Journal of the Turkish Chemical Society Section: A Chemistry
TURKISH CHEMICAL SOCIETY

Synthesis and Characterization of Benzodioxinone-Bearing Methacrylate-Based Random Copolymer via Atom Transfer Radical Polymerization

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Abstract: Methacrylate-benzodioxinone (BDMA) as a monomer was firstly synthesized and then copolymerized with methyl methacrylate and 2-hydroxyethyl methacrylate via atom transfer radical polymerization (ATRP) in the presence of CuCl/pentamethyldiethylene triamine (PMDETA) catalytic system using ethyl 2-bromopropionate (EtBrP) as an initiator. Successful formation of the block copolymer was also confirmed in detail by proton nuclear magnetic resonance spectroscopy (^{1}H NMR), Fourier-transform infrared spectroscopy (FT-IR), and gel permeation chromatography (GPC) appropriately. Secondly, photochemical acylation of obtained copolymer through hydroxyl and benzodioxinone groups led to the release of benzophenone compound and ester-linkage on the polymer backbone. The formation of ester-linkage increases the glass transition temperature and the thermal stability of the obtained copolymer.

Keywords: Atom transfer radical polymerization, ketene chemistry, photochemical acylation, random copolymer.

Submitted: February 12, 2021. **Accepted:** March 20, 2021.

Cite this: Celik C, Acik G. Synthesis and Characterization of Benzodioxinone-Bearing Methacrylate-Based Random Copolymer via Atom Transfer Radical Polymerization. JOTCSA. 2021;8(2):501–10.

DOI: https://doi.org/10.18596/jotcsa.879021.

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INTRODUCTION

Copolymers have attracted enormous interest ranging from many industrial fields to another applications in the past two decades (1-4). The development of controlled/living radical polymerizations provides many advantages for producing well-defined polymers (5, 6). The reversible addition-fragmentation chain transfer (RAFT), (7, 8) atom transfer radical polymerization (ATRP), (9-12) nitroxyl-mediated polymerization (NMP) (13, 14) are widely used CLRP methods over the past three decades. Among these methods, ATRP is the most powerful, versatile, and inexpensive method discovered by Matyjaszewski (5, 11, 15-18). Furthermore, the ATRP can be applied in various monomers under different conditions and provided control over molecular weight, polydispersity, and polymers' topology (9, 10, 14). This robust method also overcame a wide range of industrial problems, such as tolerance to solvents and impurities (9-11, 19).

Recently, benzodioxinone chemistry (20), which can easily form ketene and corresponding ketone intermediates upon UV irradiation (21-24) or temperature exposure thermolysis (25-27), has been utilized in synthetic polymer chemistry (28-30). Due to its chemical structure containing carbonyl and alkenyl groups and the possibility of their transformation into ketenes, benzodioxinone compounds are versatile organic reactive intermediates. Also, salicylate esters, one of the most important materials in the medical field (31), can be synthesized by the photochemical acylation process of benzodioxinone in the presence of either phenols or alcohols (32, 33). Recently, this photochemistry has been applied to synthesize various macromolecular architectures by combining various CLRP methods (34).

This study aims to synthesize photochemically sensitive random copolymer-bearing antagonist benzodioxinone and hydroxyl functionalities via atom transfer radical polymerization with a one-step procedure. For this purpose, methacrylated benzodioxinone was firstly synthesized by esterification reaction of 5-hydroxy-2,2-diphenyl-4H-benzo[d][1,3]dioxin-4-one with methacryloyl chloride. The methacrylated benzodioxinone monomer was copolymerized with methyl methacrylate and 2-hydroxylethyl methacrylate to get photochemically sensitive random copolymer, by using simple UV irradiation of the resulting copolymer led to photochemical acylation reaction between antagonist benzodioxinone and hydroxyl functionalities. Spectroscopic, chromatographic, and thermal analyses confirmed the formations of obtained copolymer and its acylated species.

