

Benzoin-Terminated Polyurethane as Macrophotoinitiator for Synthesis of Polyurethane–Polymethyl Methacrylate Block Copolymers

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ABSTRACT: Macromolecular photoinitiators have attracted much attention in the recent years. They combine the properties of polymers with those of low-molecular weight photoinitiators. These are polymers having side- or main-chain photoreactive groups and can be used to make tailor-made graft and block copolymers. Benzoin is an important photoinitiator, and polymers containing terminal photoactive benzoin group can initiate polymerization of vinylic monomers to give block copolymers. In the present case, we report the synthesis of polyurethane macropho-

toinitiator with benzoin end group, which was subsequently used to synthesize polyurethane–polymethyl methacrylate block copolymers. The block copolymers were characterized by FTIR, ¹H NMR, TGA, scanning electron microscopic analysis, and solution viscometry studies. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 3089–3093, 2009

Key words: macromolecule; photoinitiator; block copolymer; photopolymerization

INTRODUCTION

Photopolymerization is an important step in the preparation of synthetic polymers in both industry and academia. Photopolymerization is extensively used in various industrial processes such as manufacture of printed circuits, encapsulation of electronic components, and coating.¹ Photopolymerization can be achieved through the use of photoinitiators (PIs), photo-crosslinkable polymers, and photo-crosslinking agents.^{2,3} PIs are used for the polymerization of functional monomers, oligomers, and polymers⁴ for their use in applications including UV-curing of coatings and inks as well as for more specialized applications such as dental restorative materials^{5,6} and biomaterials.^{7,8} Polymeric PIs are also precursors for block and graft copolymers depending on the position of the PI moiety incorporated into the polymer chain.⁹ The selective incorporation of light-sensitive groups within a condensation polymer offers the possibility of formation of macroradicals in photolysis, which may initi-

ate the polymerization of vinyl monomers¹⁰ to produce block copolymers.

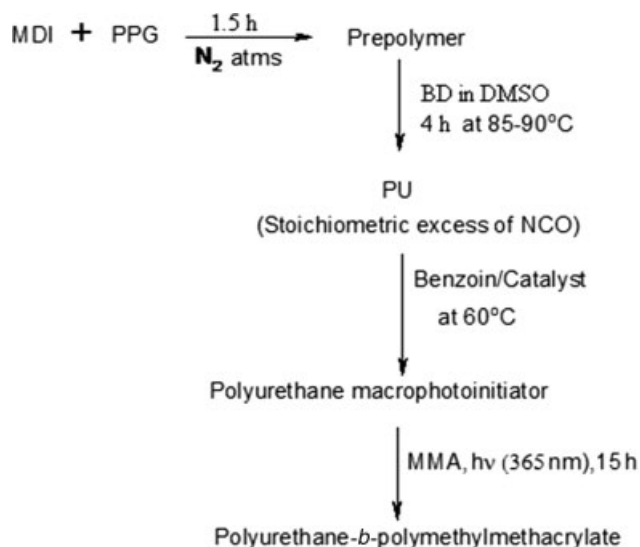
Aromatic ketones are the most versatile PIs in commercial practice as their absorptions occur at longer wavelengths and their quantum yields are higher than aliphatic ketones.¹¹ Benzoin and its derivatives are extensively used as PIs¹² because of their ability to initiate free-radical polymerization of vinyl monomers. Upon irradiation in the 300–400 nm range, these compounds undergo scission with high quantum efficiencies.

