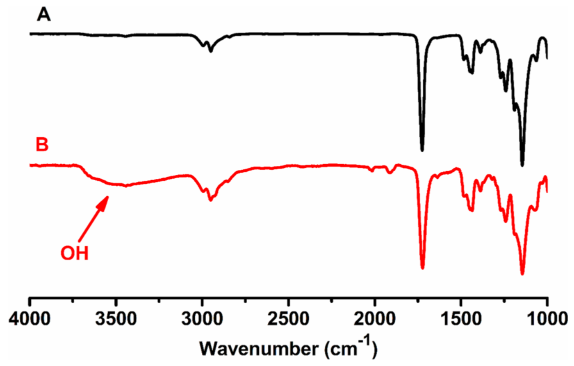


Figure 2. FT-IR spectra of bromo functional hyperbranched PMMA (A) and star-hyperbranched PMMA-*b*-PHEMA copolymer (B).

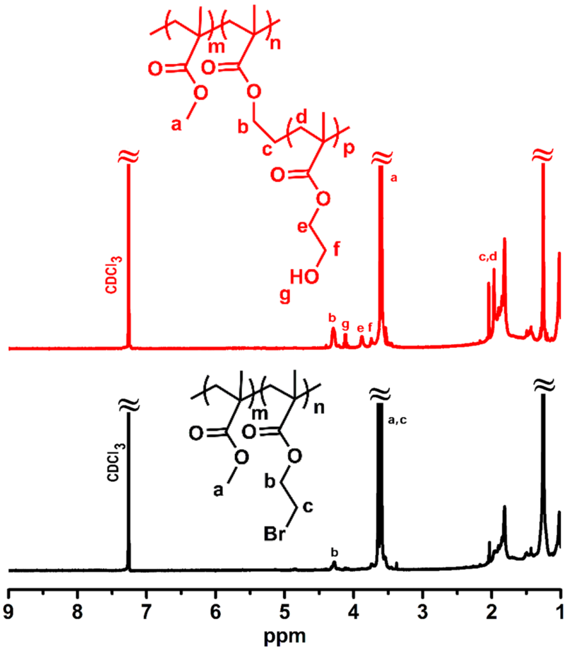
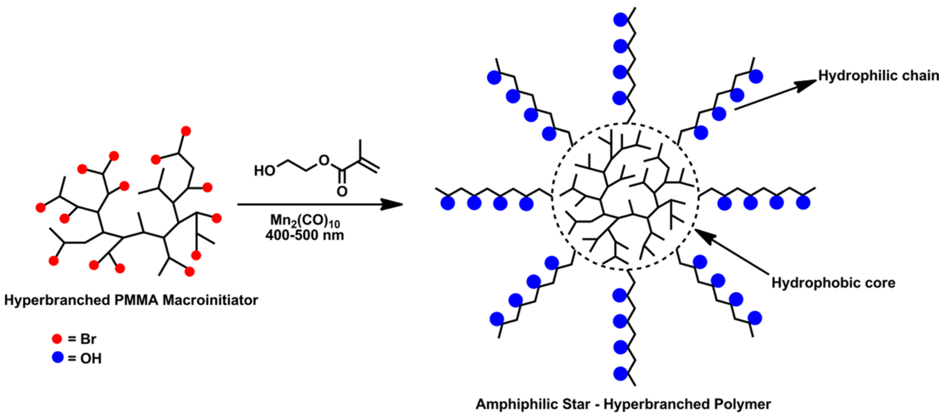
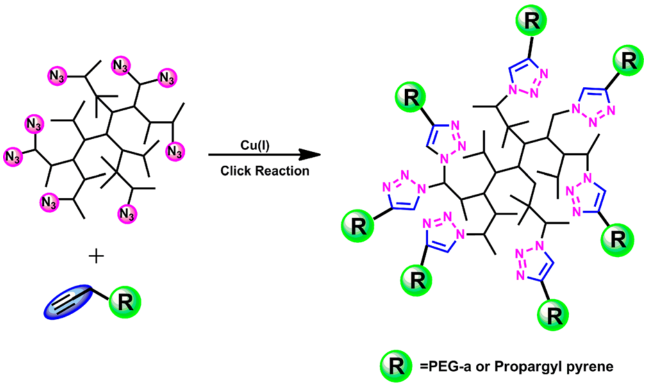


Figure 3. ^{1}H NMR spectra of the bromo functional hyperbranched polymer and its star block copolymer.

