Photopolymerization of acrylates by enzymatically synthesized PCL based macrophotoinitiator

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Abstract. Polycaprolactone based macrophotoinitiator was synthesized via enzymatic ring-opening polymerization by using commercially available Irgacure-2959 as the nucleophilic initiator and Novozyme-435 as the immobilized lipase catalyst. The macrophotoinitiator was further utilized to photopolymerize benzyl acrylate (BzA), tetrahydrofurfuryl acrylate (THFA), 2-hydroxyethyl acrylate (HEA) and poly (ethylene glycol) methyl ether acrylate ($M_n \sim 480$ g/mole) (PEGMEA-480) under Ar atmosphere. The obtained polymers were characterized by ¹H Nuclear Magnetic Resonance, Fourier Transform Infrared Spectroscopy, Differential Scanning Calorimetry and Size Exclusion Chromatography. The highest dry polymer conversions were achieved with BzA and THFA. However, due to the gel formation during the photopolymerization reactions of HEA and PEGMEA-480, the dry polymer conversions were comparably lower. The photopolymerization product of BzA demonstrated a single glass transition temperature at -6.5°C . The enzymatically synthesized macrophotoinitiator was shown to be an efficient catalyst for light-induced polymerization of the abovementioned monomers.

Keywords: biopolymers, biocomposites, polycaprolactone, macrophotoinitiator, enzymatic polymerization, photopolymerization

1. Introduction

Polycaprolactone (PCL) is among the most important polymers preferred to be applied in medicine and tissue engineering owing to its mechanical properties, low melting point ($59\text{--}64^\circ\text{C}$), crystallinity, blend compatibility with a wide range of polymers, good solubility with biocompatibility and biodegradability by numerous bacteria [1–3]. Enzymatic polymerization is a synthetic *in-vitro* polymerization technique when an isolated enzyme is used as a catalyst [4]. One of the main reasons of preferring enzymatic polymerization is the residual organometallic catalysts such as Zn, Al, Sn, Sb, Ti, Bi, Ge, remaining from the ring opening polymerization (ROP) of various lactones and condensation polymerization, since

these metallic catalysts are intrinsically toxic limiting their usage in biomedical applications [4–6]. In addition to this, enzymatic polymerization has more prevailing features as compared with the organic synthesis such as higher catalytic activity, milder reaction conditions (i.e. temperature, pressure and pH etc.), better enantioselectivity, chemoselectivity and regioselectivity, and lesser by-product formation. Lactones with various ring sizes including ϵ -caprolactone (CL) are susceptible to enzymatic ring-opening polymerization (eROP) by lipases which was studied by many research groups regarding the reactivity, kinetics, selectivity, solvent and initiator effects [7]. Photopolymerization possesses a substantial interest since it has been applied in coatings, adhesives, inks,

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printing plates, optical waveguides and microelectronics by providing economic and environmental benefits together. For instance, photoinitiated polymerization methods might accommodate room temperature or below synthesis conditions, which is deficient in synthesis methods employing thermal energy such as thermal curing and free-radical polymer synthesis with thermally degradable initiators [8, 9]. In the literature, benzoin, 2-hydroxy-2-methyl-1-phenyl propan-1-one (Darocure 1173), 2-hydroxy-1-[4-(2-hydroxyethoxy)phenyl]-2-methyl propan-1-one (Irgacure 2959) photoinitiators were used in the synthesis of PCL based macrophotoinitiators via stannous octoate catalyzed living ring-opening polymerization (ROP) to induce photopolymerization of methyl methacrylate (MMA) resulting in block copolymers of ϵ -caprolactone (CL) and MMA [10]. Similarly, mid-chain macrophotoinitiators comprised of poly(D,L-lactide) homopolymer and tetrablock poly(D,L-lactide)-poly(ϵ -caprolactone) copolymers were synthesized via ROP and they were utilized in further installation of MMA units via light induced polymerization [11].

