Journal of the Serbian Chemical Society
JSCS-info@shd.org.rs • www.shd.org.rs/JSCS
J. Serb. Chem. Soc. *85* (3) 353–367 (2020)
JSCS–5306
UDC 544.7+577.11:542.913.000.57:539.24
Original scientific paper

Porous amphiphilic biogel from a facile chemo-biosynthetic route

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(Received 25 June, revised 5 September, accepted 16 September 2019)

Abstract: Grafting of medium-chain-length poly-3-hydroxyalkanoates (mcl--PHA) with glycerol 1,3-diglycerolate diacrylate (GDD) in acetone was performed using benzoyl peroxide as the initiator. A detailed mechanism scheme provides significant improvement to previous literature. Radical-mediated grafting generated α–β carbon inter-linking of mcl-PHA and GDD, resulting in a macromolecular structure with gel properties. The thermal properties of the copolymer for different graft yields were investigated as a function of initiator concentration, GDD monomer concentration, incubation period and temperature. The water absorption and porosity of the gel were significantly improved relative to neat mcl-PHA.

Keywords: biogel; chemo-biosynthetic; biopolymer; radical grafting.

INTRODUCTION

Polyhydroxyalkanoates (PHA) are well-known biopolymers with attractive biocompatibility. They are accumulated within certain bacterial species in the form of granules when the microorganisms experience imbalanced growth conditions, *viz*., simultaneous excess carbon source and limitation of nutrients such as nitrogen and phosphorus.[1–4] Two categories of PHA could be differentiated, *i.e.*, short-chain-length polyhydroxyalkanoates or scl-PHA, comprising of monomers with four- to five-carbon atom length, and medium-chain-length polyhydroxyalkanoates or mcl-PHA, made up of 6- to 14-carbon atom length monomers.[2] Modification and functionalization of PHA, intended for tuning the features, are

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https://doi.org/10.2298/JSC190625101S

important for certain applications. Functionalization of PHA on the side chain, for example, can alter the polymer interaction behaviour by introducing elements of hydrophilicity.[5]

One of the functionalization techniques is grafting. Graft copolymerization of PHA forms a modified segmented copolymer with interesting properties, particularly in terms of wettability and thermo-mechanical strength. The grafting processes can be realised in several ways, including chemical, radiation, and plasma discharge methods.[6–8] The current grafting methods for many polymers are equally applicable in the case of PHA functionalization. For example, benzoyl peroxide-initiated graft polymerization of 2-hydroxyethylmethacrylate (HEMA) onto poly-(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBHV) enhances the crystallinity and wettability of the biopolymer.[9]

Grafting applies radical intermediates during the reaction that mediate the polymerization of a vinyl monomer as grafted branches on the main polymer chain through "grafting onto", "grafting through" and "grafting from" techniques.[7,10] Free radical grafting *via* radical initiators is widely used for the modification of polymers. Benzoyl peroxide is one of the initiators extensively used to functionalize bacterial polyesters.[7,9,11–15] It is a simple and robust method. Benzoyl peroxide has been reported to be more efficient compared to other common thermal initiators, such as azo-*bis*-isobutyronitrile (AIBN)[16] and other peroxyl initiators.[17] When the concentration of the propagating radical balances the rate of radical termination, polymers with high number average molecular weight and low dispersity can be obtained. The catalyst determines the equilibrium constant between the active and dormant species, which in turn determine the polymerization rate.[18,19]

In this study, medium-chain-length poly-3-hydroxyalkanoates (mcl-PHA), obtained from bacterial fermentation, was graft copolymerized with glycerol 1,3--diglycerolate diacrylate (GDD) by free radical polymerization. The grafted product, PHA-*g*-GDD, was prepared through a thermal incubation process with all reaction components mixed together in a selected organic solvent. The effects of different initiator concentrations, in this case benzoyl peroxide (BPO), were investigated alongside incubation temperature and time, and initial GDD concentration. The PHA-*g*-GDD copolymer was characterized and a mechanism of the grafting reaction was proposed.

EXPERIMENTAL

Materials

Lauric acid ($C_{12}H_{24}O_2$, M_w 200.23, CAS 143-07-7) for synthesis was purchased from Merck as a sole carbon source in fermentation medium to produce medium-chain-length poly--3-hydroxyalkanoates (mcl-PHA) by *Pseudomonas putida* Bet001.[20,21] The mcl-PHA was obtained by solvent extraction and purified through repeated methanol precipitation and washing steps.[21]

Benzoyl peroxide (BPO) ($C_4H_{10}O_4$, M_w 242.23, CAS 94-36-0), (with 25 % H_2O, used as received) for synthesis was purchased from Merck Millipore (Darmstadt, Germany) and applied as the sole radical initiator of the grafting reaction. Glycerol 1,3-diglycerolate diacrylate (GDD, $C_{15}H_{24}O_9$, M_w 348.35, CAS 60453-84-1) was purchased from Sigma–Aldrich (Saint Louis, CA, USA) and used as received.