Scheme 3. Synthesis of an Amphiphilic Star-Hyperbranched PMMA-*b*-PHEMA Block Copolymer by Visible Light Irradiation



Scheme 4. Postfunctionalization of Hyperbranched Polymers by "Click" Chemistry Process



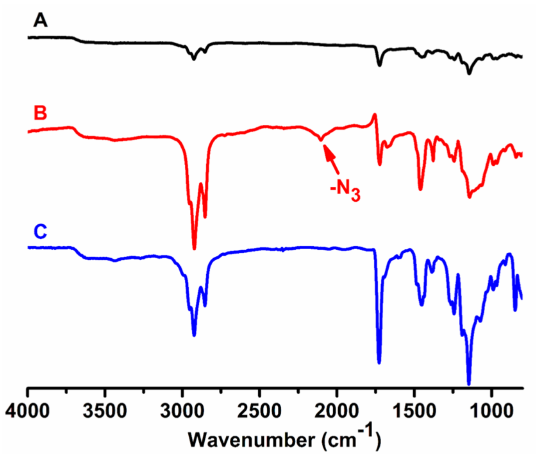


Figure 4. FT-IR spectra of bromo functional hyperbranched PMMA (A) and its azido (B) and pyrene functionalized (C) analogues.

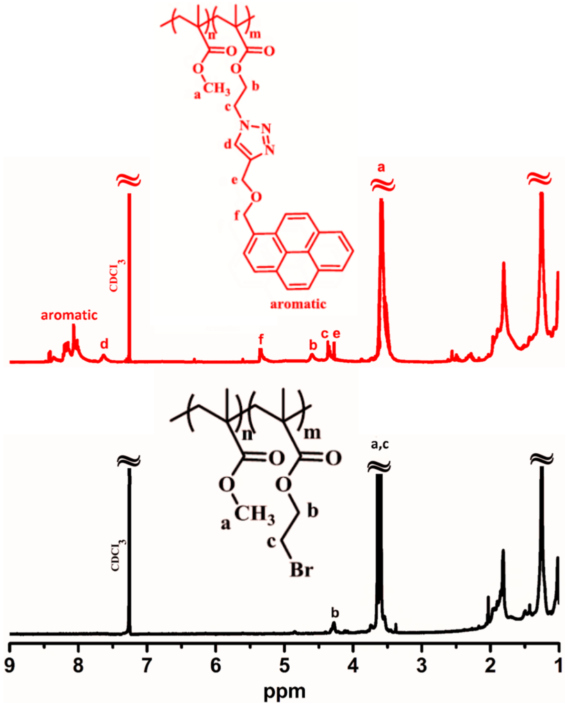


Figure 5. ^{1}H NMR spectra of the bromo functional hyperbranched polymer and its pyrene functionalized analogue.

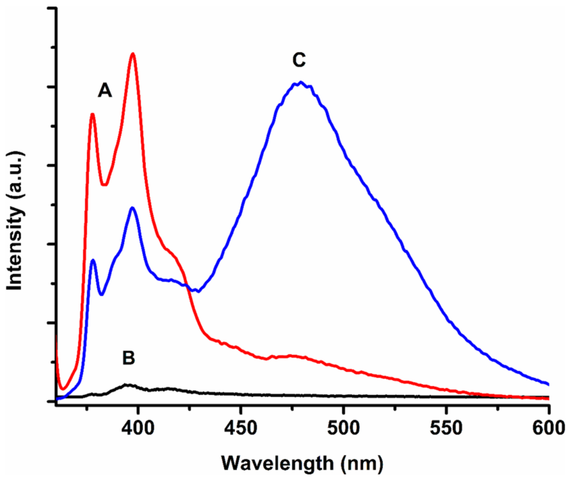


Figure 6. Fluorescence emission spectra of 1-pyrenemethanol (A), the bromo functional hyperbranched polymer (B), and corresponding pyrene-conjugated polymer (C) (λ_{ex} = 345 nm).