Nucleophiles such as water and alcohols were studied in the literature for their initiation efficiency in eROP of lactones. ω -unsaturated alcohols, alkyl glucopyranosides, bifunctional atom transfer radical polymerization (ATRP) initiators, are the examples of nucleophiles other than water which initiated eROP of lactones [12–17]. Irgacure-2959 (Ir2959) was used as the nucleophilic initiator to obtain a macrophotoinitiator by enzymatic ring opening polymerization (eROP) of oxacycloheptadec-10-en-2-one. The α -Ir2959-substituted macrophotoinitiator was also UV-cured [18].

The use of macrophotoinitiators might be helpful to decrease the migration of the photodecomposition products in packaging applications due to their relatively depleted mobility as compared to the smaller photoinitiators. The photodecomposition products of macrophotoinitiators also have lower volatility which might be an important feature in coating applications where low volatile organic component (VOC) content is crucial [19]. In biomedical applications such as bone cements and tooth fillings, prepolymers which bear photoactive groups are injected to obtain complex forms through small holes which overcomes the drawbacks of the surgical operations [20]. Hindering unpleasant odors, providing better solubility and compatibility are also the

encouraging factors for utilizing polymeric photoinitiators [11].

Poly(benzyl acrylate) (PBzA) was preferred in the literature due to its high thermal and photochemical stability and poly(tetrahydrofurfuryl acrylate) (PTHFA) was noted with its recognizable blood compatibility [21, 22]. Homopolymer and copolymers of 2-hydroxyethyl acrylate (HEA) were widely used in biomedical applications as a result of their hydrogel form, tunable properties and biocompatibility [23, 24]. Poly(ethylene glycol) based densely brushed polymers are well-known for their antifouling uses due to their highly efficient protein repelling feature [25].

In this study, an alternative method for the synthesis of a metal-free PCL based macrophotoinitiator via eROP unlike the polyesters including metal-catalyst residues by using Ir2959 as the nucleophilic initiator and Novozyme-435 as the immobilized lipase catalyst. Afterwards, the obtained macrophotoinitiator was used to allow light-induced polymerization of BzA, THFA, HEA and poly(ethylene glycol) methyl ether acrylate (PEGMEA-480). The macrophotoinitiator and the photopolymerization products were characterized via ^1H NMR, FT-IR, DSC and SEC.

2. Experimental

2.1. Materials

ϵ -Caprolactone (99%) (CL) was purchased from Alfa Aesar, Germany. Irgacure 2959 (Ir2959) (1-[4-(2-Hydroxyethoxy)-phenyl]-2-hydroxy-2-methyl-1-propane-1-one) was purchased from Ciba Specialty Chemicals, Switzerland. Novozyme-435 (N435) (*Candida Antarctica Lipase B* immobilized on acrylic resin), poly(ethylene glycol) methyl ether acrylate (PEGMEA-480) (Average molecular weight of 480 g/mole) and 2-hydroxyethyl acrylate (HEA) were purchased from Sigma-Aldrich, MO, USA. Benzyl acrylate (BzA) was purchased from TCI Chemicals, Belgium. Tetrahydrofurfuryl acrylate (THFA) was purchased from Polysciences Inc., PA USA. Solvents were supplied from Sigma-Aldrich, MO, USA, and used as received.

2.2. Methods

2.2.1. Characterization

Size exclusion chromatography

Size exclusion chromatography (SEC) measurements were performed with Agilent 1100 as tetrahydrofuran (THF) was the SEC solvent with 45 min measurement time.

Differential scanning calorimetry

Mettler-Toledo DSC-1, equipped with an automatic sample robot, a liquid nitrogen-based cooling system and a FRS5 sensor based on a star-shaped arrangement of 56 thermocouples was used for differential scanning calorimetry (DSC) measurements. Standard Al pans of 40 μL were utilized for sample preparation. The DSC measurements were performed in 3 sequential runs: (1) heating from room temperature to 60 $^{\circ}\text{C}$, (2) cooling from 60 to -100°C , (3) heating from -100 to 200°C respectively, while heating and cooling were executed in $10^{\circ}\text{C}/\text{min}$ ramps. Between each heating and cooling steps, isothermal periods of 5 minutes were applied. 2nd heating curves were taken into consideration in STARE Excellence Software for the calculation of the values.

