Degradable Polystyrene via the Cleavable Comonomer Approach

Noémie Gil,[1] Baptiste Caron,[1] Didier Siri,[1] Julien Roche,[2] Slim Hadiouch,[1] Douriya Khedaioui,[3] Stéphane Ranque,[2] Carole Cassagne,[2] Damien Montarnal,[3] Didier Gigmes,[1] Catherine Lefay,[1],* Yohann Guillaneuf[1],*

[1] Aix-Marseille Univ, CNRS, Institut de Chimie Radicalaire, UMR 7273, F-13397 Marseille, France.

[2] Aix Marseille Univ, APHM, IHU Méditerranée Infect, IRD, VITROME, Marseille, France

[3] Univ. Lyon, CPE Lyon, CNRS, Catalyse, Polymerization, Processes and Materials, UMR 5128, F-69003 Lyon, France

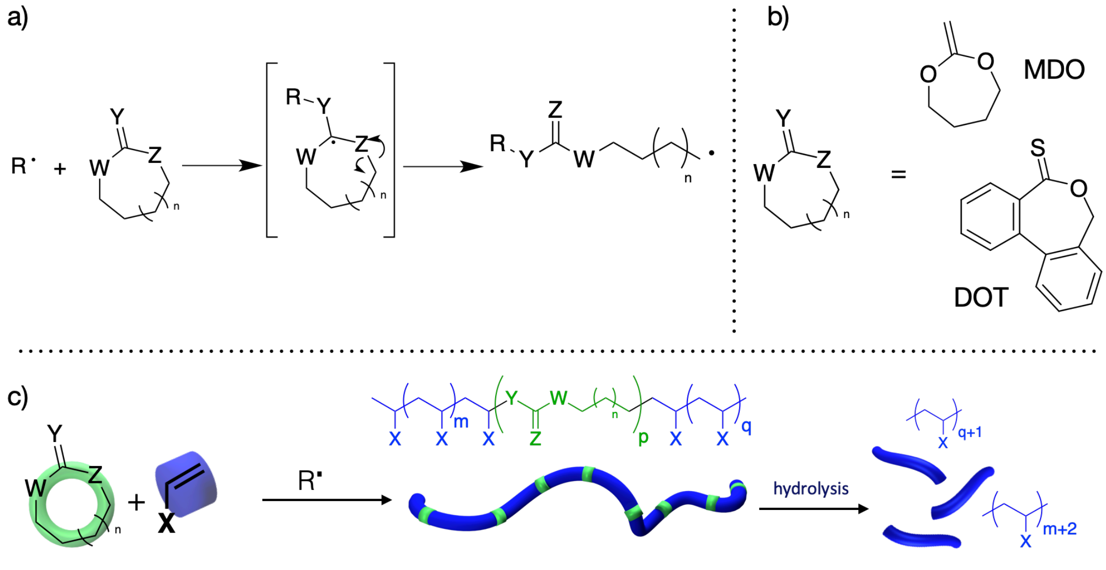
ABSTRACT: Polystyrene (PS) is a major commodity polymer, widely used in various applications ranging from packaging to insulation thanks to its low cost, high stiffness and transparency as well as its relatively high softening temperature. Similarly to all polymers prepared by radical polymerization, PS is constituted of a C-C backbone and thus is not degradable. To confer degradability to such materials, the copolymerization of vinyl monomers with cyclic monomer that could undergo radical ring-opening is an efficient methodology to introduce purposely cleavable bonds into the polymer backbone. Dibenzo[c,e]-oxepane-5-thione (DOT) is a cyclic thionolactone monomer known for its efficient copolymerization with acrylate derivatives but so far could not be incorporated into PS backbones. From a theoretical study combining DFT and kinetic models using the PREDICI software, we showed that modifying experimental conditions could overcome these limitations and that high molar mass degradable polystyrene (M_w close to 150,000 g.mol^{-1}) could be prepared via statistical insertion of thioester groups into the polymer backbone. Thanks to favorable reactivity ratios allowing only a few mol% of thioester units to be randomly incorporated, there was no major modification of the thermal and mechanical properties of the PS. The degradation of such PS could be performed in THF at RT in one hour using 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) as a base, leading to oligomers with M_n close to 1,000 g.mol^{-1}. We successfully demonstrate further applicability of these copolymerization systems for the photo-triggered decomposition of PS in solution as well as the synthesis of cross-linked PS networks degradable into soluble side-products.

Introduction

Plastic waste has become a global environmental concern, with more than 300 million tons of petroleum-based synthetic plastics industrially produced worldwide every year. Polystyrene (PS) is one of the major sources of plastic products in the world. Due to its high durability, easy processability and hydrolytic stability, PS is widely used in packaging, insulation, building and food processing industries and thus has become a major pollutant of soils, rivers, lakes, and oceans.[1]

The most common chemical approach to recycle polystyrene waste is thermal or thermocatalytic decomposition that leads either to fuel-like products[2] or to close-loop recycling through the recovery of styrene monomer[3]. Another route of recycling for PS, particularly suited for foams, proceeds through the dissolution of waste[4] in solvents[5] (including terpenics such as limonene) followed by recovery in supercritical CO2. Biodegradation of plastic waste, including that of PS, has been studied since the 1960's. Researchers have attempted to use mixed microbial cultures and have isolated bacteria from various sources such as soil, garbage or sewage sludge to biodegrade various plastics into low molecular organics or mineralize to CO_2. The ability of microorganisms to use polystyrene as a carbon source has been recently established.[6-8] However, the high molar mass of commercial PS severely limits the efficiency of these enzymatic reactions.

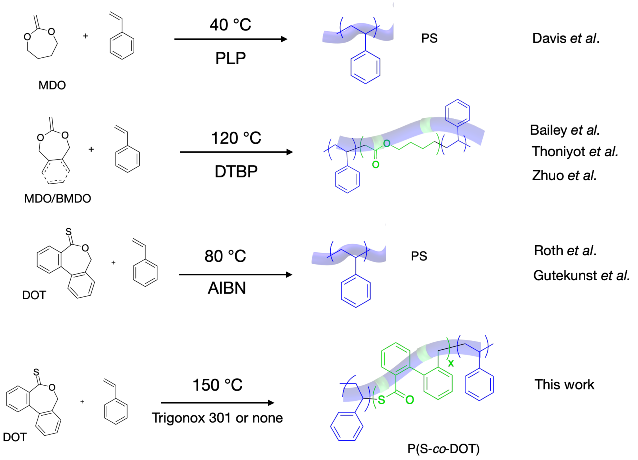
The convenience and the increasing demand for these polymers despite the environmental concerns are strong incitements to convert PS into (bio)degradable materials. A possible solution is to use, in a first degradation step, an additive capable of accelerating the cleavage of the long C-C backbone, followed in a second step by classic biodegradation of short oligomers. Radical ring-opening polymerization (rROP) combines both the advantages of ring-opening polymerization and radical polymerization, that is the production of polymers having heteroatoms and/or functional groups in the main chain together with the robustness, the ease of use and the mild polymerization conditions of a radical process (Scheme 1).[9] The polymerization occurs via the addition of radicals onto cyclic monomers bearing an exo-methylene function or equivalent groups followed by a fragmentation of the intermediate cyclic radical to afford a new radical and the incorporation of heteroatoms into the C-C backbone.



Scheme 1. a) Radical addition/fragmentation mechanism. b) Structure of the MDO and DOT monomers. c) Insertion of hydrolytically cleavable bonds into polymer backbone by the radical ring-opening copolymerization technique.