Monomer composition of mcl-PHA

The monomer content of the mcl-PHA was determined by gas chromatography. A sufficient amount of the sample was subjected to methanolysis. Two milliliters of dichloromethane (DCM) and 2 ml mixture of methanol and sulphuric acid (1:1 volume ratio) were added to the sample. The mixture was incubated at 100 °C for 2 h and 20 min in a heating block. Distilled water was added, and the mixture vortexed for about one minute before being left standing overnight or at least four hours for phase separation. The organic bottom layer containing the methylated products was transferred into a vial and mixed with sodium sulphate (Na_2SO_4) to remove excess water. The organic layer was auto-injected into a fused silica capillary column (30 m length×0.32 mm internal diameter×0.25 μm film, Supelco SPBTM-1, Bellefonte, PA, USA) fitted within a gas chromatography machine (Trace GC Ultra, Thermo Scientific, Rodano, Milan, Italy) with flame ionization detector. During the process, helium was used as a carrier gas at the rate of 48.3 ml min^{-1} and 0.41 bar pressure.[21] Four types of monomers, *i.e.*, 3-hydroxyhexanoate (3HHx), 3-hydroxyoctanoate (3HO), 3-hydroxydecanoate (3HD) and 3-hydroxydodecanoate (3HDD), at 4, 37, 38 and 21 mol %, respectively, hence, alternatively known as P(3HO-*co*-3HHx-*co*-3HD-*co*-3HDD) were identified and quantified in the mcl-PHA samples.

*Preparation of PHA-*g*-GDD copolymers*

Copolymers were prepared by incubation of 50 g dm^{-3} mcl-PHA and 0.14 mol dm^{-3} GDD in acetone at varying concentrations of BPO. Oxygen was purged from the solution with nitrogen gas for ten minutes and the vial was subsequently capped to introduce airtight conditions. The mixture was incubated within a heating block at 70 and 90 °C. The mixture was left to cool to ambient temperature (25±1 °C) post-incubation before adding methanol to allow precipitation of the gel product, and separate the non-grafted GDD monomer and GDD homo--oligomers in the soluble fraction at the same time. Successful grafting was indicated by the increase in the mass of precipitated product over the initial mass of mcl-PHA used (Eq. (1)),[9,11,13,14] calculated as follows:

$$\text{Graft yield } = 100\frac{W_f - W_i}{W_i} \quad (1)$$

where W_f is the final mass of the grafted PHA after reaction, and W_i is the initial mass of PHA before reaction.

*Characterisation of the PHA-*g*-GDD copolymers*

Fourier transform infrared-attenuated total reflectance (FTIR-ATR) spectroscopy. FTIR--ATR was used to record the spectra on Perkin–Elmer Spectrum 400 FT-IR and FT-NIR spectrometer (Perkin–Elmer Inc., Wellesley, MA, USA), equipped with Pike GladiATR hovering monolithic diamond ATR accessory (Pike Technologies Inc., USA) at room temperature. The samples were placed on the monolithic diamond ATR probe and fastened against the diamond crystal plate using a force adaptor. The spectra were recorded between 4000 and 450 cm^{-1} using cuts of 0.5 cm×0.5 cm films.

Simultaneous thermal analysis (STA) and differential scanning calorimetry (DSC). The applied thermal analysis was destructive simultaneous thermal analysis (STA) of ASTM--E2550-11 thermal stability method. The machine used was a Perkin–Elmer STA 6000 (Perkin–Elmer Inc., Wellesley, MA, USA) running on tandem differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The sample was prepared in the form of a film. The analysis was programmed to initialize from 30 °C until 800 °C at a rate of 10 °C min^{-1} under a nitrogen gas stream of 10 ml min^{-1}.

Proton nuclear magnetic resonance (^{1}H-NMR). A sufficient quantity of grafted sample was washed with deuterated chloroform ($CDCl_3$). The solvent was filtered to separate the undissolved component using a borosilicate glass syringe equipped with 0.22 μm polytetrafluoroethylene (PTFE) disposable filter (11807–25; Sartorius Stedim, Göttingen, Germany). The filtrate fraction with the dissolved component was subjected to NMR analysis. The spectrum was acquired using a JEOL JNM-GSX 270 FT-NMR spectrometer (JOEL, Tokyo, Japan) at 400 MHz against tetramethylsilane (TMS) as internal reference. For mcl-PHA, the sample was simply dissolved in $CDCl_3$ and filtered.

Carbon solid-state nuclear magnetic resonance (^{13}C-NMR). A sufficient quantity of undissolved grafted sample was washed with chloroform to remove the residue, dried and pulverized for solid-state analysis. The spectrum was acquired using a JEOL JNM-ECX500 NMR spectrometer (JOEL, Tokyo, Japan) at 500 MHz.

Water absorption and porosity studies. The samples were cut into small cubes with measured height, length and breadth, and then immersed in deionised water overnight. For the porosity study, the cubes were immersed in 95 % ethanol solution for an hour before being left overnight immersed in deionised water.[11,20,22] Gravimetric measurement was used to record the weight change for each of the samples in order to determine the degree of swelling from water absorption (Eq. (2)). To calculate the porosity of the samples (Eq. (3)), the solvent replacement method was used. The calculations involved are as follows:

$$\text{Degree of swelling } = 100\frac{W_\text{w} - W_\text{d}}{W_\text{d}} \tag{2}$$

$$\text{Porosity } = 100\frac{W_\text{w} - W_\text{d}}{\rho V} \tag{3}$$

where W_d is the weight of the sample before immersing (dry), W_w is the weight of the sample after immersing (wet), V is the volume of the sample and ρ is the density of the solvent used, in this case, denatured 95 % ethanol, which is 790 kg m^{-3}.