MATERIALS AND METHODS

Materials

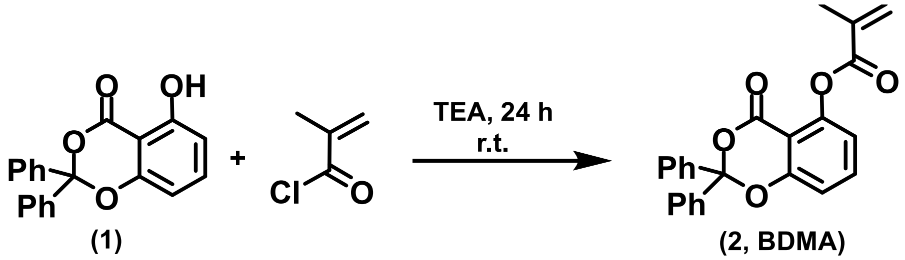
Monomers, methyl methacrylate (Aldrich, MMA, 99%,), and 2-hydroxyethyl methacrylate (Aldrich, HEMA, 99%) were purified to remove the inhibitor by passing through a basic alumina column. Copper(I) chloride (Aldrich, CuCl, 99.99%), ethyl 2-bromopropionate (99%, Aldrich), and methacryloyl chloride (Aldrich, 97%) were used without further purification. N,N,N',N",N’’-pentamethyldiethylene triamine (PMDETA; 99%, Aldrich) was used as ligand and distilled before use. Toluene (99.7%, Aldrich) and other solvents were purified prior to use by conventional distillation and drying procedures.

Instrumentation

The ^{1}H-NMR analysis was conducted by Agilent NMR System VNMRS 500 spectrometer at room temperature in deuterated chloroform ($CDCl_3$) with tetramethylsilane (TMS) as the internal standard. Additionally, Perkin-Elmer FT-IR Spectrum One B spectrometer was used for Fourier transform infrared (FT-IR) spectroscopic analysis. The molecular weights and molecular weight distributions of the resulting polymers were determined by a Viscotek GPCmax. The GPC was equipped with an autosampler system consisting of a pump module (GPCmax, Viscotek, Houston, TX), a refractive index (RI) detector (VE 3580, Viscotek), and a combined light-scattering (Model 270 dual detector, Viscotek). The GPC system was equipped with two columns (LT5000L, Mixed, Medium Organic 300x8 mm and LT3000L and Mixed, Ultra-Low Organic 300x8 mm) with a guard column (TGuard, Organic Guard Column 10x4.6 mm) using tetrahydrofuran eluent at 35 ºC (flow rate, 1 mL min^{-1}). The polystyrene standards having narrow molecular weight distribution were used for the calibration of the refractive index detector. Two scattering angles, namely 90 and 7, were used in the light-scattering detector (λ_0 = 670 nm). The GPC data were analyzed using Viscotek OmniSEC Omni-01 software. Perkin-Elmer Diamond TA/ TGA thermogravimetric analysis (TGA) analyzed the thermal stability of obtained polymers with a heating rate of 10 °C/min under nitrogen flow (200 mL/min). Also, thermal transitions of obtained polymers were analyzed by Perkin-Elmer Diamond differential scanning calorimetry (DSC) with a heating rate of 10 °C/min under nitrogen flow (10 mL /min).

Synthesis of 4-oxo-2,2-diphenyl-4H-benzo[d][1,3]dioxin-5-yl methacrylate (BDMA)

Methacrylated benzodioxinone was synthesized with a modified two-step procedure. Firstly, the 5-hydroxy-2,2-diphenyl-4H-benzo[d][1,3]dioxin-4-one (1), was prepared as reported previously (35). In the second step, hydroxyl function of (1) was converted to methacrylate (2) by esterification using methacryloyl chloride according to the procedure given below (Scheme 1);



Scheme 1. Synthesis of 4-oxo-2,2-diphenyl-4H-benzo[d][1,3]dioxin-5-yl methacrylate (BDMA).

A solution of the above-obtained benzodioxinone, (1), (0.6 g, 1.88 mmol), and a 1.05 molar equivalent of triethylamine were added into dry acetone, and the solution was cooled to 0 ºC. Then, 1.05 mol of methacryloyl chloride per mol of alcohol was added drop-wise into the solution with vigorous stirring. After that, the suspension was stirred for 24 h at room temperature. The resulting salt firstly precipitated out, and then it was filtered off. The BDMA monomer was obtained by distillation of the acetone, unreacted methacryloyl chloride, and triethylamine under low pressure. Finally, the BDMA monomer yielded an oily yellow liquid (BDMA, 70%).

