Polymer Chemistry

ROYAL SOCIETY OF CHEMISTRY

PAPER

View Article Online
View Journal | View Issue

Check for updates

Cite this: *Polym. Chem.*, 2023, **14**, 1224

Degradable vinyl polymer particles by radical aqueous emulsion copolymerization of methyl methacrylate and 5,6-benzo-2-methylene-1,3-dioxepane†

Paul Galanopoulo, ‡[a] Laura Sinniger, ‡[a] Noémie Gil,[b] Didier Gigmes,[b] Catherine Lefay,[b] Yohann Guillaneuf,[b] Maëlle Lages,[c] Julien Nicolas,[c] Franck D'Agosto *[a] and Muriel Lansalot *[a]

Received 12th January 2023,
Accepted 13th February 2023

DOI: 10.1039/d3py00040k

rsc.li/polymers

With an increasing interest in the synthesis of (bio)degradable polymers, the synthesis of (bio)degradable vinyl polymer particles is attracting growing attention. In this work, degradable poly(methyl methacrylate) (PMMA) particles were synthesized by radical emulsion polymerization in water. A cyclic ketene acetal, 5,6-benzo-2-methylene-1,3-dioxepane (BMDO) was used as a co-monomer to introduce cleavable ester functions into the PMMA backbone. The stability of BMDO in aqueous media was studied and the degradation mechanism discussed in order to better comprehend the use of BMDO in emulsion and understand the incorporation of BMDO into the copolymer chains. Stable latexes containing various amounts of BMDO inserted units (from 2 to 6.4 mol%) were obtained. The degradation of the resulting copolymers was carried out in a basic medium and an average molar mass loss of 90% was observed.

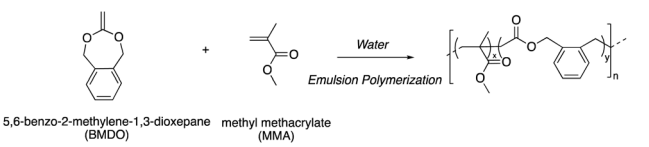
Open Access Article. Published on 13 Feabhra 2023. Downloaded on 11/05/2026 16:37:04.
This article is licensed under a Creative Commons Attribution-NonCommercial 3.0 Unported Licence.

Introduction

Vinyl polymers are widely used in many applications and are thus massively produced in industry. Their carbon–carbon backbone cannot be degraded easily, which is a valuable property for most applications. However, it also limits their use in certain fields where (bio)degradability is sought, notably in biomedical applications for, *e.g.*, nanomedicines or implantable devices.[1] In addition, considering the current quest for more environmentally friendly polymer products, including possible recycling, the synthesis of (bio)degradable vinyl polymers is a key challenge.[2–4] Degradable polymers can be synthesized by inserting cleavable units distributed in the backbone. Under external stimuli such as pH, light, temperature or enzymatic activity, the targeted units cleave, leading to low molar mass oligomers. Ideally, the ultimate goal would be to insert enough cleavable bonds to achieve complete degradation without affecting the intended properties of the final materials.

One strategy is based on the use of cyclic ketene acetals (CKAs) as comonomers, which allow the preparation by radical ring-opening polymerization (rROP) of vinyl copolymers containing cleavable ester functions.[5–7] The polymers obtained can be thus subjected to hydrolytic or enzymatic degradation leading to a decrease in their molar mass.[8] Besides, the use of CKAs in radical copolymerization is, *a priori*, less restrictive than the ring-opening anionic polymerization of cyclic monomers for introducing ester cleavable bonds into polymers.

The copolymerization of different CKAs with a variety of vinyl monomers has been widely studied in homogeneous conditions,[8,9] the most reported ones being 2-methylene-1,3-dioxepane (MDO) and 5,6-benzo-2-methylene-1,3-dioxepane (BMDO, Scheme 1). The latter has been successfully copolymerized with styrene,[5,10] *n*-butyl acrylate,[11] as well as



Scheme 1 Aqueous radical emulsion copolymerization of BMDO and MMA.

[a]*Univ Lyon, Université Claude Bernard Lyon 1, CPE Lyon, CNRS, UMR 5128, Catalysis, Polymerization, Processes and Materials (CP2M), 43 Bd du 11 novembre 1918, 69616 Villeurbanne, France. E-mail: franck.dagosto@univ-lyon1.fr, muriel.lansalot@univ-lyon1.fr*
[b]*Aix Marseille Univ, CNRS, Institut de Chimie Radicalaire, UMR 7273 Marseille, France*
[c]*Université Paris-Saclay, CNRS, Institut Galien Paris-Saclay, 17 avenue des Sciences, 91400 Orsay, France*

†Electronic supplementary information (ESI) available. See DOI: https://doi.org/10.1039/d3py00040k

‡These authors contributed to the work equally.

This journal is © The Royal Society of Chemistry 2023

Open Access Article. Published on 13 Feabhra 2023. Downloaded on 11/05/2026 16:37:04.
This article is licensed under a Creative Commons Attribution-NonCommercial 3.0 Unported Licence.

methacrylic compounds such as poly(ethylene glycol) methacrylate (PEGMA)[12] and methyl methacrylate (MMA).[13] MDO has also been copolymerized with a variety of vinyl co-monomers including styrene or MMA.[14] However, in these cases, low incorporation of MDO units was observed except when vinyl acetate (VAc) was used.[14]

Nonetheless, these copolymerizations have been extensively investigated in bulk and in solution. In contrast, only a very few examples concerning the use of CKAs in an aqueous dispersed media have been reported,[15–17,27] despite the tremendous importance of polymerization in dispersed media. This can be explained by the high sensitivity of CKAs to protic species since CKAs are known to rapidly hydrolyze in aqueous media.[18,27]

