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ORIGINAL ARTICLE

Synthesis and thermal investigation of phosphate-functionalized acrylic materials

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Abstract

Functionalized acrylic materials derived from methyl methacrylate (MMA), 2-hydroxyethyl methacrylate (HEMA), and diethyl 2-(methacryloyloxy)ethyl phosphate (DMP) were synthesized by successive free-radical polymerizations using benzoyl peroxide (BPO) as the initiator and *N*,*N*-dimethyl-*p*-toluidine (DMpT) as the activator. NMR and GPC data showed that successful random copolymerization of MMA and DMP was carried out using the BPO-DMpT system. Moreover, the resulting products were able to react with HEMA monomer, yielding polymers with P(MMA-*co*-DMP)-*b*-PHEMA chain structures. Interestingly, the glass transition of DMP/PHEMA-containing copolymers was reduced with respect to the PMMA homopolymer. In addition, the thermal stability was enhanced with increasing DMP content in P(MMA-*co*-DMP) copolymers and was further enforced by incorporating PHEMA blocks. The presence of DMP/PHEMA segments should improve the thermal behavior of acrylic materials, which is of great interest in the design of versatile bone cements for total joint arthroplasty and functional coatings in targeted drug delivery.

Introduction

Synthetic polymethacrylates derived from methyl methacrylate (MMA) and 2-hydroxyethyl methacrylate (HEMA) are considered valuable in the fields of orthopedic surgery and targeted drug delivery [1–3]. PMMA-based bone cement has a pivotal role in fixating implants to bone tissues in total joint arthroplasty [1]. In the pharmaceutical industry, PMMA derivatives are commonly used as film-coating agents for both tablet and capsule dosages [2]. Alternatively, PHEMA has been used in soft contact lenses and artificial cornea; furthermore, it is used as a substrate to prevent cellular adhesion and dispersion [3]. The block copolymerization of MMA and HEMA could be an interesting route to modify the intrinsic properties of PMMA and synthesize novel PMMA-based acrylic materials. Block copolymerization could increase the selection of polymers with variable properties available for the design and fabrication of cements and/or pharmaceuticals to achieve versatile applications.

It is well-known that PMMA bone cement materials are biologically inert and do not show activity in bone augmentation. However, biomimetic modifications via phosphorylation have greatly enhanced the heterogeneous nucleation of apatite and cell adhesion behavior [4]. Moreover, PMMA polymer systems bearing different functional groups can potentially be used in broad-spectrum drug release [5, 6]. Previous reports have shown a remarkably high affinity between the amine groups of PMMA derivatives and the phosphate groups of a model drug dexamethasone, which provided the desired release profile of the drug [6].

According to the literature, copolymers of diethyl 2-(methacryloyloxy)ethyl phosphate (DMP) and several alkyl acrylates were synthesized by radical polymerization in benzene using azobis(isobutyronitrile) (AIBN) as an

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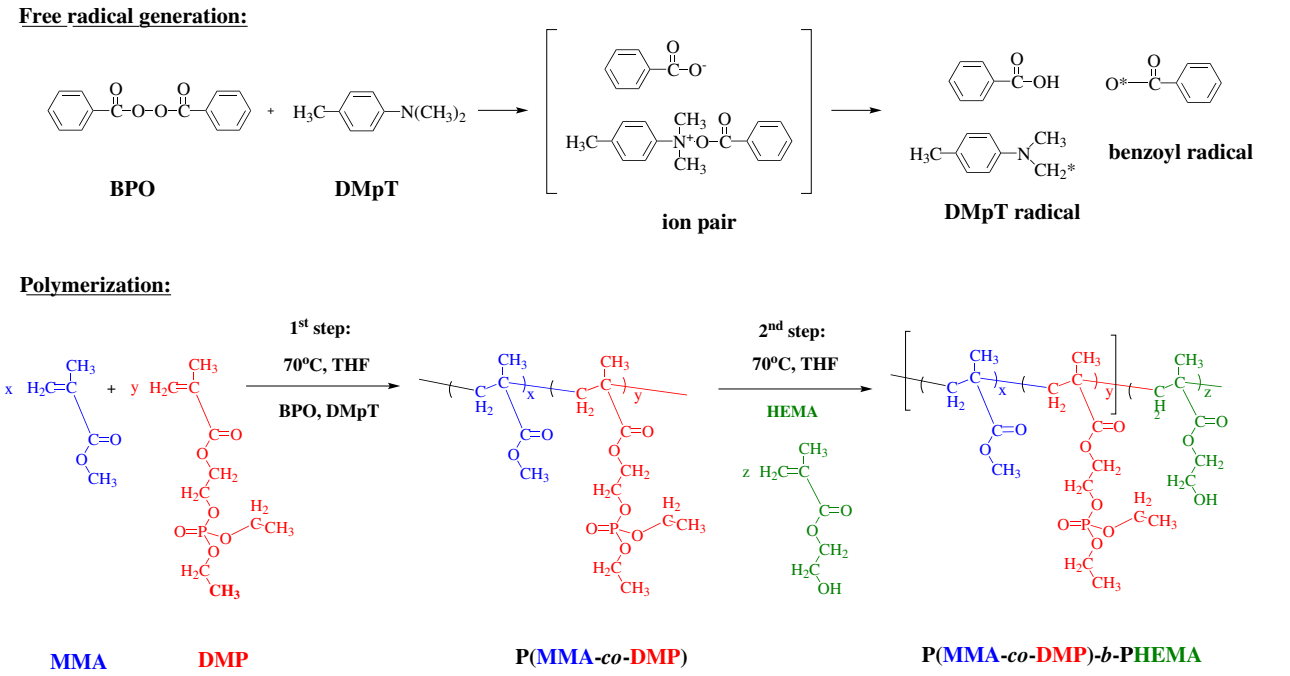