RESULTS AND DISCUSSION

Characterisation of PHA-g-GDD copolymers

FTIR-ATR Spectroscopy. Ester vibrations were detected for both the individual mcl-PHA and GDD samples. The carbonyl absorptions were observed at 1726 and 1718 cm^{-1}, respectively, while the corresponding C=O bond signals appeared at 1162 and 1189 cm^{-1}. In addition, the vibration signalling wavelength for symmetric $–CH_2–$ of the samples were observed at 2858–2855 cm^{-1}, and 2926–2925 cm^{-1} for asymmetric $–CH_3$. No asymmetric $–CH_3$ signalling was detected in the pure GDD samples (Fig. 1).

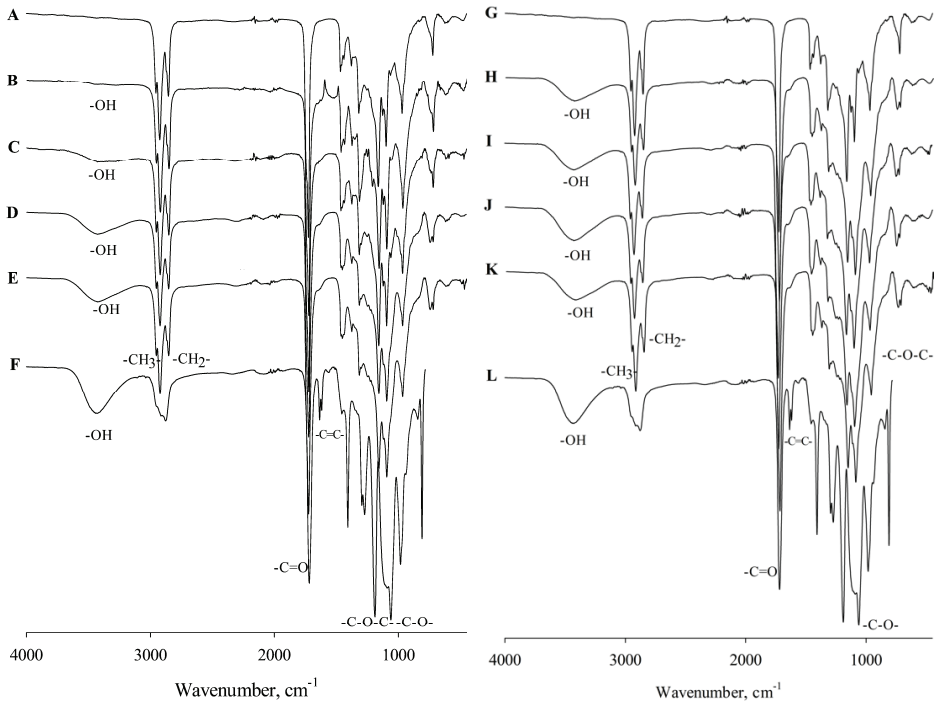

Fig. 1. FTIR spectra of grafted materials obtained from reaction mixture at 70 (left) and 90 °C (right). A & G – neat mcl-PHA; B & H – PHA-*g*-GDD with 3.0×10^{-6} mol dm^{-3} BPO; C & I – PHA-*g*-GDD with 5.0×10^{-6} mol dm^{-3} BPO; D & J – PHA-*g*-GDD with 10^{-5} mol dm^{-3} BPO; E & K – PHA-*g*-GDD with 1.5×10^{-5} mol dm^{-3} BPO; F & L – GDD monomer.

In the grafted copolymer, a signal from the presence of a hydroxyl group introduced by the GDD monomers was evident as the copolymers exhibited new broad signals of –OH group shifted to 3432–3431 cm^{-1}. In addition, a strong shift at about 1151 cm^{-1} signifying ester bond signal, available in both mcl-PHA and GDD monomer, was present in abundance for the grafted product samples compared to the neat mcl-PHA samples. Ether bond presents exclusively in pure GDD samples was also evidenced with a strong signal at about 1091 cm^{-1}. It can be concluded that grafting of mcl-PHA with GDD was successful.

^{1}H-NMR. A representative ^{1}H-NMR spectrum for the grafted products is shown in Fig. 2. The spectrum shows all typical signals for neat PHA. The signal indicating a successful grafting process was found between 1.8 and 1.9 ppm. The signal was assigned to overlapping signals of methine and methylene hydrogen atoms (CH) and (CH_2) on the backbone of polyacrylate, labelled as *h* and *i*. The peak also signifies the hydrogen atoms at the grafting position of PHA, reflecting α and β positions to the carbonyl of the terminal fatty acid of PHA, labelled as *f* and *g* in Fig. 2, respectively. Additionally, another new signal of interest was evi-

dent between 3.7 and 3.8 ppm. This is associated with hydrogens from methylene and methine groups of the triglycerol core of GDD, labelled as *j* and *k*.

