One-Step Synthesis of Degradable Vinylic Polymer-Based Latexes via Aqueous Radical Emulsion Polymerization

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RESEARCH ARTICLE

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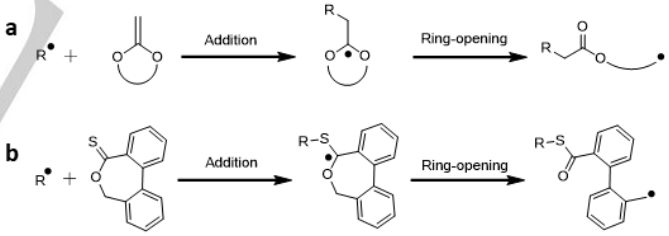
Abstract: Aqueous emulsion copolymerizations of dibenzo[c,e]oxepane-5-thione (DOT) were performed with *n*-butyl acrylate (BA), styrene (S) and a combination of both. In all cases, stable latexes were obtained in less than two hours under conventional conditions; that is in the presence of sodium dodecyl sulfate (SDS) used as surfactant and potassium persulfate (KPS) as initiator. A limited solubility of DOT in BA was observed compared to S, yielding to a more homogeneous integration of DOT units in the PS latex. In both cases, the copolymer could be easily degraded under basic conditions. Emulsion terpolymerization between DOT, BA and S allowed to produce stable latexes not only composed of degradable chains but also featuring a broad range of glass transition temperatures.

Introduction

The development of new synthetic routes to produce degradable and/or recyclable/reusable polymer materials has seen a surge of interest lately for their potential application as biomaterials or to address environmental concerns.[1,2] One possible strategy is the incorporation of specific chemical bonds into the polymer backbone. Upon external stimuli such as pH, chemical reagents, enzymes or light, these bonds break, resulting in polymer chains with lower molar masses. Such bonds can intrinsically be part of the chemical structure of the polymer chains like in polyesters that is a very well-known representative class of recyclable commodity polymers.[3] However, for vinylic polymers produced by the formation of carbon-carbon bonds, such as those obtained by radical polymerization, the challenges may consist in finding appropriate comonomers that could not only allow the easy and controllable introduction of these cleavable chemical groups along the chains, but also be compatible with the main processes used to produce the corresponding polymers.

The design of a specific class of monomers known as cyclic ketene acetals (CKAs) has made possible the synthesis of ester-containing vinylic polymers through radical polymerization.[4] CKAs are known to copolymerize with traditional vinylic monomers through radical ring-opening polymerization (rROP) (Scheme 1a).[5,6] The main advantage of such a process is to obtain a vinylic copolymer with properties similar to those of the vinylic homopolymer, but with the ability to be degraded into oligomers by cleavage of the ester functions distributed along the backbone. The possibility of forming reactive oligomers being reprocessable into valuable polymers is even more interesting for recyclability in the context of circular economy. Even though CKAs have been known since the pioneering work of Bailey in the 80's,[7] rROP has only recently attracted extensive interest and has mainly been used for the synthesis of biodegradable polymers for biomedical applications.[8] However, the use of CKAs for the synthesis of degradable vinylic polymers remains relatively restrained due to the inherent issues related to the chemical nature of CKAs.[9] Indeed, their low reactivity toward traditional vinylic monomers (notably toward more activated monomers such as (meth)acrylics and styrenics) lessens the range of accessible types of polymers.[4,9] In addition, CKAs exhibit competing radical mechanism between radical ring-opening and ring-retaining propagation; the latter leading to non-degradable ketal units in the chain.



Scheme 1. Radical ring-opening mechanism in the case of (a) CKAs and (b) DOT.

Last but not the least is the strong intolerance of CKAs to aqueous media as they are rapidly hydrolyzed.[10] This is indeed a major drawback for aqueous emulsion polymerization, one of the main production processes of polymers by radical polymerization, that leads to high solids content dispersions of polymer particles. The fact that, after 40 years exploring all types of radical (co)polymerizations of CKAs, only two examples of polymerization in dispersed aqueous media can be found, attests to the difficulty of the task.[11,12]

As an alternative to CKAs, the groups of Roth[13] and Gutekunst[14] proposed to use the biphenylic cyclic thionolactone: dibenzo[c,e]oxepane-5-thione (DOT, Scheme 1b) capable of sustaining a ring-opening mechanism to afford in-chain thioester functions. Compared to the radical ring-opening of CKAs, DOT cannot lead to any type of ring-retention meaning that all the polymerized cyclic monomers will be converted to in-chain

thioester functions. Furthermore, the authors reckon that, unlike CKAs, DOT could present favorable reactivity ratios with styrene or (meth)acrylates.

Both teams identified acrylates, among other comonomers, to be particularly suitable for copolymerization with DOT. Bingham and coworkers successfully copolymerized DOT with methyl acrylate (MA), poly(ethylene glycol) methyl ether acrylate (PEGA), acrylonitrile and *N,N*-dimethyl acrylamide through organic solution radical polymerization reaching high conversions for each monomer.[13,15] Additionally, they successfully showed that reversible-deactivation radical polymerization *via* reversible addition-fragmentation chain transfer (RAFT) can be applied to DOT copolymerizations. In parallel, Gutekunst and coworkers successfully used DOT for RAFT copolymerization in dimethylformamide with both *n*-butyl acrylate (BA) and *tert*-butyl acrylate, and showed that DOT was consumed more rapidly than the acrylates leading to copolymers with a slight gradient of comonomer distribution.[14] Eventually, the copolymers all proved to be able to degrade through several techniques ranging from methanolysis in sodium methoxide[14] to hydrolysis in aqueous NaOH solution [15] and to aminolysis with isopropylamine.[13,15,16] All degradations were performed at room temperature. Later, Roth and coworkers extended the range of comonomers able to copolymerize with DOT to maleimides to afford alternating copolymers in dimethylsulfoxide, acrylonitrile or aniline, with tunable degradation.[16]

However, the copolymerization with other vinylic monomers proved to be either difficult or impossible. Notably, Bingham *et al.* found that DOT inhibits radical polymerization of vinyl acetate and *N*-vinylcarbazole.[13] During copolymerization with methyl methacrylate, DOT remains a bystander, whereas it was originally found to retard the polymerization of styrene without being incorporated.[13] However, we recently showed that DOT and styrene could be efficiently copolymerized under appropriate experimental conditions. At high temperature (*i.e.*, 150 °C), the reactivity ratios are close to 1, allowing a statistical incorporation of the two monomers regardless of the feed ratio. At lower temperature, only a feed ratio of 5 mol% of DOT could be used due to the lower reactivity of DOT.[17] The development of this new type of monomer opens a completely new field for the synthesis of degradable polymer materials. While its use remains yet to be fully investigated, the high stability of DOT in ambient conditions, and most of all its stability toward hydrolysis, is a significant advantage compared to CKAs when considering syntheses in aqueous media and particularly their transposition to emulsion polymerization. Besides its fundamental interest, the success of such transposition would put forward an original way of introducing degradability into latex technology and related applications. It could additionally give access to original degradable particles complementary to polyester counterparts, yet obtained by tricky nanoprecipitation methods of preformed polyester chains, which usually lead to low solids content dispersions.[18,19]