Fig. 1 Schematic illustration showing the successive free-radical polymerization of MMA and HEMA with phosphate functional groups in THF, as initiated by BPO-DMpT

initiator [7, 8]. Reghunadhan Nair et al. [7] studied the copolymerization of DMP with MMA, methyl acrylate, ethyl acrylate, and butyl acrylate, as initiated by AIBN. In this reaction system, the DMP content in the resulting polymer was very close to that in the feed, revealing that DMP underwent a completely random copolymerization with MMA; however, DMP entered the polymer chain preferentially when reacted with the other acrylates. It is to be expected that the glass transition temperature (T_g) of the copolymers containing DMP may be influenced by the sequence distribution of monomers in the polymer chains. Moreover, the authors found that the T_g decreased with an increase in the weight fraction of DMP in the MMA/DMP copolymers [7]. The effect of two different initiators, AIBN and benzoyl peroxide (BPO), on the graft copolymerization of MMA onto poly(ethylene-*co*-propylene) was investigated in toluene [9]. The authors found that BPO-initiated copolymerization yields an appreciable degree of grafting compared to the AIBN initiator. Therefore, it would be interesting to study whether the block copolymerization of MMA/HEMA can be achieved using BPO as the initiator, as is typically used in the polymerization of acrylic bone cement in total joint arthroplasty [1]. Furthermore, the effect of DMP/PHEMA segments in the resulting copolymers on the glass transition properties and the thermal decomposition behaviors that are intrinsic to PMMA is still unknown, but this effect is an important parameter that dictates the quality of film coatings and success of total joint replacement surgeries.

In this study, we report the synthesis of acrylic polymers with phosphate functional groups by the successive addition of MMA/HEMA/DMP monomers, using BPO as an initiator and DMpT as an activator for free-radical polymerization (Fig. 1). The resulting copolymers were characterized by gel permeation chromatography (GPC), nuclear magnetic resonance (NMR) spectroscopy, Fourier-transform infrared spectroscopy (FT-IR), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and elemental analysis. The results are discussed in comparison to PMMA homopolymers.

Materials and methods

Materials

Methyl methacrylate (MMA), 2-hydroxyethyl methacrylate (HEMA), benzoyl peroxide (BPO), *N*,*N*-dimethyl-*p*-toluidine (DMpT), diethyl chlorophosphate, trimethylamine, copper(I) chloride (CuCl), and magnesium sulfate ($MgSO_4$) were purchased from Acros Organics (Geel, Belgium). All solvents were of analytical grade. DMP was synthesized according to the literature [7, 8]. Typically, HEMA (22.5 g, 0.175 mol) was dissolved in 100 mL of anhydrous ethyl ether in a reaction vessel with a magnetic stirrer. A molar equivalent of trimethylamine (1 M solution in THF) was added to the reaction solution, and the system was lowered to 0 °C. Then, 150 mg of CuCl was added to the solution,

followed by a dropwise addition of diethyl chlorophosphate (30 g, 0.175 mol), and the mixture was allowed to stir continuously at this temperature for 2 h. The reaction system was returned to room temperature and kept overnight. The filtrate was extracted twice with an aqueous solution of NaOH (2 wt%). The organic phase was then washed twice with distilled water, dried over magnesium sulfate, and evaporated under reduced pressure. A conversion rate of 90% was determined by ^{1}H-NMR. Yield: 30 g (65%). ^{1}H-NMR (DMSO-d_6): δ (ppm) = 1.2 (*t*, 6H, –CH_3 on phosphate ester), 1.9 (s, 3H, CH_3 on allyl), 3.9–4.4 (m, 8H, –O–CH_2–), 5.7 (s, 1H, –CH vinyl *trans* to carbonyl), 6.0 (s, 1H, –CH vinyl *cis* to carbonyl).