Miniemulsion copolymerization in water of BMDO with either MMA or styrene was described in 2012.[17] The ultimate objective justifying the use of a miniemulsion polymerization process was the encapsulation of drugs in a degradable polymer matrix. Polymer particles were obtained, and the formation of copolymers based on MMA and BMDO claimed, while their degradation was not evaluated. In addition, the known sensitivity of BMDO to protic species[11] did not appear to be an impediment to employ a broad range of surfactants and miniemulsion polymerization conditions. This process is indeed meant to protect the comonomers from the aqueous environment by trapping them into nanometric monomer droplets in which the polymerization will, in theory, exclusively take place.[19]

Emulsion polymerization provides a more universal and industry-relevant approach to polymerization in aqueous dispersed media. However, the polymerization starts in water and the hydrophobic comonomers are required to diffuse through the aqueous phase from large micrometric monomer droplets to nanometric particles. The challenge for the copolymerization of CKA with monomers commonly used in aqueous emulsion thus lies in finding suitable conditions for successful copolymerization while maintaining good control on the insertion of the ester functions, with the aim of ensuring homogeneous degradation of the copolymer. Very recently, the copolymerization of VAc with MDO was studied in aqueous emulsion polymerization.[15,16] Indeed, as mentioned above, MDO was successfully copolymerized with VAc in homogenous medium (determined reactivity ratios: r_{MDO} = 0.47 and r_{VAc} = 1.53) leading to degradable polymers.[20] P(VAc-*co*-MDO) copolymers were obtained in semi-batch emulsion conditions at 40 °C using redox initiators. The key to the success of this synthesis is the very specific formulation employed to rapidly nucleate particles in which MDO can rapidly escape from the aqueous phase. This however requires very fine adjustments in terms of pH and feeding rates, as well as the additional use of hydrophilic charged comonomers, which may not be suitable for a wide range of applications and may generate reproducibility issues.[27]

Copolymerization of BMDO with MMA, which also present favorable reactivity ratios (r_{BMDO} = 0.53 and r_{MMA} = 1.96),[13] has never been investigated in aqueous emulsion copolymerization. In this paper, we look at developing very simple protocols for the aqueous emulsion copolymerization of BMDO with MMA to yield degradable vinyl polymer particles.

Materials and methods

Materials

Methyl methacrylate (MMA, Aldrich, 99%), potassium persulfate (KPS, Aldrich, 99%), sodium dodecyl sulfate (SDS, Aldrich, 99%), sodium bicarbonate (Aldrich, Bioreagent), potassium carbonate (K_2CO_3, Aldrich, 99%), potassium hydroxide (KOH, Aldrich, 85%), dichloromethane (ACS reagent, Aldrich), methanol (VWR) and tetrahydrofuran (THF, Fisher, HPLC grade) were used as received. 5,6-Benzo-2-methylene-1,3-dioxepane (BMDO) was synthesized as reported in the literature.[5] Water was deionized before use (Purelab Classic UV, Elga LabWater).

Experimental procedures

Emulsion copolymerization of MMA and BMDO. Emulsion copolymerizations of MMA and BMDO were performed under nitrogen in a two-necked round bottom flask equipped with a condenser. First, a monomer mixture containing MMA and BMDO, and the aqueous phase containing KPS (4 mM), $NaHCO_3$ (8 mM), SDS (14 mM) and water were introduced in the flask. Both solutions were previously placed in an ice bath and degassed for 30 min by nitrogen bubbling. The flask was then placed in an oil bath at 70 °C under stirring at 500 rpm. After the desired reaction time, the polymerization was stopped by immersion in an ice bath and exposure to air. MMA consumption was followed by ^{1}H NMR for the copolymerizations, or by gravimetric analysis in the case of MMA homopolymerization. The copolymer composition was determined by ^{1}H NMR spectroscopy from dried samples. The copolymers were also analyzed by SEC and DSC and the particle diameter was determined by DLS analysis.

Degradation experiments. 40 mg of dry extract was dissolved in 3 mL of THF, to which 5 mL of KOH solution (5 wt%) in methanol were added. The mixture was stirred for 2 h at 60 °C and for one night at room temperature. Solvents were removed by evaporation. The residue was dispersed in water, filtered, and recovered by redissolution in dichloromethane. This organic phase was dried under vacuum to provide the final product that was analyzed by SEC.

Analytical techniques

Nuclear magnetic resonance (NMR). NMR spectra were recorded on a Bruker Avance III 400 MHz spectrometer (^{1}H: 400 MHz; ^{13}C: 100 MHz) at 25 °C. The samples were diluted in $CDCl_3$ at concentrations of about 30 mg mL^{-1}. NMR spectra were recorded with a 5 mm BBFO + probe with a *z*-gradient coil.

Size exclusion chromatography (SEC). SEC analyses were performed using a Viscotek system (Malvern Instruments) including a four-capillary differential viscometer, a differential refractive index (RI) detector and a UV detector. THF was used as the mobile phase at a flow rate of 1 mL min^{-1} at 35 °C. All

Open Access Article. Published on 13 Feabhra 2023. Downloaded on 11/05/2026 16:37:04.
This article is licensed under a Creative Commons Attribution-NonCommercial 3.0 Unported Licence.

samples were injected at a concentration of 3 to 5 mg mL^{-1} after filtration through a 0.45 μm PTFE membrane. The separation was carried out on three Polymer Standard Service columns (SDVB, 5 μm, 300 × 7.5 mm) and a guard column. The average molar masses (number-average molar mass, M_n, and weight-average molar mass, M_w) and the dispersity, $Đ = M_w/M_n$, were calculated from the RI signal with a calibration curve based on poly(methyl methacrylate) standards (Polymer Standards Service).

Dynamic light scattering (DLS). The intensity-weighted mean diameter (or *Z*-average diameter), Z_{ave}, of the latex particles and the polydispersity index (PDI) were measured at 25 °C using a Zetasizer Nano Series (Nano ZS) from Malvern Instruments. Before measurements, the latex was diluted with water. The mean particle diameter was averaged over three consecutive runs. The data were collected at a 173° scattering angle using the fully automatic mode of the Zetasizer system and fitted with the cumulant analysis.