General procedure for Random Copolymerization by ATRP

Methacrylated benzodioxinone (BDMA, 0.1 g, 2.6×10^{-4}mol), 2-hydroxyethyl methacrylate (2.5 mL, 2×10^{-2} mol) and methyl methacrylate (9.25 mL, 9×10^{-2} mol) dissolved in deoxygenated solvent toluene (0.5 mL), PMDETA as a ligand (17 µL, 8×10^{-5} mol), ethyl 2-bromopropionate as an initiator (17 µL, 1.35×10^{-5} mol) and catalysts Cu(I), (0.016 g, $1.6\times10^{-}$

^{4} mol) were added to a Schlenk tube equipped with a magnetic stirring bar. The reaction tube was then degassed by three freeze-pump-thaw cycles and was placed in an oil bath (90 °C) for 48 h. The ATRP of BDMA, MMA, and HEMA was stopped by exposing to air. The reaction mixture was diluted with THF and passed through a short basic silica column to remove the copper catalyst. Then the reaction solution was concentrated by rotary evaporation and precipitated in 10-fold excess cold methanol. The obtained copolymer (PBDMA-*co*-PHEMA-*co*-PMMA) was filtered and dried under a vacuum oven at room temperature (yield: 20%; determined gravimetrically).

Photochemical acylation process of PBDMA-*co*-PHEMA-*co*-PMMA

Previously synthesized PBDMA-*co*-PHEMA-*co*-PMMA in THF (30 mL) were added to a quartz tube and irradiated for 48 h by a merry-go-round type UV-reactor equipped with 16 Philips 8W/06 lamps and a cooling system. All lamps emitted light at λ>350 nm. After the given time, the acylated copolymer first was precipitated in methanol, then collected by filtration. The filtrated copolymer was then dried under vacuum for 24 h at room temperature. Upon UV irradiation, benzophenone was released as a by-product removed by precipitation step using methanol as solvent.

RESULTS AND DISCUSSION

Based on previous literature studies that gave information about benzodioxinone photochemistry for various synthetic approaches, we synthesized copolymer including photosensitive benzodioxinone benefiting from ketene's chemoselective reactions intermediates toward hydroxyl groups in the copolymer backbone. For this purpose, firstly, methacrylated benzodioxinone (BDMA) was synthesized by esterification reaction of phenolic benzodioxinone 5-hydroxy-2,2-diphenyl-4H-benzo[d][1,3]dioxin-4-one with methacryloyl chloride (Scheme 1). The chemical structure of BDMA was confirmed by ^{1}H-NMR spectroscopy detecting characteristic protons of benzodioxinone (c, d, e, f, g, h, i, j) and methacrylate (a and b) at 6.5-7.6, 1.6, and 6.1 ppm (Figure 1).

In the second step, the random copolymerization of BDMA, 2-hydroxylethyl methacrylate, and methyl methacrylate was done by ATRP at 90 °C in toluene using EtBrP and CuCl/ PMDETA as initiator and catalyst, respectively (Scheme 2).