Building on the very recent works with DOT mentioned above, we anticipated that (co)polymerizations involving DOT would provide a sustainable system for the formation of degradable particles obtained by aqueous emulsion polymerization. Since BA has shown good reactivity with DOT[14] and is one of the most widely used vinylic monomers for aqueous emulsion, the copolymerization of DOT and BA under emulsion conditions is first addressed in the present paper. Furthermore, while the copolymerization of DOT with styrene was shown to occur efficiently under harsh conditions in homogeneous media (T = 150 °C),[17] we also anticipated in a second step that emulsion copolymerization of DOT and styrene could benefit from a compartmentalization of the polymerization into nanoparticles in an emulsion process and allow successful copolymerization under milder conditions. Finally, terpolymerizations of DOT with styrene and BA were studied to demonstrate the ability of DOT to implement the synthesis of degradable polymers with tuneable thermal properties.

Results and Discussion

Emulsion copolymerization of DOT with *n*-butyl acrylate. *Preliminary experiments*. With the aim of identifying the simplest system possible, aqueous emulsion copolymerizations of DOT and BA were thus conducted using the most basic *ab initio* batch system, with sodium dodecyl sulfate (SDS) as surfactant and potassium persulfate (KPS) as the sole water-soluble initiator. In a first experiment, a mixture of BA containing 5 mol% of DOT was prepared prior to its addition to the aqueous medium to target a 18 wt% solids content (A1, Table 1). Despite stirring, the monomer mixture remained biphasic as BA seemed to be unable to fully solubilize DOT, the latter remaining visible as a fine solid. After addition of the aqueous phase, the polymerization carried out at 80 °C led to a white milky dispersion in about one hour (Figure 1). Coagulum was however formed, to the extent of 18 wt% of initial monomer mass preventing an accurate conversion of BA through gravimetric analysis (estimated to 66% for the stable latex fraction). The success of an emulsion polymerization is subjected to the use of a hydrophobic monomer with some solubility in water, even very low. This not only ensures an efficient initiation in water but also its diffusion from the monomer droplet reservoirs to the nucleated particles through the aqueous phase. While this is the case for BA, the very low solubility in water for DOT, combined with its low solubility in BA, may not allow for an efficient diffusion of both monomers through the water phase leading to some bulk copolymerization. Nonetheless, as shown by DLS analyses of the filtered recovered latex, the synthesis led to stable monodisperse particles of about 110 nm in diameter (see also the cryo-TEM image in Figure 1).

^{1}H NMR spectrum of the dry extract of this latex is presented in Figure 2. Compared to DOT monomer, the lower chemical shift and the broadening of the signals corresponding to the aromatic protons confirm the presence of ring-opened DOT units in the chains. This spectrum can be compared to that of PBA chains obtained from the dry extract of a latex synthesized under the exact same conditions but without DOT (A0 in Table 1, stable latex, particle diameter by cryo-TEM of 103 nm). A shoulder (*e'*) broadens the signal of the methylene protons adjacent to the ester moiety in BA units at ca. 4 ppm. In accordance with previous work on DOT copolymerization with acrylates,[13,14] this signal is attributed to the proton corresponding to a BA unit next to a thioester group. The presence of additional aromatic resonances in the spectrum corresponding to latex A1 and the resonance assignments made in Figure 2 indeed confirm the incorporation of DOT into the PBA backbone during copolymerization.

Table 1. *Ab initio* and sonicated-assisted emulsion copolymerization of DOT and BA. Experimental conditions, results and molar mass characteristics of the copolymers and their degradation products.

Run	f_{DOT} [a] (%)	τ_{th} [b] (wt%)	t (min)	τ_s [b] (wt%)	τ_c [c] (wt%)	Yield BA [d] (%)	F_{DOT} [e] (%)	T_g [f] (°C)	Z_{ave} [g] (nm) PDI	M_n [h] (kg mol^{-1}) $Đ$	Degradation products depending on degradation method				
												dry extract treated with TBD	dry extract treated with IPA	latex treated with TBD	
											$M_{n,deg}$ th [i] (kg mol^{-1})	M_n [h] (kg mol^{-1}) $Đ$	M_n [h] (kg mol^{-1}) $Đ$	M_n [h] (kg mol^{-1}) $Đ$	Z_{ave} (nm) PDI
Conventional emulsion polymerizations:															
A1	4.8	17.5	120	12.5	18.0	66	3.2	n.d.	110 0.01	161 4.0	3.1	n.d.	16.4 3.9	n.d.	n.d.
A0	-	17.5	65	17.7	-	99	-	-49	61 0.04	insoluble	Insoluble	n.d.	insoluble	n.d.	n.d.
Sonicated-assisted experiments:															
A1*	1.0	10.7	60	10.5	-	98	0.8	-47	60 0.02	360 3.0	15.5	15.7 6.9	30.1 7.7	18.8 8.2	108 0.29
A2*	2.0	10.0	70	9.7	-	97	1.8	-45	52 0.02	330 3.0	7.3	8.8 6.4	10.1 7.5	8.9 7.8	75 0.21
A3*	3.0	9.8	90	9.3	4.5	93	2.2	-45	45 0.03	307 3.1	5.9	7.0 3.8	12.4 3.5	6.6 2.8	n.d
A4*	4.8	8.9	140	7.7	13	84	3.9	-43	44 0.04	143 3.5	3.4	4.2 4.0	16.8 2.6	4.6 4.1	n.d
A0*	-	9.9	20	9.7	-	96	-	-49	71 0.04	insoluble	n.d.	insoluble	insoluble	n.d.	n.d.

[a] Molar fraction of DOT in the initial monomer mixture. [b] Theoretical solids content (τ_{th}) and experimental final solids content (τ_s) measured by gravimetric analysis. [c] Weight fraction of coagulum in the final medium compared to the initial monomer mass. [d] Yield of polymers under the form of particles calculated from the solids content after filtration. Equivalent to conversion when no coagulum is formed. [e] Average molar fraction of inserted DOT in the resulting copolymers estimated by ^{1}H NMR. [f] Glass transition temperature estimated from DSC analysis. [g] Intensity-average diameter and polydispersity of the final particles from DLS. [h] Experimental number-average molar mass, M_n, and dispersity, M_w/M_n, of the copolymer or degradation product determined by SEC-THF using a calibration based on PMMA standards. [i] Calculation of the theoretical M_n for degradation products (equation S1). IPA stands for isopropylamine and TBD for 1,5,7-triazabicyclo [4.4.0]dec-5-ene.

