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Two-steps solvent-free synthesis of poly(hydroxybutyrate)-based photocurable resin with potential application in stereolithography

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A bio-based polymeric ink for stereolithography developed through a two-steps solvent-free process is herein proposed. Specifically, low molecular weight poly(hydroxybutyrate) (PHB)-diol oligomers were prepared via molten transesterification of bacterial PHB with 1,4-butanediol. Transesterification conditions such as diol concentration, catalyst amount and reaction time were studied for optimizing the final oligomers molecular weight and structural features. In the second step, the oligomeric hydroxyl terminals are converted into methacrylate moieties through a solvent-free end-capping reaction and diluted in propylene carbonate in order to obtain a photo-polymerizable ink with suitable viscosity. The ink was UV-cured, and the obtained material properties are investigated by FT-IR and DSC measurements. The proposed method provides valuable and environmental-friendly alternative to nowadays available synthetic routes, overcoming their typical disadvantages related to the used solvents and harsh conditions. Moreover, it opens up a sustainable route for converting polyesters in functionalized oligomeric derivatives, which can potentially find application in 3D printing of customized biomedical devices.

In the last decades a growing interest has been addressed to additive manufacturing thanks to the quick development of several 3D printing techniques.^[1] Among them, stereolithography apparatus (SLA)^[2] allows to fabricate solid objects with complex geometries,^[3] barely achievable with conventional techniques, through a selective layer-by-layer UV-irradiation of a photopolymerizable resin starting from a 3D computer-aided design (CAD) model of the desired object. As reviewed by Chartrain and co-workers,^[4] such high resolution is a crucial aspect in the manufacturing of custom-made scaffolds for tissue engineering, making SLA an innovative fabrication approach in medical fields as dentistry, maxillofacial surgery and orthopedic reconstruction. Typically, a suitable resin for SLA consists of methacrylate or acrylate terminated low molecular weight (MW) polymer or oligomers mixed with a suitable high boiling reactive^[5] or non-reactive^[6] diluent, which is required for dealing with highly viscous^[7], or even solid macromonomers.^[8] Indeed, both suitable viscosity (lower than 5 Pa·s)^[2] and presence of photo-sensitive terminals are key-factors to have a tailored and localized 2D solidification through a photo-induced cross-linking process.^[9] In the specific field of biomedical devices, the use of biocompatible and in some cases bioresorbable resins play an important role.^[8] A representative example is the work of Jansen and colleagues who proposed a poly(D,L-lactide)-based resin for the preparation of scaffolds through vat photopolymerization.^[10] In particular, they prepared several photopolymerizable resins, using three-armed terminated fumarate oligoesters as macromonomers diluted in reactive N-vinyl-2-pyrrolidone. The UV irradiation of such resins leads to effective photo-cured materials characterized by different hydrophilicity and mechanical properties, accordingly to the amount of reactive diluent added. Despite the acceptable biocompatibility shown by photo-crosslinkable resins, most of them are composed of synthetic oligomers and their industrial preparation still have several open issues that have to be addressed. For instance, the harsh reaction conditions and the use of toxic feedstocks, solvents and catalysts are typical disadvantages of these processes.^[11] A possible solution for overcoming these drawbacks is the

development of UV-curable formulations based on biodegradable polymers obtained by a sustainable process, which starts from biomasses or wide types of wastes^[12-15] according to the circular economy framework.^[16] In this view, poly(hydroxyalkanoate)s (PHAs) are the most attractive bacterial polymers,^[17] thanks to their exceptional properties in terms of biodegradability, biocompatibility and bioresorbability.^[18] According to the feedstock characteristics and used bacterial strain, different types of PHAs, either homopolymer or copolymer, can be obtained.^[19] Among them, the poly(3-hydroxybutyrate) (PHB) has been recently proposed in several studies as material for scaffolds to support tissue regeneration.^[20-22] Despite PHB is outstanding for biomedical application, its very high MW and the lack of photo-polymerizable groups^[23] makes this polyester unsuitable for the preparation of resins for SLA. For this reason, in the past decades, several approaches have been presented to chemically modify PHB chains according to specific need.^[24-26] Since the PHB thermal degradation starts few degrees above its melting point (approx. 180°C),^[27] all reported synthetic pathways propose a process in solution. This usually requires large amounts of toxic and expensive solvents for processing gram-scale quantity of PHB, making such procedures barely suitable for a sustainable and scalable productions. For this reason, in this study we propose a simple two-step and solvent-free process to prepare a PHB-based ink suitable for 3D vat photopolymerization. Bis-hydroxyl terminated PHB oligomers are obtained through a transesterification reaction in molten with 1,4-butanediol (schematic representation in **Figure 1a**) and successively end-capped with photo-curable methacrylate functionalities. This type of functionalization is the most widespread in commercial products thanks to the typical high UV-induced reactivity of the methacrylate groups, allowing to envisage the application of the herein presented material in commercial equipment for SLA. An ink with suitable viscosity is finally obtained diluting the as-prepared UV-curable oligomers in a non-reactive environmental-friendly solvent such as propylene carbonate.^[6] Indeed, this solvent does not take part to photopolymerization process and its post-printing complete removal is feasible,^[8] leading to a