Cyclic ketene acetals (CKA) were reported by Bailey and coworkers in the 80's as suitable monomers for rROP.[9-11] This monomer family was then extensively studied as a way to produce polymers similar to classic aliphatic polyesters, but through a radical pathway. This technique has been recently rejuvenated by the possibility to copolymerize CKA with classic vinyl monomers, enabling the introduction of cleavable functions into the copolymer backbone. This led to a broad range of novel (bio)degradable polymers suitable for a large scope of applications.[9, 10] Among the various CKAs, 2-methylene-1,3-dioxepane (MDO) and 5,6-benzo-2-methylene-1,3-dioxepane (BMDO) were the most studied and used monomers thanks to their very efficient ring-opening ability. The main limitation of such polymerization process is related to the specific reactivity of the CKA compared to common vinyl monomers. In particular, the copolymerization of CKA and styrene is hardly performed in the literature due to unfavored reactivity ratios (Bailey *et al.*[12] reported values of $r_{\mathrm{MDO}} = 0.021$ and $r_{\mathrm{sty}} = 22.6$ in bulk at 120 °C and Aggarwal *et al.*[13] $r_{\mathrm{BMDO}} = 1.08$ and $r_{\mathrm{sty}} = 8.53$ in bulk using ATRP at 120 °C). With these values, an initial fraction of 80 mol % MDO leads to a PS with only 12 mol% of ester units.[14] The high discrepancy between the reactivity of the two monomers could led to very heterogenous materials, as recently highlighted by Thoniyot *et al.*[14] Moreover, our group recently showed by a theoretical approach that such unfavorable reactivity ratios led to heterogeneous degradations with some chains being only slightly affected.[15]

To circumvent such drawbacks, Roth and coworkers[16] followed by Gutekunst *et al.*[17] recently proposed thionolactones as new cyclic monomers for rROP. In particular they both showed that dibenzo[c,e]-oxepane-5-thione (DOT) is able to copolymerize with acrylate derivatives, acrylonitrile and *N,N*-dimethylacrylamide and thus enables the insertion of thioester functionalities into the polymer backbone in a efficiently manner. The thioester linkages that were inserted into the polymer chain confer degradability by both basic hydrolysis,[18] aminolysis[16] (*e.g.* using isopropylamine in dichloromethane), oxidative hydrolysis,[18] and methanolysis[17]. Nevertheless, both studies claimed that these new monomers cannot homopolymerize nor copolymerize with styrene.[16, 17] In the latter case, only polystyrene is obtained with DOT remaining spectator. Since these preliminary studies, we sought to understand the peculiar reactivity of thionolactone derivatives, and in particular of the DOT monomer.



Scheme 2. Preparation of degradable polystyrene by the radical ring opening copolymerization of cyclic rROP monomers and styrene.

Starting from a theoretical study combining both quantum chemistry (DFT calculations) and numerical modeling using the PREDICI software, we describe in this work that the copolymerization of DOT with styrene works well provided that high temperatures are used, and that statistical copolymers can be obtained.

We illustrate the wide possibilities that arise by synthesizing high molar mass copolymers of styrene and DOT, with only minor modification of properties, but amenable to complete degradation (Scheme 2). A comparison study with CKA monomers (MDO and BMDO) was also performed showing the impact of the reactivity ratios on the degradation of the polymers. Random incorporation of such DOT comonomers is thus an efficient manner to introduce cleavable bonds inside the PS backbone and we will highlight its impact on the degradability of the resulting materials.

Results and discussion

Preparation of PS-*co*-CKA and PS-*co*-DOT

The aim of this work is to investigate the preparation of degradable polystyrene via the copolymerization of styrene and cyclic monomers. We thus started by performing the copolymerization of styrene with MDO using experimental conditions recently reported by Thoniyot and coworkers.[14] The polymerizations were performed initially at 120°C with an optimized reaction time to avoid compositional drift (Table 1). Initial feed ratio in MDO was 20 mol% and 1 mol% of di-*tert*-butyl peroxide (DTBP) was used as the initiator. After 6 hours, a PS with a M_n of 67,300 g.mol^{-1} and a Đ of 2.2 was obtained. The analysis of the purified copolymer showed that only 3 mol% of MDO units was inserted into the backbone, in rather good agreement with Thoniyot *et al.*[14] This copolymer was degraded using accelerated conditions (KOH 5 wt% in THF/MeOH for 96 h) leading to degraded products of M_n = 12,800 g.mol^{-1} and Đ of 2.9. To decrease the length of the degraded products, a similar experiment was performed with a MDO initial feed ratio of 50 mol%. In that case, due to a lower concentration of styrene, the M_n decreased to 45,800 g.mol^{-1} with a Đ of 1.9.

Table 1. PS containing either MDO or DOT comonomer before and after degradation

	Ratio S/Comonomer	Comonomer	M_n (Đ) before degradation g.mol^{-1}	M_n (Đ) after degradation g.mol^{-1}
P1[a,b]	80/20	MDO	67,300 (2.2)	12,800 (2.9)
P2[a,b]	50/50	MDO	45,800 (1.9)	5,400 (2.3)
P3[a,c]	50/50	MDO	90,000 (2.0)	6,300 (2.0)
P4[d,e]	95/5	DOT	7,800 (1.8)	3,000 (2.1)
P5[d,e]	70/30	DOT	4,500 (1.5)	-
P6[d,e]	50/50	DOT	3,000 (1.5)	-
P7[d,f]	95/5	DOT	16,300 (2.0)	2,500 (1.9)

[a] bulk, 120 °C, [b] 1 mol% DTBP, [c] 0.1 mol% DTBP, [d] 80 °C, 1 mol% AIBN, [e] 80 mol% anisole, [f] 10 mol% anisole

Nevertheless, the amount of ester units increased to 6 mol% and led to degraded product of M_n = 5,400 g.mol^{-1} and Đ of 2.3. To increase the M_n of the initial polymer, a lower amount of initiator (0.1 mol%) could be used but at the expense of the overall conversion (70 instead of 85 %).

Since it is not possible to degrade the copolymers into oligomers of less than 5,000 g.mol^{-1}, we thus investigated the use of DOT as comonomer in the polymerization of styrene. Indeed, this comonomer pair was only hardly investigated previously.[16, 17] We started with the experimental conditions used by Roth and coworkers[16] (80 °C, anisole with only 20 mol% of monomers since the DOT is hardly soluble in common vinyl monomers) and tested 3 initial feed ratio, *i.e* $[S]_0$:$[DOT]_0$ = 95:5, 70:30 and 50:50. With the lowest amount of DOT (5 mol%), the conversion of styrene reached only 50 % after 24h and produced a PS with a M_n of 7,800 g.mol^{-1}. With higher DOT amount, $f_{DOT,0}$ = 30 and 50 mol%, the conversion lowered to 35 and 25 % and the M_n decreased to 4,500 and 3,000 g.mol^{-1}, respectively, impeding its practical use to prepare high molecular weight polystyrene. The experiment with $f_{DOT,0}$ = 5 mol% was then investigated in more details. The kinetics of the copolymerization is shown in the ESI Figure S1, with the conversion of DOT being half the conversion of styrene. This led to an incorporated amount of DOT inside the backbone close to 2.5 mol%. The isolated copolymer was degraded using different accelerated conditions, that is KOH 5 wt% in THF/MeOH, *N*-isopropylamine 50 wt% in DCM and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) 2.5 wt% in THF. We obtained a degraded product with a M_n close to 3,000 g.mol^{-1} (Figure 1).