Differential scanning calorimetry (DSC). DSC analyses were performed on a Mettler Toledo DSC 3. Samples were passed using 40 μL alumina pans. Two heating steps separated by one cooling step were performed at a rate of 10 °C min^{-1}. The second heating was used to determine the glass transition temperature (T_g) of the polymers. For the calculation of the theoretical T_g, the Fox equation (eqn (1)) was used with the assumption that the obtained copolymers were statistical. The T_g of PBMDO homopolymer was set at 16 °C according to the literature[13] and the T_g of PMMA was set at 125 °C according to our experimental results.

$$\frac{1}{T_g} = \frac{W_{MMA}}{T_{g\,PMMA}} + \frac{W_{BMDO}}{T_{g\,PBMDO}} \quad (1)$$

Results and discussion

Emulsion copolymerization of MMA and BMDO

P(MMA-*co*-BMDO) copolymer latexes were successfully synthesized under very conventional emulsion polymerization conditions, *i.e.* using SDS as surfactant and KPS as thermal initiator. $NaHCO_3$ was also added to the medium to start at a basic pH (~8.8) since we reckoned that BMDO hydrolysis would be kept to a minimum under these conditions.[18]

A first synthesis was conducted with 5 mol% of BMDO at 70 °C (E1BMDO, Table 1). The conversion of MMA was monitored by ^{1}H NMR, following the evolution of the signals characteristic of the vinyl protons of MMA (5.5 and 6 ppm) in relation to the signal characteristic of methoxy protons present in the copolymer (3.6 ppm). For E1BMDO (Table 1), the MMA conversion reached 99% (Fig. 1) and a stable latex was obtained. As mentioned in the introduction, CKAs are sensitive to protic species and thus easily hydrolyzed in water. We thus conducted a brief study of BMDO stability on storage and two distinct degradation products were identified as detailed in the ESI (D1 and D2 in Fig. S1 and S2†), at least one of them (D1) being volatile (see ESI†). Subsequently, we also studied its stability in aqueous dispersed media. However, due to the complexity of the NMR spectra associated with the presence of

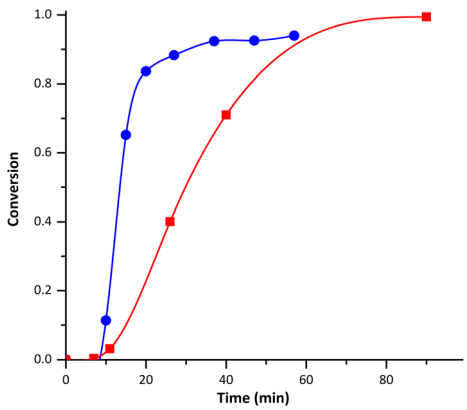


Fig. 1 Evolution of MMA conversion with time during emulsion (co) polymerization of MMA and BMDO for experiments E1MMA (blue) and E1BMDO (red).

Table 1 Emulsion copolymerizations of MMA and BMDO. Experimental conditions and characterization of the formed copolymers and latexes

Run	$f_{BMDO,0}$ [a] (%)	Base	*t* (min)	Conv.[b] (%)	F_{BMDO} [c] (%)	Z_{ave} [d] (nm)	PDI[d]	T_g [e] (°C)	M_n [f] (kg mol^{-1})	$Đ$ [f]
E1MMA	0	$NaHCO_3$	60	94	—	67	0.03	125	660	2.6
E1BMDO	5	$NaHCO_3$	90	99	3.8	45	0.07	76	61.5	5.8
E2BMDO	5	K_2CO_3	90	94	4.6	39	0.06	56	27.8	3.3
E3BMDO	5	None	90	73	0.05	60	0.05	n.d.	n.d.	n.d.
E4BMDO	2	$NaHCO_3$	90	98	2.0	45	0.07	87	98.2	5.9
E5BMDO	10	$NaHCO_3$	90	98	6.4	47	0.06	67	28.5	1.9

Experiments were conducted at 70 °C targeting a solid content of 10 wt%, with [SDS] = 14 mmol L^{-1}, [Base] = 8 mmol L^{-1}, [KPS] = 4 mmol L^{-1}. Most of the experiments were performed with $NaHCO_3$, leading to an initial pH (pH_0) around 8.8 and a final pH (pH_f) close to 8. For E2BMDO, K_2CO_3 was used instead (pH_0 = 11.0/pH_f = 7.7), while E3BMDO was run without a base (pH_0 = 6.0/pH_f = 2.3). [a] Molar fraction of BMDO in the initial monomer mixture. [b] Conversion of MMA determined by gravimetric analysis in the case of E1MMA and by ^{1}H NMR for the copolymerizations. [c] Average molar fraction of BMDO in the copolymer calculated according by ^{1}H NMR. [d] Intensity-average diameter and polydispersity index of the final particles from DLS. [e] Glass transition temperature estimated from DSC analyses. [f] Experimental number-average molar mass, M_n, and dispersity, $Đ = M_n/M_w$, of the copolymer determined by SEC-THF using a conventional calibration based on PMMA standards. n.d.: not determined.

This journal is © The Royal Society of Chemistry 2023

Open Access Article. Published on 13 Feabhra 2023. Downloaded on 11/05/2026 16:37:04.
This article is licensed under a Creative Commons Attribution-NonCommercial 3.0 Unported Licence.

volatile compounds, the quantification of the different species was difficult. Likewise, the BMDO conversion was thus delicate to evaluate considering a similar potential degradation during polymerization, which is indeed shown by the presence of D2 product when monitoring E1BMDO reaction by ^{1}H NMR (Fig. 1). It was thus not possible to determine BMDO conversion by ^{1}H NMR nor gravimetrically. Compared to the homopolymerization of MMA (E1MMA, Table 1), the addition of BMDO induced a decrease of the polymerization rate (Fig. 1), despite the lower particle size (45 *vs.* 67 nm, respectively, Table 1) and thus the higher number of particles (N_p) obtained in the presence of BMDO. The threefold increase of N_p cannot be clearly explained at this stage. The lower polymerization rate could be linked to the decrease of the apparent rate constant of propagation $\langle k_p \rangle$ considering the low k_p values of BMDO.[21] The monomer concentration into the particles could also be lower, and so could be the average number of radicals per particle.