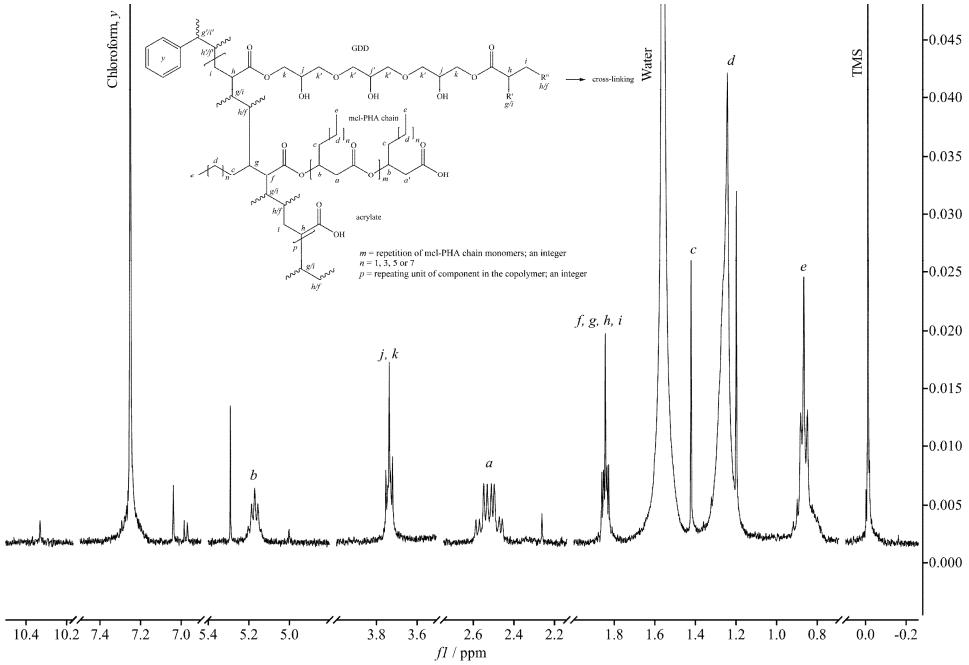

Fig. 2. ^{1}H-NMR spectrum for PHA-*g*-GDD copolymer.

A broad signal, overlapping with the chloroform peak at 7.3 ppm (labelled as *z*), most likely indicates the presence of a benzene ring, originating from the phenyl radical, which is generated by the initiator BPO and attaches to the very first monomer during the polymerization process.

Extensive cross-linking in the copolymer, due to the divalent structure of GDD, leads to a gel-like material, which is insoluble in the solvent applied for recovery and purification in this study *i.e.* methanol. However, some of the grafted mcl-PHA copolymer could be dissolved in hydrophobic solvent, such as chloroform, and subsequently investigated for NMR studies. This separated component represents a fraction of the grafted copolymer with a relatively lower molecular weight from less extensive cross-linking, thereby providing an organic solvent–soluble material for structural authentication.

^{13}C-NMR. Solid-state ^{13}C-NMR authentication was also performed since the major fraction of the grafting product exhibited gel-like morphology, which is virtually insoluble in any organic solvent. However, the signal resolution was rather poor with several combined peaks especially related to the aliphatic components of both mcl-PHA and GDD. Nevertheless, an additional signal of minute

amount of carbonyl ketone groups was observed at around 210 ppm on the spectrum (*see* Supplementary material to this paper, Fig. S-5), indicating oxidation of secondary alcohol hydroxyl group within GDD, occurring as a side reaction due to the cascading radical reaction environment. Elaboration on the spectrum signals is made available in the Supplementary material.

Mechanism of mcl-PHA grafting with GDD

From structural studies, a detailed grafting reaction mechanism was proposed, which presented a significant improvement to previous literature.[11,13] While the proposed reaction scheme still follows a typical three-step radical polymerization, which includes initiation, propagation and termination phases, it introduces a thorough revision of participating reactive components in the reaction.

Firstly, the grafting process involving mcl-PHA requires an unsaturated terminal monomer unit, referring to a double bond between α- and β-carbon atoms, most likely originating from thermal degradation of mcl-PHA. There are several possibilities to introduce the double bond *via* elimination processes, as corroborated by other similar studies[23,24] and shown in Fig. 3.

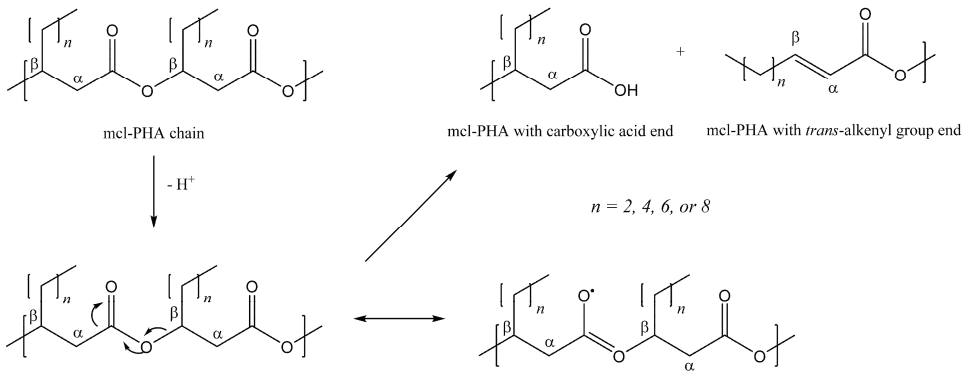

Fig. 3. Possible routes of mcl-PHA degradation that contribute to alkenyl end groups able to participate in grafting reaction *via* proton abstraction.