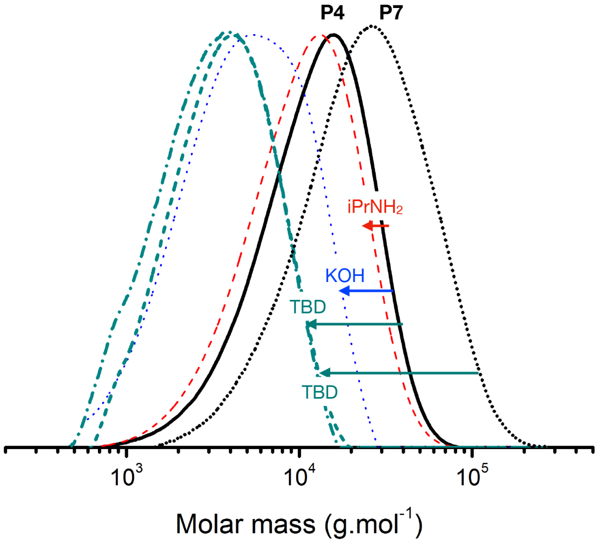


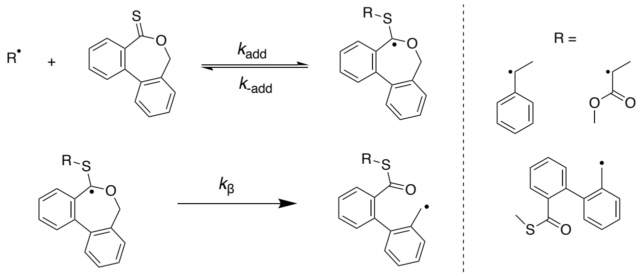
Figure 1. Molar mass distribution of P(S-*co*-DOT) before and after degradation: **P4** before degradation (solid line dark), **P7** before degradation (short-dotted line dark), **P4** after 18h of degradation using iPrNH2 in DCM (dashed line red), **P4** after 18h of degradation using 5 wt% KOH in THF/MeOH (dotted line blue), **P4** after 18h of degradation using 2.5 wt% TBD in THF (short-dashed line cyan) and **P7** after 18h of degradation using 2.5 wt% TBD in THF (dashed dotted line cyan).

It has to be noted that the aminolysis conditions did not lead to degradation unlike it usually occurs for thioester moieties into polyacrylate and polyacrylamide derivatives.[16-18] On the contrary, the use of TBD revealed to be very efficient (the kinetics and different mode of degradation are detailed in the degradation paragraph). Since only 5 mol% of DOT is used, we thus decreased the amount of anisole to improve the kinetics and the length of the polystyrene while keeping the DOT soluble. By using 10 mol% of anisole instead of 80 mol% used previously, we obtained in two hours 70 % of conversion for the styrene and close to 40% for the DOT, producing a PS with M_n of 16,250 g.mol^{-1} incorporating 3 mol% of thioester units. The degradation using TBD led to oligomers of M_n = 2,500 g.mol^{-1} (Figure 1). A similar degradation product is obtained showing that the incorporation of the DOT is identical to the previous experiment and only the M_n of the polymer before degradation changed with a decrease amount of solvent. These results showed that unlike the results of both Gutekunst[17] and Roth,[16] the copolymerization of DOT and styrene occurred even though only half of the thioester units were successfully incorporated into the backbone. Secondly, at higher DOT amount, the lower reactivity and the solvent that is necessary to dissolve it impedes its use in copolymerization with styrene at high ratio. Such behavior is thus different to the one of acrylate and acrylamides derivatives and this difference will be studied by quantum chemistry.

Theoretical considerations

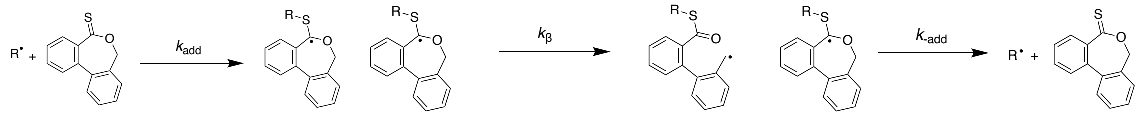
As discussed previously, the radical copolymerization of DOT monomer with acrylate derivatives was reported to be efficient, with a statistical incorporation of the thioester functionality inside the vinyl-based backbone.[16, 17] In contrast, copolymerization with styrene led only to the preparation of polystyrene without incorporation of the thionolactone into the backbone.

To have a better understanding of this phenomenon, DFT calculations were performed to determine the enthalpies of reaction as well as the activation energies of i) the addition of alkyls radicals onto the thionolactone functionality and ii) the β-scission of the intermediate radical that either leads to thioester and a second released alkyl radical or gives back the thionolactone and the propagating vinyl macroradical (Scheme 3).To perform such theoretical study, we choose the UB3LYP/6-31G(d) level of theory due to the large number of atoms that are involved in the system. Moreover we already showed that this level of theory allowed us to have a good understanding of the homopolymerization of CKA[19] or the copolymerization behavior of CKA with various vinyl monomers.[20, 21]



Scheme 3. Kinetic scheme that has been theoretically investigated by DFT calculations.

In such previous study, more complex level of theory (G3MP2RAD, BMK, etc.) led to similar results but with increased computational time.[19, 20, 22] The results of the calculations are gathered in Table 2. We can first observe that the β-scission reaction of the radical intermediate is not affected by the nature of the radical adduct since both enthalpies of reaction ΔH_r and activation energies are rather similar (close to -23 kJ mol^{-1} for ΔH_r and close to 60 kJ mol^{-1} for the $E_{a,\beta}$). The main difference evidenced from the calculations is the higher activation energy for the addition onto DOT monomers of styryl or DOT-based radicals ($E_{a,add}$ close to 28 kJ mol^{-1}) than of acrylate radicals ($E_{a,add}$ = 12 kJ mol^{-1}). This results in the more favorable addition of acrylate derivatives during the copolymerization and thus could explain a better statistical incorporation of DOT in such copolymerization system. In the case of styrene, the calculations showed that the addition-fragmentation mechanism is still possible but should be favored at higher temperature. A qualitative assessment of the copolymerization behavior can be obtained through the determination of transfer rate constant, by analogy with methods developed for kinetics of RAFT polymerization.



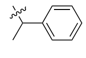
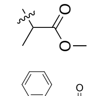
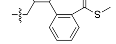
	$E_{a,\,add}$ (kJ mol^{-1})	ΔHr (kJ mol^{-1})	$E_{a,\,\beta}$ (kJ mol^{-1})	ΔHr(kJ mol^{-1})	$E_{a,\,-add}$ (kJ mol^{-1})	ΔHr (kJ mol^{-1})
	29	-14.6	62.6	-23.1	41.2	14.6
	11.7	-26.5	58.8	-22.1	35.8	26.5
	27.3	-22.4	61.5	-23.8	47.3	22.4

Table 2. Energies of activation and enthalpies of reaction for the different radical addition on the DOT monomer and the β-scission of the intermediate radical.

This complex rate constant allows the estimation of the efficiency of a RAFT agent by taking into account the combination of the radical addition (*add*), inverse radical addition (*-add*) and β-scission reaction (*β*) that occurred during the RAFT process.[23] The transfer rate constant is given by the following equation:

$$k_{tr} = k_{add} \times \frac{k_\beta}{k_{-add} + k_\beta} \qquad (1)$$

This rate coefficient could then be compared to the propagation rate constant of the vinyl monomer to estimate the copolymerizability of the two monomer pairs. To determine the kinetic rate constants, we have to calculate or estimate the Arrhenius pre-exponential factor. It is known that the DFT calculation of such entropy-based parameter is difficult due to the treatment of all vibrations as harmonic oscillators.[24]

While the entropy associated for certain vibrations is correct, hindered rotations occurring in cyclic molecules cannot be properly taken into account. We rather opted for conservative estimations of the pre-exponential factors using previously reported values.[19, 22] This approach was experimentally validated with cyclic ketene acetals.[19, 22] In particular for radical addition reaction, we used $A_{add} = 10^8$ L mol^{-1} s^{-1} for secondary radical as recommended by Fischer and Radom.[25] For the unimolecular β-fragmentation, a value of $A_\beta = 10^{13}$ s^{-1} was used.[26-28] A similar value is also used for the reverse addition rate constant $A_{-add} = 10^{13}$ s^{-1}. The results for each rate coefficient and transfer coefficient are summarized in Table 3 as well as the influence of the temperature on such values. Experimentally, both Roth[16] and Gutekunst[17] showed good incorporation of thionolactones with acrylate derivatives at 80 °C. With such monomers, the ratio between k_p and k_{tr} is close to 13. With styrene, this ratio is higher (above 30) showing a lower reactivity of DOT with styrene. Nevertheless, by increasing the temperature up to 150 °C, the value reached the threshold value of 19 that is closer to the one determined for acrylate derivatives copolymerization at 80 °C. Such conditions seemed thus more compatible with a good copolymerization behavior between styrene and DOT.