^{1}H NMR analysis was then run on the dried extract of both latexes. The assignments proposed in Fig. 2 were based on a previously published ^{1}H NMR analysis of a copolymer obtained by bulk atom transfer radical copolymerization of MMA and BMDO.[13] The signal at 5.0 ppm is characteristic of protons next to the ester functions (signal *2*, Fig. 2). The presence of BMDO inserted units is further confirmed by the multiplicity of the signals associated to the protons *a* and *c* of the MMA units. Indeed, it is possible to distinguish the different triads in the copolymer according to the full investigation of the microstructure of P(MMA-*co*-BMDO) that has already been reported.[13]

Notably, while signal *a* appears as a single resonance in the spectrum of PMMA, it is displayed as four distinct resonances in the spectrum of the dry extract of E1BMDO (Fig. 2). This change confirms the formation of triads containing two MMA units and one BMDO unit. As expected, *c* is already displayed as three distinct resonances in the case of PMMA. The incorporation of BMDO is also shown by the appearance of several other signals in the 0.6–1.3 ppm region, characteristic of the methyl protons from a MMA unit in triads containing BMDO units (Fig. 2).[13]

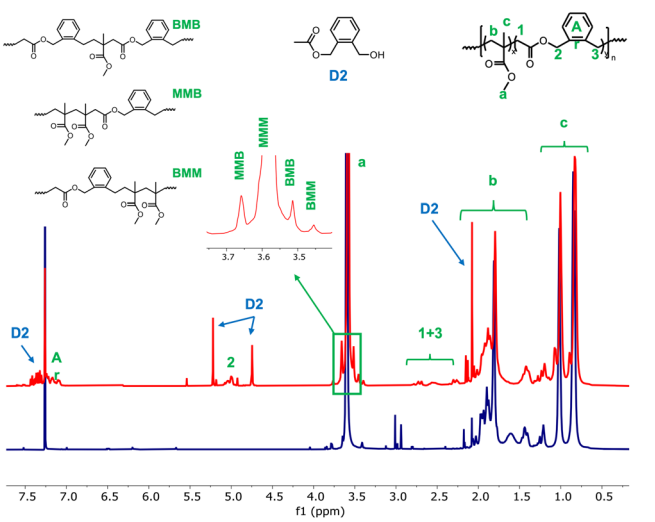


Fig. 2 ^{1}H NMR spectra of the dried extract of latexes E1BMDO (red) and E1MMA (blue) ($CDCl_3$, 256 scans). Assignments were made according to a previous report.[13] B stands for BMDO units and M for MMA units in a triad. D2 corresponds to one of the identified degradation products of BMDO (see ESI, Fig. S1†).

The composition of the copolymer was determined by integrating *2* at 5.0 ppm corresponding to two protons of a BMDO unit and signal *a* corresponding to the methoxy protons of MMA units (Fig. 2). According to the integration, 3.8 mol% of BMDO were incorporated into the PMMA chains. The rather low fraction of BMDO in the copolymer (F_{BMDO}) leads to small intensity and poorly defined signals and does not allow for an accurate signal integration. The F_{BMDO} values determined by NMR may therefore be slightly flawed. Nevertheless, the molar fraction of BMDO in the copolymer is lower than the initial molar fraction of BMDO in the monomer mixture. As mentioned above, a small part of BMDO degrades thus preventing full incorporation of the BMDO into the copolymer chains. In addition, copolymerization of CKAs with vinylic monomers generally leads to compositional drift and thus requires high amount of CKA in the initial feed.[8] For instance, the bulk radical copolymerization of MMA with BMDO ($f_{BMDO,0}$ = 0.5) conducted at 50 °C using AIBN leads to a copolymer containing only 13 mol% of BMDO units after 45 h of reaction,[5] in agreement with the reactivity ratios reported for these monomers (r_{BMDO} = 0.53; r_{MMA} = 1.96).[10] In emulsion polymerization, the reactivity ratios combined with the higher solubility of MMA in water probably lead to the formation of polymer chains richer in MMA units at the beginning the polymerization, or even to PMMA chains. Degradation of BMDO during polymerization, even if limited, could also lead to complete depletion of BMDO, resulting in the formation of PMMA chains.

SEC analysis performed on the dry extract gave additional information on the impact of BMDO during emulsion copolymerization with MMA. Indeed, the molar mass of the copolymer (M_n = 61 500 g mol^{-1}) is significantly lower than that of the PMMA homopolymer (M_n = 660 kg mol^{-1}) obtained from the emulsion polymerization of MMA under the same conditions. Additionally, the SEC trace is seemingly broader, as evidenced by an increased dispersity (5.8 for E1BMDO *vs.* 2.1 for E1MMA, Table 1). This feature may be the result of side reactions, including chain transfer, originated from BMDO itself[13] and/or its degradation products. Together with the impact of $\langle k_p \rangle$, all these events could also explain why the polymerization is slower in the presence of BMDO, despite lower particle sizes.

The multi-wavelength UV detector of the SEC can bring additional information on the chain composition (Fig. 3a). The carbonyl groups of the MMA units absorb at 217 nm and the aromatic protons from BMDO at 260 nm. The UV analysis was thus used to study whether BMDO was evenly distributed within the copolymer chains. The blue and red chromato-

Open Access Article. Published on 13 Feabhra 2023. Downloaded on 11/05/2026 16:37:04.
This article is licensed under a Creative Commons Attribution-NonCommercial 3.0 Unported Licence.