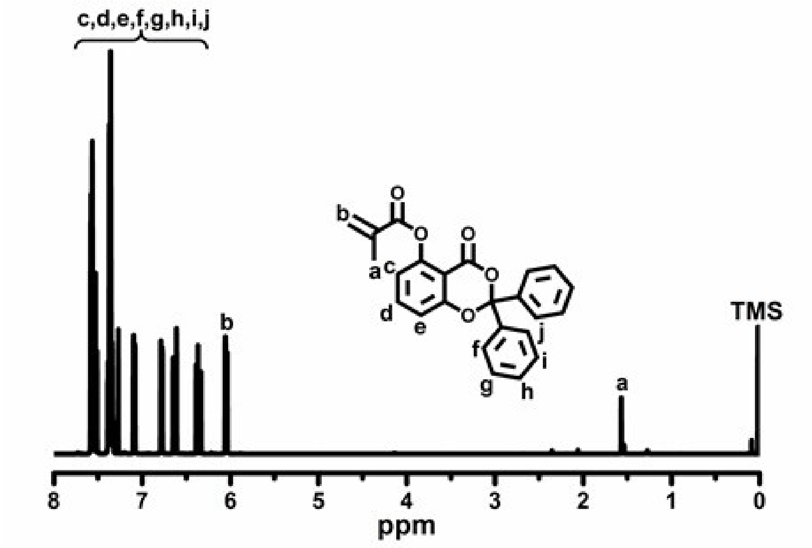
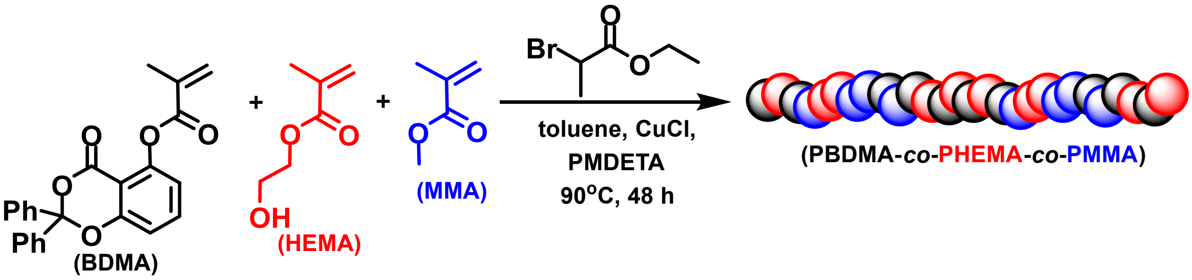
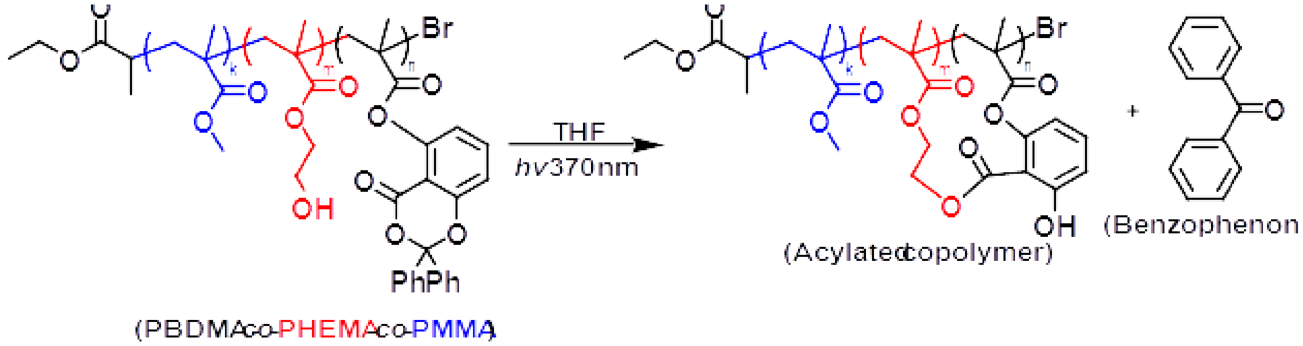


Figure 1. ^{1}H-NMR spectrum of BDMA.



Scheme 2. Copolymerization of BDMA, HEMA and MMA via ATRP. (BDMA:HEMA:MMA:PMDETA:EtBrP:CuCl = 1:80:350:0.3:0.05:0.6 in 0.6 mL xylene)

The successful ATRP copolymerization led to photochemically active copolymer (PBDMA-*co*-PHEMA-*co*-PMMA), including benzodioxinone, which can absorb near UV light. In the final stage, the photochemical acylation process of the obtained PBDMA-*co*-PHEMA-*co*-PMMA was achieved throughout 48 h under UV light (Scheme 3).



Scheme 3. Photochemical acylation of PBDMA-*co*-PHEMA-*co*-PMMA.

Based on spectroscopic (FT-IR and ^{1}H-NMR) and chromatographic (GPC) data of obtained copolymer by ATRP, the random copolymer was obtained with good yield as evaluated by acceptable monomer conversion (20%) and molecular weight (M_n= 73.730 g/mol) and molecular weight distribution (PDI= 1.26). The FT-IR spectra of untreated and UV-treated PBDMA-*co*-PHEMA-*co*-PMMA copolymer were shown in Figure 2. The spectrum for the neat PBDMA-*co*-PHEMA-*co*-PMMA displayed the characteristic bands such as broad O-H band at 3500 cm^{-1}, aromatic C-H band at 2950 cm^{-1}, sharp C=O band at 1700 cm^{-1}, aromatic C=C band at 1450 cm^{-1} at and C-O band at 1250 cm^{-1}. After the photochemical acylation process, all characteristic bands of PBDMA-*co*-PHEMA-*co*-PMMA were presented, whereas a new band at 1625 cm^{-1} attributed to the intramolecular hydrogen-bonded carbonyl group was formed.