Fourier transform infrared spectroscopy

Fourier Transform Infrared Spectroscopy (FT-IR) measurements were performed with ATR-FT-IR (Affinity-1 FT-IR, Shimadzu) in the range between 600 and 4000 cm^{-1} .

 ^1H nuclear magnetic resonance

^1H Nuclear Magnetic Resonance (NMR) measurements were performed with Agilent VNMRS 500 MHz (CDCl_3).

2.2.2. Enzymatic synthesis of PCL-based macrophotoinitiator

The eROP mechanism of CL as N435 was the enzymatic catalyst and Ir2959 the nucleophilic initiator was demonstrated in Figure 1. For the enzymatic synthesis of PCL-based macrophotoinitiator, firstly, Ir2959 was dissolved in CL at room temperature and the mixture was treated with freshly activated 4 Å molecular sieves for two days. N435 (200 mg) was dried at 50°C for 3 days in a vacuum oven; the glass reactor was treated with flame under vacuum and closed with rubber septum. Monomer/initiator mixture was added via syringe to the reactor and the reaction proceeded for 8 hours at 80°C . CL/initiator ratio (mole/mole) was 10 and the total mixture of the monomer and the initiator was 4.5 g. The reaction was stopped by adding chloroform and enzyme was filtered. Excess chloroform was evaporated from the mixture and the polymer was precipitated via ice-cold methanol for 4 times. The resulting polymer was washed with methanol to ensure the successful removal of the unreacted Ir2959 from the macrophotoinitiator. Sequentially, the polymer was dried under vacuum at 30°C for 4 days.

2.2.3. Photopolymerization reactions initiated by PCL based macrophotoinitiator

Light Emitting Diode (LED) lamps with 360–400 nm wavelength emission were utilized. 15° of optical

Figure 1. Enzymatic ring-opening polymerization mechanism of CL with lipase as Ir2959 was the initiator [4]

lenses were used for effective focusing to the reaction mixtures. The advantage of the LED lamps is the ignorable heating of the reaction medium, consequently prevention of the solvent evaporation and pressure build-up and loss of solvent from the reaction medium. PCL based macrophotoinitiator, acrylic monomer, magnetic stirring bar and 0.4 mL of dimethylacetamide (DMA) were put into a 10 mL snap-capped glass vial. The vial was purged with Ar gas. The mixture was kept at 35 °C for 2–3 min and subsequently in ultrasonic bath again for 2–3 min to ensure good solubility of the compounds in the solvent. Then UV polymerization was started; the reaction time was kept as 20 minutes for each monomer. The amount of the macrophotoinitiator was 40 mg, the ratio of acrylate/macrophotoinitiator (mole/mole) was kept constant at 200 in all of the photopolymerization experiments.

The resulting polymers were dissolved in chloroform when BzA and THFA were used as monomers and precipitated in ice cold diethyl ether for two times. However, since gel formation observed when HEA and PEGMEA-480 were used as monomers, it was not possible to dissolve the gels in chloroform, dichloromethane, dimethylacetamide, dimethylsulfoxide, toluene and tetrahydrofuran. Hence, the gels were rinsed with chloroform and ice-cold methanol

respectively in order to remove the residual macrophotoinitiator, PEGMEA-480, HEA and DMA trapped inside the gels. The rinsed polymers were dried under vacuum oven at 40 °C for 2 days.