Grafting of mcl-PHA with GDD to obtain PHA-*g*-GDD copolymer starts with the dissociation of BPO into a benzene radical. It is proposed that the radicals start the initiation step by attacking the β-carbon of the double bond to introduce a radical on the α-carbon.

The reaction is possible at either end of GDD molecules. In the process, the benzene ring is covalently bonded to the monomer to become part of the terminal monomer unit of the copolymer. Although initiation could also occur at the unsaturated terminal fatty acid of mcl-PHA, the probability is small owing to low concentration density of mcl-PHA molecules compared to the acrylate monomer.

Nevertheless, grafting reaction with mcl-PHA does not hinder the propagation of the vinyl polymerization (Fig. 4).

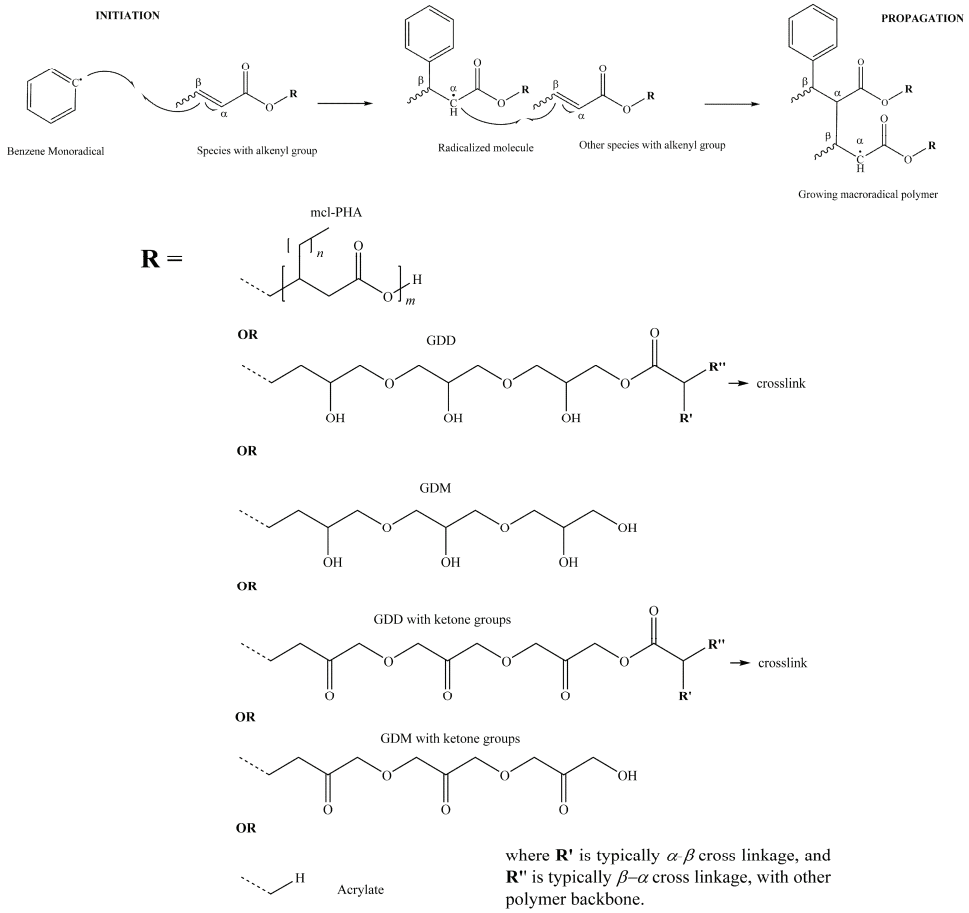

Fig. 4. Initiation and propagation mechanism scheme involving species with alkenyl reactive group **R** groups that are available within the biogel.

The chain process of the polymerization is continuously repeated to produce a growing macromolecule consisting of a mixture of GDD monomers, acrylate monomers and mcl-PHA with random connection pattern. The cascade of growing copolymer consistently assembles radicalized α-carbon to be bound to β-carbon of monomers, thereby transferring the radical to the α-carbon of the newly attached monomer.[25] concurrently, the same process is presumably occurring at the other end of GDD monomers as well. The bivalent nature of GDD, thereby, is giving rise to a cross-linked copolymer. This cross-linking affects the properties of the resulting gel, accounting for almost zero solubility in aqueous solution and

a rigid shape. Further complexity of the macromolecule arose from hydroxyl groups in GDD monomer being exposed to dehydration to form carbonyl groups, albeit in minute amount due to the radical transfer propagation process.

Termination step occurs when two different growing macroradical copolymers react with each other, thereby losing their radical character that is associated with unpaired electrons. Termination by disproportionation is more likely than combination of radicals, as shown in Fig. 5.