Smets and Doi^{13,14} incorporated benzoin methyl ether (BME) groups into polycarbonate by performing the polycondensation of bisphenol A with phosgene in the presence of 4,4'-dihydroxybenzoin methyl ether. This on UV irradiation with methyl methacrylate (MMA) resulted in block copolymer. Yagci and coworkers^{15–17} reported the block copolymers of vinyl monomers using azobenzoin initiators. Yagci and coworkers⁹ also synthesized novel end-chain- and mid-chain-functional macrophotoinitiator of poly(ϵ -caprolactone) using benzoin and 2-hydroxy-2-methyl-1-phenyl propan-1-one (HMPP) as PIs. Corrales et al.¹⁸ also reported some new polymeric PIs that were used for UV curing. They reported polymeric PIs such as benzoin ether derivatives having benzoin methyl moieties connected to the main chain through benzyl aromatic. Bossmann and coworkers¹⁹ reported photoinitiated synthesis and characterization of P(MMA/DPB) polymer nanoparticles using poly(*N*-isopropylacrylamide) in

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Scheme 1 Synthesis of polyurethane-*b*-polymethyl methacrylate.

aqueous solutions as a template. They used benzoin and BME as PIs. Barner-Kowollik and coworkers² used high-resolution electrospray ionization-mass spectrometry (ESI-MS) to study the polymeric product spectrum generated by the pulsed laser polymerization (PLP) of MMA at temperatures $\leq 0^\circ\text{C}$ in the presence of the photoinitiators 2,2-dimethoxy-2-phenylacetophenone (DMPA), benzoin, benzil, benzoin ethyl ether (BEE), and 2,2-azobisisobutyronitrile (AIBN), which were further employed frequently in UV-curing applications, photoimaging, etc.

The incorporation of photolabile benzoin groups into the polyurethane (PU) chain enables it to act as a macrophotoinitiator. Such a PU macrophotoinitiator may be utilized to initiate the photopolymerization of vinylic monomers to synthesize PU-

polyvinyl block copolymers. Herein, we report the use of a PU macrophotoinitiator with benzoin group at the chain end to synthesize polyurethane-poly-methyl methacrylate block copolymers (PU-*b*-PMMA) (Scheme 1).

EXPERIMENTAL

Solvent and reagents

Dimethyl sulphoxide (DMSO, E-Merck) was dried over calcium hydride for 1 week and distilled under reduced pressure. *N,N*-Dimethylformamide (DMF, Qualigens) was dried over barium oxide for 3 days and then distilled under reduced pressure. Polypropylene glycol MW 1000 (PPG, E-Merck) was heated at 100°C in a rotary evaporator under reduced pressure for 10 h. Diphenyl methane-4,4'-diisocyanate (MDI, Aldrich) was distilled under reduced pressure and stored over silica gel at 4°C . MMA (E-Merck) was washed with 5% aqueous sodium hydroxide solution to remove the inhibitor. It was then washed with distilled water, dried over CaCl_2 , and distilled under reduced pressure. 1,4-Butane diol (BD, E-Merck) was distilled under reduced pressure. Benzoin (E-Merck) and dibutyl tin dilaureate (DBTDL, Aldrich) were used as supplied.

Synthesis of polyurethane macrophotoinitiator

Polyurethane macrophotoinitiator (PUMPI) was synthesized with benzoin as the photolabile group. PU was first synthesized from MDI, PPG, and BD with stoichiometric excess of isocyanate groups. This PU was reacted with required amount of benzoin to produce benzoin-terminated PU macrophotoinitiator. The molar ratio of MDI, PPG, and BD+benzoin used