Synthesis of PMMA

MMA (9.3 g, 0.093 mol), BPO (2 wt%, 0.000826 mol), and DMpT (2.5 wt%, 0.001722 mol) were dissolved in 50 mL of THF in a round-bottomed vessel equipped with a mechanical stirrer, and the solution was allowed to stir at 70 °C under a dry argon atmosphere for 5 h. Polymerization of MMA at different BPO/MMA ratios and reaction times was carried out using the same procedure. The product was collected by re-precipitation with THF as the solvent and diethyl ether as the non-solvent, followed by filtration and vacuum drying. ^{1}H-NMR (DMSO-d_6): δ (ppm) = 0.7–1.0 (d, 3H, CH_3), 1.6–2.0 (d, 2H, CH_2), 3.5 (s, 3H, OCH_3).

Synthesis of P(MMA-*co*-DMP)

To synthesize the copolymer with an MMA/DMP weight ratio of 95/5, MMA (9.5 g, 0.095 mol), DMP (0.5 g, 0.00187 mol), BPO (2 wt%, 0.00083 mol), and DMpT (2 wt %, 0.00148 mol) were dissolved in 50 mL of THF in a round-bottomed vessel equipped with a mechanical stirrer, and the solution was allowed to stir at 70 °C under a dry argon flow for 5 h. Copolymerization of MMA and DMP at different weight ratios was carried out using the same procedure. All polymers were recovered by re-precipitation with THF as the solvent and diethyl ether as the non-solvent, followed by filtration and vacuum drying.

Synthesis of PMMA-*b*-PHEMA

The block copolymerization of MMA and HEMA follows a two-step process. Typically, in the first step, MMA (2.2 g, 0.022 mol), BPO (2 wt%, 0.000272 mol), and DMpT (2 wt %, 0.000463 mol) were dissolved in 50 mL of THF in a round-bottomed vessel equipped with a mechanical stirrer, and the solution was allowed to stir at 70 °C under a dry argon atmosphere for 3 h. In the second step, HEMA (2.2 g, 0.017 mol) was added dropwise through a dropping funnel, and the reaction solution was maintained at the same temperature under a dry argon environment for another 2 h. The product was recovered by re-precipitation with THF as the solvent and diethyl ether as the non-solvent, followed by filtration and vacuum drying. ^{1}H-NMR (DMSO-d_6): δ (ppm) = 0.75–1.05 (d, 6H, CH_3), 1.76 (d, 4H, CH_2), 3.5 (s, 5H, OCH_3; CH_2), 3.9 (s, 2H, OCH_2), 4.8 (s, 1H, OH).

Synthesis of P(MMA-*co*-DMP)-*b*-PHEMA

A terpolymer comprised of P(MMA-*co*-DMP) and PHEMA blocks was synthesized in the same manner as PMMA-*b*-PHEMA, with a mixture of MMA/DMP monomers instead of only MMA in the first step. Typically, MMA (1.1 g, 0.011 mol), DMP (1.1 g, 0.041 mol), BPO (2 wt%, 0.000272 mol), and DMpT (2 wt%, 0.000463 mol) were dissolved in 50 mL of THF in a round-bottomed vessel equipped with a mechanical stirrer, and the solution was allowed to stir at 70 °C under a dry argon atmosphere for 3 h. In the second step, HEMA (1.1 g, 0.0085 mol) was added dropwise through a dropping funnel, and the reaction solution was maintained at the same temperature under a dry argon environment for another 2 h. The product was recovered by re-precipitation with THF as the solvent and diethyl ether as the non-solvent, followed by filtration and vacuum drying. ^{1}H-NMR (DMSO-d_6): δ (ppm) = 0.75–1.05 (d, 9H, CH_3), 1.28 (*t*, 6H, CH_3), 1.76 (d, 6H, CH_2), 3.54 (s, 5H, OCH_3; CH_2), 3.9 (s, 2H, OCH_2), 4.03–4.11 (m, 8H, OCH_2), 4.8 (s, 1H, OH).