completely PHB-based object. After an initial optimization of the process parameters, the PHB-based ink formulation is successfully photo-crosslinked by UV irradiation, demonstrating the suitability of the proposed material for SLA.

Due to the previously mentioned PHB thermal instability, its in-melt processability temperature range is particularly limited by both melting point and thermal degradation temperature.^[27, 28] Such well-known thermal degradation process results in an overall drop of polymer MW^[29] that becomes relevant and uncontrollable only for temperatures close to 200°C.^[30] Thus, 190°C is the typically reported temperature that allows to have a homogeneous stirring of the melted polymer and, at the same time, minimize the occurrence of degradation processes.^[31] Moreover, the addition of a suitable transesterification catalysts can speed up the in-melt process, therefore reducing the reaction time and further suppressing the thermal depolymerization. For instance, the great catalytic efficiency of a very small amount of titanium(IV) butoxide (Ti(OBu)₄) was already successfully shown in analogues processes.^[32]

Initial investigations for optimizing the transesterification conditions were performed on a poly(3-hydroxybutyrate) named as PHB(1) (polymer details in Table S1), varying the amount of 1,4-butanediol (1,4-BDO) (reaction in Figure 1a). Specifically, diol amount is expressed as equivalent with respect to polymer repeating units moles in the initial mass of PHB. Therefore, 1 molar equivalent of diol would theoretically lead to complete depolymerization of the whole polymeric mass.

Given amounts of PHB(1) and 1,4-BDO were loaded in a double-neck glass reactor and heated at 190°C, by a pre-heated oil bath, under mechanical stirring. After 5 minutes from the catalyst addition, the reaction was quenched by immersing the reactor in an ice bath to limit the possible thermal degradation (detailed procedure in SI). The so-obtained polymeric product was carefully washed with deionized water and analyzed by proton Nuclear Magnetic Resonance (¹H-NMR, experimental details in SI). ¹H-NMR investigations (Figure 1a and S1) do not show any PHB thermal degradation that is typically confirmed by the formation of crotonate moieties,

which are the main products of such phenomena.^[29] Specifically, the absence of crotonate vinylic proton signal at 5.8 ppm^[33] in the spectra in Figure 1a and S1, confirms that the selected temperature and short reaction time deeply suppress degradative phenomena, as desired.

As expected, a correlation between quantity of used diol and the MW of the prepared PHB-diols was evidenced by Gel Permeation Chromatography measurements (GPC, experimental details in SI) as shown in Figure 1b. Indeed, oligomers characterized by lower MWs can be also prepared by simply increasing the initial 1,4-BDO equivalents (**Figure 1b**). This is in good agreement with Differential Scanning Calorimetry (DSC) results, since the decrease of oligomers chains length (chromatograms in Figure 1b) is accompanied by a decrease of the PHB-diol melting temperature as displayed in **Figure 1c**. Besides, a more detailed insight on chains structure and reaction mechanisms were also achieved analyzing the content of hydroxyl groups and calculating the hydroxyl value (*OHV*), by the previously published ¹⁹F-NMR-based technique.^[34] Briefly, the terminal hydroxyl groups (*OH*) of the macromolecule were derivatized with a fluorinating agent (trifluoroacetic anhydride) and the consequent analysis, of the fluorinated product, by ¹⁹F-NMR leads to the differentiation and quantification of each type of *OH* (details in SI). Considering that the product of the transesterification reaction presents a primary (*OH^I*) and secondary hydroxyl group (*OH^{II}*) (Figure 1a), a molar *OH* ratio can be calculated by integral comparison (**Figure 1d**). By combining the calculated *OH* ratio values with ¹H-NMR spectra (Figure 1a and S1) is possible to understand how both PHB-diol MW and structure are affected by the 1,4-BDO amount initially added. In particular, as schematized in **Figure 1e**, using 0.2 equivalent of 1,4-BDO, in addition to the desired transesterification derivative (named PHB-diol A, green arrow in Figure 1e), a product with a comparable melting temperature of the PHB(1) is obtained (DSC curves in Figure 1c). This is also confirmed by GPC chromatogram (Figure 1b) in which two signals can be observed, indicating the presence of unreacted high MW PHB mixed with the desired product (peak at lower retention time). This is further supported by hydroxyl groups analysis, which shows an unbalanced *OH* ratio (*OH^I* <