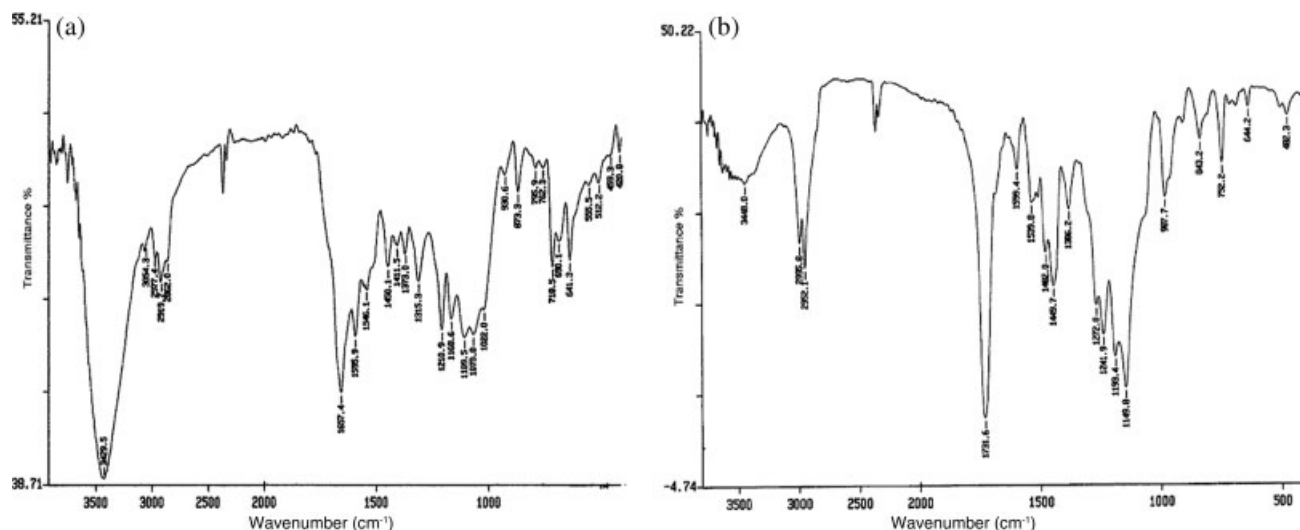


Figure 1 FTIR spectrum of (a) PUMPI and (b) PU-*b*-PMMA.

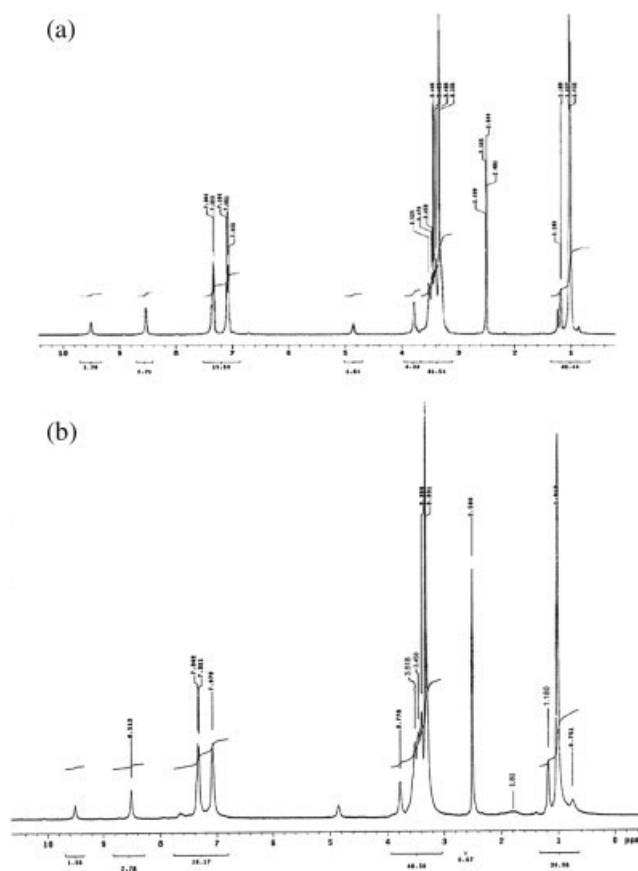


Figure 2 ^1H NMR spectrum of (a) PUMPI and (b) PU-*b*-PMMA.

in the synthesis was 3 : 1 : 2. The general reaction scheme is given in Scheme 1.