3. Results and discussion

^1H NMR spectrum of the Ir2959 end-functionalized PCL based macrophotoinitiator was demonstrated in Figure 2. The characteristic peaks of the structure were as follows: $\delta = 7.90\text{--}7.95$ ppm (2H, m, $\mathbf{H_a}$); $\delta = 6.93\text{--}6.98$ ppm (2H, m, $\mathbf{H_b}$); $\delta = 4.43\text{--}4.47$ ppm (2H, t, $\mathbf{H_d}$); $\delta = 4.23\text{--}4.27$ ppm (2H, t, $\mathbf{H_c}$); $\delta = 4.00\text{--}4.15$ ppm (2H, t, $\mathbf{H_5}$); $\delta = 3.61\text{--}3.67$ ppm (2H, t, $\mathbf{H_{5'}}$); $\delta = 2.23\text{--}2.38$ ppm (2H, t, $\mathbf{H_1}$); $\delta = 1.50\text{--}1.75$ ppm (4H, m, $\mathbf{H_2}$, $\mathbf{H_4}$); $\delta = 1.64$ ppm (6H, s, $\mathbf{H_e}$); $\delta = 1.30\text{--}1.45$ ppm (2H, t, $\mathbf{H_3}$). The end-group fidelity of the macrophotoinitiator was found according to the Equation (1), where I_d and $I_{5'}$ were the peak integrals of the peaks **d** and **5'** respectively. The peak **5'** presented in every polymer chain as the $-\text{CH}_2-$ neighboring the chain-end hydroxyl group; while the peak **d** only presented in the successfully Ir2959 end-functionalized PCL chains. The end-group fidelity (the molar ratio of Ir2959 end-functionalized PCL chains to the total PCL chains in the dry polymer mixture) was calculated as the direct ratios of the peak areas of these two peaks. The molecular weight of the

Figure 2. ^1H NMR of the PCL based macrophotoinitiator

macrophotoinitiator was calculated as 3875 g/mole according to ^1H NMR result. On the other hand, the M_n value was calculated as 5150 g/mole from the SEC results. The dry polymer conversion was found as 52% and the end-group fidelity was calculated as 93% according to Equation (1):

$$\text{End-group fidelity} = \frac{I_d}{I_{s'}} \quad (1)$$

^1H NMR spectrum of the PCL-*b*-PBzA was shown in Figure 3. The characteristic peaks of the structure were as follows: $\delta = 7.90\text{--}7.95$ ppm (2H, m, H_a); $\delta = 7.11\text{--}7.38$ ppm (5H, m, H_A , H_B , H_C); $\delta = 6.93\text{--}6.98$ ppm (2H, m, H_b); $\delta = 4.82\text{--}5.06$ ppm (2H, s, H_D); $\delta = 4.43\text{--}4.47$ ppm (2H, t, H_d); $\delta = 4.23\text{--}4.27$ ppm (2H, t, H_c); $\delta = 4.00\text{--}4.15$ ppm (2H, t, H_5); $\delta = 3.61\text{--}3.67$ ppm (2H, t, H_5'); $\delta = 2.23\text{--}2.38$ ppm (2H, t, H_1); $\delta = 1.78\text{--}1.99$ ppm (1H, b, H_G); $\delta = 1.50\text{--}1.75$ ppm (6H, m, H_2 , H_4 , H_H); $\delta = 1.30\text{--}1.45$ ppm (2H, t, H_3). According to the ^1H NMR of the purified dry polymer of this reaction Figure 3, the conversion was calculated as 93% confirming the conversion calculation from the crude reaction mixture, where $[I]_D^d$ and $[I]_5^d$

were the peak integrals of the peaks **D** and **5** of the dry polymer and $[I]_D^f$ and $[I]_5^f$ were the peak integrals of the peaks **D'** and **5** of the feed before photopolymerization Equation (2). The molar feed ratio of the benzyl acrylate monomer to the CL repeating units in the macrophotoinitiator before the light induced polymerization was 200/31 (mole/mole):

Dry polymer conversion benzyl acrylate [%] =

$$= \frac{\frac{[I]_D^d}{[I]_5^d}}{\frac{[I]_D^f}{[I]_5^f}} \cdot 100 \quad (2)$$

