Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information to:

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,*] Muriel Lansalot[a,*]

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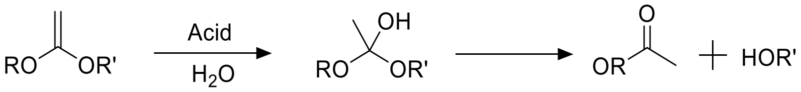
[a] *Univ Lyon, Université Claude Bernard Lyon 1, CPE Lyon, CNRS, UMR 5128, Catalysis, Polymerization, Processes and Materials (CP2M), 43 Bd du 11 novembre 1918, 69616 Villeurbanne, France.*
[b] *Aix Marseille Univ, CNRS, Institut de Chimie Radicalaire, UMR 7273, Marseille, France.*
[c] *Université Paris-Saclay,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

‡ These authors contributed to the work equally.

1. Hydrolysis of BMDO

Prior to the emulsion copolymerization experiments, we tried to study the hydrolysis of BMDO in aqueous dispersed media. If the aqueous sensitivity of CKAs is known and acknowledged as a drawback to its use in aqueous media, no specific study has yet focused on the identification of the products of CKAs hydrolysis or on the degradation kinetics. According to the work of Kresge *et al.*,[1] hydrolysis of ketene acetals is acid-catalyzed and happens in a two-step mechanism: acid-catalyzed hydration of the carbon-carbon double bond followed by elimination of one of the alkoxy groups (Scheme S1). Experimentally, degradation of the ketene acetal groups mainly occurs in acidic conditions. In addition, it was observed that cyclic derivates were hydrolyzed at a faster rate than non-cyclic ones.[1]



Scheme 1. Proposed mechanism for the acid-catalyzed hydrolysis of ketene acetal functions.[1]

BMDO was previously found to quantitatively degrade when dissolved in “as received” DMF.[2] It was stated that this degradation was due to the presence of acidic impurities that could add on the double bond of BMDO to yield an orthoester (D1, Figure S1).

Very briefly, we found out that BMDO takes the form of a solid that alters upon daily exposure to air to become slimy clusters, indicating a particular sensitivity to air moisture. We thus recovered the oily part to identify the degradation products. Figure S1 presents the ^{1}H NMR spectra of pure BMDO and of the oily part resulting from exposure to air. If the signals attributed to D1 were indeed present and no residual BMDO could be detected, other unassigned signals could also be found (Figure S1). Acknowledging the mechanism associated with the acid-catalyzed hydrolysis of ketene acetals (Scheme S1), we assumed that D1 could be the intermediate species on the way to the opened hydrolyzed form D2 (Figure S1). Attributions of the signals according to simulation from Chemdraw® software and to their integration tend to confirm the presence of both D1 and D2 in the degraded BMDO. ^{13}C NMR analyses and DEPT 135 analysis were performed on partially degraded BMDO (Figure S2). The obtained spectra were in agreement with the presence of the two degradation products D1 and D2. Notably, the presence of negative signals at 172 ppm and 117 ppm on the DEPT 135 spectrum showed the presence of the quaternary carbons 14 and 10 attributed to the ester of D2 and the orthoester of D1, respectively.