OH^I) that is consistent with an incomplete transesterification (Figure 1e). On the other hand, a OH ratio close to one can be obtained using 0.4 equivalent of 1,4-BDO. In addition, both DSC and GPC analyses (Figure 1b and 1c) clearly suggest that a remarkable decrease of the MW takes place in these conditions. Therefore, PHB-diol chains bearing both primary and secondary hydroxyl terminals are present only in the product characterized by A structure. It is also noteworthy that, dealing with such structured oligomers, a spectroscopically-determined number average molecular weight (M_n) can be obtained.^[34] Such M_n , calculated from ^{19}F -NMR integral values, are in good agreement with the chromatographic results as summarized in Table S2 of Supporting Information (see sample PHB-diol(1)).

A further increase of the 1,4-BDO reagent amount (0.6 equivalent, Figure 1e) results in a slight decrease of both MW (Figure 1b) and melting point (Figure 1c). However, an unexpected and unbalanced OH ratio was obtained. Even in this case, a significant amount of secondary hydroxyl groups was observed, but GPC and DCS results clearly exclude the persistence of unreacted PHB. The reason that leads to an unbalanced OH ratio lies in the development of a side-reaction. Performing PHB transesterification with a high amount of 1,4-BDO results in a rapid formation of PHB-diol A. Its concentration quickly reaches a critical value at which the PHB-diol A starts competing with 1,4-BDO for the transesterification of the starting PHB with the formation of PHB-diol with structure B (named as PHB-diol B, magenta arrow in Figure 1e). It is clear that the formation of PHB-diol B takes place through the reaction with the primary hydroxyl groups of PHB-diol A, which are more reactive than secondary ones. For this reason, a decrease of the primary hydroxyl groups content is observed despite the MW decrement. Although a low MW was achieved, the reaction performed in such conditions is of poor interest, since a mixture of products hardly separable is obtained. Moreover, the advantage derived from achieving a low MW is completely lost by taking into account the extremely low yield detected (Figure 1e).