average molecular weight value of this polymer determined by refractive index ($M_{n,GPC\text{-}RI}$ = 99 600 g mol^{-1}) is close to that determined by light scattering ($M_{n,GPC\text{-}LS}$ = 106 800 g mol^{-1}).

Subsequently, bromine functional hyperbranched polymer was further used as macroinitiator in the visible light induced polymerization of MMA in the presence of $Mn_2(CO)_{10}$. After 180 min of irradiation, a polymer with 45% conversion and molecular weight of $M_{n,GPC\text{-}RI}$ = 84 000 g mol^{-1} and $M_{n,GPC\text{-}LS}$ = 445 000 g mol^{-1} was obtained. The huge difference between RI and LS measured molecular weights indicates highly branched structure, and also BEMA units induce further chain initiation due to the presence of bromine atoms.

As a consequence of the process, some of the bromine groups may not be activated and remain in the branched polymer which allows postfunctionalization through further polymerization and a Cu(I)-catalyzed click reactions. Principally, any vinyl monomer can be polymerized by the activation of the remaining halide groups in the presence of $Mn_2(CO)_{10}$ by a similar photochemical process. For our convenience, we have selected hydroxyethyl methacrylate (HEMA) as the second monomer, and visible light induced polymerizations yielded amphiphilic star block copolymers possessing hydrophobic hyperbranched core and hydrophilic dangling chains (Scheme 3).

Successful block copolymerization was confirmed by spectral analyses of the precursor hyperbranched polymer and final star block copolymer. In the FT-IR spectrum of the block copolymer, the OH stretching band of poly(hydroxyethyl methacrylate) (PHEMA) star arms is clearly detectable (Figure 2).

Similarly, in addition to the characteristic bands of the PMMA core, the NMR spectrum also exhibits signals at 3.5–4.4 ppm region corresponding to $-CH_2O$, $-OCHH_2$, and $-OH$ protons of PHEMA segments (Figure 3).

The composition of the hyperbranched PMMA–PBEMA is found by ^{1}H NMR data. Thus, the peak around 3.59 ppm corresponding to the protons of methyl group of PMMA segment and methylene protons adjacent to the bromine moiety of PBEMA is compared to the methylene peaks of PBEMA next to the ester functionality, which appears at 4.27 ppm. By this comparison, the ratio of PMMA to PBEMA is calculated.