MDI (2.001 g) and PPG (2.660 g) were first heated for 1.5 h at 90°C under nitrogen. Then 10 cm³ DMSO was added slowly. The reaction mixture was cooled to 50°C, and BD (0.2423 g) dissolved in 5 cm³ DMSO was added dropwise through a pressure equalizing funnel. The reaction mixture was then heated again at 85–90°C for 4 h. Then it was cooled to 60°C, and then benzoin (1.135 g) dissolved in DMSO was added slowly followed by the addition of the catalyst DBTDL (2 drops). The mixture was further heated for another 3 h at 60°C and finally, the polymer was precipitated from water. It was then dried in a vacuum oven at 60°C for several days.

Block copolymerization

The photoblock copolymerization was carried out in a Heber Multilamp Photochemical Reactor (COMPACT-LP-MP-88) at 365 nm. The mixture of PUMPI (0.1001 g) and MMA (1.001 g) dissolved in 10 mL DMF was placed in a reactor tube made of borosilicate. The tube was then closed under nitrogen atmosphere and irradiated at 365 nm in the reactor

for 15 h. At the end of the reaction, the polymer was recovered by pouring into large excess of methanol. The homopolymer (PMMA) was removed by Soxhlet extraction with acetone. The block copolymer was dried in vacuum oven for several days.

RESULTS AND DISCUSSION

The PU macrophotoinitiator and its block copolymer were synthesized according to Scheme 1. They were characterized by FTIR and ^1H NMR. The block copolymer was further studied by thermogravimetry and scanning electron microscopy (SEM). The viscosity measurements indicated a rise in viscosity as a result of block copolymerization.

FTIR spectra were recorded using a Perkin Elmer RX1 FTIR spectrophotometer. The polymers were analyzed in the form of KBr pellets. The spectra of PUMPI and its block with PMMA are shown in Figure 1(a,b) respectively. In the PU macrophotoinitiator, the urethane N–H stretch was observed at 3428 cm⁻¹. The carbonyl absorption due to the

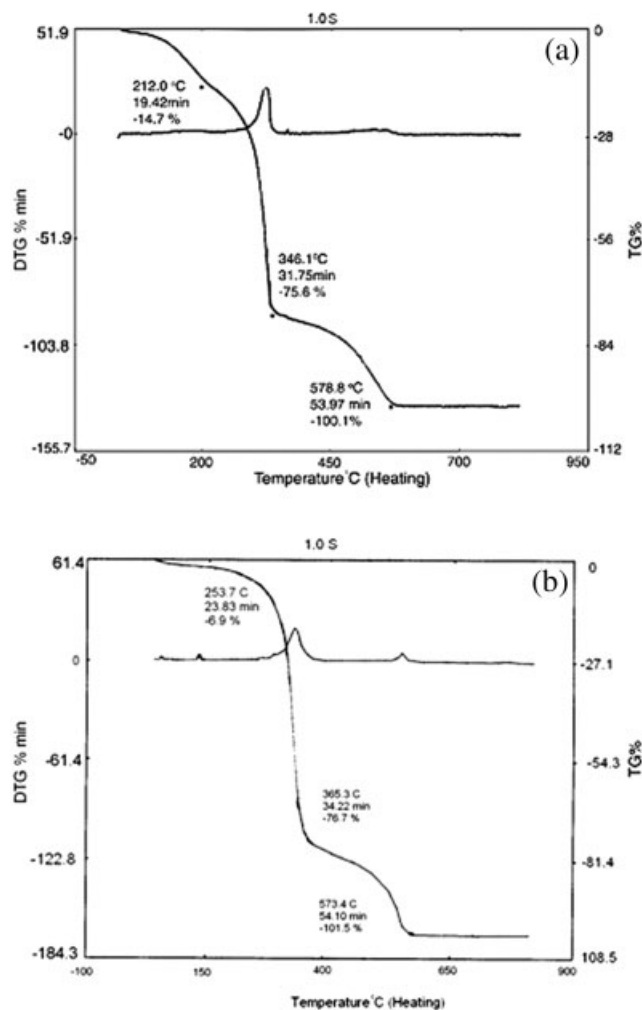


Figure 3 TG thermogram of (a) PUMPI and (b) PU-*b*-PMMA.