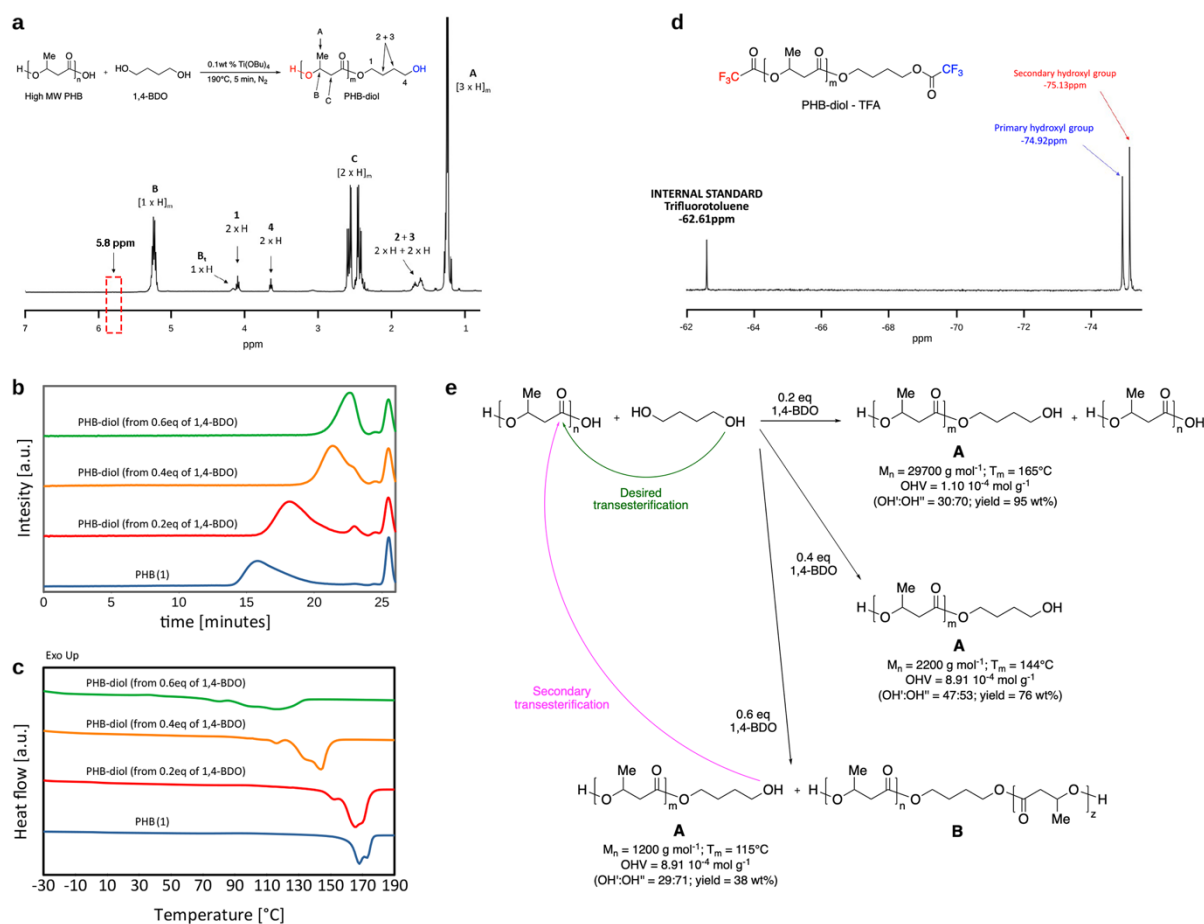


Figure 1. (a) ¹H-NMR spectrum of PHB-diol A (in blue primary hydroxyl group and in red secondary hydroxyl group) and related signal assignments. Dashed red rectangle highlights the absence of the signal at 5.8 ppm due to the most common thermal degradation product; (b) GPC chromatograms and (c) DSC thermograms of starting PHB and transesterificated products obtained with different amount of 1,4-butanediol; (d) ¹⁹F-NMR spectrum of trifluoroacetylated PHB-diol with A-like structure used for OHV determination; (e) reaction scheme as a function of different amounts of 1,4-BDO. Desired (green arrow) and secondary (magenta arrow) transesterification reactions.

Once established the most advantageous reaction conditions for obtaining the desired oligomers with PHB-diol A-like structure (see also ¹³C and 2D-NMR spectra reported in Figure S2 and S3 respectively), a further tuning of the oligomers MW was attempted. Since increasing the 1,4-BDO equivalents mainly results in formation of undesired products mixture and the reaction

temperature cannot be modified considering the previously mentioned reasons, the only parameters that can be varied are the reaction time and catalyst amount. Even in this case, an increase of both parameters only leads to an OH ratio variation from the desired value of one, with OH^I remarkably lower than OH^{II} , as shown in Figure S4. These findings can be reasonably explained considering that either increasing the reaction time or using a higher amount of catalyst result in a similar overproduction of PHB-diol A. As previously explained, upon a critical concentration of PHB-diol A is reached, the competing side-reaction occurs, thus resulting in PHB-diol B formation (characterized by $OH^I \ll OH^{II}$).

Although both parameters lately studied do not affect as desired the PHB-diol A MW, a different approach has to be followed. Assuming that the process takes place with similar mechanisms, a correlation between the MWs of the starting PHB and yielded PHB-diol can be expected. Since the enzymatic process to produce PHB allowed to obtain polymers with different MWs,^[35] transesterification was performed applying the previously optimized conditions that ensure the desired OH ratio, but using starting PHBs with different MWs. In particular, two polyesters, named PHB(2) and PHB(3), characterized by a lower MW (polymer details in Table S1), were transesterificated (reaction scheme in **Figure 2a**) following the procedure used for the previous PHB(1).