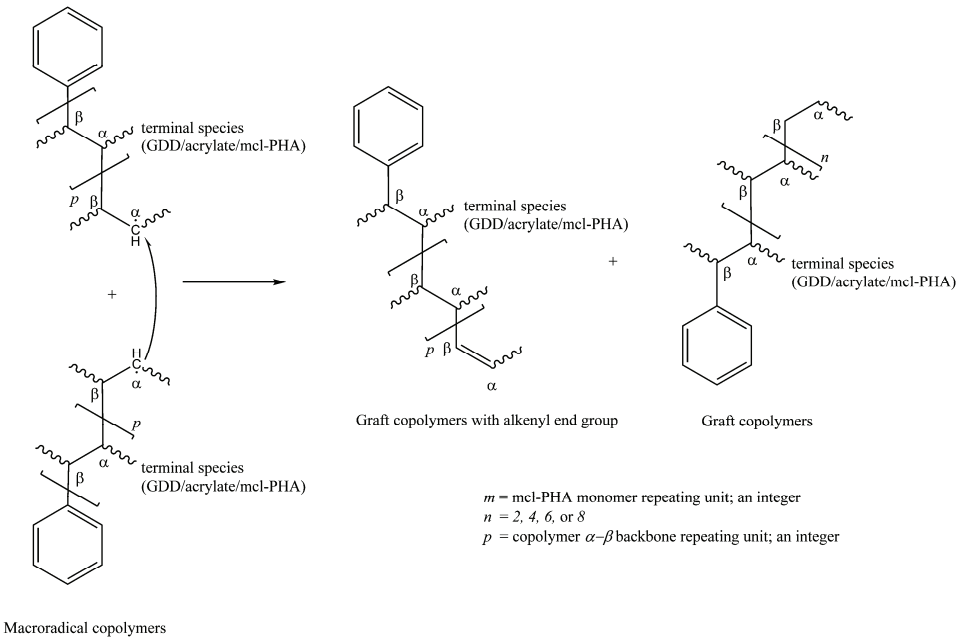

Fig. 5. Termination step.

During the grafting process, GDD monomers may also react with each other to form a densely cross-linked homopolymer gel following the same mechanism that applies for the grafting process. Owing to the divalent character of GDD and the nature of the vinyl polymerization, a high molecular weight is achieved. The crosslinking converts most of the monomers into a highly crosslinked gel, which consists of only a few interwoven polymer networks. The separation of these is practically impossible. However, GDD-polymers with low crosslinking, owing to incorporation of substantial contents of mono-valent acrylates, may be separated from grafted mcl-PHA based on their solubility in methanol, while highly crosslinked gels and polymers containing higher portions of mcl-PHA are expected to form a precipitate.

In general, the grafted material may comprise of mcl-PHA with varying degrees of grafting component based on different reaction parameters, depending

on the initiator concentration, temperature and the concentration of GDD monomer itself.

*Thermal properties of PHA-*g*-GDD copolymer*

Thermal properties of PHA-*g*-GDD samples were determined using TGA and DSC analyses. The grafted samples showed changes in terms of their thermal degradation behaviour, Fig. 6.

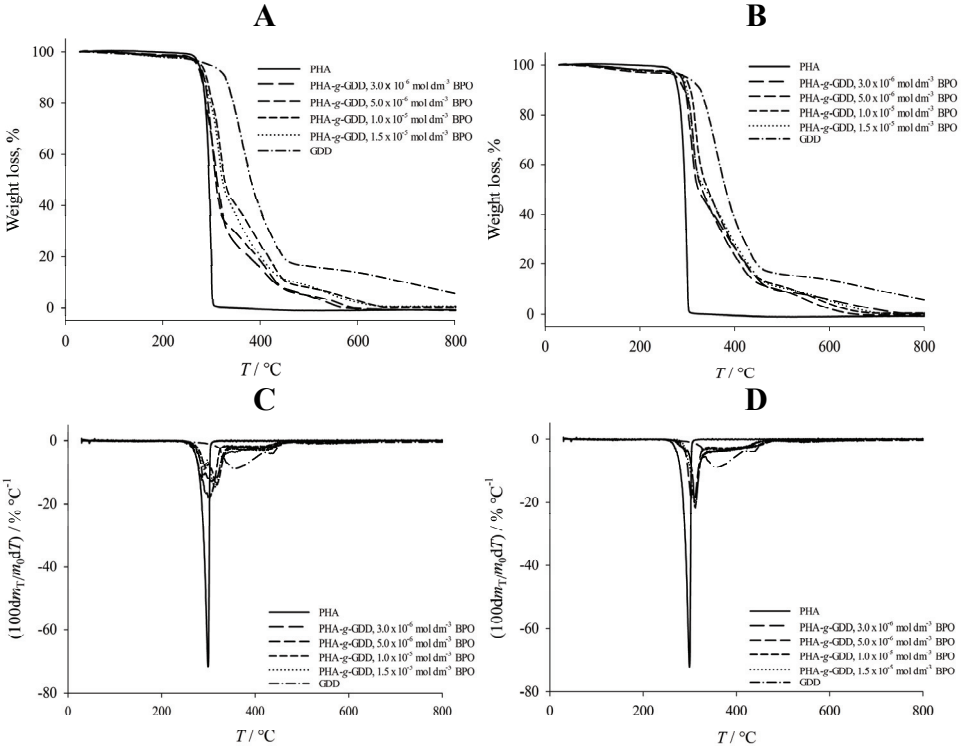

Fig. 6. TGA analysis for PHA, PHA-*g*-GDD and GDD samples for different initiator concentrations, A & B weight percentage curves, and C & D derivative weight percentage curves. **A** and **C** represent samples incubated at 70 °C, while B and D represent samples incubated at 90 °C.