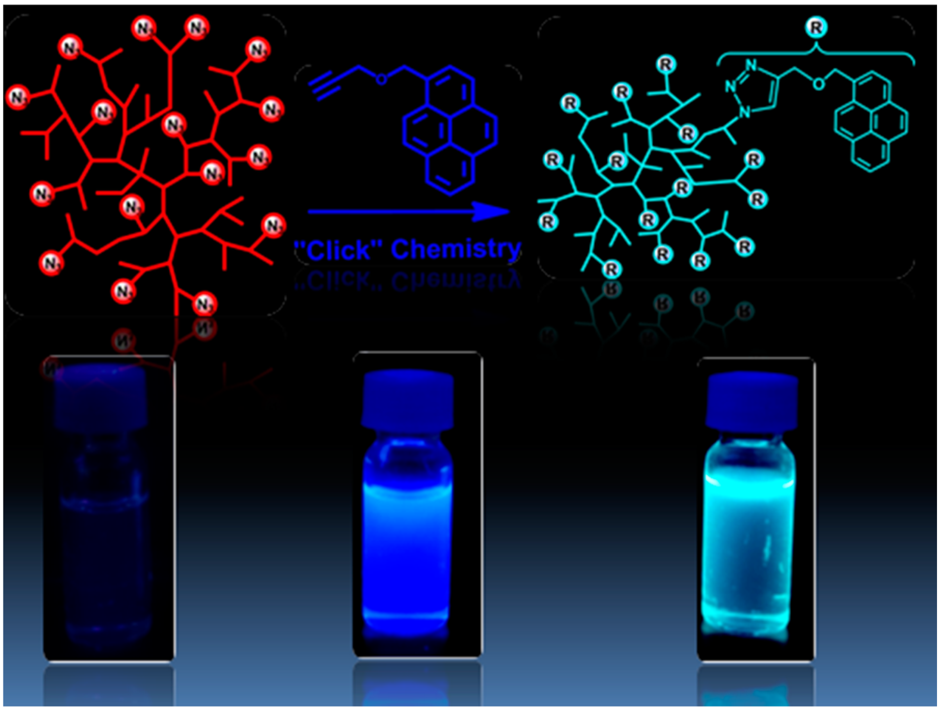


Figure 7. Photograph of azide-functionalized hyperbranched PMMA, propargylpyrene, and pyrene-functionalized hyperbranched PMMA dispersed in $CHCl_3$ which was taken when irradiated with a 366 nm UV lamp.

The hyperbranched polymers were modified by Huisgen type click reactions (Scheme 4).[40−44] For this purpose, bromine groups were converted into azide functions by condensation with NaN_3 in DMF solution. In the FT-IR spectrum of the azidated sample, the characteristic vibration band of N_3 group is observed as a sharp peak at 2106 cm^{-1}.

Propargylpyrene and poly(ethylene glycol)−acetylene (PEG-a) as model and hydrophilic polymer click components, respectively, were prepared independently according to the described literature procedures[36,37] (see Experimental Section). The model click reaction with propargylpyrene and azide-modified hyperbrached PMMA was performed using Cu(I) catalyst in DMF at 45 °C. The pyrene-functionalized hyperbranched polymer was characterized by FT-IR spectra (Figure 4), where disapperance of the azide vibration peak at 2106 cm^{-1} was observed.

The ^1H NMR spectrum of the pyrene functionalized polymer also confirms successful click reaction. As can be seen from Figure 5, the aromatic protons of pyrene units appear at 7.9−8.6 ppm while triazole ring protons resonate at 7.6 ppm.

Even more convincing evidence for pyrene incorporation was obtained from fluorescence measurements. Peaks corresponding to the emission from propargyl pyrene at 350 and 400 nm appear as a weak broad band for the pyrene functionalized PMMA. Moreover, the polymer exhibits structureless excimer emission centered at 480 nm, indicating strong interaction of pyrene groups present in the hyperbranched structure also in the excited state (Figure 6).

Pyrene incorporation can also be verified by the visual observation of the fluorescence properties of propargylpyrene and hyperbranched polymer in $CHCl_3$ before and after click reaction when irradiated with a 366 nm UV lamp (Figure 7).

The click reactions with PEG-a and azide-modified hyperbrached PMMA was carried out under similar experimental conditions. The resulting PEG-a functionalized hyperbranched polymer was characterized by FT-IR, ^1H NMR, and GPC measurements. In the FT-IR spectra, the disappearance of the alkyne peak around 1965 cm^{-1} and azide peak around 2106 cm^{-1} was noted. The ^1H NMR spectra exhibits characteristic PEG protons as well as the triazole protons that appear at 8.01 ppm (see Supporting Information). Molecular weight of the polymer is $M_{n,GPC\text{-}IR}$ = 91 000 g mol^{-1} and $M_{n,GPC\text{-}LS}$ = 465 000 g mol^{-1}. The difference between RI and LS measured molecular weight indicates that highly branched structure is preserved after the click process.