For both PHB(2) and PHB(3), PHB-diol with the desired structure (PHB-diol A) was obtained, as confirmed by ^{19}F -NMR spectroscopic investigations summarized in Figure 2a (^{19}F -NMR spectra in Figure S5). As hypothesized, PHB-diols A characterized by a decreasing chain length were actually obtained starting from PHBs with lower MWs as also observed by GPC measurements reported in **Figure 2b**. These results are then further supported by DSC measurements (**Figure 2c**), which show that decreasing the MW of the starting PHB also the melting temperature of the associated PHB-diol decreases accordingly. Furthermore, a correlation between the MW of the starting PHB and the MW of the obtained PHB-diols with the optimized esterification process can be observed, as depicted in **Figure 2d**.

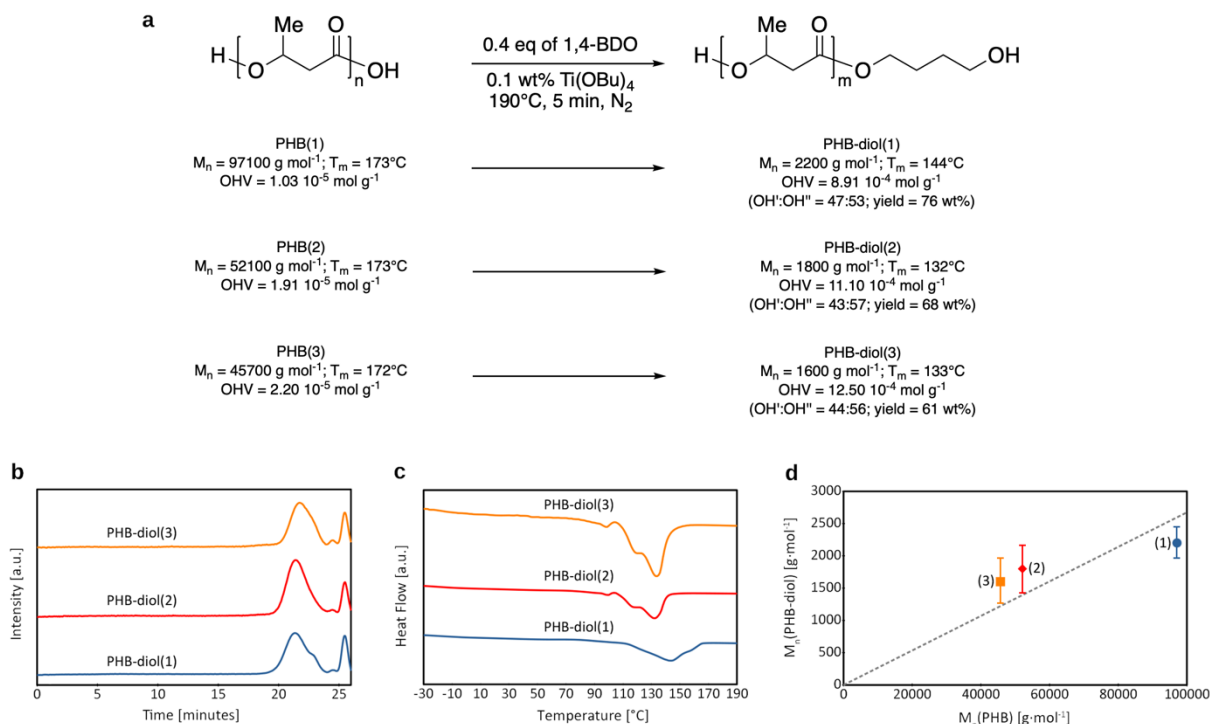


Figure 2. (a) Schematic representation and characterization results of starting PHBs and synthesized PHB-diols; (b) GPC chromatograms and (c) DSC thermograms of the prepared PHB-diols with A-like structure; (d) correlation between number average molecular weights (M_n determined by ^{19}F -NMR-based method described in SI) of starting PHBs and synthesized PHB-diols.