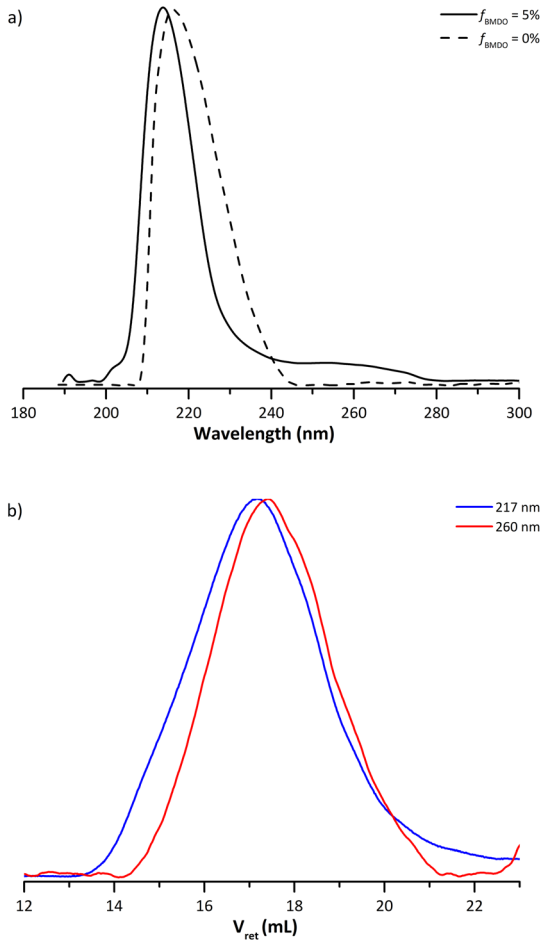


Fig. 3 (a) SEC traces from the UV detector obtained for the dried extract from experiments E1MMA ($f_{BMDO,0}$ = 0%) and E1BMDO ($f_{BMDO,0}$ = 5%, Table 1), normalized on the maximum of absorption. (b) SEC traces from the UV detector set at 217 nm (blue) and 260 nm (red) obtained for experiment E1BMDO (Table 1).

grams (Fig. 3b) do not fully overlap, indicating a slight difference in composition of the chains depending on the molar mass. The higher molar mass chains appear to contain more MMA units than the lower molar mass ones. In other words, lower molar mass chains are richer in BMDO units than higher molar mass chains. Most of the distribution nevertheless exhibit BMDO inserted units.

Eventually, the curve obtained from DSC analysis performed on the dried extract showed one thermal transition at 86 °C (Fig. 6) that is likely attributed to the T_g of P(MMA-*co*-BMDO) copolymer chains as the T_g of PBMDO[10] and of a PMMA sample prepared by emulsion polymerization[22] have been reported at 16 °C and 127 °C, respectively.

Overall, this first experiment conducted with BMDO indicated that very classical emulsion conditions could lead to the formation of a stable latex made of P(MMA-*co*-BMDO) copolymers. This copolymerization system was then investigated in more detail.

Influence of the pH on the copolymerization

As the stability of BMDO is conditioned to the absence of acidic species, we anticipated above that successful emulsion copolymerizations should take place at basic pH. In the following, we conducted emulsion copolymerizations using a different base while keeping the other experimental parameters constant (*i.e.*, temperature, initiator, solid content). The use of K_2CO_3 (E2BMDO, Table 1) instead of $NaHCO_3$ (E1BMDO, Table 1) had no significant influence on the conversion (94% and 99%, respectively) and particle size. In both experiments the conversion was high, the particles rather small and the final pH similar (~8). Nevertheless, the incorporation of BMDO was slightly increased as experiment E2BMDO yielded a copolymer with an average of 4.6 mol% of BMDO units in the chains. A third experiment was performed without adding any base to the medium (E3BMDO, Table 1). Only 73% conversion of MMA was achieved after 90 min and barely any BMDO was incorporated in the copolymers. The final pH dropped to 2.3. It is very likely that, in this case, BMDO was hydrolyzed at a much faster rate compared to the experiments conducted in the presence of either $NaHCO_3$ or K_2CO_3. The use of a base is thus of paramount importance to achieve a successful copolymerization of MMA with BMDO under aqueous emulsion conditions. $NaHCO_3$ was selected for the following experiments, as it represented the better option to achieve full conversion of MMA with high incorporation of BMDO units.

Influence of the initial fraction of BMDO in the monomer feed

In the next series of experiments the initial fraction of BMDO in the feed of monomers was varied between 2 and 10 mol% (Table 1). The syntheses all led to nearly full conversion of MMA (>98%) in less than 90 min. Stable latexes were formed in every case (Fig. 4). According to the DLS analysis, the hydrodynamic diameter of the particles decreased with the increase in BMDO (from 67 nm to 45 nm, for $f_{BMDO,0}$ = 0 and 2%,

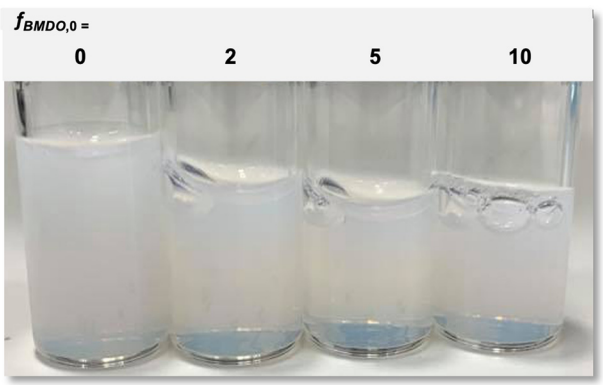


Fig. 4 Photos of the latexes prepared with different initial molar fraction of BMDO. From left to right: experiments E1MMA, $f_{BMDO,0}$ = 0%; E4BMDO, $f_{BMDO,0}$ = 2%; E1BMDO, $f_{BMDO,0}$ = 5%; E5BMDO, $f_{BMDO,0}$ = 10% (Table 1).