Measurements

GPC was performed at 40 °C using a setup composed of an HPLC pump, a refractive index detector, and two size-exclusion columns connected in series: one guard column (PLgel 5 μm, 7.5 × 50 mm) and one Mixed-D column (PLgel 5 μm, 7.5 × 300 mm) (Agilent Technologies, Inc. UK). The mobile phase was THF, and the flow rate was 0.8 mL min^{-1}. The weight-average molecular weight (M_w) and polydispersity index (M_w/M_n) of the polymer were expressed with respect to PMMA standards (Polymer Standards Service, Inc., Amherst, MA, USA). ^{1}H-NMR and two-dimensional diffusion ordered spectroscopy (2D DOSY) NMR measurements were performed at 300 K on a 600 MHz Varian VNMRS-600 NMR spectrometer (Varian, Palo Alto, CA, USA) with DMSO-d_6 as the solvent and tetramethylsilane (TMS) as the reference. ^{31}P NMR spectra were obtained with a Varian UNITYINOVA-500 NMR spectrometer. IR spectra were recorded with a PerkinElmer Spectrum 100 FT-IR spectrometer (PerkinElmer, Santa Clara, CA, USA). DSC measurements were obtained on a LT-Modulate DSC 2920 calorimeter (TA Instruments, New Castle, DE, USA). The samples were first heated from 25 to 105 °C under a nitrogen atmosphere and then kept at 105 °C

Table 1 Molecular characteristics of PMMA and its copolymers

Sample	Homo/copolymer	$W_{MMA}/W_{DMP}/W_{HEMA}$		M_w[c] (×10^4 g mol^{-1})	M_w/M_n[c]	T_g[d] (°C)	T_d[e] (°C)
		Feed[a]	Product[b]				
M4	PMMA	100/0/0	100/—	4.5	1.5	118	208
P1	P(MMA-*co*-DMP) 95/5	95/5/0	97/3/—	4.3	1.6	116	223
P2	P(MMA-*co*-DMP) 90/10	90/10/0	90/10/—	4.3	1.5	109	237
P3	P(MMA-*co*-DMP) 50/50	50/50/0	50/50/—	2.6	1.9	109	250
E1	PMMA-*b*-PHEMA	50/0/50	56/—/44	11.0	2.3	115	219
E2	P(MMA-*co*-DMP)-*b*-PHEMA	33/33/33	46/27/28	5.6	2.0	93	262

[a]Weight ratio

[b]Calculated by ^{1}H-NMR spectra

[c]Determined by GPC

[d]Measured by DSC

[e]Detected by TGA

for 5 min, followed by rapid cooling to room temperature. A second heating was performed from 30 °C to 200 °C at a heating rate of 10 °C min^{-1}. TGA was carried out on a TA Instruments SDT Q600 thermogravimetric analyzer (TA Instruments, New Castle, DE, USA). The samples were heated from 25 to 600 °C at a rate of 10 °C min^{-1}. Elemental analyses for carbon (C) and hydrogen (H) were recorded on a Vario EL cube apparatus (Elementar, Germany), and the amount of oxygen (O) was recorded on a Flash 2000 Instrument (Thermo Fisher Scientific Inc., Italy). From these data, the amount of phosphorus (P) was quantified.

Results and discussion

A series of functionalized acrylic materials derived from MMA, HEMA and DMP were synthesized by successive free-radical polymerization in THF using a BPO-DMpT-initiated system (Fig. 1). When BPO and DMpT are mixed together, DMpT causes the decomposition of BPO in a reduction/oxidation electron-transfer process, resulting in benzoyl and DMpT radicals [10]. In the first step of the polymerization, one free-radical attacks the alkene double bond of a methacrylate monomer, MMA or DMP, propagating the polymerization process until it is terminated by another free radical. In the second step, the unterminated polymeric-free radical serves as a macro-initiator and is allowed to react with HEMA, rendering copolymers with PMMA/PHEMA segments bearing phosphate functional groups. Table 1 shows the composition and molecular characteristics of the various homo/copolymers.

A pilot study concluded that the free-radical polymerization of MMA initiated by the formation of benzoyl/DMpT radicals is an efficient and convenient method to form PMMA (Supplementary Figure S1 and Table S1). The conversion of monomer to polymer was very fast, as the increase in molecular weight occurred dramatically during the first 3 h, and more than 90% of the loaded MMA monomer was converted into PMMA. After this, the molecular weight increased slightly and reached a steady state after 5 h. An increase in the BPO/monomer ratio led to a decrease in the molecular weight of the polymer, from $M_w = 53{,}000$ g mol^{-1} for 0.2 wt% BPO to $M_w = 20{,}000$ g mol^{-1} for 5 wt% BPO. From these preliminary experiments, it was concluded that the free-radical polymerization of MMA initiated by the formation of the benzoyl radical is an efficient and convenient method to form PMMA.