^1H NMR spectrum of the product obtained via photopolymerization THFA as Ir2959 end-functionalized PCL was the macrophotoinitiator was shown in Figure 4. The characteristic peaks of the structure were as follows: $\delta = 4.23\text{--}4.27$ ppm (2H, t, H_c); $\delta = 3.93\text{--}4.17$ ppm (5H, H_5 , H_D , H_E); $\delta = 3.69\text{--}3.91$ ppm (2H, m, H_A); $\delta = 2.23\text{--}2.53$ ppm (3H, H_1 , H_F); $\delta = 1.78\text{--}2.07$ ppm (3H, m, H_{B1} , H_{B2} , H_{C1}); $\delta = 1.45\text{--}1.78$ ppm (7H, H_G , H_{C2} , H_2 , H_4); $\delta = 1.30\text{--}1.45$ ppm (2H, t, H_3). The dry polymer conversion was calculated

Figure 3. ^1H NMR of the product synthesized via photopolymerization of BzA by PCL based macrophotoinitiator

Figure 4. ^1H NMR of the product synthesized via photopolymerization of THFA by PCL based macrophotoinitiator

following Equations (3)–(5). m/n referred to the ratio of the number of the repeating units of THFA to the repeating units of CL in the macrophotoinitiator which was calculated according to Equation (4) and (5). I_A , I_D , I_E and I_5 were the integral values of the peaks **A**, **D**, **E** and **5** respectively. $(m_{\text{feed}})/(n_{\text{feed}})$ was the feed molar ratio of the THFA monomer to the CL repeating units in the macrophotoinitiator before the light induced polymerization, which was the same as BzA photopolymerization, 200/31 (mole/mole):

$$\text{Dry polymer conversion of THFA [\%]} = \frac{\frac{m}{n}}{\frac{(m_{\text{feed}})}{(n_{\text{feed}})}} \quad (3)$$

$$I_D + I_E + I_5 = 3m + 2n \quad (4)$$

$$I_A = 2n \quad (5)$$

The ^1H NMR of the photopolymerization product of HEA and PEGMEA-480 macromonomer couldn't be measured due to the insolubility of the resulting polymers in solvents such as, dichloromethane, dimethylformamide, dimethylsulfoxide, N,N -dimethylacetamide, toluene, hexane, acetonitrile and water.

Therefore only DSC and FT-IR measurements of the resulting gels could be executed. The chemical structure of the target block copolymer, PCL-*b*-PHEA was shown in Figure 5.

The FT-IR spectra of Ir2959 end-functionalized PCL based macrophotoinitiator and the polymer obtained after photopolymerization of HEA were shown in Figure 6. In both of the spectrums, asymmetric stretching of CH_2 , symmetric stretching of CH_2 , $\text{C}=\text{O}$ carbonyl stretching and symmetric $\text{C}-\text{O}-\text{C}$ stretching at 2945, 2864, 1720 and 1165 cm^{-1} respectively were the common peaks remained the same after photopolymerization. On the other hand, after polymerization of HEA, the appearance of an $\text{O}-\text{H}$ stretching region around 3000–3700 cm^{-1} together with $\text{O}-\text{H}$ bending at 1073 cm^{-1} were attributed the

Figure 5. Chemical structure of the target block copolymer PCL-*b*-PHEA

Figure 6. FT-IR spectrum of the PCL based macrophotoinitiator and the gel obtained after photopolymerization of HEA

HEA repeating units confirming the hydrogen bonds occurred chiefly driven by the $-OH$ functionalities. However, FT-IR technique is not sufficient enough to reveal whether the resulting polymer was a mixture of polymers or a block copolymer as well as 1H NMR.

The chemical structure of the target block copolymer after photopolymerization of PEGMEA-480 macromonomer by the PCL based macrophotoinitiator was demonstrated in Figure 7. In the FT-IR spectrum of photopolymerization product of PEGMEA-480, it can be seen that after the photopolymerization of PEGMEA-480, the resulting polymer had a slight wide O–H stretching region between $3000\text{--}3700\text{ cm}^{-1}$, which was attributed to the moisture uptake of the PEGMEA-480 segments in the final polymer due to the nature of PEG even though the PEGMEA-480 macromonomer was not containing hydroxyl end-groups. All of the other peaks related to PCL structure were the same as asymmetric stretching at 2945 cm^{-1} , symmetric stretching at 2864 cm^{-1} , carbonyl stretching at 1720 cm^{-1} and C–O–C stretching at 1165 cm^{-1} . Additionally, the peak with small absorbance at 1637 cm^{-1} was associated with the double bonds of the unreacted PEGMEA-480 macromonomer residue trapped