The dry extract from latex A1 was treated with isopropylamine, as thioester containing polymers are known to be sensitive to aminolysis.[13,15,16] The SEC trace of the recovered product (Figure 3) showed a much lower molar mass (from 160.8 kg mol^{-1} to 16.4 kg mol^{-1} after isopropylamine treatment), which accounts for a decrease in M_n of ~90%.

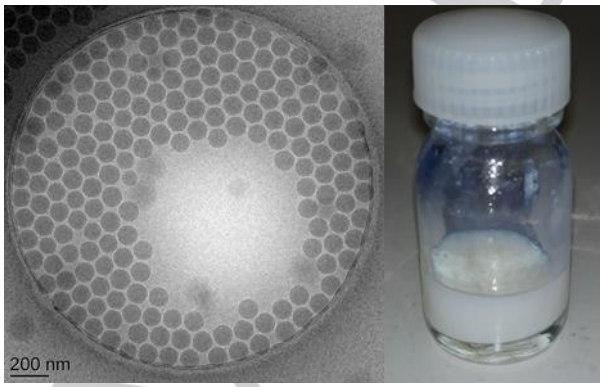


Figure 1. Cryo-TEM image and photo of latex A1 (Table 1) obtained by copolymerizing DOT and BA in emulsion (F_{DOT} = 3.2 %).

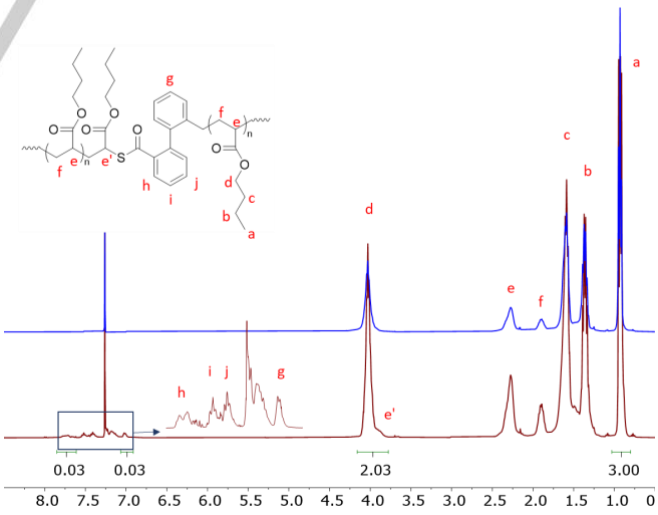


Figure 2. ^{1}H NMR spectrum ($CDCl_3$, 256 scans) of the dried extract obtained from latex A1 (red, Table 1) with the corresponding assignments, and from latex A0 obtained with BA as sole monomer (blue).

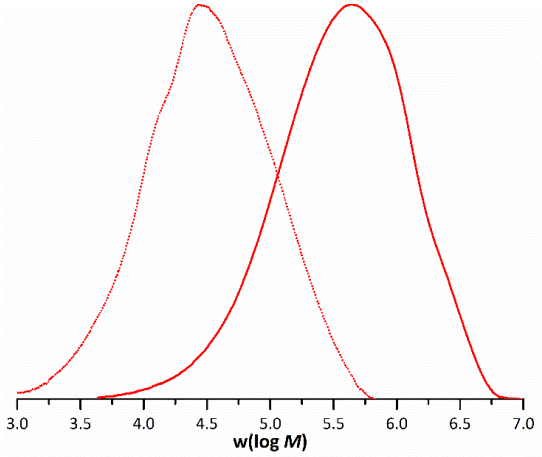


Figure 3. Molar mass distribution for latex A1 (plain line) and its degradation product after treatment of the dry extract with isopropylamine (dotted line).

Several experiments were then conducted to reduce the amount of coagulum and increase the yield (see Supporting Information, Table S1). Lowering the solids content to 10 wt% and varying the DOT content in the monomer mixture from 5 mol% in A1 down to 1 mol% in A5 (Table S1) allowed to recover a stable latex in absence of coagulum incorporating 0.9 mol% of DOT after conversion of 98% of BA in 75 min. Again, degradation was quite significant with a decrease in M_n of ~95%. This last experiment shows that the simplest emulsion polymerization system allows to yield, in less than an hour, stable nanoparticles made of a degradable polymer resulting from the copolymerization of DOT with BA.

Pseudo-miniemulsion / sonication-assisted emulsion copolymerization of DOT and n-butyl acrylate. Miniemulsion polymerization protocols were then investigated to decrease the impact of DOT solubility issues in BA and monomer diffusion issues through the aqueous phase. Indeed, in a miniemulsion polymerization, the nucleation takes place in pre-stabilized monomer droplets formed after applying high shear to the polymerization mixture.[20] Hexadecane was added in the monomers as a co-stabilizer, and after addition of the aqueous phase, the mixture was sonicated. However, this protocol did not provide well-defined miniemulsions as DLS analysis showed the presence of droplets with various sizes. Yet the dispersions remained visually rather stable and looked quite homogenous even for high DOT content (for f_{DOT} = 5% for instance). Even though this process did not allow to provide a proper miniemulsion system, polymerization of the resulting dispersion can be regarded as sonication-assisted emulsion polymerizations.[21]
These polymerizations indeed showed better reproducibility and much less or no coagulum, which allows to obtain representative samples and thus run kinetic measurements up to a content of 2 mol% of DOT in the initial feed. Syntheses with DOT feed ranging from 1 mol% to 4.8 mol% were thus conducted using those media as they stood (Table 1). The temperature was reduced to 70 °C to afford slower reaction and enable kinetics monitoring aiming for 10 wt% solid content.
Those kinetic studies (Figure 4a) give an insight into the reactivity of both monomers. While almost complete conversion was reached in less than 20 min for a DOT-free formulation (A0* in Table 1), 40 and 60 min are required for DOT feeds of 1% and 2% (A1* and A2* in Table 1), respectively. This is nevertheless in strike contrast to the copolymerizations of DOT carried out in organic solution where reactions last at least several hours and for which conversions were not always quantitative.[14-16] This is due to the beneficial effect of compartmentalization of the emulsion polymerization process. DOT seems to have a retarding effect on the emulsion polymerization of BA. As mentioned previously, those results are in accordance with the already observed retardation in the cases of radical copolymerization of methyl acrylate with DOT by Bingham *et al.*[11] The authors explained this behavior by analogy to retardations due to slow fragmentation in the case of RAFT polymerization using dithiobenzoates.[22] In addition, the previously observed tendency of DOT to be inserted at a faster rate than acrylates [13,14] is confirmed here meaning that a drift in composition, *i.e.,* in the content of degradable units in the chains over the course of the copolymerization, should be expected. Indeed, the observed decrease of the average molar fraction of DOT units in the copolymers over the course of the reaction (Figure 4b) corroborates this assumption. The formation of PBA chains might therefore take place towards the end of the reaction when DOT has been entirely consumed.