Table 3. Theoretical calculation of the transfer rate constant k_{tr} as defined in equation 1 and the ratio between this constant and the propagation rate constant k_p of styrene and acrylate derivatives

	80 °C	120 °C	150 °C
k_{tr} (acrylate on DOT), kJ mol^{-1}	737	2452	5201
k_p/k_{tr} (acrylate on DOT)	13	10	8.5
k_{tr} (styrene on DOT), kJ mol^{-1}	3.5	20.2	60.3
k_p/k_{tr} (styrene on DOT)	33	23	19

To go a step further, kinetic modellings using the PREDICI software were performed to have a better idea of the copolymerization behavior.

Kinetic simulations

DFT calculations were interesting to understand the behavior of the radical processes, but, due to too many assumptions, cannot describe macroscopically the results of the polymerization. To do this, we first tried to simulate the polymerization using a simplified copolymerization kinetic scheme using the PREDICI software.[29] In this scheme, the main adjustable parameters are the reactivity ratios r_S and r_{DOT} as well as the propagation rate constant of the DOT homopolymer. (the details of the model and its validation on homopolymerization of styrene are presented in ESI, Figure S2). We could fit the experimental conversion of the DOT/S copolymerization at 80 °C with a feed ratio of $[S]_0$:$[DOT]_0$ = 95:5 with a $r_S = 2.0$, a $r_{DOT} = 0.36$ and a $k_{p,DOT} = 30$ L.mol^{-1}.s^{-1} (Figure 2).

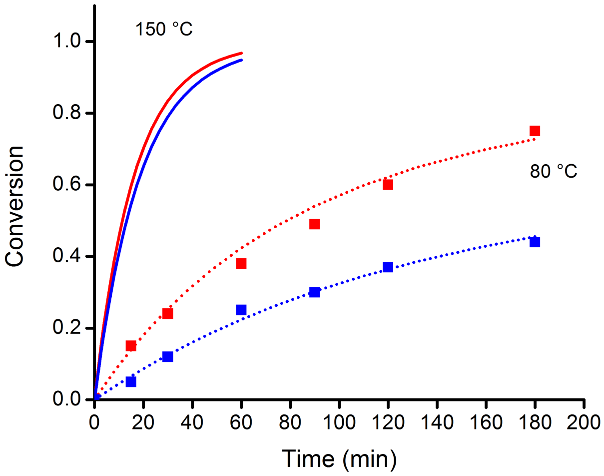


Figure 2. Kinetic plot of the experimental copolymerization of styrene (red squares) and DOT (blue squares) at 80 °C in presence of anisole (10 mol%) with feed ratio $[\text{Styrene}]_0 : [\text{DOT}]_0 = 95 : 5$. The dashed lines are the PREDICI fits using $r_S = 2.0$, $r_{DOT} = 0.36$ and $k_{p,DOT} = 30$ L.mol^{-1}.s^{-1}. The solid lines are the corresponding PREDICI simulations at 150 °C, assuming that the kinetic parameters follow a pseudo-Arrhenius behavior and E_a values determined by DFT calculations.

The reactivity ratios values obtained are interesting since they can be compared to the k_{tr} values that were previously calculated via DFT calculations. In this approach, k_p/k_{tr} is equals to r_S and the experimental value is one order of magnitude lower than the calculated one (2.0 instead of 33). This is in rather good agreement with the assumption of a gas phase and the pre-exponential factors that were only approximated according to the nature of the reaction. Nevertheless, the main interest of the DFT calculations combined with PREDICI simulations relies on the determination of the activation energies that could help us to find optimized experimental temperature. We thus performed also DFT calculations to determine the activation energies and also k_{tr} between the open form of the DOT radical onto the DOT. This allows us to estimate the $k_{p,DOT}$

and the addition of the open form of the DOT radical onto styrene to determine the r_{DOT} value (the details of these calculations are given in ESI). The interesting feature relies on the pseudo-Arrhenius dependency of the two reactivity ratio values. The r_{S} has a -10 kJ.mol^{-1} ($E_{\mathrm{a,p}}$-($E_{\mathrm{a,add}}$+$E_{\mathrm{a}\beta}$-$E_{\mathrm{a,-add}}$)) whereas the r_{DOT} has a 16 kJ.mol^{-1} dependance, meaning that increasing the temperature will lead to bring the two reactivity ratios closer to the value 1 and thus should lead to better incorporation of the two comonomers into the backbone. By using the value determined by fitting and used the calculated pseudo-Arrhenius behavior, we simulated the copolymerization of styrene and DOT with $f_{\mathrm{S,0}}$ =0.95 at 150 °C in 10 % anisole (Figure 2). In that case, simulated r_{S} and r_{DOT} were set to 1.14 and 0.88, with $k_{\mathrm{p,DOT}}$ = 500 L.mol^{-1}.s^{-1}. The results presented in Figure 2 confirm the better copolymerization behavior with rather similar conversion for both styrene and DOT.

Optimized preparation of P(S-*co*-DOT) at 150 °C

The previous theoretical studies comforted us in performing the copolymerization of DOT and styrene at high temperature (150 °C). At this temperature, we used either a peroxide as initiator (Trigonox 301) or the thermal autopolymerization of styrene. The copolymerizations were also carried out with initial feed ratios $[\mathrm{S}]_0 : [\mathrm{DOT}]_0$ of 95 : 5 and 80 : 20 to investigate the influence of DOT content on the degradability of the copolymers. To perform the polymerization with 20 mol% of DOT, 80 mol% of anisole to ensure the good solubility of DOT (*i.e.* $[\mathrm{S}]_0:[\mathrm{DOT}]_0:[\mathrm{Anisole}]_0$ = 8:2:40]) was still used for the two experiments. The resulting P(S-*co*-DOT) copolymers were isolated and analyzed by ^{1}H and ^{13}C NMR spectroscopy. ^{13}C NMR (Supporting Information, Figure S3) confirmed the introduction of the thioester bond into the copolymer backbone with a signal at 192 ppm, characteristic of the thioester functionality (See complete NMR analyses in ESI).

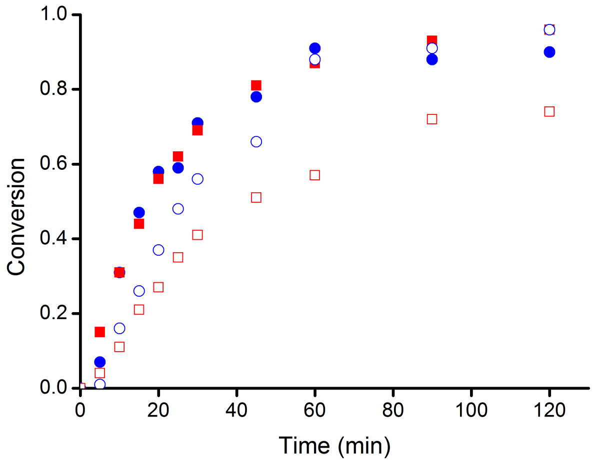


Figure 3. Kinetic plot of the experimental copolymerization of styrene (square) and DOT (dot) at 150°C with 80 mol% anisole with feed ratio $[\mathrm{S}]_0 : [\mathrm{DOT}]_0$ = 95 : 5 (full symbol) and 80 : 20 (empty symbol) initiated with 1 mol% of Trigonox 301.