We next investigated the synthesis of MMA/DMP random copolymers by the free-radical polymerization of a mixture containing MMA and DMP, using BPO as an initiator and DMpT as an activator. The reaction was performed for 5 h at a fixed BPO/monomer ratio of 2 wt%. After purification by dissolution/precipitation, the BPO-initiated MMA/DMP copolymers were recovered as a dough-like mass and changed from white to yellow as the DMP content increased. As the solvent evaporated, a hard, cement-like complex was formed. The MMA/DMP weight ratios of the feeds were selected to be 95/5, 90/10 and 50/50.

As shown in Table 1, the molecular weight of the MMA/DMP copolymers did not change significantly as the DMP content increased from 0 to 10% under the same conditions (2 wt% BPO and 2 wt% DMpT). However, when the DMP content in the MMA/DMP copolymer reached 50%, a strong decrease in the molecular weight of the copolymer was observed. This finding may result from the bulky structure of the DMP monomers, which causes difficulties

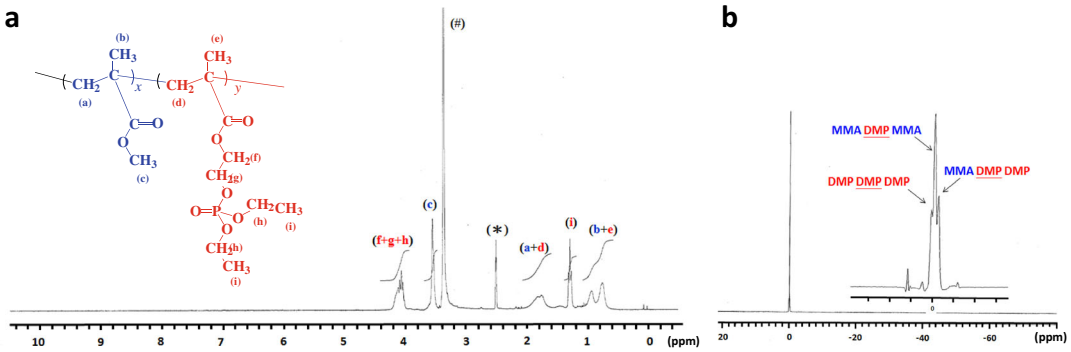

Fig. 2 Chemical structures and **a** ^{1}H-NMR and **b** ^{31}P NMR analyses of a P(MMA-*co*-DMP) copolymer (sample P3) in DMSO-d_6 (*: DMSO; #: H_2O)

when MMA and DMP were incorporated into the polymer chain. Additionally, the hydrodynamic volume of the MMA/DMP copolymers bearing DMP segments changed compared with the parent PMMA homopolymer.

Figure 2a shows a typical ^{1}H-NMR spectrum and the chemical structure of the resulting copolymer. Typical signals for PMMA were observed as follows: 1.8 ppm (protons **a**), 0.7–1.0 ppm (protons **b**), and 3.6 ppm (protons **c**) [11, 12]. The presence of DMP units was confirmed by the appearance of signals at 4.0–4.2 ppm (protons **f** + **g** + **h**) and 1.3 ppm (protons **i**) and by the increase in the signals at 1.8 ppm (protons **d**) and 0.7–1.0 ppm (protons **e**). The MMA/DMP weight ratio was calculated from the integration of signal **c** of the MMA units at 3.6 ppm and signals **f** + **g** + **h** of the DMP units at 4.0–4.2 ppm. The results are summarized in Table 1. It appears that the MMA/DMP weight ratios in the copolymers, as obtained by ^{1}H-NMR, are very close to those of the initial feeds, indicating a very good conversion of both MMA and DMP monomers. Figure 2b shows the ^{31}P NMR spectrum of the P(MMA-*co*-DMP) copolymer (sample **P3**). It contains three split peaks, which were attributed to different triads of MMA and DMP repeating units. Notably, only a single peak can be observed for the DMP monomer.