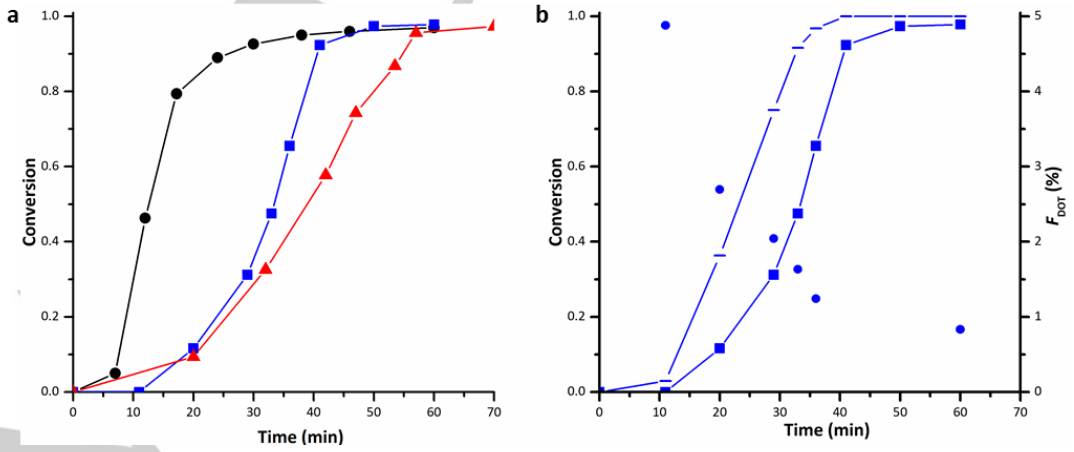


Figure 4. (a) Evolution of BA conversion *versus* time during sonication-assisted emulsion copolymerizations of DOT and BA (Table 1) for experiments A0* (black circles), A1* (blue squares) and A2* (red triangles). (b) Evolution of BA conversion (squares), DOT conversion (dash) and average molar fraction of DOT in the copolymers (F_{DOT}, circles) *versus* time for experiment A1*.

It is worth mentioning that the size of the particles decreases as the molar fraction of DOT in the initial feed increases (from 71 nm (A0*) to 45 nm (A3*)). This phenomenon is not necessarily expected and remains difficult to explain in such a system were several factors influence the particle size.

Moreover, the curves obtained from DSC analysis performed on the dried latex all showed a single glass transition temperature which increases with the average molar fraction of DOT in the copolymers (Figure 5 and Figure S6). Those results prove that the final material is made of random copolymers and tends to show that although a composition drift may take place, homopolymer chains of PBA did not form as it should have led to two distinct glass transition temperatures. However, given the low DOT content the T_gs of the different copolymers remain rather close to each other and a second glass transition would be difficult to identify in a such narrow range. Knowing that DOT homopolymerization is challenging and is yet to be fully investigated, the T_g value for PDOT homopolymer based on Fox equation can be estimated at around 110 °C.[14,16] In addition, in the case of homogeneous copolymerization of styrene and DOT, we found a similar T_g than the reference polystyrene, suggesting that the T_g value of the PDOT is close to 100 °C.[14,17] It is thus expected that the T_g of P(BA-*co*-DOT) would increase with the fraction of DOT units in the copolymer as the T_g of PBA is around -50 °C.

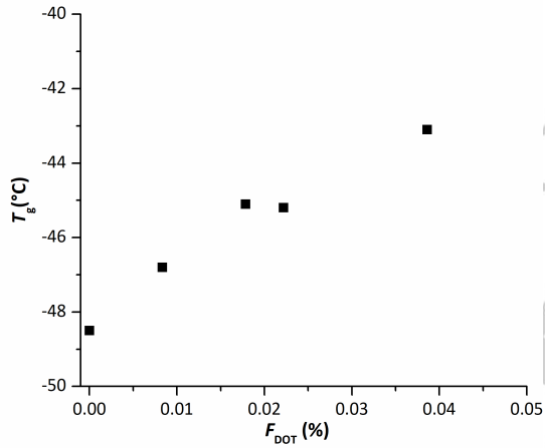
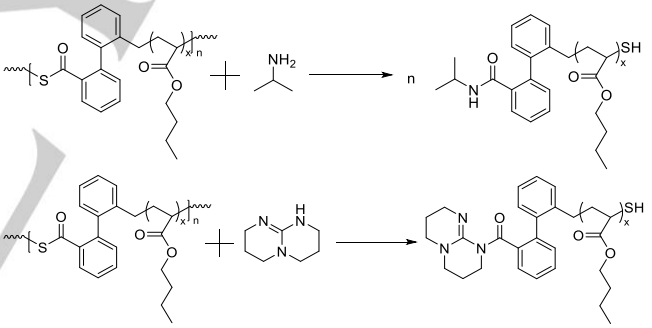


Figure 5. Evolution of the T_g depending on the average molar fraction of DOT units in the P(BA-*co*-DOT) copolymers for sonication-assisted emulsion process (Table 1).

Eventually, molar mass distributions and degradation experiments provide very valuable data. First, it can be noticed that overall, the molar masses of the copolymers tend to decrease with the increase of the molar fraction of DOT (Table 1). Interestingly, the molar mass distributions present a shoulder toward the higher molar mass values that seems to increase as the content of DOT decreases (Figure S3). BA, and more generally acrylic monomer polymerization, is prone to irreversible chain transfer to polymer leading to branching, especially at higher temperature.[23] The presence of this shoulder may thus rather be linked to chain transfer reactions. Anyhow, the increase in DOT contents seems to reduce the phenomenon as the shoulder disappears for latex A4* (Figure S3) for which $f_{DOT,0}$ = 4.8%. It is possible that DOT exerts some sort of control over branching during BA polymerization as styrene is known to.[24] Indeed, for the control experiments with only BA (A0 and A0*, Table 1) it was not possible to perform any SEC analysis; neither on the original copolymers nor after the degradation procedure (see below), as the samples could not be filtered before injection, while no issues were found with any of the samples obtained from synthesis involving DOT.