■ CONCLUSION

In conclusion, we described a facile method for the synthesis of well-defined soluble bromine-functional hyperbranched PMMA. The method is based on the polymerization of AB* methacrylic monomers, in the presence of $Mn_2(CO)_{10}$. Visible light irradiation efficiently produces carbon-centered radical without using high temperature and hard reaction conditions. At sufficiently high concentrations of BEMA and $Mn_2(CO)_{10}$ gelation was observed. Both effects essentially favor radical coupling and consequently gelation. The polymer structures as well as branching degree and polymer compositions were investigated by ^1H NMR and GPC LS/IR measurements.

Such polymers obtained by photochemical means may be used in numerous applications such as biomedical and drug delivery systems. In the described synthetic methodology, bromine functionalities provide possibility to use hyperbranched PMMA as a macroinitiator in the polymerization of HEMA and MMA and as a starting material in "click chemistry" reactions. The amphiphilic characters of hyperbranched polymer can be adjusted by incorporating polymeric segments of hydroxylic monomers. For the synthesis of functional materials by simple coupling and polymerization reactions, the bromine end groups of hyperbranched polymer can be a perfect starting point.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H NMR and FT-IR spectra of star-hyperbranched PMMA-*b*-PEG copolymer. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors are thankful for Istanbul Technical University Research Fund and TUBITAK (The Scientific and Technical Research Council of Turkey) Project no. 113Z234. M.C. thanks TUBITAK for the financial support by means of a graduate program.