PMMA-*b*-PHEMA block copolymer was synthesized by the free-radical polymerization of successively added MMA and HEMA in the presence of BPO-DMpT initiator. The process of block copolymerization involves two steps. In the first step, the polymerization of MMA, initiated by BPO-DMpT, occurred in the first 3 h. Then, in the second step, the obtained PMMA-free radical served as a macroinitiator and was allowed to react with HEMA over the next 2 h. P(MMA-*co*-DMP)-*b*-PHEMA terpolymer was synthesized in the same manner using a predetermined amount of a MMA/DMP mixture, instead of only MMA monomer (Fig. 1). The GPC chromatograms of PMMA-*b*-PHEMA and P(MMA-*co*-DMP)-*b*-PHEMA tend towards a broad bimodal molecular weight distribution, suggesting the presence of two species with different molecular weights (Fig. 3a). Figure 4a shows a DOSY NMR spectrum of the P(MMA-*co*-DMP)-*b*-PHEMA copolymer. Typical signals for PMMA, PDMP, and PHEMA components were observed. The presence of PHEMA units was confirmed by the appearance of signals at 4.7 ppm (protons **n**). Signals characteristic of MMA, DMP, and HEMA diads or triads were detected in the ^{31}P NMR spectra (Fig. 4b), indicating that copolymerization occurred. Figure 3b shows the FT-IR spectra of PMMA and the synthesized copolymers. In the spectrum of PMMA, the bands at 1726 and 1150 cm^{-1} were assigned to C=O and C–O stretching vibrations. The spectrum also shows two characteristic absorptions at 2955 and 1450 cm^{-1}, which are attributed to the stretching vibrations of C–H and C–O, respectively [12–14]. MMA/DMP copolymers exhibited bands at 982 and 1027 cm^{-1}, which is in agreement with the presence of DMP units [15, 16]. In the spectrum of P(MMA-*co*-DMP)-*b*-PHEMA, another C–O stretching band appeared at 1075 cm^{-1}, and an O–H stretching band appeared at 3400–3500 cm^{-1}, which is in agreement with the presence of PHEMA blocks [15]. In the present study, the MMA/DMP weight ratios in the resulting polymers, as obtained by ^{1}H-NMR (Table 1) and elemental analyses (Table 2), are very close to those of the initial feeds, indicating that a successful random copolymerization was carried out using the BPO-DMpT initiator-activator system. Moreover, the resulting products were able to react with the HEMA monomer, rendering a polymer with a chain structure of P(MMA-*co*-DMP)-*b*-PHEMA. We also attempted to synthesize a block copolymer of MMA/HEMA via the successive addition of HEMA and MMA; however, no product could be recovered after dissolution/precipitation. This result was attributed to the fact that the products from the polymerization of HEMA led to cross-linked aggregates in the solvent (THF), rather than dissolution. This result revealed that block copolymerization of MMA/HEMA cannot be achieved using this procedure.

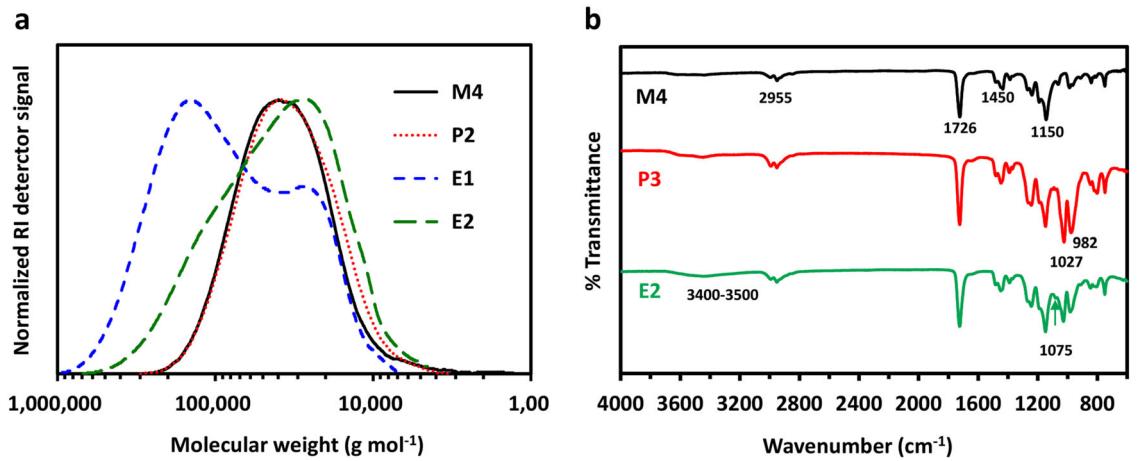

Fig. 3 **a** GPC traces, **b** FT-IR spectra of PMMA and its copolymers. PMMA (sample M4), P(MMA-*co*-DMP) (samples P2 or P3), PMMA-*b*-PHEMA (sample E1), and P(MMA-*co*-DMP)-*b*-PHEMA (sample E2)