Figure 7. Chemical structure of the target block copolymer PCL-*b*-PPEGMEA

inside the gel, despite the resulting gel was rinsed with chloroform numerous times. The peak with highest absorbance value at 1099 cm^{-1} , which was the result of C–O, C–C stretching together with C–H rocking (trans) vibrations, implied the PEGMEA-480 segments in the resulting polymer (Figure 8). In Figure 9, the 2nd heating curves on the DSC thermograms of the macrophotoinitiator and the photopolymerization products of BzA, THFA, HEA and PEGMEA-480 were demonstrated. For the photopolymerization reaction when BzA was the monomer, the only endothermic transition was the broad and high step change glass transition of the resulting polymer. The T_g of the polymer was evaluated as -6.5°C . Thus, the resulting polymer had a completely amorphous

structure. Since there was a only one glass transition observed, the resulting polymer might be the block copolymer of PCL and PBzA. On the other hand, the polymer might also be the homogeneously mixed block copolymer, unreacted PCL chains and the homopolymer of PBzA, since two different free radicals occurred during the photodecomposition of the macrophotoinitiator one of which was including the PCL chain and the other was the ketyl radical. For photopolymerization of THFA, the broad and high step change in the glass transition of the polymer with an onset value of -12.2°C revealed the amorphous domains in the photopolymerization product. Interestingly, the glass transition of the macrophotoinitiator at -53.3°C couldn't be observed. The two melting points at closed values to each other were observed (52.4 and 56.7°C) was an indication of two different crystalline domains. The melting at 52.4°C was attributed to the unreacted PCL chains and the melting at 56.7°C was associated with either the block copolymer or the mixture of block copolymer with the homopolymer of THFA.

For the photopolymerization of HEA, since there were two distinct glass transitions (at -55.3 and

16.5°C) and two melting peaks (at 55.9°C and a broad peak around 160°C) were observed, the resulting polymer might be evaluated as the mixture of the unreacted PCL, homopolymer of HEA and the block copolymer PCL-*b*-PHEA. The T_g value at -55.3°C and T_m value at 55.9°C were the characteristic peaks of the PCL based macrophotoinitiator. On the other hand, the broad and highly inclined T_g value at 16.5°C was ascribed to the block copolymer and/or the homopolymer of HEA. Therefore, the photopolymerization product was in the rubbery state and had an elastic behavior. The broad endothermic transition around 160°C was due to the high melting point of HEA including polymer chains equipped with dense hydrogen bonds due to the hydroxyl functionality of HEA repeating units, which was also confirmed by FT-IR measurements. For the photopolymerization reaction of PEGMEA-480, the only one glass transition (at -61.2°C) temperature was attributed to either the homo-brush polymer of PEGMEA-480 macromonomer, or the block copolymer PCL-*b*-PPEGMEA-480. Additionally, there were two melting transitions (a peak at 6.6°C and a small peak with multiple shoulders around 54°C) were observed.

Figure 8. FT-IR spectrum of the PCL based macrophotoinitiator and the gel obtained after photopolymerization of PEGMEA-480

The T_m at 54 °C was considered as the residual unreacted PCL chains, and the T_m at 6.6 °C as the melting of the block copolymer. The low T_g and T_m values signified the rubbery and elastic state of the resulting polymer similar to the photopolymerization products conducted with the other monomers.