TABLE I
Degradation Temperature and Percentage of Weight Loss for PUMPI and PU-*b*-PMMA

Sample	1st degradation (% of weight loss)	2nd degradation (% of weight loss)	3rd degradation (% of weight loss)
PUMPI	212.2 (14.7%)	346.1 (75.6%)	578.8 (100%)
PU- <i>b</i> -PMMA	253.7 (6.9%)	365.3 (76.7%)	573.4 (100%),

urethane group is generally observed at around 1700 cm^{-1} . However, the macrophotoinitiator carbonyl absorption was observed as a broad peak at 1657.4 cm^{-1} . This was due to the presence of additional carbonyl in benzoin where α - β -unsaturation lowers the absorption frequency. A strong peak at 1595.9 cm^{-1} was due to C=C of benzene ring of MDI. The band at 1070.0 cm^{-1} and 1109.5 cm^{-1} correspond to C—O—C stretching mode in polyether soft segment of PU.

Figure 1(b) shows the urethane N—H stretch at 3448.0 cm^{-1} . The peak centered at 1149.8 cm^{-1} and 752.2 cm^{-1} could be assigned to the blocked PMMA as the PMMA homopolymers were removed by soxhlet extraction with acetone.^{20,21} The carbonyl peak of PMMA chain was observed at 1731.6 cm^{-1} .

^1H NMR spectra were recorded on a Bruker AC 200MHz spectrophotometer using d_6 -DMSO as solvent. ^1H NMR spectrum of macrophotoinitiator is presented in Figure 2(a). The peak centered at 1.01–1.1 ppm was due to methyl protons from PPG. The multiple peaks between 3.3 and 3.5 ppm were observed due to CH and CH_2 protons of PPG. The peak at 3.778 is due to the CH_2 protons of the MDI unit²² and the one at 4.9 was probably due to the CH-protons of PPG next to the urethane linkage.²³ The peaks observed at 7.063 to 7.341 ppm were due to the aromatic protons of the MDI unit and phenyl groups of the benzoin group. The peaks at 8.58 and 9.51 ppm were due to the urea proton and urethane protons, respectively.

^1H NMR spectrum of block copolymer of PU macrophotoinitiator with MMA is presented in Figure

2(b). All characteristic peaks of the PU macrophotoinitiator were present in this spectrum. The peak at 0.751 ppm was due to the $-\text{CH}_3$ proton of PMMA for syndiotactic configuration.²⁴ Protons peaks due to ester methyl protons at 3.5 to 3.7 ppm cannot be differentiated because of the overlapping between proton peaks of PPG and $-\text{OCH}_3$ of PMMA. A small peak at 1.80 ppm may be due to the $-\text{CH}_2$ protons of PMMA.²⁴

TG spectra were recorded in TG/DTA 32, Seiko spectrometer, Japan. The TG/DTA studies were carried out in the temperature range between 25 and 700°C in N_2 atmosphere at the heating rate of $10^\circ\text{C}/\text{min}$. The thermograms of the macrophotoinitiator and the corresponding block copolymer with MMA are shown in Figure 3(a,b), respectively. The two thermograms are similar but not identical, which indicated the differences in their chemical composition. This was due to the block copolymerization process. The temperatures corresponding to different stages of weight loss are shown in Table I.

Leica Cambridge 440 scanning microscope was used to study the surface morphology of polymers. The samples were coated with thin layer of gold and kept on a copper grid, then run the SEM under high vacuum. Figure 4(a,b) shows the SE-micrographs of the PU macrophotoinitiator and the corresponding block copolymer with PMMA. The micrograph for PUMPI shows the phase-separated morphology with well-developed domain structures. The formation of block copolymer with PMMA evidently altered the morphology of the precursor macrophotoinitiator. This was evident from the micrographs [Fig. 4(b)].