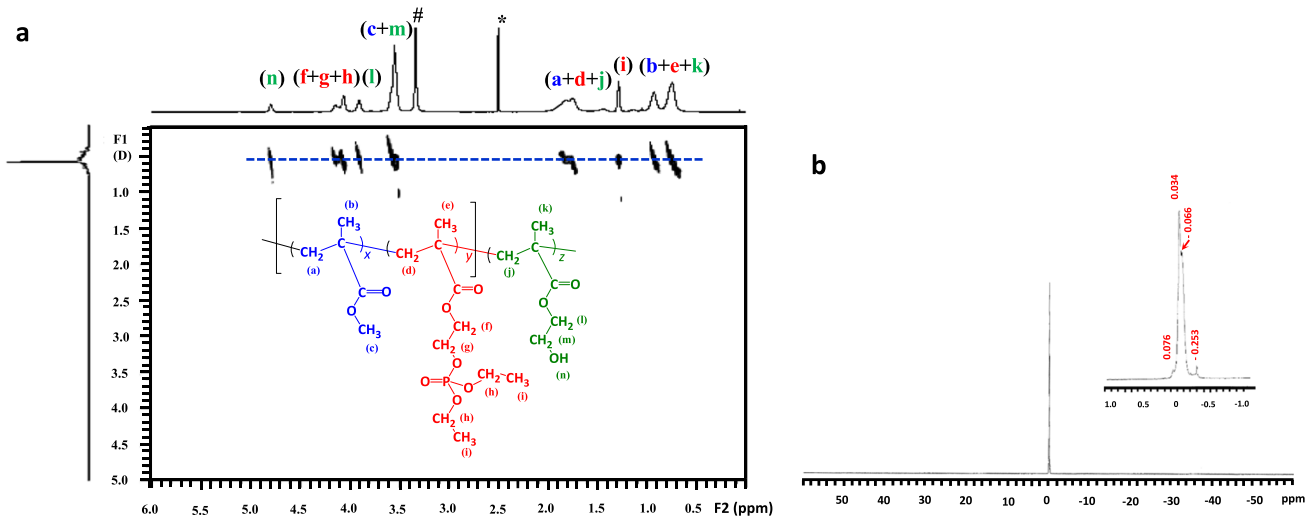

Fig. 4 Chemical structure and **a** DOSY and **b** ^{31}P NMR analyses of a P(MMA-*co*-DMP)-*b*-PHEMA copolymer (sample E2) in DMSO-d_6 (*: DMSO; #: H_2O)

Table 2 Elemental analyses of PMMA and MMA/DMP/HEMA copolymers

Sample	Theoretical values (%)				Elemental analysis (%)			
	C	H	O	P	C	H	O	P
M4	60.0	8.0	32.0	0.0	59.8	8.4	32.5	0.0
P3	49.2	7.4	35.0	8.5	50.6	7.6	30.9	10.9
E1	57.4	7.8	34.8	0.0	56.3	7.8	32.3	0.0
E2	50.8	7.4	35.5	6.3	53.2	7.8	31.2	7.8

The thermal properties of the various copolymers were investigated using DSC and TGA and were compared with the corresponding PMMA homopolymer. For DSC measurements, samples were first heated from 25 °C to 105 °C and then rapidly cooled to room temperature to erase the thermal history. For T_g measurements, a second heating step from 30 °C to 200 °C was carried out at a heating rate of 10 °C min^{-1}. The DSC thermograms are shown in Fig. 5a. The T_g of the PMMA homopolymer (sample **M4**) was detected at 118 °C, indicating that PMMA is an organic glass at room temperature. Notably, the T_g values agree with those predicted by the Flory–Fox equation, i.e., the T_g increased with increasing molecular weight (Supplementary Table S1). Introducing 5% DMP into the PMMA chain (sample **P1**) slightly decreased the T_g to 116 °C. However, when another 5% DMP was incorporated into the PMMA (i.e., sample **P2**), the T_g decreased to 109 °C. Interestingly, sample **P3** showed a T_g value very close to that of sample

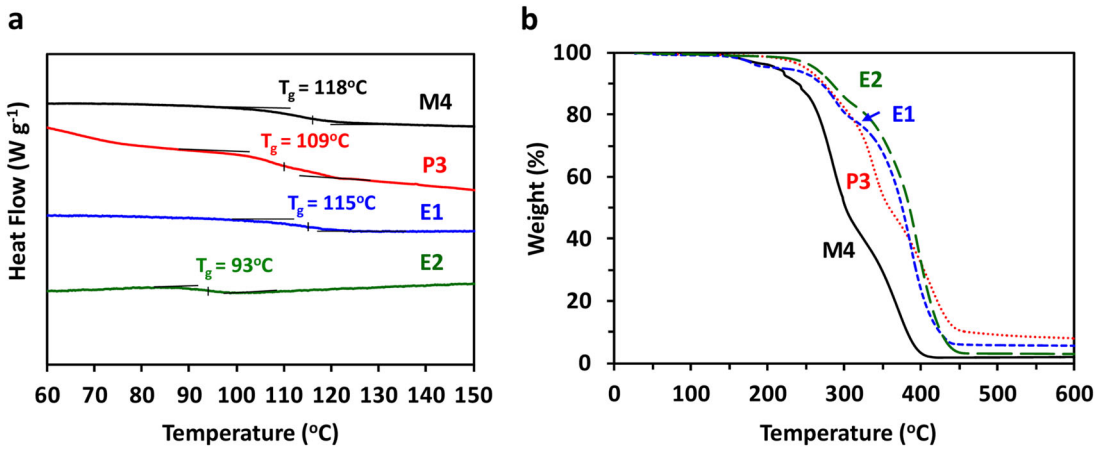

Fig. 5 Thermal behavior of PMMA and its copolymers. **a** DSC and **b** TGA thermograms: PMMA (sample M4), P(MMA-*co*-DMP) (sample P3), PMMA-*b*-PHEMA (sample E1), and P(MMA-*co*-DMP)-*b*-PHEMA (sample E2)