Although FT-IR results confirmed the copolymer formation and acylation, the ^{1}H-NMR analysis provided a powerful indication. As can be seen, the Figure 3, the presence of aromatic protons belonging to PBDMA appear very clear between 6.10 and 7.50 ppm (**n, o, p, r, s, t, u and v**), PHEMA at 3.85 and 4.10 ppm (**k and j**), and PMMA at 3.58 ppm (**g**) prove the successful formation of copolymer bearing UV light-sensitive benzodioxinone. In addition, the chemical composition of the copolymer could be calculated from the integration ratio of methoxy protons of MMA (-O-CH$_3$, **g**) at 3.58 ppm, methylene protons (-CH$_2$-, **j and k**) of HEMA at 4.10 ppm and 3.95 ppm and the aromatic protons (**n, o, p, r, s, t, u and v**) of benzodioxinone at 6.10 and 7.50 ppm. According to the ^{1}H-NMR calculation, the copolymer composition was found as 8.7, 29.0, and 62.3% for PBDMA, PHEMA, and PMMA, respectively.

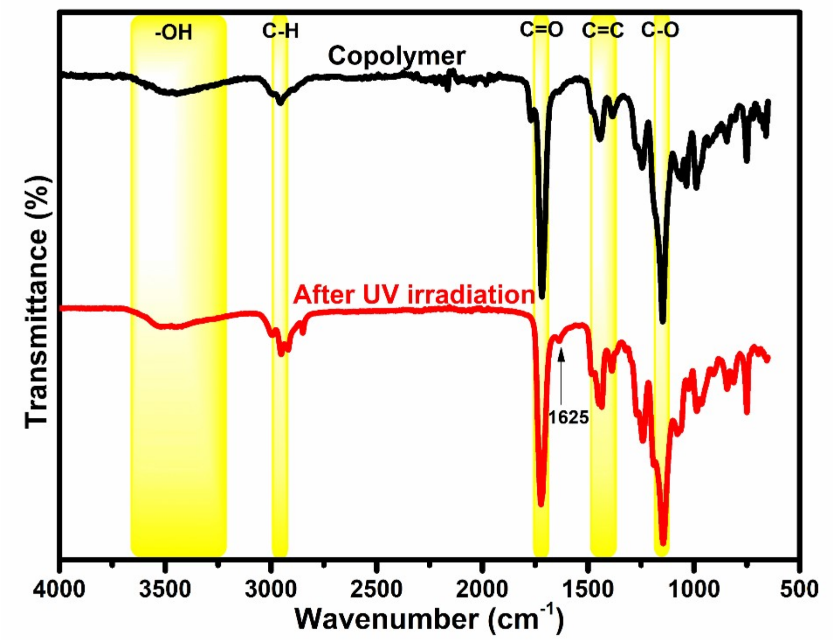


Figure 2. FT-IR spectra of PBDMA-*co*-PHEMA-*co*-PMMA and it's acylated species after UV irradiation.

The photoinduced acylation reaction antagonist benzodioxinone and hydroxyl groups of the PBDMA-*co*-PHEMA-*co*-PMMA led to the acylated product. After the acylation process, the aromatic peaks at 6.10 ppm and 6.18 ppm (**n, o, and p**) coming from benzodioxinone were remarkably decreased, whereas the aromatic peaks at 6.98 ppm and 7.08 ppm (**r, s, t, u and v**) belonging benzene rings of leaving benzophenone were almost disappeared.

Additionally, the acylation process was monitored by gel permeation chromatography in the THF system (Figure 4). After the photoinduced acylation process, the molecular weight of PBDMA-*co*-PHEMA-*co*-PMMA was moderately decreased due to the leaving benzophenone compound as a by-product. Furthermore, the polydispersity indexes of both untreated and UV-treated PBDMA-*co*-PHEMA-*co*-PMMA copolymer displayed unimodal traces.