It has to be noted that the characteristic loss of color is also observed in such copolymerization system (Supporting Information, Figure S4), originating from the isomerization of the colored (C=S)-O- group after the ring-opening of the thionolactone monomer into a (C=O)-S- functionality. The kinetics of the polymerization are reported in Figure 3. Interestingly, and as expected after the PREDICI simulations, the conversion of both monomers are in these conditions rather similar, independently of the initial feed ratio. This indicates a better statistical incorporation of two monomer units into the polymer backbone. As already observed by Gutekunst *et al.*[17] with DOT being incorporated slightly faster than *tert*-butyl acrylate, the experimental incorporation of DOT is also faster compared to styrene, this feature not being expected via the PREDICI simulations.

At the view of these results, we determined the reactivity ratios by fitting the evolution of the feed ratio versus the overall molar conversion (Figure 4), using the Skeist equation and a non-linear least square method (NLLS).[20, 30, 31] This method provides reactivity ratios at 150 °C of r_{S} = 0.55 and r_{DOT} = 1.68 with a $r_{\mathrm{sty}} \times r_{\mathrm{DOT}}$ = 0.92, that is very close to the ideal value of 1. These values are in accordance with the ones determined via DFT calculations and PREDICI simulations (r_{S} = 1.14 and r_{DOT} = 0.88). Despite a slight composition drift at high conversion, a random incorporation of the two monomers was thus demonstrated, which appears essential in the scope of inserting cleavable bonds into the polystyrene backbone. The higher reactivity ratio for the cyclic monomer compared to the vinyl monomer has never been observed and is certainly due to the high rate of radical addition onto the C=S group compared to the cyclic ketene acetal group. The reactivity ratios are also totally different from the values determined at 80 °C by Roth and coworkers[16] on the methyl acrylate – DOT pair (r_{MA}= 0.424 and r_{DOT} = 0.003).

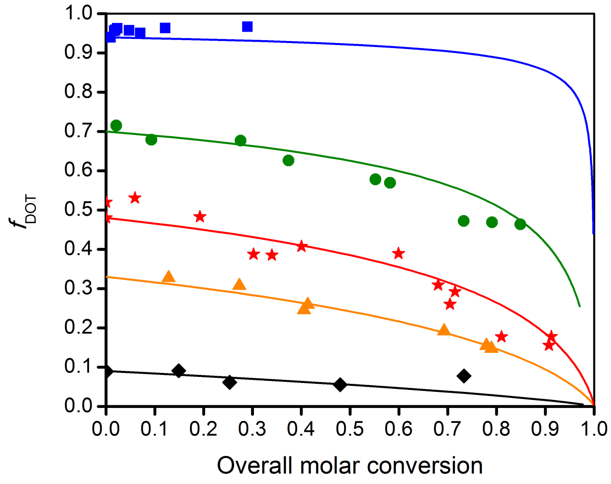


Figure 4. Experimental and theoretical DOT monomer composition versus overall molar conversion with r_{S} = 0.55 and r_{DOT} = 1.68 during the bulk copolymerization of DOT and Styrene at 150 °C initiated with 1 mol% of Trigonox 301.

	Ratio S:DOT	Time (h) Overall conversion	Initiator	Anisole (mol%)	F_{DOT}	M_n (g.mol^{-1})	M_w (g.mol^{-1})	Đ	T_g (°C)	$T_{5\%}$ (°C)
Copo1	80:20	20 0.63	no	80	31	14290	28420	2	94	335
PS1	100:0	17 0.8	no	80	-	45300	88400	2.2	105	386
Copo2	95:5	2 0.91	TG301 (1mol%)	80	4	10700	24600	2.3	91	357
PS2	100:0	2 0.95	TG301 (1mol%)	80	-	11400	26100	2.3	93	332
Copo3	95:5	17 0.88	no	10	5	74900	149900	2	106	357
PS3	100:0	1h45 0.95	no	10	-	85000	180500	2.1	107	386

Table 4 Experimental conditions used to prepare P(S-*co*-DOT) copolymer and reference Polystyrene and their thermal properties

These values supposed a tendency to alternating sequences and thus are not in agreement with the degradation profiles presented into the same study.

Copolymers were then prepared at larger scale (about 3-5 g), targeting to obtain high molecular weight materials, at 150 °C using various polymerization conditions (presence of anisole or thermal initiator, See **Copo1-3** in Table 4). In all cases, corresponding homopolymers were synthesized in the same conditions (**PS1-3**).

As expected, the M_n of the obtained copolymers varies with the use of solvent and quantity of initiators (Trigonox 301 or none). The higher M_n is obtained with only 10 mol% solvent and without initiator, using only thermal auto-polymerization of styrene to initiate polymer chains. It is interesting to note that when using only 5 mol% of DOT, the M_n are rather similar to the refence polystyrene (**Copo2**, **PS2**, and **Copo3**, **PS3**). The main difference relies on the use of an higher $f_{0,DOT} = 0.2$, that decreases the M_n from 45,300 to 14,300 g.mol^{-1} (**Copo1**). This difference could be ascribed to enhanced termination reaction due to the lower rate of the overall polymerization when high amounts of DOT are used.

Thermal and mechanical properties of P(S-*co*-DOT)

The glass transition temperatures of **PS1-3** and **Copo1-3** polymers were analyzed by DSC. As expected, the T_g decreases with the molar masses[32] but more surprisingly, copolymers containing from 5 to 20 mol% DOT display T_gs with only weak differences (1 to 5 °C) from their corresponding homopolystyrenes. Thermogravimetric analyses (TGA) show however 5% degradation temperature T5% significantly lower (about 30 to 50 °C) for **Copo1-3** than for the corresponding PS. This interesting feature is consistent with the incorporation of cleavable DOT units with lower chemical stability. The decomposition temperatures remain yet in all cases above 330 °C, which still constitutes an excellent heat resistance for most applications. The thermomechanical properties of high molar mass polymers **Copo3** and **PS3** were investigated with Dynamic Mechanical Analysis (DMA) (Figure 5). Both materials displayed extremely similar behaviors, with comparable moduli at room temperature and T_α transitions.

Melt rheology was more informative on changes brought by incorporation of DOT units to the viscoelastic properties of the copolymers. To this end, we gathered the frequency-dependent response of small amplitude oscillatory shear (SAOS) over a temperature range from 110 to 190 °C, and constructed the corresponding master curves by time-temperature superposition (TTS) (Figure 6). The large difference in the mastercurves of **PS1-3** illustrates, as expected from the corresponding molar masses, a transition from unentangled (**PS2**) to barely entangled (**PS1**) and significantly entangled melts (**PS3**), evidenced by the appearance of an elastic plateau in the storage moduli.

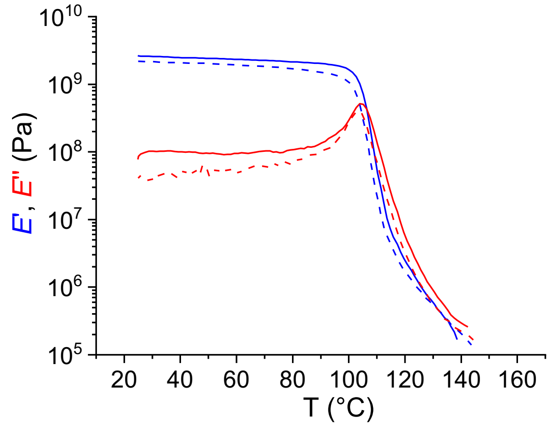


Figure 5. DMA analysis of **PS3** (solid lines) and **Copo3** (dashed lines) at 1 Hz and a heat rate of 3 °C min^{-1}.