■ REFERENCES

(1) Hawker, C. J.; Frechet, J. M. J. *J. Chem. Soc., Perkin Trans. 1* **1992**, *0* (19), 2459−2469.
(2) Wooley, K. L.; Fréchet, J. M. J.; Hawker, C. J. *Polymer* **1994**, *35* (21), 4489−4495.
(3) Sunder, A.; Mülhaupt, R.; Frey, H. *Macromolecules* **1999**, *33* (2), 309−314.
(4) Sunder, A.; Mülhaupt, R.; Haag, R.; Frey, H. *Adv. Mater.* **2000**, *12* (3), 235−239.
(5) Voit, B. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38* (14), 2505−2525.
(6) Voit, B. I.; Lederer, A. *Chem. Rev.* **2009**, *109* (11), 5924−5973.
(7) Gao, C.; Yan, D. *Prog. Polym. Sci.* **2004**, *29* (3), 183−275.
(8) Sendijarevic, I.; McHugh, A. J. *Macromolecules* **2000**, *33*, 590−596.
(9) Kim, Y. H. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36* (11), 1685−1698.
(10) Romagnoli, B.; Hayes, W. *J. Mater. Chem.* **2002**, *12* (4), 767−799.
(11) Inoue, K. *Prog. Polym. Sci.* **2000**, *25* (4), 453−571.
(12) Yates, C. R.; Hayes, W. *Eur. Polym. J.* **2004**, *40* (7), 1257−1281.
(13) Jikei, M.; Kakimoto, M.-a. *Prog. Polym. Sci.* **2001**, *26* (8), 1233−1285.
(14) Gaynor, S. G.; Edelman, S.; Matyjaszewski, K. *Macromolecules* **1996**, *29* (3), 1079−1081.
(15) Frechet, J. M. J.; Henmi, M.; Gitsov, I.; Aoshima, S.; Leduc, M. R.; Grubbs, R. B. *Science* **1995**, *269* (5227), 1080−1083.
(16) Wang, Z.; He, J.; Tao, Y.; Yang, L.; Jiang, H.; Yang, Y. *Macromolecules* **2003**, *36* (20), 7446−7452.
(17) Hawker, C. J.; Frechet, J. M. J.; Grubbs, R. B.; Dao, J. *J. Am. Chem. Soc.* **1995**, *117* (43), 10763−10764.
(18) Sunder, A.; Hanselmann, R.; Frey, H.; Mülhaupt, R. *Macromolecules* **1999**, *32* (13), 4240−4246.
(19) Liu, J.; Huang, W.; Zhou, Y.; Yan, D. *Macromolecules* **2009**, *42* (13), 4394−4399.
(20) Ciftci, M.; Kahveci, M. U.; Yagci, Y.; Allonas, X.; Ley, C.; Tar, H. *Chem. Commun.* **2012**, *48* (82), 10252−10254.
(21) Yagci, Y. *Macromol. Symp.* **2006**, *240* (1), 93−101.
(22) Fouassier, J.-P. *Photoinitiation, Photopolymerization, and Photocuring: Fundamentals and Applications*; Hanser: Munich, 1995.
(23) Bamford, C. H.; Mullik, S. U. *J. Chem. Soc., Faraday Trans. 1* **1973**, *69*, 1127−1142.
(24) Bamford, C. H.; Paprotny, J. *Polymer* **1972**, *13* (5), 208−217.
(25) Tasdelen, M. A.; Yagci, Y. *Aust. J. Chem.* **2011**, *64* (8), 982−991.
(26) Koumura, K.; Satoh, K.; Kamigaito, M. *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47* (5), 1343−1353.
(27) Koumura, K.; Satoh, K.; Kamigaito, M. *Macromolecules* **2008**, *41* (20), 7359−7367.
(28) Koumura, K.; Satoh, K.; Kamigaito, M. *Macromolecules* **2009**, *42* (7), 2497−2504.
(29) Asandei, A. D.; Adebolu, O. I.; Simpson, C. P. *J. Am. Chem. Soc.* **2012**, *134* (14), 6080−6083.
(30) Yagci, Y.; Hepuzer, Y. *Macromolecules* **1999**, *32* (19), 6367−6370.
(31) Kahveci, M. U.; Acik, G.; Yagci, Y. *Macromol. Rapid Commun.* **2012**, *33* (4), 309−313.
(32) Iskin, B.; Yilmaz, G.; Yagci, Y. *Macromol. Chem. Phys.* **2013**, *214* (1), 94−98.
(33) Gunes, D.; Karagoz, B.; Bicak, N. *Des. Monomers Polym.* **2009**, *12* (5), 445−454.
(34) Bally, F.; Ismailova, E.; Brochon, C.; Serra, C. A.; Hadziioannou, G. *Macromolecules* **2011**, *44* (18), 7124−7131.
(35) Tsarevsky, N. V.; Sumerlin, B. S.; Matyjaszewski, K. *Macromolecules* **2005**, *38* (9), 3558−3561.
(36) Amici, J.; Kahveci, M. U.; Allia, P.; Tiberto, P.; Yagci, Y.; Sangermano, M. . *J. Mater. Sci.* **2012**, *47* (1), 412.
(37) Gacal, B. N.; Koz, B.; Gacal, B.; Kiskan, B.; Erdogan, M.; Yagci, Y. *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47* (5), 1317−1326.
(38) Ates, S.; Durmaz, Y. Y.; Torun, L.; Yagci, Y. *J. Macromol. Sci., Part A: Pure Appl. Chem.* **2010**, *47* (8), 809−815.
(39) Zheng, J.; Goh, S. H.; Lee, S. Y. *Polym. Bull.* **1997**, *39* (1), 79−84.
(40) Kolb, H. C.; Finn, M. G.; Sharpless, K. B. *Angew. Chem., Int. Ed.* **2001**, *40* (11), 2004−2021.
(41) Rostovtsev, V. V.; Green, L. G.; Fokin, V. V.; Sharpless, K. B. *Angew. Chem., Int. Ed.* **2002**, *41* (14), 2596−2599.
(42) Tasdelen, M. A.; Yagci, Y. *Angew. Chem., Int. Ed.* **2013**, *52* (23), 5930−5938.
(43) Tasdelen, M. A.; Yilmaz, G.; Iskin, B.; Yagci, Y. *Macromolecules* **2012**, *45* (1), 56−61.
(44) Tasdelen, M. A.; Yagci, Y. *Tetrahedron Lett.* **2010**, *51* (52), 6945−6947.