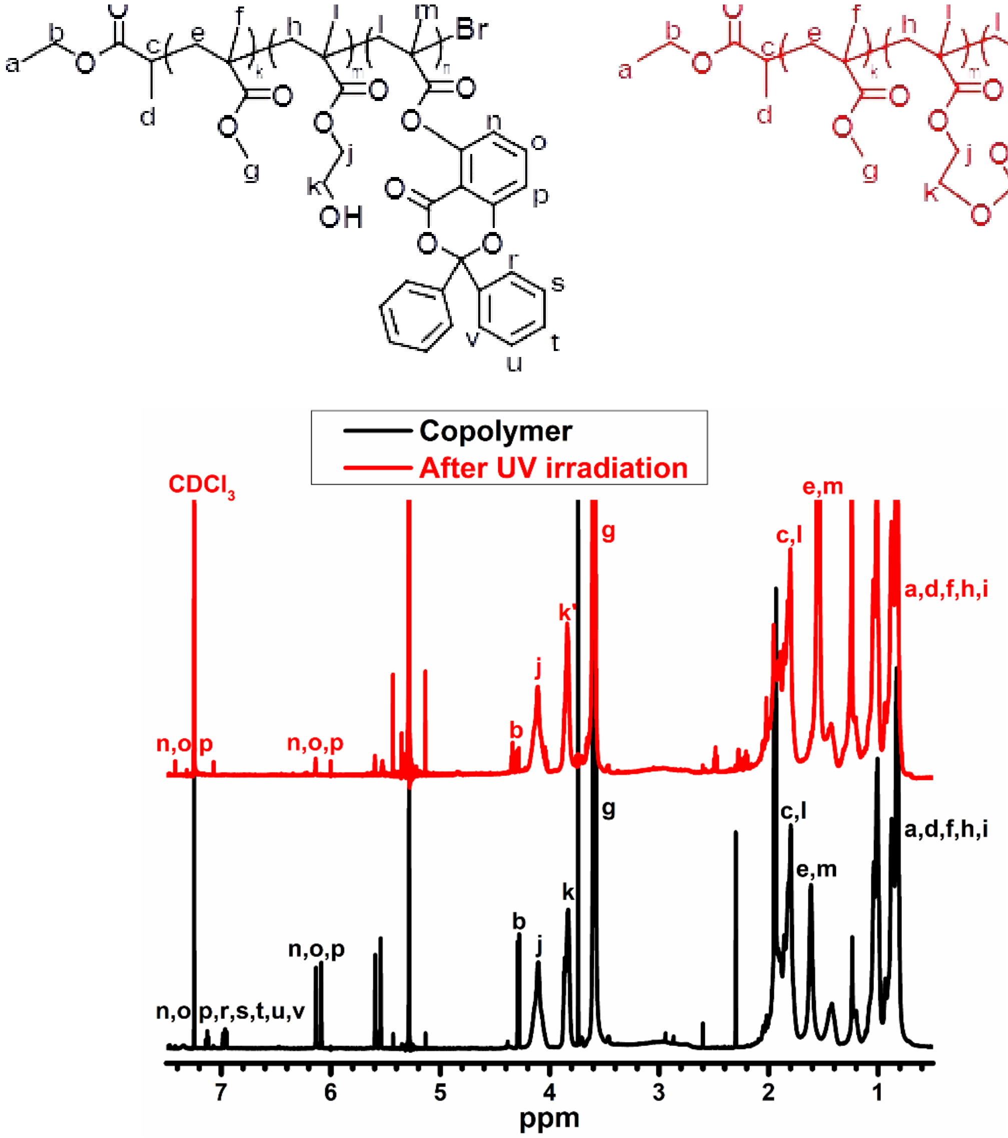


Figure 3. ^{1}H-NMR spectra of BDMA-*co*-PHEMA-*co*-PMMA and its acylated species after UV light irradiation. The random copolymer composition was calculated by ^{1}H-NMR analysis using the following formula: (Composition=(**n+o+p+r+s+t+u+v**)/(**n+o+p+r+s+t+u+v+g+j+k**)x100 and (**j+k**)/(**n+o+p+r+s+t+u+v+g+j+k**)x100, where **n+o+p+r+s+t+u+v** represents the integrated peak area at between 6.10 ppm and 7.50 ppm corresponding to aromatic protons of benzodioxinone, **j+k** represents the integrated peak area at 4.10 ppm and 3.95 ppm methylene protons ($-CH_2-$) of HEMA and **g** represents the integrated peak area at 3.58 ppm methoxy protons ($-O-CH_3$) of MMA).