While sample **Copo3** containing 5 mol% DOT also displays a well entangled regime, it is interesting to note that its entanglement modulus G_N (measured at the reduced frequency corresponding to minimal value of tanδ[33]) is about 140 kPa, i.e. significatively lower than that of **PS3** (about 190 kPa). This variation can be related to changes of molecular weight between entanglement, $M_e = G_N / (\rho RT)$. While the obtained M_e value at T=120 °C for **PS3** about 18 kg mol^{-1} is in complete agreement with previously reported values,[34] the higher M_e value about 24 kg mol^{-1} of **Copo3** indicates less flexible conformation of the polymer chain, which is consistent with the high rigidity expected from DOT units incorporated the polymer backbone.

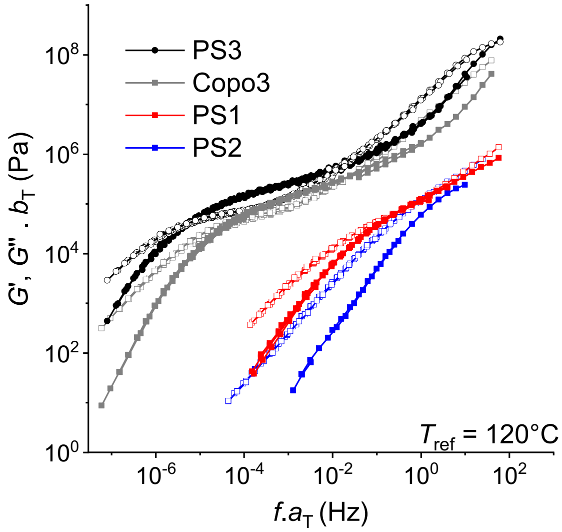


Figure 6. Rheological mastercurves constructed from SAOS analysis of samples **PS1-3** and **Copo3** and referenced at T_{ref} = 120 °C. Storage (G') and loss (G'') moduli are shown using solid and open symbols, respectively.

Degradation studies

Degradation studies of the various copolymers were demonstrated in various conditions. First hydrolysis of PS copolymers in solution was investigated in accelerated conditions by using 5 wt% potassium hydroxide in THF for 18 h (Figure 7). In all cases, we observed a strong decrease of the M_n for the degraded products (M_n between 900 and 3,000 g.mol^{-1}). The reference PS (**PS1-3**) treated in the same conditions did not display any variation of molar mass (Supporting Information, Figure S5), confirming that degradation occurred by the hydrolysis of the cleavable thioester bonds.

The **Copo1** has a higher amount of DOT (31 mol%) and thus led to smaller oligomers (900 g.mol^{-1}). **Copo2** and **Copo3** have the same initial feed ratio of DOT (5 mol%) but the analyses of the isolated copolymer showed a slightly higher incorporation of DOT in **Copo3** (5 mol% in **Copo3** compared to 4 mol% in **Copo2**). This led to a slightly higher M_n for the oligomers (2500 instead of 1600 g.mol^{-1}). The decomposition of the three copolymers using KOH showed nevertheless the expected trend, that is, an increase of M_n for the degraded products in the order **Copo2** > **Copo3** > **Copo1** that is directly correlated with the fraction of thioester units in the polymer backbone. The more interesting result is the 40 times decrease in molar mass that occurs during the degradation of **Copo3**. Considering the theoretical incorporation of 5 mol% of DOT, we could expect an oligomer with 20 styrene units and a degraded DOT at chain ends. The M_n/M_w of the degraded products are rather close to such oligomer length since 15/30 units were measured. The inaccuracy of theoretical and experimental M_n for such oligomers could be due to the non-negligible chain-end effect on the SEC elution.

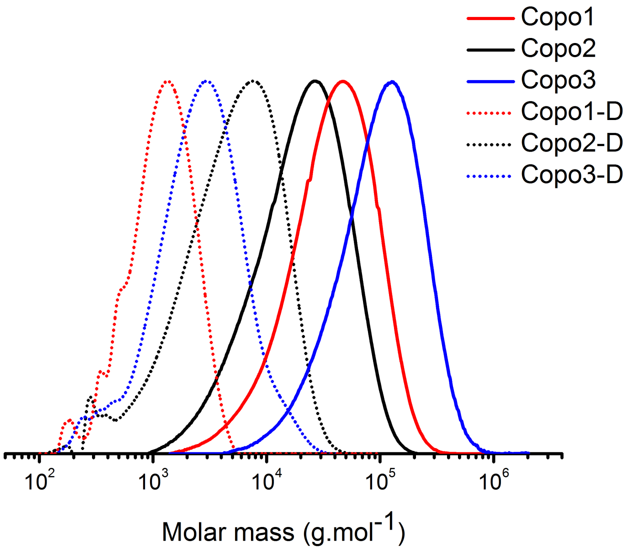


Figure 7. Evolution of the molar mass distribution of the P(S-*co*-DOT) after the degradation process (KOH 5 wt% in THF/MeOH during 18 h): **Copo3** (blue), **Copo2** (black), **Copo1** (red),

The kinetics of hydrolysis was monitored and is rather low (18 h for the complete decomposition, see details in Figure S6) compared to the one reported by Nicolas and coworkers on poly(methyl methacrylate) containing ester units coming from the MPDL CKA copolymerization where degradation in similar conditions lasted only minutes.[35] The kinetics of decomposition is then comparable with the duration that is described by Thoniyot and Van Herk[14] for the degradation of their polystyrene containing ester units.

Other degradations conditions were also tested as discussed previously. First, aminolysis using *N*-isopropylamine in dichloromethane as already reported[16] were still unable to degrade the copolymers (See ESI for details). We thus tried various amines with different steric hindrance such has ethanolamine or even ammonia in THF but without success. Similarly, we tried the heterogeneous degradation of the polystyrene in basic water also without success.

Lastly, we investigated organic acids and bases to induce degradation. Addition of organic acids such as trifluoroacetic acid (TFA) or para-toluene sulfonic acid (PTSA) in THF (2.5 wt%) did not trigger important changes (Supporting information, Figure S7). While 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in THF was recently found very efficient to degrade polythioesters,[36] our tests in similar conditions showed again very little effect (Figure 8).

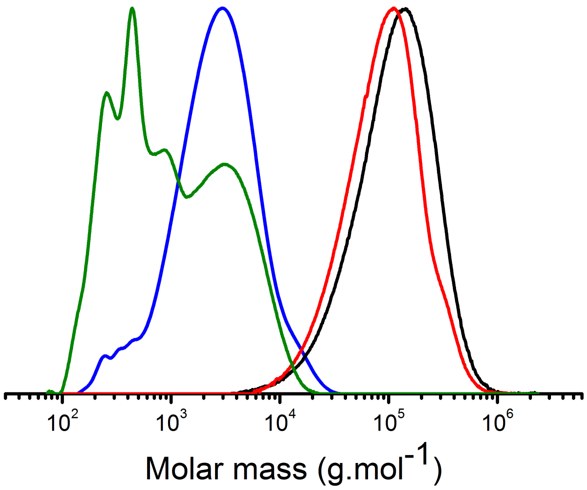


Figure 8. Evolution of the molar mass distribution of P(S-*co*-DOT) during the degradation process: **Copo3** before degradation (dark), **Copo3** after 17h of degradation using DBU (red), **Copo3** after 18h of degradation using KOH (blue), **Copo3** after 1h of degradation using TBD (green).