The degradation of the copolymer chains incorporating ring-opened monomer units is convenient and already well documented. Several routes are possible for acrylic polymers containing in-chain thioester link as shown by the experiments conducted by the groups of Roth[13] and Gutekunst.[14] The most convenient way is to use isopropylamine. It was notably shown to be particularly efficient in the case of BA-based copolymers. It is also possible to use concentrated solutions of KOH.[15] Hence, alternative routes were studied, and a very fast and complete degradation was achieved through use of 1,5,7-triazabicyclo [4.4.0]dec-5-ene (TBD), a strong organo-soluble base.[17] In the frame of the present paper, the chain degradation can be considered on the dry extract itself or after an appropriate treatment of the latex. As such, particle degradation is more challenging as the degradation process will also depend on the ability of the nucleophile to diffuse through the water phase and reach the (inside of) the particles. To evaluate the efficiency of the degradation, we compared the SEC traces of dry extracts before and after treatments with isopropylamine and TBD (Scheme 2), first for latex A2* (Table 1).



Scheme 2. Degradation of P(BA-*co*-DOT) with isopropylamine and TBD. The polymer chains are shown as having acyl-TBD chain-ends. Please note that these could readily hydrolyze into carboxylic acids in water.

Figure 6 shows in both cases the formation of much lower molar masses than observed in the starting samples confirming once again the incorporation of the DOT units. As expected, the molar masses of the degradation products decrease with the increase of the molar fraction of DOT in the copolymer (Table 1, Figure 7). It is possible to estimate the molar mass after degradation by assuming a perfect distribution of DOT units along the PBA chain and no consecutive DOT units, leading to a statistical copolymer (see Supporting Information). The comparison between the experimental molar mass of the degraded products and the theoretical one (Table 1) shows that, even if isopropylamine is convenient and most of the time sufficient to degrade in-chain thioester functions, TBD is more suitable to ensure complete degradation. Control experiments A0 and A0* (Table 1) also underwent the degradation treatment to attest that the observed shift in molar masses was specific of the in-chain thioester

linkages. Neither the original dried latex (as mentioned above) nor the treated one were soluble enough for SEC, indirectly showing that treatment with TBD or isopropylamine was not efficient.

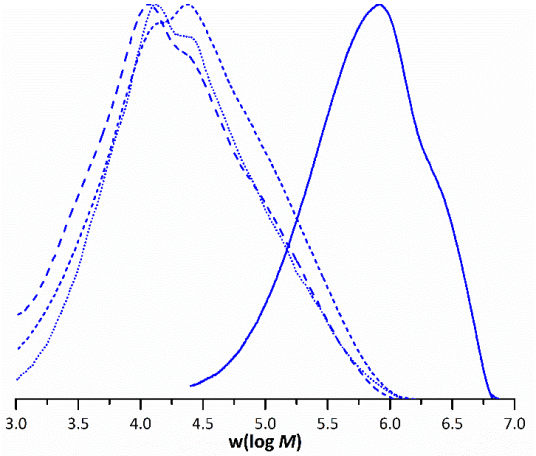


Figure 6. Molar mass distribution of the dry extract for latex A2* (Table 1, plain line) and its degradation product after treatment of the dry extract with isopropylamine (dotted line) and TBD (dashed line), and direct treatment of the latex with TBD (short dashed line).

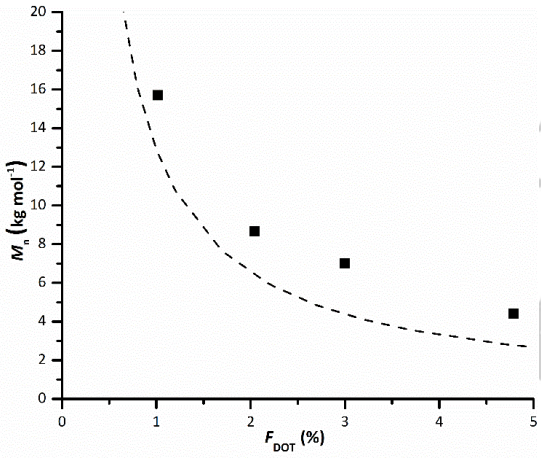


Figure 7. Evolution of experimental (dotted line) and theoretical (dashed line) number-average molar masses of the degradation products as a function of the average molar fraction of inserted DOT units in the copolymers (from A1*, A2*, A3* and A4*, Table 1).

For every experiment, degradation products also present a broadened molar mass distribution as shown by the chromatograms and the dispersity of the degradation product (Table 1, Figure S3). Relation between the molar mass of the degraded product and the reactivity ratios of both the vinylic and the monomer bringing the degradable units have already been simulated in the case of copolymerization of 2-methylene-1,3-dioxepane (MDO).[25] It was notably shown that the copolymerization of comonomers with disparate reactivity ratios would result in a drift of composition leading to intermolecular heterogeneity in the case of radical polymerization (or intramolecular heterogeneity with gradient copolymer in the case of controlled radical polymerization), which would result on degradation products presenting broad molar mass distribution in both cases. As for radical emulsion copolymerization of DOT and BA, the increased dispersity of degradation products thus settles the kinetic results, as this phenomenon is symptomatic of an uneven distribution of DOT units in the different polymer chains.

Eventually straightforward approaches to degrade the latex were probed. First, dilution of the latex in KOH solutions was tried but without success. SEC analyses of the resulting chains did not show any sign of decrease of molar mass compared to the starting latex. In addition, the aspect of the latex remained visually unchanged apart when high KOH concentration was used for which the latex ended up precipitating/coagulating probably through a salting out effect. Isopropylamine led to partial degradation of the copolymers and larger particles. Ultimately, by diluting the latex in a concentrated aqueous TBD solution, complete degradation of the copolymers was observed as shown by the SEC results (A1*, A2*, A4*, Table 1, Figure S4). It was expected that TBD could readily degrade polymer chains inside dispersed particles as it is both water-soluble and organosoluble and may thus be able to diffuse from the aqueous phase to the core of the particles. Interestingly, the aspect of the latex did not change substantially after treatment with TBD although SEC of the resulting product did show that the copolymers were degraded (Table 1). Nonetheless, DLS analyses performed on the resulting medium attest that it was still composed of particles even though they were larger, and the particle size distribution was much broader. For instance, degradation on latex A2* led to particles almost twice as big as the initial ones (Z_{ave} = 75 nm, PDI = 0.21). This feature is indeed very interesting on an applicative point of view, as it allows to employ the target latex and manipulate the degraded chains as stable dispersions if required.