P2, indicating that no significant effect on the T_g occurred by increasing the DMP content from 10 to 50%. For the PHEMA-containing copolymers, similar thermograms were found with slightly lower T_g values. These findings showed that PHEMA blocks decreased the chain mobility of the PMMA or P(MMA-*co*-DMP) blocks. It is worth noting that the T_g of a random copolymer is a monotonic function of the composition, while block copolymers can present two or more transitions [17].

TGA thermograms of the samples were recorded from 25 to 600 °C, as shown in Fig. 5b. PMMA exhibited uniform thermal degradation behavior. For the copolymers, a two-step degradation profile was detected. It is assumed that the first degradation step corresponds to the MMA moiety. The value of the decomposition temperature (T_d) was reported at 5% weight loss of the sample. A T_d value of 208 °C was obtained for PMMA, and values of 223, 237 and 250 °C were obtained for the P(MMA-*co*-DMP) copolymer samples **P1**, **P2**, and **P3**, respectively (Table 1). The TGA curve of the MMA/DMP copolymer shifted to a higher temperature compared to PMMA, i.e., the overall stability increased due to the presence of DMP segments.

In pharmaceutical formulations, T_g is a critical parameter in terms of sustained release dosage forms. It is generally believed that the coating process must be carried out at a temperature (called the minimum film-forming temperature) above the T_g of the film-coating materials, which facilities uniform distribution of the coating [2]. In total joint replacement, radical polymerization is an exothermic reaction that consequently increases the temperature of the cement mixture. This factor can cause serious complications in vivo, such as aseptic loosening by necrosis of the surrounding tissues [1]. Therefore, next-generation bone cements need to incorporate monomers with low heats of reaction in order to reduce thermal necrosis and enhance biocompatibility. Sabino et al. reported the curing properties of bone cements with MMA as the base monomer and either methacrylic acid (MAA) or diethyl amino ethyl methacrylate (DEAEMA) as co-monomers [18]. The addition of MAA to MMA produced bone cements with a maximum temperature during polymerization (T_{max}) of 73 °C, while the addition of DEAEMA resulted in a T_{max} of 38 °C. In addition, they also found that low T_{max} values corresponded to a low T_g for the bone cement. Therefore, investigating the transition temperature of homo/copolymers is important for predicting the curing properties of new bone cement formulations. In this work, DSC analysis demonstrated that the T_g of the MMA/DMP copolymers was lower than that of the PMMA homopolymer and was further decreased by the incorporation of PHEMA blocks (Table 1). For this reason, using DMP or PHEMA to modify PMMA improves the glass transition properties for bone cement applications. Regarding treatment by thermal processes, Yang et al. studied the thermal degradation behavior of hybrid copolymers of MMA and ε-caprolactone (CL) under a nitrogen atmosphere [19]. All MMA/CL copolymers exhibited improved thermostability in comparison with the two homopolymers, and the T_d increased with the MMA molar fraction over the range of 30 mol% to 70 mol %. In the present study, we also found that the T_d increased with increasing DMP content in P(MMA-*co*-DMP) copolymers, and was further increased by incorporating PHEMA blocks. From a processing viewpoint, block copolymers of PMMA/PHEMA with phosphate functional groups provide a wide temperature range for thermal treatment.

Conclusion

Herein, we reported the synthesis and characterization of functionalized acrylic materials prepared by the successive addition of MMA/DMP/HEMA monomers, using BPO-DMpT-initiated polymerization. At low DMP/MMA ratios, DMP underwent a random copolymerization with MMA; however, the bulky structure of DMP restricted chain propagation at high DMP contents. In this reaction system, the resulting products were able to react with the HEMA monomer, rendering polymers with a chain structure of P(MMA-*co*-DMP)-*b*-PHEMA. Analysis of the thermal properties found that the incorporation of DMP or PHEMA in PMMA rendered a copolymer with a low T_g and high T_d compared to the PMMA homopolymer, thus increasing the overall stability of the main chain polymer. These features are of great interest for designing novel biomedical materials and particularly show potential for applications in bone cements and coating system additives.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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