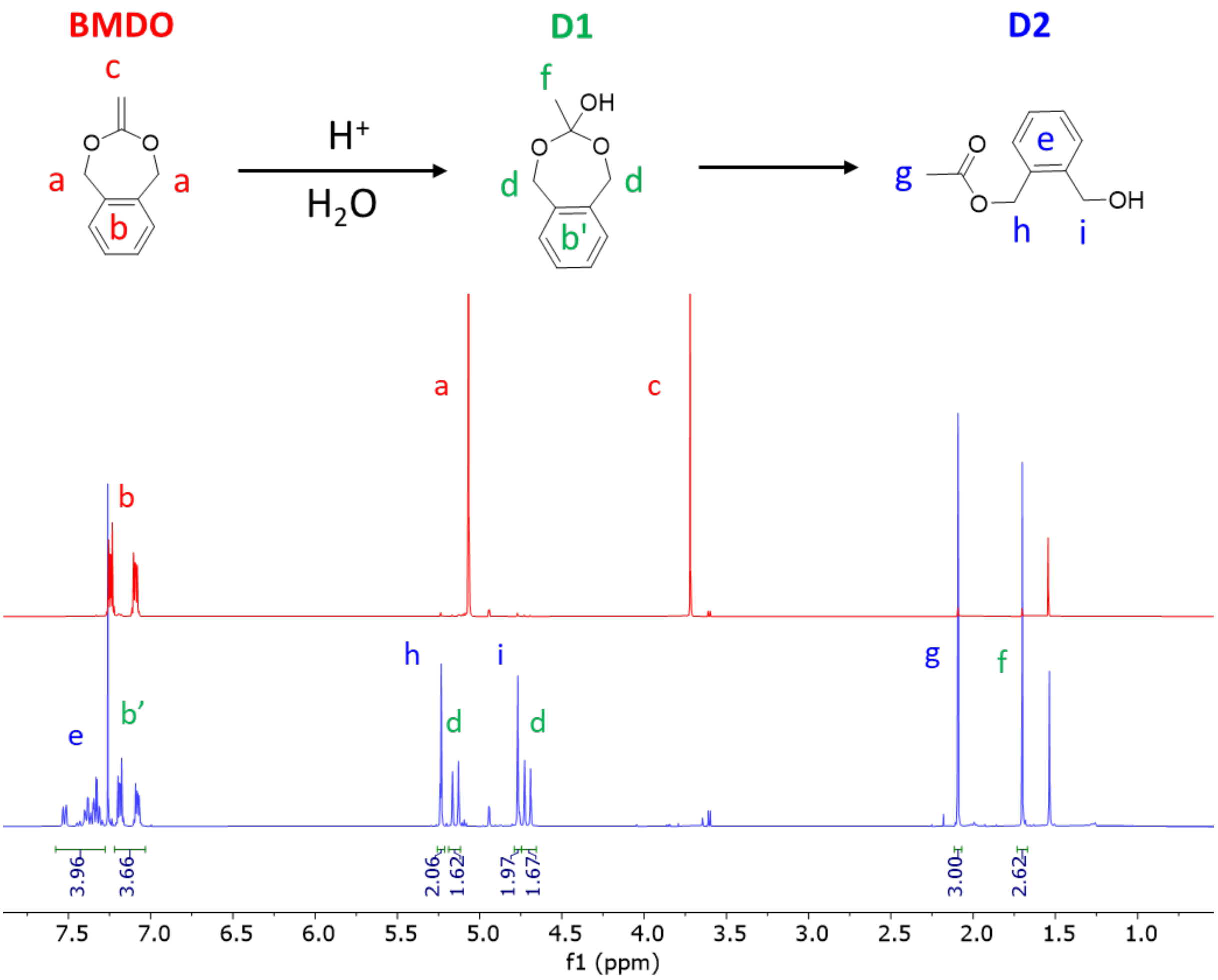


Figure S1. Suggested route for the hydrolysis of BMDO leading to D1 and D2 and ^{1}H NMR spectra ($CDCl_3$, 64 scans) of pure BMDO (red) and degraded BMDO (blue).