Emulsion copolymerization of DOT with styrene. Following the promising results obtained for emulsion copolymerization of DOT and BA, we suspected DOT to be able to readily copolymerize with styrene in emulsion under appropriate conditions. While copolymerization of styrene and DOT in homogeneous media was found to be only accessible at high temperature or in presence of a low amount of DOT,[17] we reckon that the mechanism of compartmentalization associated with emulsion polymerization may be a trigger to the copolymerization.[26]

The temperature was raised to 80 °C as a high-energy activation is required to achieve the copolymerization between DOT and styrene, varying the DOT content between 0 and 5 mol% (Table 2).[17] The use of styrene instead of BA very slightly improved the solubility of DOT in the monomer (2 mol% (3.5 wt%) in BA against 3 mol% (6 wt%) in styrene). Syntheses led to the formation of coagulum at DOT content above 3 mol% although the impact on the stability of the latex seems to be less prominent as shown by the lower coagulum content for S4 (Table 2) *versus* A4* (Table 1) . Nonetheless, from 1 to 5 mol% of DOT in the initial monomer feed, syntheses led to stable latex and high conversion for styrene (> 90 %) (Table 2).

Table 2. A*b initio* aqueous emulsion copolymerization of styrene and DOT. Experimental conditions, results and molar mass characteristics of the copolymers and their degradation products.

Run	f_{DOT} [a] (%)	τ_{th} [b] (wt%)	t (min)	τ_s [b] (wt%)	τ_c [c] (wt%)	Yield *Styrene* [d] (%)	F_{DOT} [e] (%)	Z_{ave} [f] (nm)	PDI[f]	Before degradation		Degradation on dry extract treated with TBD		
										M_n [g] (kg mol^{-1})	$Đ$ [h]	M_n [g] (kg mol^{-1})	$Đ$ [g]	$M_{n,deg}$ th [h] (kg mol^{-1})
S0	-	10.2	70	10.2	-	100	-	51	0.02	108.7	3.8	-	-	-
S1	1.0	10.0	110	9.6	-	93	1.1	48	0.04	101.7	3.6	7.4	2.9	9.7
S2	2.0	10.4	120	10.7	-	95	1.9	45	0.03	76.5	3.0	4.2	2.7	5.6
S3	3.0	10.1	120	9.7	7	96	3.0	45	0.03	60.7	4.7	2.7	2.7	3.6
S4	5.0	10.1	120	9.5	6	91	4.7	43	0.06	47.5	3.9	1.9	3.1	2.3

[a] Molar fraction of DOT in the initial monomer mixture. [b] Theoretical solids content (τ_{th}) and experimental final solids content (τ_s) measured by gravimetric analysis. [c] Weight fraction of coagulum in the final medium compared to the initial monomer mass. [d] Yield of polymers under the form of particles calculated from the solid content after filtration. Equivalent to conversion when no coagulum was formed. [e] Average molar fraction in the resulting copolymers estimated by ^{1}H NMR. [f] Intensity-average diameter and polydispersity of the final latex from DLS. [g] Experimental number-average molar mass, M_n, and dispersity, M_w/M_n, of the copolymer or degradation product determined by SEC-THF using a calibration based on polystyrene standards. [h] Calculated theoretical M_n for degradation products (equation S1).

The incorporation of DOT into the polystyrene backbone was confirmed by ^{1}H NMR spectroscopy of the dried latexes, all of which showing a broad signal at 4.1 ppm (as illustrated in Figure 8 for latex S3, Table 2), which is absent from the spectrum of pure polystyrene. This signal is attributed to the proton *b'* characteristic of a styrene unit next to the thioester of a DOT unit. The multiplicity of the signal is presumed to be linked with polymer tacticity.[13] The integration of this signal was compared to that of signal *a* to estimate the molar fraction of DOT units in the copolymer, giving very consistent results. For every synthesis, the molar fraction of DOT in the obtained copolymer remains very close to the molar fraction of DOT in the initial monomer mixture (Table 2).

FTIR spectra recorded for the powders obtained after drying the latex confirm further the incorporation of DOT units in the copolymers (Figure 9). In accordance with Spick *et al.* works,[16] the presence of an absorbance band between 1650 and 1680 cm^{-1}, which intensity increases with the amount of DOT, attests to the presence of -SC=O bond in the copolymer.

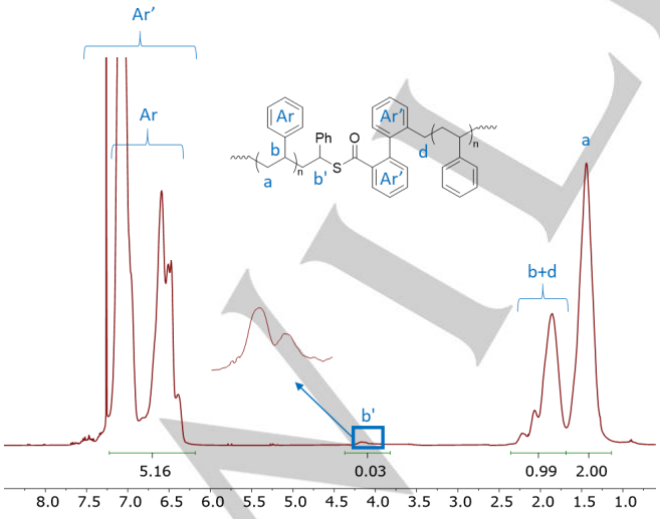


Figure 8. ^{1}H NMR spectrum ($CDCl_3$, 256 scans) of the dried extract from latex S3 (Table 2) with the corresponding assignments.

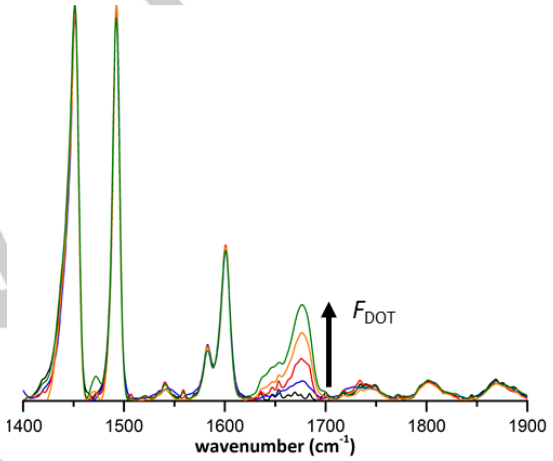


Figure 9. FTIR spectra of dried extract from latex S0 (black), S1 (blue), S2 (red), S3 (orange) and S4 (green). All the curves were normalized based on the absorbance band at 1440 cm^{-1} that is linked with methylene group both present in styrene and DOT unit (C-H bending).