According to the technical SLA requirements discussed above, the terminals functionalization was carried out only on the PHB-diol characterized by A structure and the lowest MW (PHB-diol(3)). In details, PHB-diol hydroxyl terminal groups were converted into methacrylate functionalities upon using 2-isocyanatoethyl methacrylate following the reaction scheme in **Figure 3a** (procedure details in SI). Indeed, such a bifunctional reactant is widely used for converting polyol terminals into photocurable moieties.^[36] Dealing with low MW PHB-diol characterized by very low melting point (133°C , Figure 2a) permits to obtain a homogeneous molten at temperature considerably below the thermal degradation onset. Therefore, an uncatalyzed and solvent-free end-capping process was performed at 150°C and the reaction was

monitored by FT-IR spectroscopy (experimental details in SI) and reported in **Figure 3b**. Specifically, the decrease of the peak intensity associated to the isocyanate group (2268 cm^{-1})^[37] is typically used as evidence that the end-capping reaction is taking place. After only 10 minutes the isocyanate peak completely disappeared (Figure 3b) and the process was considered complete. This was also confirmed by $^1\text{H-NMR}$ spectrum of the product PHB-diol-ma presented in **Figure 3c**, which clearly shows the typical signals of amide protons at approx. 5.1 ppm and vinylic protons peaks at 5.5 and 6.2 ppm due to the newly introduced terminal groups.^[38]

The methacrylated oligomers were then diluted at 90°C in propylene carbonate ($1.54\text{ mg}\cdot\mu\text{L}^{-1}$) to obtain a photocurable biobased polymeric ink with the desired viscosity. A photo-initiator (Irgacure[®] 819) was added (2 wt.% with respect to the oligomer) and the formulation was irradiated under UV light for 10 minutes (details in SI) in order to induce the photopolymerization as schematically reported in **Figure 3d**. The obtained photocured resin (see samples photo in Figure S6) was analyzed both by FT-IR and DSC. Specifically, as shown in **Figure 3e**, the FT-IR peak corresponding to methacrylic terminal groups (carbon double bond at 1637 cm^{-1}) completely disappears after the UV irradiation.^[39] On the contrary, the UV irradiation experiment in absence of photo-initiator, results in a not cross-linked material as shown by the diverse response to heating of the two materials in Movie S1. DSC thermograms presented in **Figure 3f** are in good agreement with the latest presented result (Figure 3e), revealing that after the UV curing, the peak associated to the melting process of the uncured oligomer disappears. It is also noteworthy that a remarkable increase of the glass transition temperature (T_g) from -11°C to 7°C , was observed (Figure 3f).^[39]