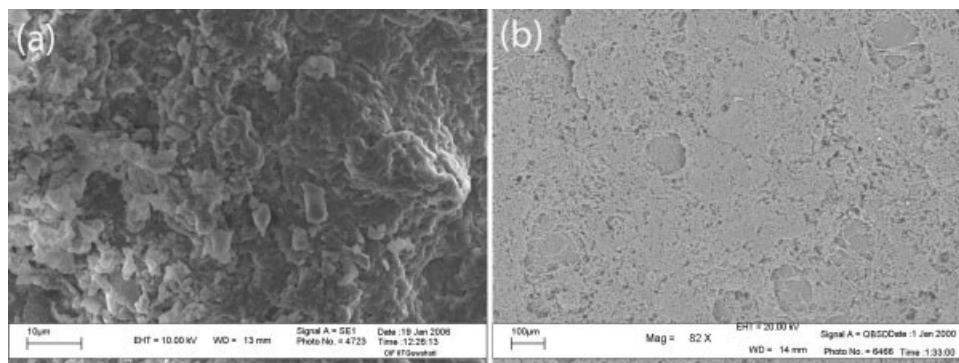


Figure 4 SEM photograph of (a) PUMPI and (b) PU-*b*-PMMA.

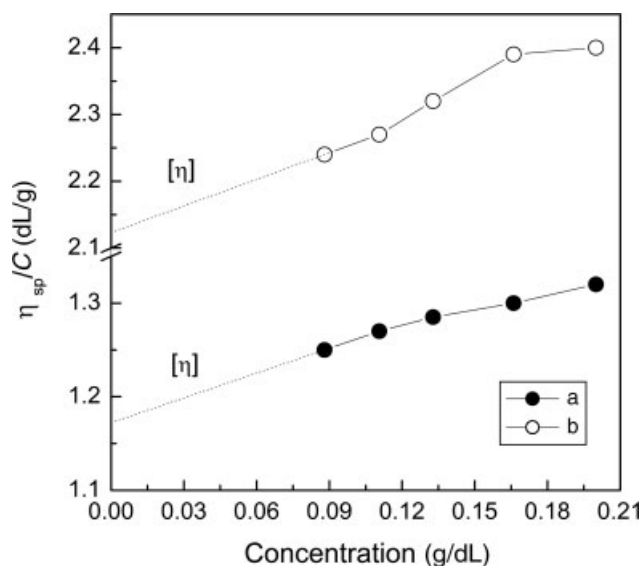


Figure 5 Reduced viscosity against concentration of (a) PUMPI and (b) PU-*b*-PMMA.

In the block copolymer, a scaly continuous morphological feature appeared to mask the original morphological features of the macrophotoinitiator.

The viscosity behavior of the macroinitiator and its block copolymer was also investigated using a standard Ubbelohde viscometer at 25°C in a thermostatted water bath. Dilute solution viscometry is concerned with the measurement of the increase in viscosity and allows the determination of intrinsic ability of a polymer to increase the viscosity of a particular solvent at a given temperature. Wang and Huang²⁵ studied the inherent viscosity of some PU macroiniferters based on MDI-PTMG-TPED. They found that with increasing monomer concentration at constant polymerization time, inherent viscosity increased due to the increasing molar mass of the resulting polymer. The viscosities of the PU macrophotoinitiator and PU-PMMA block copolymers were studied at different concentrations using DMF as solvent (Fig. 5). The block copolymer showed a higher value of intrinsic viscosity than that of the macroinitiator. The rise in the intrinsic viscosity may be because of the rise in the molar mass due to block copolymerization of PU with MMA.

CONCLUSION

PU macrophotoinitiator with chain-end benzoin group was successfully synthesized and further used for the synthesis of PU-PMMA block copolymer. The block copolymers were characterized and their physicochemical properties were studied using FTIR, ¹H NMR, TGA, SEM, and solution viscometric techniques.

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