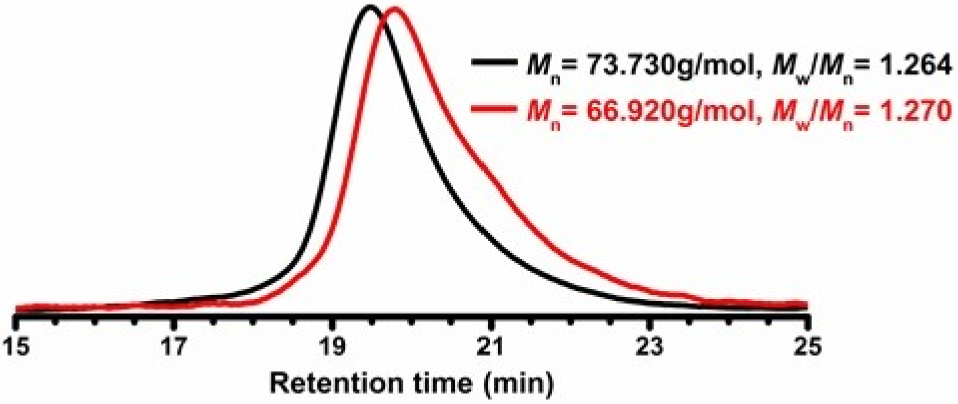


Figure 4. The GPC traces of PBDMA-*co*-PHEMA-*co*-PMMA and its acylated species after UV light irradiation (All GPC measurements were conducted using tetrahydrofuran as eluent with flow rate, 1 mL min^{-1} at 35 ^{0}C).

The thermal properties of the PBDMA-co-PHEMA-co-PMMA and its acylated species after esterification were determined by differential scanning calorimetric (DSC) analysis under a nitrogen atmosphere, and compared with pristine PHEMA-*co*-PMMA (Figure 5). The PHEMA-*co*-PMMA exhibited a glass transition temperature (T_g) at 88°C, whereas the obtained PBDMA-co-PHEMA-co-PMMA and its acylated species copolymers displayed higher T_g values at 98 and 109 °C, respectively. Due to the rigid benzodioxinone segments, the T_g value of PBDMA-*co*-PHEMA-*co*-PMMA higher than PHEMA-*co*-PMMA. After the acylation process, the linear polymer chains become entrapped within the particle, leading to decreased free volume. Therefore, the acylated species have the highest T_g value compared to the PBDMA-co-PHEMA-co-PMMA and PHEMA-*co*-PMMA (36-40).

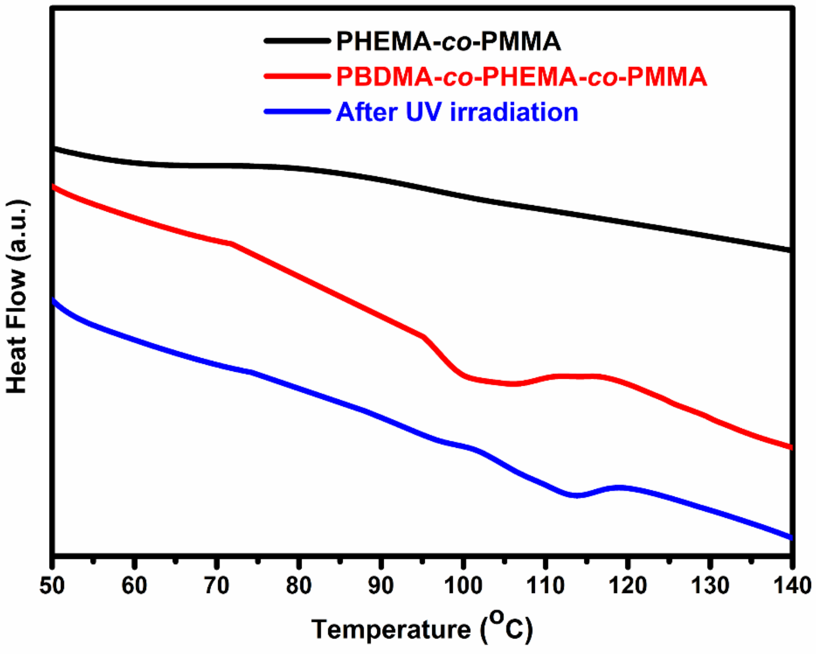


Figure 5. DSC thermogram of PHEMA-co-PMMA, PBDMA-co-PHEMA-co-PMMA, and its acylated species after UV light irradiation.