This journal is © The Royal Society of Chemistry 2023

Open Access Article. Published on 13 Feabhra 2023. Downloaded on 11/05/2026 16:37:04.
This article is licensed under a Creative Commons Attribution-NonCommercial 3.0 Unported Licence.

respectively, Table 1), which translates in the aspect of latex that was less turbid (Fig. 4). The hydrodynamic diameter did not vary significantly when the BMDO content further increased (45 nm to 47 nm, for $f_{BMDO,0}$ = 2 and 10%, Table 1).

The BMDO content in the copolymer (F_{BMDO}), determined by ^{1}H NMR, increased with the initial fraction of BMDO. However, the more BMDO in the initial feed, the less is proportionally incorporated into the chains. While an initial fraction of BMDO of 2 mol% (E4BMDO, Table 1) led to 100% of the BMDO being incorporated in the copolymer (F_{BMDO} = 2%), the synthesis starting with 10 mol% of BMDO (E5BMDO, Table 1) led to the incorporation of 64% of the BMDO in the copolymer (F_{BMDO} = 6.4%). Yet, thanks to the emulsion polymerization process, an incorporation of 64% into the copolymer after only 2 h is still in stark contrast with what can be obtained for the bulk copolymerization of BMDO with MMA. Indeed, as mentioned above, the bulk copolymerization of MMA with BMDO (50/50 mol/mol) conducted at 50 °C using AIBN led to a copolymer containing only 13 mol% of BMDO units after 45 h of reaction.[5,13]

The molar mass of the copolymer significantly decreased as the amount of BMDO increased. The presence of secondary backbiting reactions due to the insertion of BMDO units in the chains could explain this phenomenon.[10] It is nevertheless difficult to conclude on the evolution of the dispersity. It tends to increase with the addition of BMDO, except for the copolymer formed in the presence of 10 mol% BMDO (Table 1). Indeed, the SEC chromatogram of this copolymer does not exhibit a shoulder towards the high molar masses, unlike copolymers formed with 2 and 5 mol% of BMDO in the initial feed (Fig. 5a). Furthermore, the UV chromatograms at 217 nm and 260 nm are perfectly superimposed for this copolymer, attesting that all the chains would contain an even fraction of BMDO (Fig. 5b) contrary to what was shown for the copolymer formed with 5 mol% of BMDO (Fig. 3b).

The DSC curves also showed that for all the samples containing BMDO units, a single T_g could be detected (Fig. 6). This T_g decreases when the BMDO content increases (Table 1). Again, these results are in good agreement with what was expected from the T_g of the respective homopolymers.[10,22] One can note that the width of this transition is increasing as the number of incorporated BMDO units increases, which seems to indicate a stronger heterogeneity in the polymer chains, consistent with the reactivity ratios of BMDO and MMA.

To better comprehend the evolution of T_g with BMDO content in the copolymer, the experimental values were compared to those obtained by calculation according to Fox equation (eqn (1)).[23] Although the T_g of the copolymers was systematically lower than predicted (Fig. 7), the experimental trend follows the theoretical one.

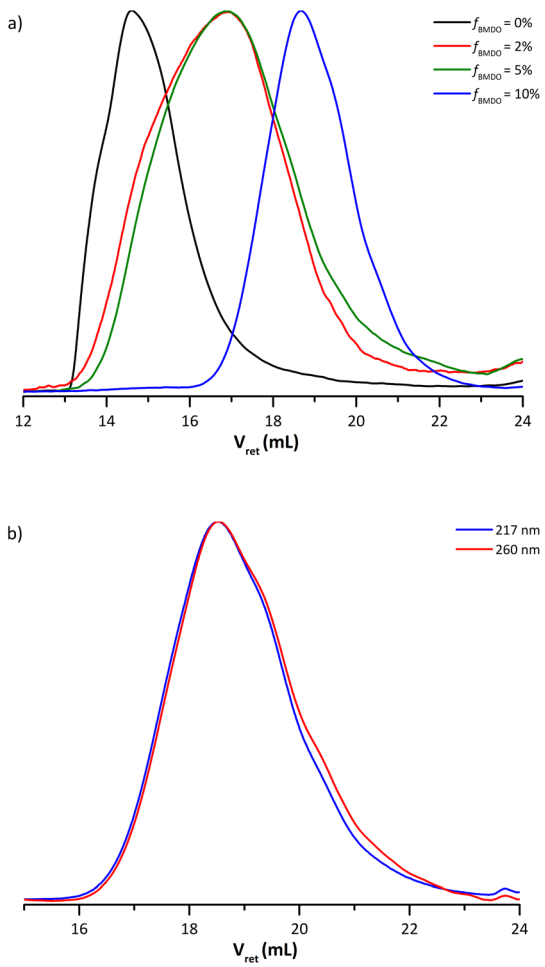


Fig. 5 (a) Molar mass distributions of dry extracts for latexes E4BMDO (red), E5BMDO (blue), E1BMDO (green) and EMMA1 (black) (Table 1). (b) UV chromatograms from SEC-THF analysis at 217 nm (blue) and 260 nm (red) for the dried latex E5BMDO.

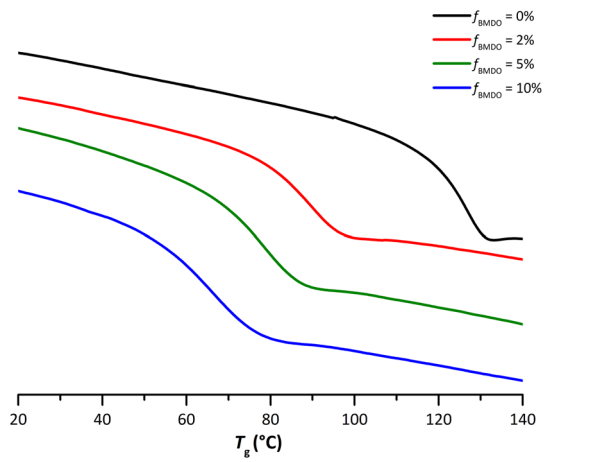


Fig. 6 Thermograms from DSC analyses performed on the dried extract of latexes of PMMA (E1MMA) and P(MMA-*co*-BMDO) with increasing amounts of BMDO: $f_{BMDO,0}$ = 2% (E4BMDO), $f_{BMDO,0}$ = 5% (E1BMDO), $f_{BMDO,0}$ = 10% (E5BMDO) (Table 1).

