



Methacrylated benzophenone as triple functional compound for the synthesis of partially crosslinked copolymers

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ABSTRACT

This contribution reports on one-pot synthesis of crosslinked and branched copolymers via simple photoinduced free radical copolymerization strategy in the presence of methacrylated benzophenone, methyl methacrylate and *N*-methyl-diethanolamine. Methacrylated benzophenone is used as a co-monomer and it is also responsible for the photoinitiation and coupling reactions simultaneously. Copolymerization experiments were carried out in several feed ratios of methacrylated benzophenone and the co-initiator upon ultraviolet irradiation. Polymerization results indicate that molecular weight values are directly depended on the concentrations of methacrylated benzophenone and co-initiator molecule. It is also observed that use of methacrylated benzophenone in mono-acrylate formulations may cause junction points in the copolymer structures.

1. Introduction

Photochemistry is one of the most preferable techniques to reduce energy consumption and important for green chemistry applications [1–3]. Besides, radical photopolymerization technique has been used in several commercial areas such as curing of coatings [2,4], polymeric thin film applications [5], nanocomposites [6–9] and polymeric nanoparticles [10–12]. So far, various polymeric materials with different morphologies have been developed via photoinduced polymerization strategies such as molecular weight controlled polymers [13,14], hydrogels [15–18], macromolecular photoinitiators [19–24], hyper-branched polymers [25,26] and star/block polymers [27–30]. In free radical photopolymerization, while type I (α -cleavage) photoinitiators directly decompose under ultraviolet (UV) irradiation [31–33], type II structures (H-abstraction type) require an additional hydrogen donor molecule for the initiation (Scheme 1) except one component type II photoinitiators which contain chromophore and hydrogen donating sides in the same molecular structure [34–41].

According to mechanism in Scheme 1, after hydrogen abstraction of diaromatic ketone, only resulted alkyl radical is able to initiate the free radical polymerization. It is known that, ketyl radicals are not as reactive as alkyl radicals for the polymerization due to the resonance stability and delocalization of unpaired electron on the molecule. These radicals may undergo termination reactions and benzopinacol structure is easily formed with ketyl–ketyl combination during irradiation [35,36,42,43].

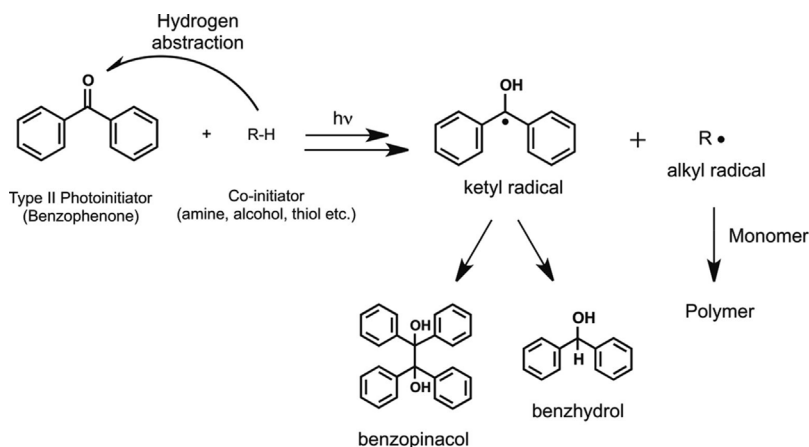
UV curing processes have paid attention because of their very rapid

reaction time at room temperature in the absence of volatile solvent environment and it has been widely used in industrial applications [2,44]. Photo-cured materials have been much more important properties than those of linear equivalents due to their individual characteristics such as high degree of crosslinking and higher mechanical properties. Generally, network structures are formed by mixture of monomers and crosslinker molecules during polymerization. In photo-initiated free radical crosslinking technique, initiator molecule rapidly decomposes, subsequently mono and multi-functional monomers transform interconnecting chains according to radical polymerization mechanism.

In this work, we introduce a new perspective in order to achieve soluble branched and crosslinked polymeric materials using a versatile photoinitiator via similar to self-condensing vinyl polymerization strategy. For this purpose, commercially available hydroxybenzophenone was converted to a methacrylated photoinitiator by simple esterification method [45,46]. Upon UV irradiation, obtained compound can be incorporated into polymer backbone due to the possessing monomeric part and it also acts as a crosslinking agent resulted by ketyl moieties during polymerization process. These attractive features of the multifunctional photoinitiator provide crosslink and branching points on the side chain of the copolymers. We characterized photoactive compound and copolymers with ^1H NMR, gel permeation chromatography (GPC) and UV spectroscopy techniques as well.

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Scheme 1. Type II photoinitiation mechanism of benzophenone with a co-initiator and termination reactions of ketyl radicals.