Neat PHA samples degraded earlier at around 260 °C compared to the other samples (Fig. 6A–D). The GDD sample was the most stable among all, with higher degradation temperature at around 300 °C. The thermal curves of PHA-*g*--GDD samples from 90 °C incubation temperature were more similar to the GDD curve (Fig. 6), indicating that these samples were more stable compared to those incubated at 70 °C (Fig. 6). The shapes of the curves were closely related due to molecular composition similarity. From DSC analysis, the T_m of the grafted

samples was in the range of 53.0 – 55.5 °C, which was slightly higher compared to neat mcl-PHA at 52.7 °C, due to the presence of GDD monomer (Table I).

TABLE I. Thermal properties of PHA and PHA-*g*-GDD for different initiator concentrations and incubation temperature, initial rate of reaction, graft yield percentages after two hours incubation, water uptake swelling and porosity percentages

t_{incub} / °C	Sample	Initial rate of reaction, % min^{-1a}	Thermal analysis		Graft yield, %	Water uptake (swelling), %	Porosity, %
			T_m / °C	T_d / °C			
	mcl-PHA	–	52.7	294.4	–	~ 0	~ 0
70	BPO, mol dm^{-3}			PHA-*g*-GDD			
	3.0×10^{-6}	1.0	55.5	297.9	72 ± 5	2.4 ± 0.2	7 ± 1
	5.0×10^{-6}	1.8	53.0	305.3	73 ± 11	4.6 ± 0.2	9 ± 1
	10^{-5}	2.6	53.7	298.1	77 ± 2	8.2 ± 1.1	10 ± 1
	1.5×10^{-5}	3.0	54.5	292.8	90 ± 9	6.6 ± 0.1	11 ± 1
90	BPO, mol dm^{-3}			PHA-*g*-GDD			
	3.0×10^{-6}	4.7	53.5	295.6	73 ± 4	6.5 ± 0.9	12 ± 1
	5.0×10^{-6}	4.8	54.7	295.0	86 ± 6	7.2 ± 1.0	10 ± 2
	10^{-5}	4.6	53.8	291.6	88 ± 3	7.3 ± 0.4	10 ± 1
	1.5×10^{-5}	4.4	53.9	298.7	85 ± 3	9.7 ± 0.5	8 ± 1

[a]Maximum standard deviation ±10 %

Generally, the thermograms were only slightly different from each other, since the grafting parameters, *viz.*, mcl-PHA concentration and GDD concentration were the same throughout the sample preparation reaction. On the other hand, the increase in initiator concentration contributed to the increase in graft yield (Table I), hence resulting in more thermostable functionalized product with higher GDD concentration that were successfully grafted to the mcl-PHA backbone. The findings also agreed with the results from TGA analysis (Fig. 6).

In terms of water absorption ability, the grafted samples exhibited increased in swelling percentage with higher initiator concentration used, although grafted samples from lower incubation temperature showed slightly lower water absorption. Neat PHA material showed negligible water absorption due to its strong hydrophobicity. For samples obtained from grafting reaction at 70 °C and different initiator concentrations, approximately similar porosity percentages were determined except at the lowest concentration of BPO used (Table I) attributed to lower degree of grafting. For grafted samples from 90 °C incubation, the increase in starting radical initiator concentration resulted in lower porosity percentages (Table I). Neat PHA material showed no evidence of porosity. It is suggested that the increase in initial concentration of BPO and incubation temperature may have contributed to more extensive grafting of PHA that resulted in lower porosity percentages of the resulting materials.

Effects of starting initiator concentration, incubation temperature and time

The grafting reaction of mcl-PHA with GDD made use of BPO as the sole initiator. As seen in Fig. 7A, at 70 °C incubation, the graft yield (%) increased with increasing starting BPO concentration. A similar trend was observed in Fig. 7B for an incubation temperature of 90 °C. At an incubation temperature of 70 °C, the rate of increase in graft yield was gradual for lower starting concentrations of initiator, *i.e.*, 3.0×10^{-6} and 5.0×10^{-6} mol dm^{-3}. When the initial concentration was increased to 1.0×10^{-5} and 1.5×10^{-5} mol dm^{-3}, a steep increase in the graft yield with time was observed (Fig. 7A). On the other hand, when incubation temperature was at 90 °C, similar fast rates of graft yield were observed for all used starting initiator concentrations (Fig. 7B). Nevertheless, for both temperatures, the grafting reaction eventually reached a plateau indicating termination of reaction following exhaustion of grafting sites and/or depletion of the radical initiator.