Other strong organic bases such as TBD were however much more efficient, leading to a very rapid and complete decomposition of the thioester moieties achieving oligomers of M_n = 600 g.mol^{-1} and M_w = 1,950 g.mol^{-1} for the degradation of **Copo3**. This very low M_n compared to the theoretical one (2200 g.mol^{-1}) could be due to the non-linearity of the calibration curve at such low molecular weight but also in the presence of residual TBD that cannot be separated of such small oligomers.

In order to analyze with a faster time-resolution the quick degradation of the copolymers by TBD, we set-up an *in-situ* rheology experiment using a Couette cell (volume 5 mL) and concentrated polymer solutions (20 wt%), The evolution of the specific viscosity η_{sp} was monitored upon addition of a concentrated TBD solution in THF (overall concentration 1.25 wt%) and thorough mixing (Figure 9).

While no significant differences upon addition of TBD can be seen on **PS3** solutions, the decrease of viscosity starts readily for **Copo3** solutions. Based on the final values of viscosities obtained after 2.5h, the 90% decrease is obtained in less than 20 min.

Finally, **PS3** and **Copo3** were tested for bacterial degradation. As said previously, the biodegradation of polystyrene has been investigated using a wide range of fungi, microbes and invertebrates.[6, 37] According to literature data and the availability of the various bacteria, *Pseudomonas aeruginosa* and *Aspergilus niger* were selected.[38, 39] The two polystyrenes were then incubated as powders with the bacteria in a culture medium without carbon source. To monitor the antimicrobial activity, we chose to use microcalorimetry. This technique has been shown to serve as an indirect measurement of a particular bioactivity that is not easily measurable in complex biosystems and bioprocesses.[40] Moreover, the high degree of sensitivity, precision and accuracy of this technique is interesting to observe very small change between reference **PS3** and **Copo3**. The experiments are detailed in ESI. After 70 h, the **Copo3** presented a slightly higher activity than the reference **PS3** (Figure S8), which shows premises for the degradation of such materials. The complete study focusing on the bacterial degradation of p(S-*co*-DOT) copolymers will be further detailed in a subsequent article.

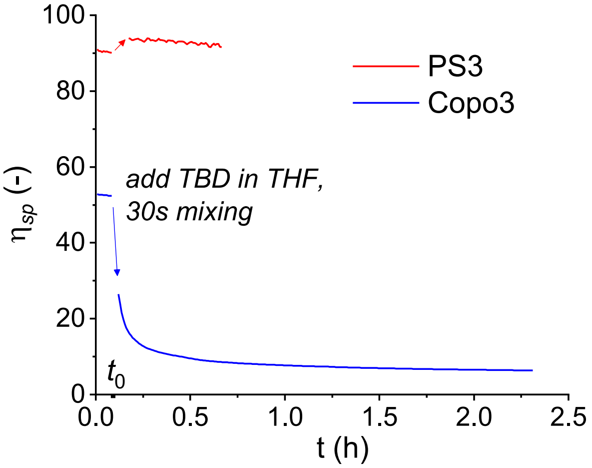


Figure 9. Evolution of specific viscosity of solutions of **PS3** and **Copo3** in THF (20 wt%) upon addition of concentrated TBD solution in THF leading to an overall TBD concentration of 1.25 wt%.

Triggered degradation

The efficient degradation of p(S-*co*-DOT) copolymers in presence of TBD is a good promise for the controlled degradation of polystyrene materials. Indeed, such degradation as shown previously is very fast after the introduction of the organic base. To selectively trigger the degradation, we sought to prepare a photolatent TBD also known as photobase generator.[41] Usually, these compounds are quaternary ammonium salts that generate, upon irradiation, the corresponding amine after a decarboxylation process[41] (Figure 10b). As a proof of concept, we prepared the TBD ammonium salt of phenylglyoxylic acid in one straightforward step, following an adapted procedure[42] (Figure 10a).

The photolatent TBD (4 wt% to mimic 2 wt% TBD) and **Copo3** was then mixed in THF at room temperature and analyzed by SEC 120 h later. The results are presented in Figure 10c and confirmed the non-degradation of the **Copo3** with the protected TBD.

The THF solution was then irradiated using a mercury lamp for 10 times 2.5 min with hand shaking between the irradiations and analyzed by SEC one hour later. As expected, the base was released and led to the degradation of the **Copo3**, confirming the efficiency of the controlled degradation. This approach open the way to a new procedure to both keep the usage materials properties of a product and thus accelerated its degradation after use by irradiation. Phenylglyoxylic acid has a strong absorption at 254 nm and thus required to use a mercury lamp. Chromophores absorbing at higher wavelength will be needed to improve the irradiation but this result open the way for a triggered degradation with such polymers.

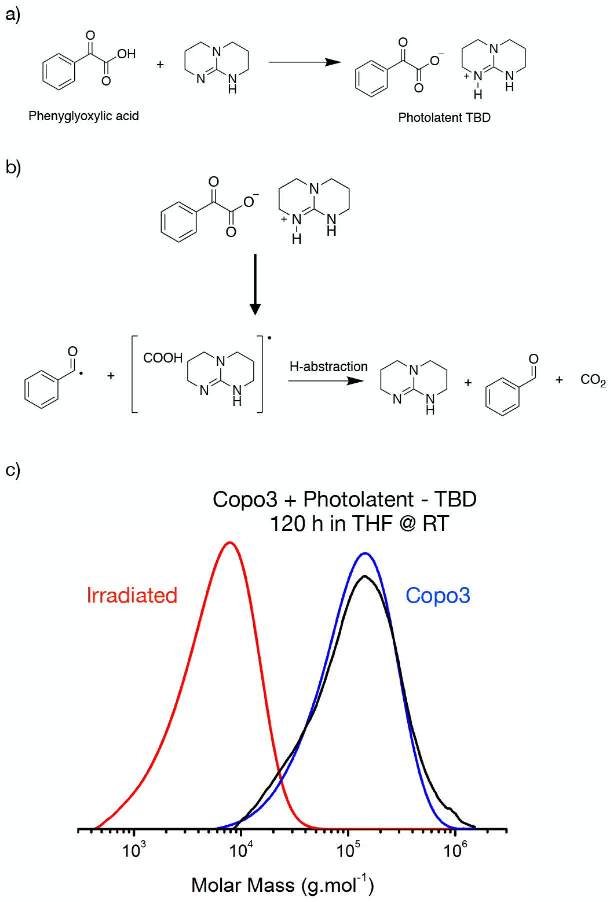


Figure 10. a) Synthesis of the photolatent – TBD. b) Deprotection mechanism of the Photolatent – TBD upon irradiation. c) Evolution of the molar mass distribution of the **Copo3** P(S-*co*-DOT) in THF (blue), after mixing with Photolatent – TBD (2 wt%) during 120 h at RT (black) and after 10 times 2.5 min of irradiation and one hour of reaction.