SEC results of the photopolymerization reactions performed by using BzA, THFA and PCL-based macrophotoinitiator were demonstrated in Figure 10. The PCL-based macrophotoinitiator had a PDI value of 1.46 and M_n of 5150 g/moles calculated from SEC measurement. There are two free-radicals forming due to photoactivation of Ir2959: (a) the radical

Figure 9. DSC 2nd heating curves of (a) PCL based macrophotoinitiator and the photopolymerization products of (b) BzA, (c) THFA, (d) HEA, (e) PEGMEA-480

bearing the benzyl group and the PCL chain, (b) the ketyl radical. Both radicals may initiate the photopolymerization reactions of (meth)acrylates [26]. Hence, it was possible to obtain the homopolymers of the acrylates inside the photopolymerization products initiated by the ketyl radical. In the polymerization performed with THFA, there was a wide peak comprising three shoulders all of which shifted to higher molecular weight values as compared with the macrophotoinitiator. The SEC curve of the product of the experiment conducted with BzA, had a smoother curve than THFA. BzA photopolymerization had also two other molecular weight distributions considering the slightly recognizable shoulders in the curve. This result revealed a second and a third distribution in the dry polymer. If the monomer and the dry polymer conversion values were considered, the dry polymer conversion of THFA was found to be much lower than that of BzA due to the loss of a portion of the resulting polymer during purification procedure (Table 1). This result was in agreement with the bigger shoulder of the lowest molecular weight chains in SEC result of THFA photopolymerization as compared to BzA. The monomer conversion values

Figure 10. SEC results of the dry polymer after photopolymerization reactions performed by using BzA, THFA and the PCL based macrophotoinitiator

Table 1. The M_n , PDI, monomer conversion, dry polymer conversion, T_g and T_m values of the macrophotoinitiator and the polymers obtained via photopolymerization of BzA, THFA, HEA and PEGMEA-480. *Monomer conversion was calculated from the ¹H NMR of the reaction mixtures after photopolymerization. **Measured by weighing.

Experiment	M_n^{SEC} [g/mole]	PDI	Monomer conv. [%]*	Dry polymer conv. [%]	T_g		T_m	
					$T_{g,1}$ [°C]	$T_{g,2}$ [°C]	$T_{m,1}$ [°C]	$T_{m,2}$ [°C]
Ir2959-PCL	5 150	1.46	—	52	-53.3	—	52.3	—
BzA	113 000	—	90	93	-6.5	—	—	—
THFA	108 000	—	94	73	-12.2	—	52.4	56.7
HEA	—	—	—	65**	-55.3	16.5	55.9	160
PEGMEA-480	—	—	—	48**	-61.2	—	6.6	54

of BzA and THFA were calculated from the ^1H NMR results of the reaction mixtures of the photopolymerization products. It is noteworthy to mention that there was only one glass transition observed in the DSC thermogram of the photopolymerization product of BzA. Even though there was only one glass transition temperature was observed for BzA photopolymerization, the two slight shoulders at lower molecular weights in SEC curve might be the indication of homopolymers of PBzA and unreacted PCL. The PCL chains which were not functionalized with Ir2959 were not able to initiate the photopolymerization of the acrylates. Hence, the unreacted residues of homoPCL chains might have been recognized in DSC and SEC measurements.

4. Conclusions

The Ir2559 end-functionalized PCL based macrophotoinitiator was successfully synthesized via eROP. The macrophotoinitiator was further employed for the photopolymerization of the benzyl acrylate, tetrahydrofurfuryl acrylate, 2-hydroxyethyl acrylate and poly (ethylene glycol) methyl ether acrylate ~480 g/mole. The photopolymerization reactions of benzyl acrylate and tetrahydrofurfuryl acrylate were found to be the most effective synthesis regarding the dry polymer conversions calculated from ^1H NMR results. On the other hand, PEG based macromonomer and 2-hydroxyethyl acrylate photopolymerizations eventualized with lower conversion values compared to BzA and THFA due to the dramatic viscosity increase during photopolymerization which resulted in gelation. Among the photopolymerization reactions, the best result was achieved with BzA regarding the conversion, thermal behaviour and SEC results, since there was only one T_g observed indicating the 100% amorphous structure. However, according to the SEC results, the photopolymerization product of BzA also had impurities possibly including the unreacted PCL and/or homopolymer of BzA. The light-induced polymerization of different acrylates showed that the enzymatic synthesis route of PCL based macrophotoinitiator as an efficient method to synthesize macrophotoinitiators.

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