Open Access Article. Published on 13 Feabhra 2023. Downloaded on 11/05/2026 16:37:04.
This article is licensed under a Creative Commons Attribution-NonCommercial 3.0 Unported Licence.

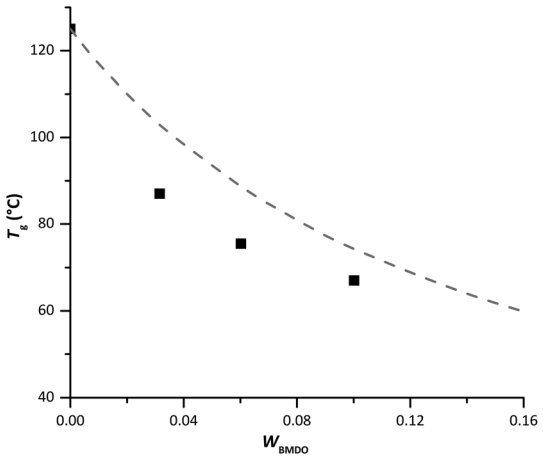


Fig. 7 Evolution of experimental (square) and theoretical (dashed line) T_g with the mass fraction of BMDO. Theoretical values were calculated with the Fox equation.

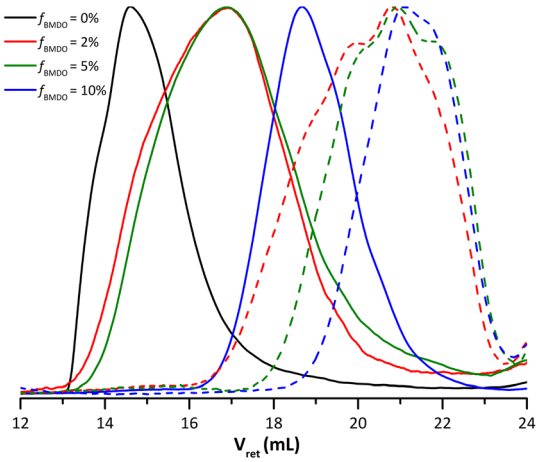
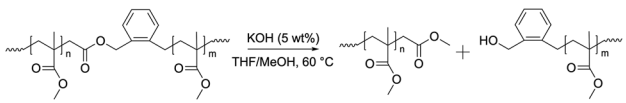


Fig. 8 Molar mass distribution of dry extracts (plain lines) and degradation products (dashed lines) obtained by degradation of dry extracts using KOH in THF/MeOH for latexes synthesized with varying fraction of BMDO in the feed of monomers (black: E1MMA; red: E4BMDO; green: E1BMDO; blue: E5BMDO, Table 2).

Degradation of the P(MMA-*co*-BMDO) copolymers

The degradation of the P(MMA-*co*-BMDO) copolymers was probed on the dry extract of the latexes. Several methods can be used to degrade CKA-containing vinyl copolymers. Yet, the most convenient and broadly used technique is the degradation under accelerated hydrolytic conditions, *i.e.* in basic conditions using a strong base such as KOH.[11,24,25] Dry extracts were thus dissolved in THF and degraded by adding a solution of potassium hydroxide in methanol (Scheme 2).

This protocol was first applied to the PMMA sample. As expected, its molar mass did not change significantly after treatment of the dry extract by KOH (from 660 kg mol^{-1} initially, to 632 kg mol^{-1} after degradation, Table 2). On the other hand, SEC traces corresponding to experiments performed in the presence of BMDO shifted toward the lower molar masses after treatment of the dried extracts with KOH in THF/MeOH (Fig. 8). All copolymers exhibited a loss of molar mass of more than 80% (Table 2).



Scheme 2 Degradation of P(MMA-*co*-BMDO) copolymers under accelerated conditions in the presence of KOH.

Those results proved the degradability of the copolymers and confirmed the incorporation of BMDO units. It is worth mentioning that molar mass values obtained remain higher than the calculated theoretical ones. Several factors may explain this observation. The rROP of CKAs is known to lead to some ring retention.[8] The inserted ring-closed BMDO units would not degrade. The presence of such units can usually be assessed by ^{13}C NMR analysis. However, in our case, the relatively low BMDO content did not allow us obtaining exploitable data by this technique. It is also possible that the mole fraction of BMDO in the copolymer, as determined by NMR, is overestimated due to the inaccuracy of the ^{1}H NMR signal integration. Eventually, it is very likely that the distribution of the degradable ester functions along the chain is uneven resulting in asymmetrical degradation products.[26] Nevertheless, the dispersity tends toward 2 when increasing the BMDO content (Table 2), which is indeed what one would expect for a statistical polymer degradation. In any case, the results of this degradation proved that we did obtain stable latexes made of degradable PMMA-based polymers.

Table 2 Results of the degradation of dry extracts in THF/MeOH/KOH medium

Run	F_{BMDO} [a] (%)	M_n [b] (kg mol^{-1})	$Đ$	$M_{n,deg}^{th}$ [c] (kg mol^{-1})	$M_{n,deg}^{exp}$ [b] (kg mol^{-1})	$Đ$	% M_n loss
E1MMA	0	660	2.6	660	632	2.9	4
E4BMDO	1.9	98.2	5.9	5.1	8.6	3.1	91
E1BMDO	3.8	61.5	5.8	2.7	5.9	2.5	90
E5BMDO	6.4	28.5	1.9	1.6	5.2	1.9	82

[a] Average molar fraction of BMDO in the copolymer. [b] Experimental number-average molar mass determined by SEC-THF using a calibration based on PMMA standards. [c] Theoretical number-average molar mass calculated according to the following equation: $M_{n,deg}^{th} = M_{MMA} \times (1/F_{BMDO} - 1) + M_{BMDO}$.