Cross-linked polystyrene

Besides linear polystyrene chains, polystyrene has been also widely used in cross-linked materials thanks to straightforward radical copolymerization with divinyl benzene. Such cross-linked polymers have notably found applications as supports for polymer-bound reagents and catalysts, ion exchange resins and separation media.[43-45] Recently, Johnson and coworkers[46] reported that the incorporation of a small amount of cleavable bond into the linear segments of a network afforded very efficient degradability (Figure 11). Building upon this concept, cross-linked poly(S-*co*-DOT) networks were prepared via the copolymerization at 150 °C of styrene : divinyl benzene : DOT mixtures with molar ratios of 94 : 1 : 5. A non-cleavable network was also prepared for comparison purposes with molar ratios of styrene : divinyl benzene of 99 : 1. At the end of the polymerization we obtained cross-linked solid polystyrene pellets (Figure 11a). When DOT was incorporated inside the materials, the orange/yellow color was maintained due to the non-complete conversion of all monomers during the reaction. Extensive washings were performed using acetone to remove the unreacted DOT to the thermoset, but a pale-yellow color still remained. Both reference thermoset and the DOT-containing one were then degraded in THF using both TBD and 5 w% KOH. In both cases, the reference thermoset was not degraded and did not lose weight whereas the thermoset containing DOT led to opaque solution without any remaining solid materials (Figure 11b). The TBD degradation is far more effective than the one using KOH due to solubility issues. This result demonstrates that a small amount of DOT (5 mol%) is thus efficient to allow the complete degradation of cross-linked polystyrene.

CONCLUSION

Thionolactones have been recently reported to be a new promising family of monomers able to undergo radical ring-opening. It was especially noted that the copolymerization of DOT with styrene was unsuccessful. In this article, we first reinvestigated in details the copolymerization of DOT and styrene and we showed that, contrary to what was claimed in the literature, DOT could be incorporated into the PS backbone but with a lower reactivity that led to roughly half of the initial feed ratio inserted. We thus performed some DFT calculations coupled with PREDICI simulation that suggested to increase the reaction temperature to allow a better randomly incorporation of the DOT unit into the PS backbone. The copolymerization was thus carried out at 150 °C using either Trigonox 301 or the thermal auto-initiation of styrene. The insertion of both monomers was then measured and led to reactivity ratios of $r_S = 0.55$ and $r_{DOT} = 1.68$ with a $r_{sty} \times r_{DOT} = 0.92$, showed a more statistical incorporation of DOT inside the polymer chains. Using this temperature, a high molecular weight PS containing 5 mol% of DOT was then obtained that presented similar thermal and mechanical properties than the reference PS. These copolymers were then degraded and showed peculiar degradation conditions: they are rather stable in acidic conditions, impervious to aminolysis regardless of the primary amine used but presented a good degradation profile when strong bases such as KOH or TBD are used. In the latter case, total degradation in less than one hour was observed.

The use of TBD let us envision a controlled degradation using a photolatent-TBD compound based on the phenylglyoxylic acid chromophore. The proof of concept was demonstrated in solution. Lastly, we also extent this work to cross-linked polystyrene. The solid pellets coming from the introduction of a small amount of divinylbenzene could be made soluble by the introduction of 5 mol% of DOT in the initial recipe followed by a degradation using either TBD or KOH.

In summary, this article showed that the use of 5 mol DOT as a comonomer in an industrial-scalable recipe leads to a material that are similar properties (molecular weight, thermal, mechanical, etc.) than polystyrene but that could be degraded in oligomers with less than 10 units long after a mild chemical treatment

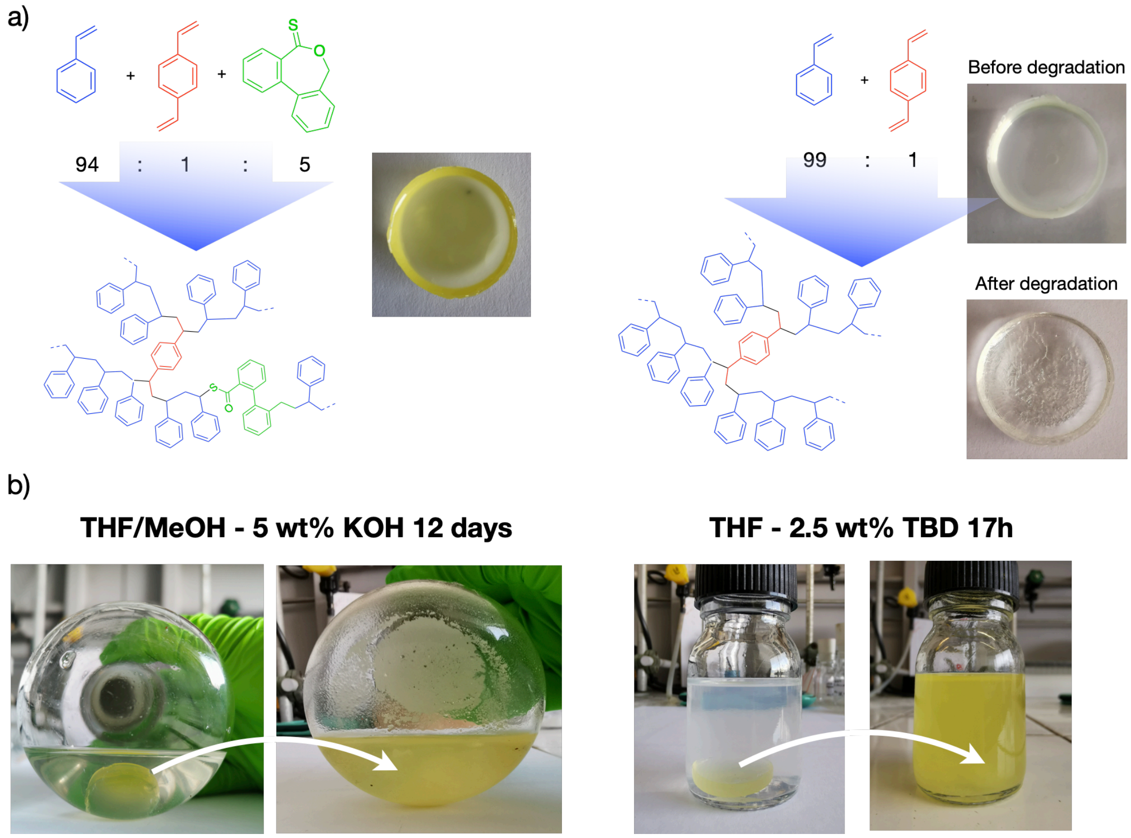


Figure 11. a) Preparation of cross-linked polystyrene using 1 mol% of divinylbenzene with and without 5 mol% of DOT. b) Degradation of the P(S-co-DOT) thermoset either using KOH (5 mol% in THF/MeOH) or 2.5 wt% TBD in THF.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website. ^{1}H NMR and ^{13}C NMR spectra of the various polymers, kinetic rate constants used in the modeling part,

AUTHOR INFORMATION

Corresponding Author

Catherine.lefay@univ-amu.fr ;
yohann.guillaneuf@univ-amu.fr

Author Contributions

The manuscript was written through contributions of all authors.

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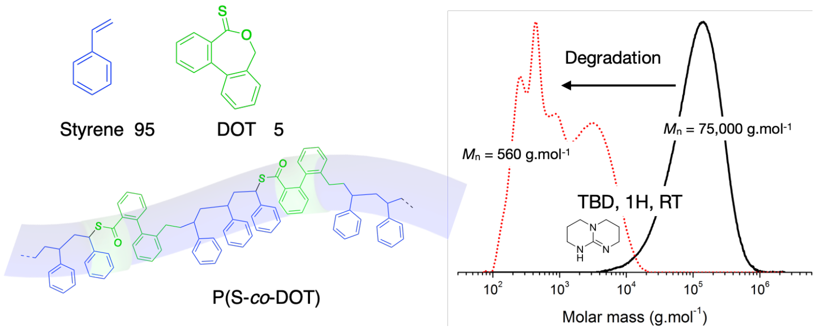
TOC


Styrene 95
DOT 5
S
O
P(S-*co*-DOT)
Degradation
M_n = 75,000 g.mol^{-1}
M_n = 560 g.mol^{-1}
TBD, 1H, RT
N
H
10^2
10^3
10^4
10^5
10^6
Molar mass (g.mol^{-1})