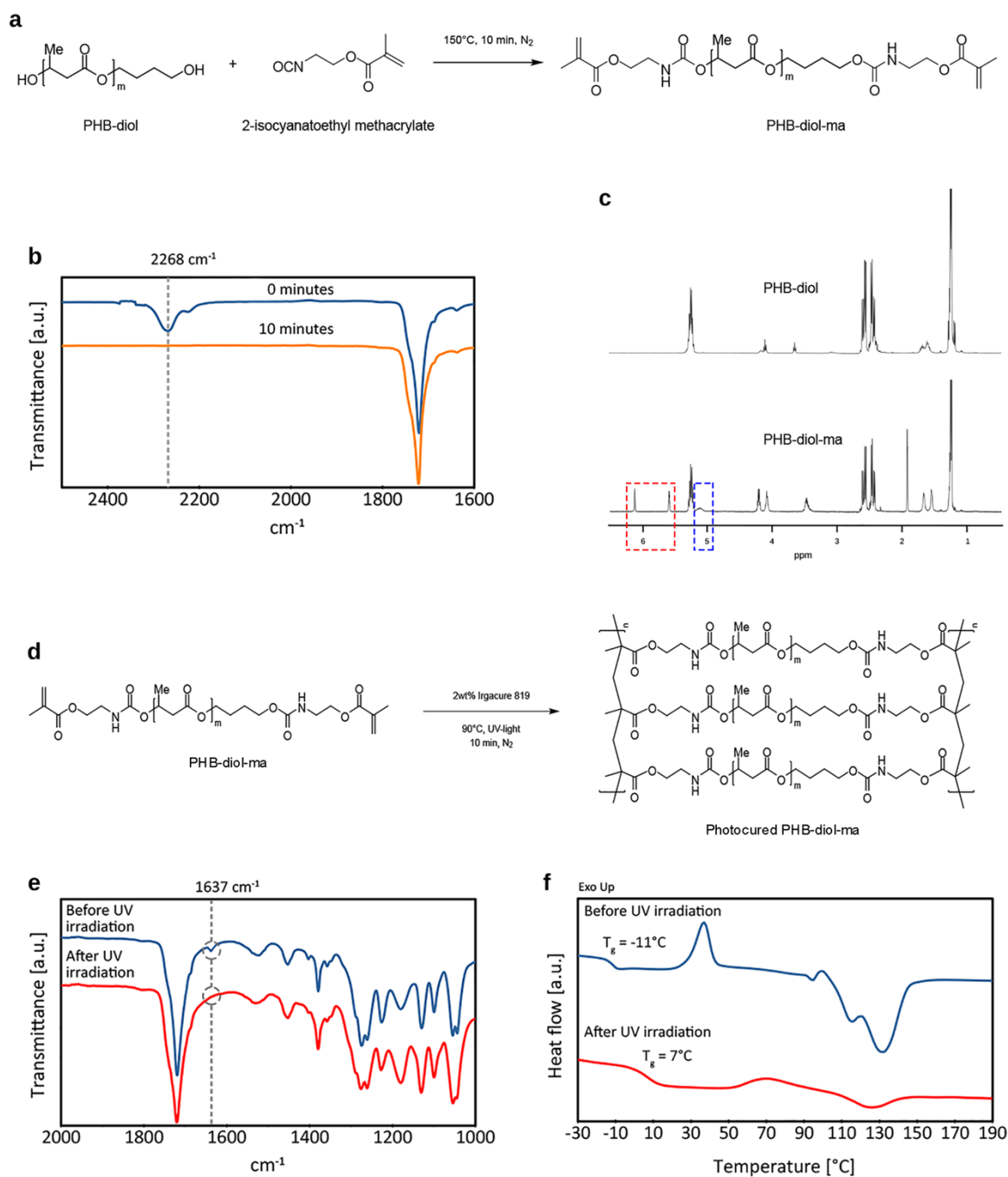


Figure 3. (a) Scheme of the end-capping reaction performed on the selected PHB-diol with A-like structure; (b) FT-IR spectra at the beginning and after 10 min of the end-capping reaction; (c) $^1\text{H-NMR}$ spectra of the starting PHB-diol and end-capped product (PHB-diol-ma), dashed red rectangle highlights the signals due to vinylic protons and dashed blue rectangle highlights the signal due to amide protons; (d) schematic representation of UV-induced crosslinking reaction; (e) FT-IR spectra and (f) DSC thermograms recorded before and after the UV irradiation of PHB-diol-ma.

In conclusion, we have shown a very fast and solvent-free two-step process to prepare UV-curable PHB-based oligomers. In particular, the herein proposed process is based on an in molten transesterification of high molecular weight bio-based PHB with 1,4-butanediol. The reaction was initially optimized by varying the reaction conditions such as diol amount, reaction time and catalyst amount. This optimization allowed to obtain PHB-diol with a molecular weight and viscosity as low as required for the application in stereolithography. Consecutively, hydroxyl terminals of the PHB-diol were end-capped by an in-melt reaction in order to obtain photocurable bis-methacrylic terminated PHB-diol oligomers.

Preliminary tests reveal the actual possibility to implement the prepared photocurable resin, properly diluted in propylene carbonate, as an ink for stereolithographic 3D printing. Specifically, UV irradiation carried out in presence of a commercial photo-initiator showed that the synthesized PHB-based resin can be photo-crosslinked. The herein proposed process can have widespread applicability, providing a simple and sustainable synthetic tool that can be also used on any type of polyester or for preparation of several differently terminated oligomers by varying the hydroxyl end-group functionalization. Moreover, the synthesized PHB-diol oligomers can be also envisioned as bio-based building block for the synthesis of block copolymers or for preparing customized biomedical devices by vat-polymerization.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Two-steps solvent-free synthesis of poly(hydroxybutyrate)-based photocurable resin with potential application in stereolithography

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Text for the Table of Contents

This study presents a facile solvent-free method to produce UV-curable ink based on high molecular weight poly(hydroxybutyrate) that can find potential application in 3D printing by vat-polymerization technology.

Graphic for Table of Contents