This journal is © The Royal Society of Chemistry 2023

Open Access Article. Published on 13 Feabhra 2023. Downloaded on 11/05/2026 16:37:04.
This article is licensed under a Creative Commons Attribution-NonCommercial 3.0 Unported Licence.

Conclusion

Ab initio aqueous emulsion copolymerization of BMDO with MMA was performed for the first time and provided a straightforward route for the synthesis of nanoparticles made of degradable vinyl polymers. Indeed, very conventional conditions allowed yielding stable latexes made of P(MMA-*co*-BMDO) copolymers in a simple and fast process in water compared to the already published studies published so far on solution or bulk copolymerization. Emulsion copolymerization proved to be successful only in basic media, which is probably due to an increase rate of hydrolysis of BMDO under acidic conditions. By adjusting the pH to basic conditions with $NaHCO_3$, the incorporation rates of BMDO varied from 2 to 6.4 mol% depending on the initial BMDO fraction. The incorporation of BMDO units was however higher than what is obtained in the case of homogeneous copolymerization. Eventually, all copolymers could be degraded under accelerated conditions with a loss of molar mass of at least 80% for every BMDO-containing copolymer.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

The authors acknowledge the financial support from the Agence Nationale de la Recherche (grant number ANR-18-CE06-0014 CKAPART).

References

1 V. Delplace and J. Nicolas, *Nat. Chem.*, 2015, **7**, 771–784.
2 P. Eyerer and A. Franck, in *Polymers – Opportunities and Risks I: General and Environmental Aspects*, ed. P. Eyerer, Springer, Berlin, Heidelberg, 2010, pp. 391–427.
3 *Nature*, 2021, **590**, 363–364.
4 M. Häußler, M. Eck, D. Rothauer and S. Mecking, *Nature*, 2021, **590**, 423–427.
5 W. J. Bailey, Z. Ni and S. R. Wu, *Macromolecules*, 1982, **15**, 711–714.
6 W. J. Bailey, S.-R. Wu and Z. Ni, *Makromol. Chem.*, 1982, **183**, 1913–1920.
7 W. J. Bailey, *Makromol. Chem.*, 1985, **13**, 171–190.
8 A. Tardy, J. Nicolas, D. Gigmes, C. Lefay and Y. Guillaneuf, *Chem. Rev.*, 2017, **117**, 1319–1406.
9 A. Tardy, N. Gil, C. M. Plummer, C. Zhu, S. Harrisson, D. Siri, J. Nicolas, D. Gigmes, Y. Guillaneuf and C. Lefay, *Polym. Chem.*, 2020, **11**, 7159–7169.
10 H. Wickel and S. Agarwal, *Macromolecules*, 2003, **36**, 6152–6159.
11 G. G. d'Ayala, M. Malinconico, P. Laurienzo, A. Tardy, Y. Guillaneuf, M. Lansalot, F. D'Agosto and B. Charleux, *J. Polym. Sci., Part A: Polym. Chem.*, 2014, **52**, 104–111.
12 C. Riachi, N. Schüwer and H.-A. Klok, *Macromolecules*, 2009, **42**, 8076–8081.
13 H. Wickel, S. Agarwal and A. Greiner, *Macromolecules*, 2003, **36**, 2397–2403.
14 W. J. Bailey, Z. Ni and S.-R. Wu, *J. Polym. Sci., Polym. Chem. Ed.*, 1982, **20**, 3021–3030.
15 M. C. D. Carter, A. Hejl, S. Woodfin, B. Einsla, M. Janco, J. DeFelippis, R. J. Cooper and R. C. Even, *ACS Macro Lett.*, 2021, **10**, 591–597.
16 M. C. D. Carter, J. DeFelippis, R. C. Even and A. Hejl, United States, US11111328B2, 2021.
17 J. M. Siebert, D. Baumann, A. Zeller, V. Mailänder and K. Landfester, *Macromol. Biosci.*, 2012, **12**, 165–175.
18 A. J. Kresge and T. S. Straub, *J. Am. Chem. Soc.*, 1983, **105**, 3957–3961.
19 J. M. Asua, *Prog. Polym. Sci.*, 2002, **27**, 1283–1346.
20 S. Agarwal, R. Kumar, T. Kissel and R. Reul, *Polym. J.*, 2009, **41**, 650–660.
21 A. Tardy, J.-C. Honoré, D. Siri, J. Nicolas, D. Gigmes, C. Lefay and Y. Guillaneuf, *Polym. Chem.*, 2017, **8**, 5139–5147.
22 J. G. Tsavalas and D. C. Sundberg, *Langmuir*, 2010, **26**, 6960–6966.
23 T. G. Fox and S. Loshaek, *J. Polym. Sci.*, 1955, **15**, 371–390.
24 G. G. Hedir, C. A. Bell, N. S. Ieong, E. Chapman, I. R. Collins, R. K. O'Reilly and A. P. Dove, *Macromolecules*, 2014, **47**, 2847–2852.
25 C. Zhu and J. Nicolas, *Polym. Chem.*, 2021, **12**, 594–607.
26 D. Gigmes, P. H. M. V. Steenberge, D. Siri, D. R. D'hooge, Y. Guillaneuf and C. Lefay, *Macromol. Rapid Commun.*, 2018, **39**, 1800193.
27 B. R. Kordes, L. Ascherl, C. Rüdinger, T. Melchin and S. Agarwal, *Macromolecules*, 2023, **56**, 1033–1044.