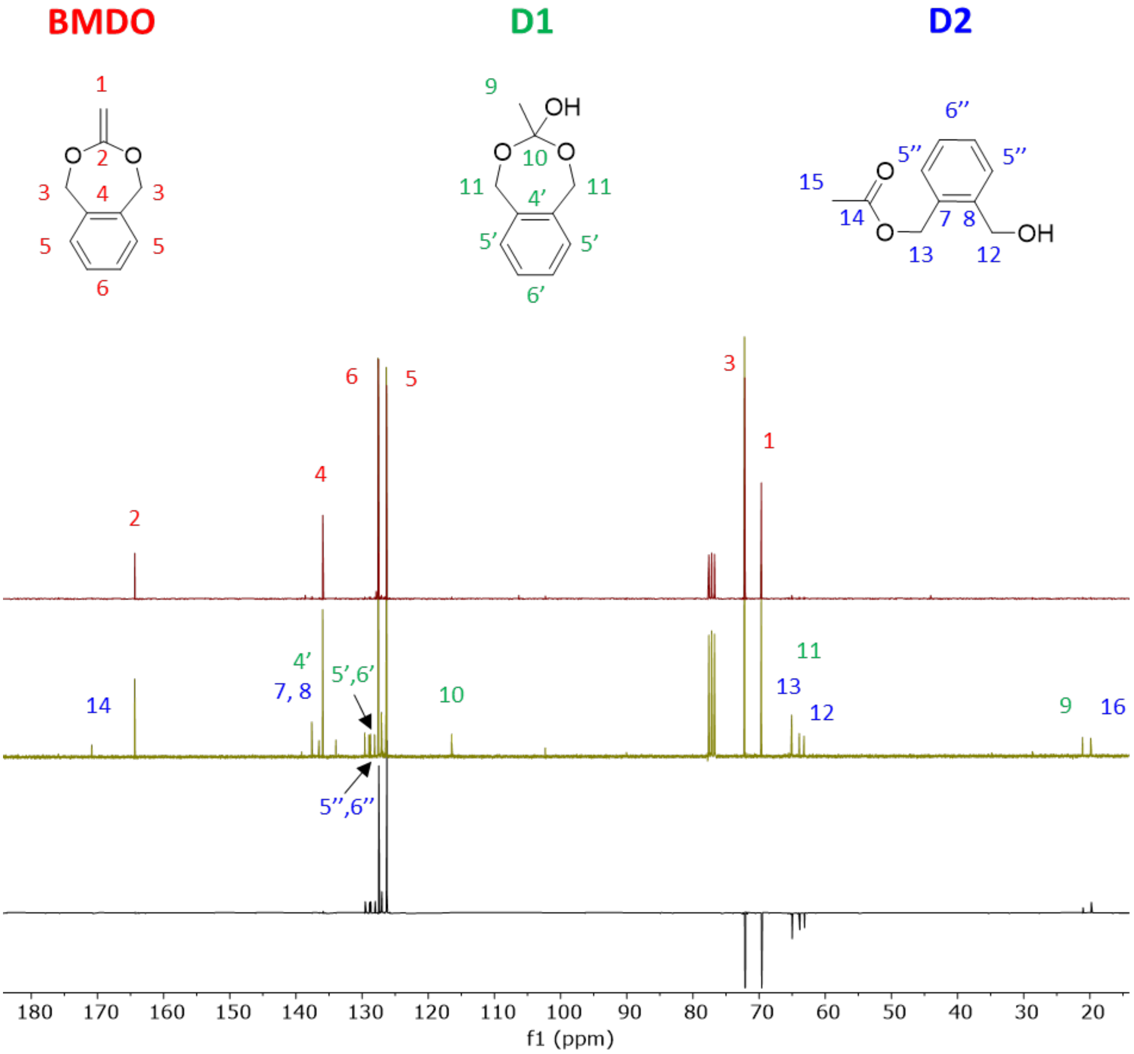


Figure S2. ^{13}C NMR spectra of pure BMDO (red) and partially degraded BMDO (yellow) and DEPT 135 analysis of the degraded BMDO (black) ($CDCl_3$, 2048 scans).

To assess the features of BMDO hydrolysis further and knowing it could be degraded by air moisture, accelerated hydrolysis conditions were considered to estimate whether D1 was indeed formed first to eventually lead to D2. BMDO was heated at 60 °C and the degradation was followed by NMR and gravimetry. Figure S3 shows the ^{1}H NMR spectra of the samples collected at different times. After 2 h, BMDO was completely degraded as shown by the disappearance of the characteristic signals of the presence of the double bond at 5.05 ppm and 3.8 ppm, and by the appearance of the characteristic signals of both D1 (singlet at 1.7 ppm, doublets at 4.7 and 5.1 ppm) and D2 (aromatics above 7.3 ppm, singlet at 2.1 ppm). After 24 h, the signals attributed to D1 started vanishing and completely disappeared after 72 h. This feature could be the results of the mechanism stated in Scheme S1 as D1 would only be the intermediate state toward D2 and would thus continue to degrade even once all the BMDO is consumed.