2. Experimental

2.1. Materials

Benzophenone (BP, 99%) was purchased from Aldrich and recrystallized from ethanol. Dichloromethane (DCM, Merck), methacryloyl chloride (97%, Aldrich), triethylamine (99%, Merck), 4-Hydroxybenzophenone (98%, Aldrich), *N*-methyl-diethanolamine (MDEA, 99%, Aldrich) and methanol (Merck) were used as received. Methyl methacrylate (MMA, Aldrich, 99%) was deinhibited by passing over basic alumina. All other reagents were used as received.

2.2. Characterization

^1H NMR spectra were recorded on a Bruker Avance Spectrometer (500 MHz) in CDCl_3 . UV spectra were recorded on a Shimadzu UV-1601 spectrometer. Fourier transform infrared spectroscopy (FT-IR) analyses were performed on a Perkin Elmer FT-IR Spectrum One B spectrometer. Gel permeation chromatography (GPC) measurements were performed on a Viscotek GPC max auto sampler system consisting of a pump, a Viscotek light scattering detector, and a Viscotek differential refractive index (RI) detector with three ViscoGEL GPC columns (G2000H HR, G3000H HR, and G4000H HR, 7.8 mm internal diameter, 300 mm length) in series. The effective molecular weight ranges were 456–42800, 1050–107000, and 10200–2890000, respectively. Tetrahydrofuran was used as an eluent at a flow rate of 1.0 mL min^{-1} at 35°C . The light-scattering detector ($\lambda_0 = 670 \text{ nm}$) included two scattering angles: 7° and 90° . Refractive index detector was calibrated with polystyrene standards having a narrow molecular weight distribution. 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} .

2.3. Synthesis and characterization of methacrylated benzophenone (BPMac)

Methacryloyl chloride (2.18 mL, 22.5 mmol) dissolved in dichloromethane (3 mL) was added dropwise to a solution of 4-hydroxybenzophenone (3.0 g, 15 mmol) and triethylamine (2.1 mL, 15 mmol) in dichloromethane (15 mL) at 0°C under nitrogen atmosphere. After the addition of methacryloyl chloride solution, the resulting mixture was stirred at room temperature overnight. Then the mixture was washed with saturated aqueous solution of NaHCO_3 (200 mL), two times with water (100 mL) and a saturated aqueous solution of NaCl (100 mL). The organic layers were dried over anhydrous Na_2SO_4 , filtered and then the solvent was evaporated. The resulting

residue was purified by recrystallization from *n*-hexane. Yield: 75%, ^1H NMR (500 MHz, CDCl_3): 7.89–7.19 ppm (m, 9H, Ar H), 6.39 and 5.81 ppm (s, 2H, $\text{CH}_2 = \text{C}(\text{CH}_3)$), 2.09 ppm (s, 3H, $\text{CH}_2 = \text{C}(\text{CH}_3)$), FT-IR (ATR): $\nu = 3060, 2363, 1732, 1649, 1594 \text{ cm}^{-1}$, GC–MS (EI, 70 eV): 266 (M^+).

2.4. General syntheses of copolymers

Appropriate solutions of the BPMac, MMA and co-initiator (MDEA) were transferred in Pyrex tubes (10 mm internal diameter) and solutions were irradiated in a photo-reactor consisting of 12 lamps and emitting light at $\lambda = 350 \text{ nm}$ in air atmosphere. At the end of the irradiation period, resulting copolymers were precipitated in excess methanol, filtered and dried in vacuum. All yields were calculated gravimetrically. All the polymerizations were performed under experimental conditions depicted in Tables 1 and 2.

2.5. Linear copolymerization of BPMac and MMA (LBPMMA)

BPMac (0.131 g, 0.49 mmol), MMA (1 mL, 9.34 mmol) and AIBN (0.008 g, 0.049 mmol) were dissolved in 1 mL of toluene in a Schlenk tube and the solution was bubbled with nitrogen for 10 min and vacuumed at room temperature. Subsequently, tube was kept at 85°C for 2 h. At the end of the period, copolymer was isolated by precipitation in excess methanol. The white product was filtered and dried in vacuum at room temperature.

3. Results and discussion

Synthesis of methacrylated benzophenone (BPMac) was performed by simple esterification procedure and characterized by FT-IR, GC–MS and ^1H NMR successfully. BPMac is a multifunctional compound possessing photoinitiator, monomeric part and it also conducts as a coupling agent after triplet excitation. Monomeric type II photoinitiator (BPMac) produces junction points on the side chain of the copolymers

Table 1

One-pot synthesis of photoinduced partially and highly crosslinked copolymers with MMA and BPMac in the presence of MDEA using $\lambda_{\text{max}} = 350 \text{ nm}$ photoreactor under air atmosphere.^a

Sample	BPMac [mol%]	MDEA [mol%]	Conversion (%)	M_n^b [g mol^{-1}]	M_w/M_n^b
P-1	1.0	1.0	18.9	9635	1.93
P-2	3.0	3.0	29.4	16100	1.72
P-3	5.0	5.0	46.7	Insoluble	Insoluble
P-4	0.5	0	0	–	–

^a MMA = 1 mL, polymerization time = 2 h.

^b Determined by GPC according to linear polystyrene standards with RI detector.

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