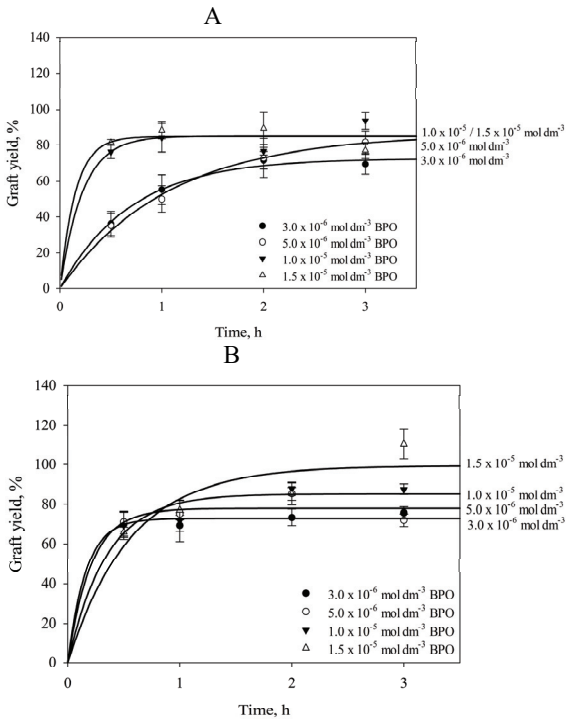

Fig. 7. Graft yield as a function of incubation time for: A) 70 and B) 90 °C incubation temperature. Initial BPO concentrations at 3.0×10^{-6}, 5×10^{-6}, 1.0×10^{-5} and 1.5×10^{-5} mol dm^{-3} for both temperatures.

Effects of initial GDD concentration

The plots in Fig. 8 show the graft yields for different GDD concentrations as a function of time. The initiator reaction is considered a fast one and hence, is expected to enter the termination phase as the concentrations of the radicals

and/or reactive sites start to deplete. With higher initial GDD concentration, higher graft yields were also observed. A similar trend was evident for different starting initiator concentrations, as shown in Fig. 7.

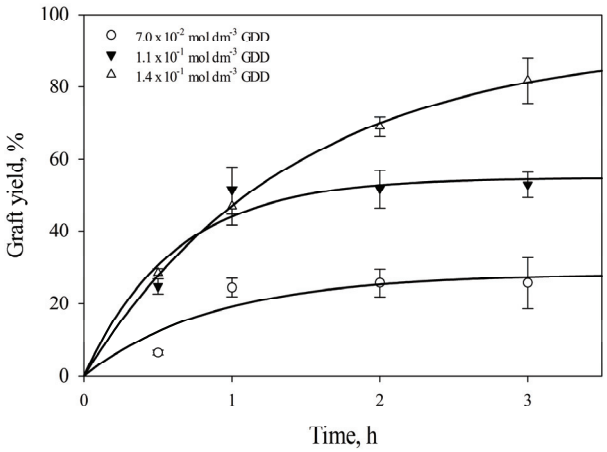

Fig. 8. Graft yield as a function of incubation time for different GDD concentrations at 70 °C incubation. Initial mcl-PHA and BPO concentrations were 50 g L^{-1} and 10^{-5} mol dm^{-3}, respectively.

Initial rate of reaction

The initial rates of grafting at two different temperatures, *i.e.*, 70 and 90 °C, for different starting initiator concentrations are given in Table I. At 70 °C, the initial rate was increasing gradually from 1.0 to 3.0 % min^{-1} as BPO concentration was increased, suggesting that the BPO dissociation has yet to reach its maximum level. However, at 90 °C, the initial rate of reaction was almost constant within a narrow range of 4.4 to 4.8 % min^{-1} for all initial BPO concentrations studied (Table I). It is suggested that at this temperature, generation of radical initiator from its parent molecule was relatively faster than at 70 °C and hence the higher initial rate of grafting. This is supported by the fact that half-life of BPO is one hour at 91 °C.

CONCLUSIONS

The graft copolymerization of mcl-PHA with GDD was successfully performed using benzoyl peroxide as the sole initiator. Elucidation of its mechanism indicates that both species could be incorporated into the same backbone of mcl--PHA polymer consisting of α–β carbon linkages due to the random nature of radical polymerization involved. The grafted product yields an amphiphilic copolymer with improved wettability, thus potentially refining its facility for cellular interaction. In addition, grafting of mcl-PHA to yield P(3HO-*co*-3HHx-*co*--3HD-*co*-3HDD)-*g*-GDD adds to the available repertoire of functional materials.

Acknowledgment. This work was supported by the Universiti Malaya under Grant No. BR008-2015.

ИЗВОД

ПОРОЗНИ АМФИФИЛНИ БИОГЕЛОВИ ДОБИЈЕНИ ЈЕДНОСТАВНИМ БИО-СИНТЕТСКИМ ПОСТУПКОМ

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Реакција калемљења глицерол-1,3-диглицеролат-диакрилата (триглицерол-диакрилата) (GDD) на поли(3-хидрокси-алканоат) средње дужине бочних алкил ланаца (mcl-PHA) је извођена у раствору ацетона у присуству бензиол-пероксида, као иницијатора. Механизам реакције калемљења на полимерне ланце је детаљно приказан и знатно побољшан у односу на претходно описане у литератури. Слободним радикалима иницирано калемљење омогућава међусобно повезивање mcl-PHA и GDD молекула преко α–β угљеничне везе, при чему настаје умрежена структура полимера са својствима гела. Термичка својства кополимера са различитим садржајем калемљених грана су анализирана у зависности од концентрације иницијатора и GDD мономера, као и времена извођења реакције полимеризације и температуре. Показано је да су апсорпција воде и порозност синтетисаних гелова знатно повећани у поређењу са полазним полимерном, mcl-PHA.

(Примљено 25. јуна, ревидирано 5. септембра, прихваћено 16. септембра 2019)

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