Both styrene conversion and the composition of the copolymer were followed over the course of the synthesis for $f_{DOT,0}$ = 3% and compared to the DOT-free synthesis (respectively S3 and S0, Figure 10, Table 1). Unlike BA, styrene copolymerizations did not seem to be impacted by the presence of DOT as both experiments reached quantitative conversion at similar rates within about one hour. The DOT content in the polymer increased slightly over the course of the reaction as the lowest average content of DOT units observed is about 2.5 mol% for 50% styrene conversion and reaches 3 mol% at higher conversion. In homogeneous solution, the incorporation of DOT is halved compared to that of styrene at 80 °C and reached a similar conversion at 150 °C.[17] In emulsion, the compartmentalization seems to even lower the reactivity difference between styrene and DOT and thus it is not necessary to increase the temperature to 150 °C as for solution copolymerization to have a statistical incorporation of thioester moieties into the PS backbone.[17]

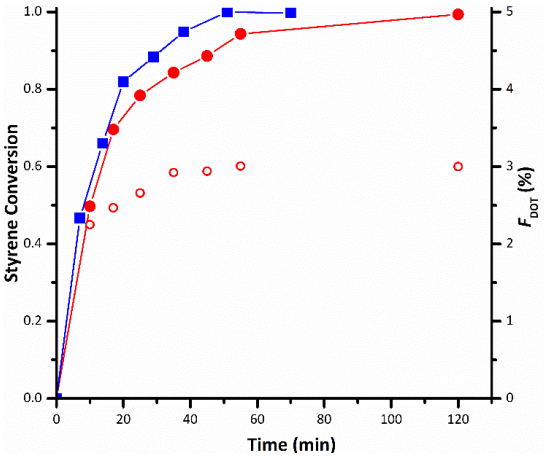


Figure 10. Evolution of styrene conversion *versus* time for experiments S0 (blue squares) and S3 (plain red circles) and the molar fraction of DOT units in the copolymer for S3 (open red circles). See Table 2 for details on S0 and S3.

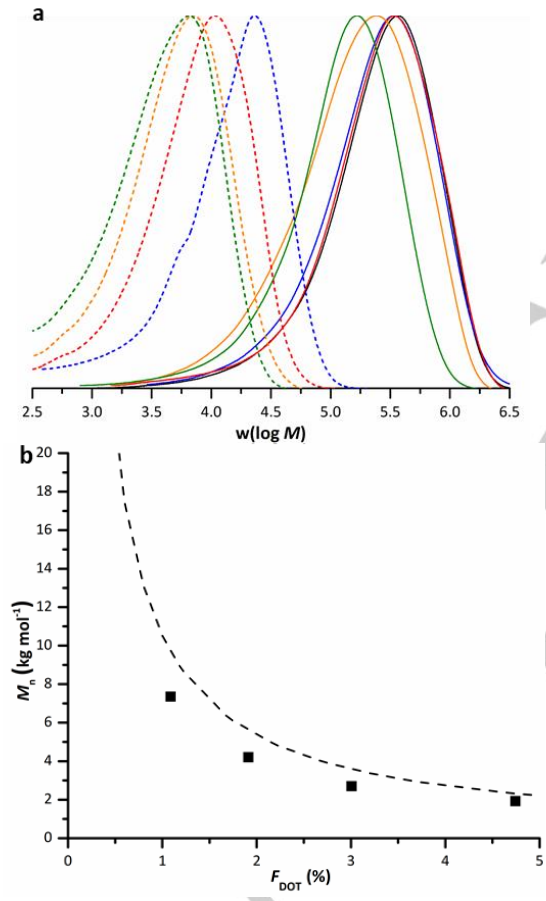


Figure 11. a) Molar mass distribution of dry extracts (plain lines) and degradation products (dashed lines) obtained through degradation of dry extracts using TBD obtained from latexes S1 (blue), S2 (red), S3 (orange) and S4 (green). (b) Evolution of experimental (squares) and theoretical molar masses (dashed line) of the degradation products as a function of the average molar fraction of inserted DOT units in the copolymers (from S1, S2, S3 and S4, Table 2).

Unlike the copolymers obtained by the copolymerization of DOT and BA, molar mass distributions do not show sign of tailing and present rather narrow traces. Degradation experiments yielded oligomers that seem to keep the same molar mass distribution as their original copolymer with no enlargement of the signal or increase in the dispersity after treatment of the dried latex by TBD (Figure 11). In addition, the molar mass of the degraded copolymers decreases with the increase of their DOT fraction following the trend of the theoretical values. Combining those results with the kinetic data shows that the insertion of DOT units in the case of copolymerization with styrene seems to be much more regular thus yielding truly random copolymers.

Unlike what was achieved with P(BA-*co*-DOT), it was however not possible to degrade the P(S-*co*-DOT) copolymers as waterborne particles with TBD. Several factors may hinder TBD diffusion inside the particle core, among which the ability of the degrading agent to swell the entangled polymer chains, which may itself be linked with the T_g of the copolymers. Whereas PBA-based copolymers present T_g way below ambient temperature (-40/-50 °C, Table 1), PS-based copolymers present T_g way above (about 100 °C, Figure 12). In the case of PS, the "glassiness" of the particles may thus limit the access to the core.

Emulsion copolymerization of DOT, *n*-butyl acrylate and styrene. As DOT proved to readily copolymerize with both styrene and BA, we sought to implement the emulsion terpolymerization of DOT with both BA and styrene in order to obtain degradable copolymer latexes with a wide range of T_g. A series of experiments was thus conducted with 2 mol% of DOT in a mixture of styrene and BA with varying molar ratios. Syntheses all led to stable and coagulum-free latexes (Table 3), with conversion of BA and styrene above 90% in about 60 min. DSC results show a single glass transition temperature that increases with the amount of styrene, suggesting the formation of a statistical copolymer (Figure S7). As expected, it was possible to vary the T_g of the copolymers in a range between -45 °C and 100 °C by adjusting the molar ratio BA/styrene in the initial monomer mixture (Figure 12).

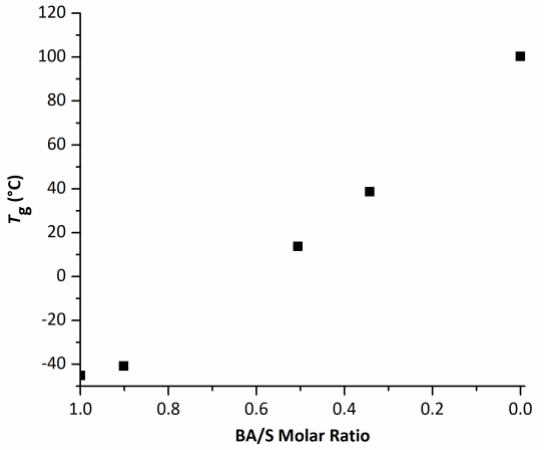


Figure 12. Evolution of the T_g depending on the average molar fraction BA/styrene in the monomer mixture for emulsion polymerization with 2 mol% of DOT (Table 3).