TGA further explored the thermal stabilities of the PHEMA-co-PMMA, PBDMA-co-PHEMA-co-PMMA, and its acylated species under nitrogen atmosphere. As shown in Figure 6, the weight loss of PHEMA-co-PMMA began at about 322 °C, reached its maximum at 440 °C, and displayed a single peak indicating one-step thermal degradation. The inclusion of benzodioxinone compounds on to polymer backbone, the rigid aromatic rings improved the thermal stability of the PBDMA-*co*-PHEMA-*co*-PMMA. However, the PBDMA-*co*-PHEMA-*co*-PMMA showed two-step degradations due to benzophenone's release and degradation of the polymer backbone. After the acylation process, the copolymer displayed one-step degradation and enhanced thermal stability again compared to the PBDMA-*co*-PHEMA-*co*-PMMA (40-42).

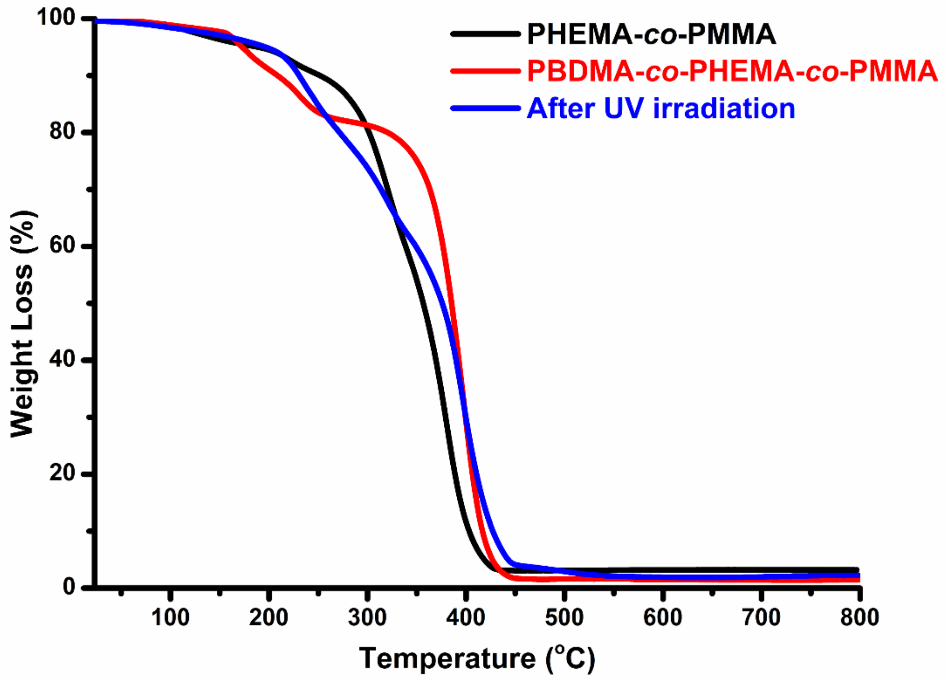


Figure 6. TGA thermogram of PHEMA-co-PMMA, BDMA-co-PHEMA-co-PMMA, and its acylated species after UV light irradiation.

CONCLUSION

In summary, a methacrylated benzodioxinone was synthesized under a mild condition and used as a co-monomer with 2-hydroxyethyl methacrylate and methyl methacrylate in the ATRP process to obtain random copolymer in one-step. The ester formation occurred through benzodioxinone's carbonyl group and the hydroxyl group of HEMA via acylation reaction upon UV photolysis. The formations of the obtained copolymer and its acylated species were confirmed by spectroscopic, chromatographic, and thermal analyses. The characteristic aromatic bands of benzodioxinone in the FT-IR and ^{1}H-NMR spectroscopies confirmed the chemical attachment of methacrylated benzodioxinone onto the linear polymer chain. In addition to this, the successful detection of ester bands in the FT-IR and ^{1}H-NMR spectroscopies was also proved the acylation process between antagonist benzodioxinone and hydroxyl groups of the PBDMA-*co*-PHEMA-*co*-PMMA. A slight decrease of the molecular weight after the photochemical acylation process was remarkably detected by gel permeation chromatography. Furthermore, thermal stabilities of the PBDMA-*co*-PHEMA-*co*-PMMA and its acylated product were also compared by DSC and TGA analyses. After the photochemical acylation process, thermal stability and glass transition temperature were clearly increased compared to the pristine PBDMA-*co*-PHEMA-*co*-PMMA.

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