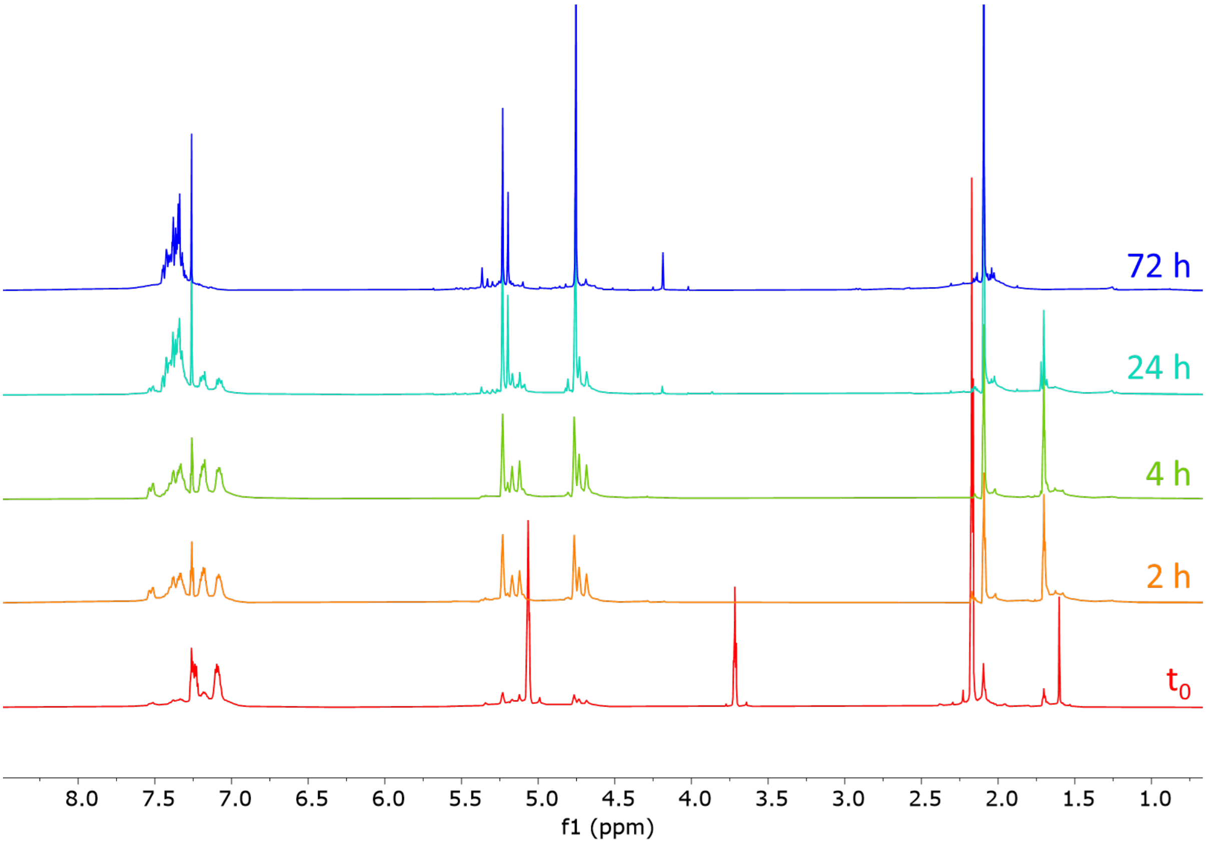


Figure S3. Evolution of the ^{1}H NMR spectra for a sample of BMDO heated at 60 °C as a function of time ($CDCl_3$, 64 scans).

Gravimetric analysis was also led in parallel to evaluate mass loss during the process and showed that volatile species were present. As shown by Figure S4, 44 wt % of the sample has evaporated after 24 h in the oven and 69 wt % after 72 h. It is thus difficult to assert that BMDO hydrolyzes following the mechanism suggested in Figure S1 as the disappearance of the signals associated with D1 are also likely due to its volatility. Accordingly, D1 and D2 might also be the products of two distinct and competitive mechanisms occurring concomitantly.

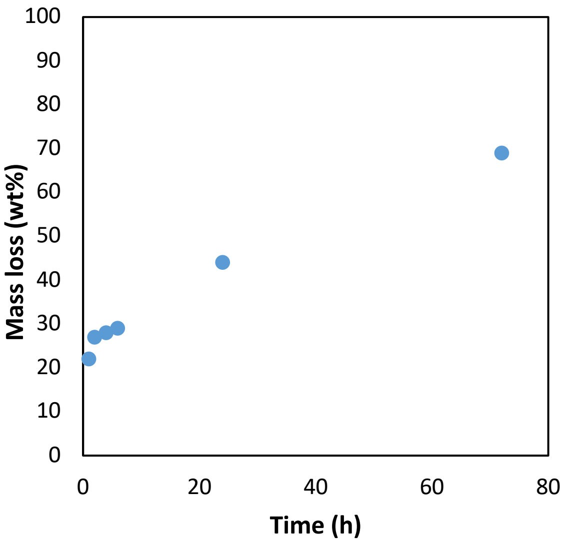


Figure S4. Evolution of the mass loss during degradation of BMDO at 60 °C.

References

1 A. J. Kresge and T. S. Straub, *J. Am. Chem. Soc.*, 1983, 105, 3957–3961.
2 G. G. d’Ayala, M. Malinconico, P. Laurienzo, A. Tardy, Y. Guillaneuf, M. Lansalot, F. D’Agosto and B. Charleux, *J. Polym. Sci. A: Polym. Chem.*, 2014, 52, 104–111.