Table 3. *Ab initio* aqueous emulsion copolymerization of DOT, BA and styrene. Experimental conditions, results and molar mass characteristics of the copolymers and their degradation products.

Run	BA/S molar ratio (%)	f_{DOT} [a] (%)	τ_{th} [b] (wt%)	t (min)	τ_s [b] (wt%)	Conv. [c] (%)	T_g [d] (°C)	Z_{ave} [e] (nm) PDI	M_n [f] (kg mol^{-1}) $Đ$	Degradation on dry extract using IPA M_n [f] (kg mol^{-1}) $Đ$	Degradation on dry extract using TBD M_n [f] (kg mol^{-1}) $Đ$
A3	100	1.9	9.8	70	9.7	91	-45	36/0.04	300 3.9	18.9 2.7	7.4 5.5
AS1	90	1.9	10.0	60	9.5	95	-40.7	39/0.16	214.5 3.6	20.1 3.2	6.6 3.8
AS0	51	0.0	11.0	60	10.6	96	10.3	40/0.04	170.0 3.6	170 3.5	n.d.
AS2	50	2.1	10.8	65	9.9	91	13.7	47/0.20	150.0 3.5	32.0 2.0	5.7 2.4
AS3	34	2.0	11.3	80	10.9	96	38.7	43/0.10	127.9 2.9	61.7 2.4	4.3 2.9
S2	0	2.0	10.4	120	10.7	95	100.3	45/0.03	76.5 3.0	n.d.	4.2 2.7

[a] Molar fraction of DOT in the initial monomer mixture. [b] Theoretical solids content (τ_{th}) and experimental final solids content (τ_s) measured by gravimetric analysis. [c] Total conversion of BA and styrene determined by gravimetric analysis. [d] Glass transition temperature estimated from DSC analysis. [e] Intensity-average diameter and polydispersity of the final latex from DLS. [f] Experimental number-average molar mass and dispersity, M_w/M_n, of the copolymer or degradation product determined by SEC-THF using a calibration based on polystyrene standards.

SEC analysis on dry extracts and their corresponding degradation products gives an insight on the impact of styrene in this copolymerization system (Figure 13). Indeed, molar mass distribution of the copolymers and their degradation products differ significantly depending on the amount of styrene in the initial batch of monomers. The shoulder toward high molar masses observed for the styrene-free synthesis disappears as the amount of styrene increases. In addition, molar mass distributions of degradation products show the disappearance of the tailing toward the higher molar masses and overall narrower molar mass distributions for the syntheses using styrene and BA compared to the ones using only BA (Figure 13). Once again, this is shown by the decrease of the dispersity but also in lower M_n for degradations products. Combining the fact that the shape of the distribution and the dispersity are left almost unchanged after the degradation process, it is reasonable to assume that the incorporation of DOT units is more homogeneous in these systems than in the ones involving BA and DOT.

The average fraction of DOT units in the copolymers could not be determined by NMR. The spectra of those copolymers did not present any isolated-enough signals that can be specifically related to a DOT unit. Nonetheless, incorporation of DOT could be indirectly confirmed by degradation experiments. Indeed, while degradation occurred for the copolymers obtained using DOT in the initial feed, no degradation was observed in the case of DOT-free synthesis (AS0, Table 3).

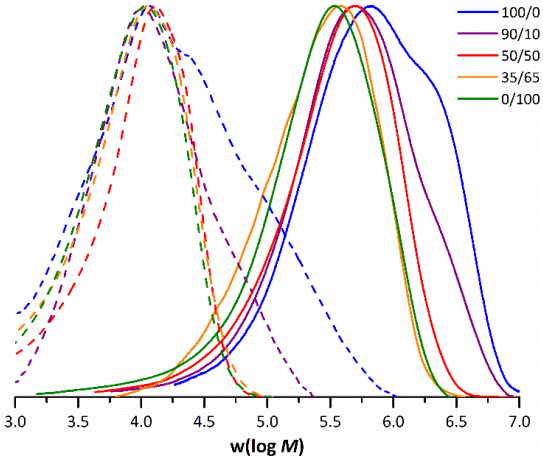


Figure 13. Molar mass distribution of dry extracts (plain lines) and degradation products (dashed lines) obtained through degradation of dry extracts using TBD for latexes synthesized with varying BA/S molar ratio (blue: A3; purple: AS1; red: AS2; yellow: AS3; green: S2, Table 3).

Conclusion

The aqueous emulsion copolymerization of dibenzo[c,e]oxepane-5-thione with either *n*-butyl acrylate, styrene or both was conducted under standard emulsion polymerization conditions to afford stable latexes in less than two hours. Syntheses all led to the quantitative incorporation of thioester units into the backbone of the vinylic copolymers. Relatively low content of cleavable thioester functions is required to obtain degradable copolymers. Indeed, successful degradation of the copolymers through the use of isopropylamine or TBD led to oligomers with molar masses in agreement with the molar fraction of integrated DOT units. The terpolymerization of DOT with both styrene and *n*-butyl acrylate allowed to afford degradable copolymers with tunable glass

transition temperature. The emulsion copolymerization of DOT thus provides a straightfoward one-step process to obtain waterborne particles made of degradable vinylic polymers. The development of more specific systems may open new perspectives in latex production for a broad range of applications in various fields, such as coatings and drug delivery, by producing degradable copolymers additionnaly addressing environmental issues.

Acknowledgements

The authors acknowledge the financial support from the Agence Nationale de la Recherche (grant number ANR-18-CE06-0014 CKAPART). Pierre-Yves Dugas (CP2M) is acknowledged for the cryoTEM observations.

Keywords: Degradable • Emulsion • rROP • Thionolactone • Particles

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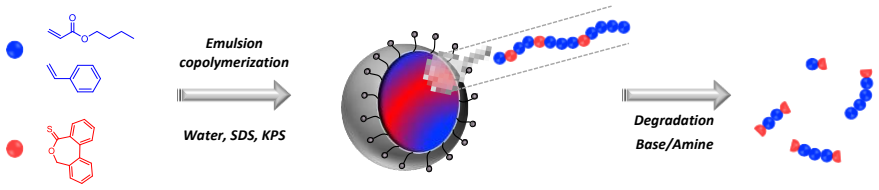

Emulsion copolymerization of dibenzo[c,e]oxepane-5-thione (DOT) with either styrene, *n*-butyl acrylate or a mixture of both were carried out in water using SDS as surfactant and KPS as initiator. Stable waterborne particles of vinylic polymers (red) bearing cleavable thioester units (blue) along the chains were obtained. The polymer chains were degraded to oligomers using a strong base (1,5,7-triazabicyclo [4.4.0]dec-5-ene) or isopropylamine.

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