

Mechanical Acceleration of Ester Bond Hydrolysis in Polymers

Jian Wang, Xiaobin Gao, Alice Boarino, Frédéric Célerse, Clémence Corminboeuf, and Harm-Anton Klok*



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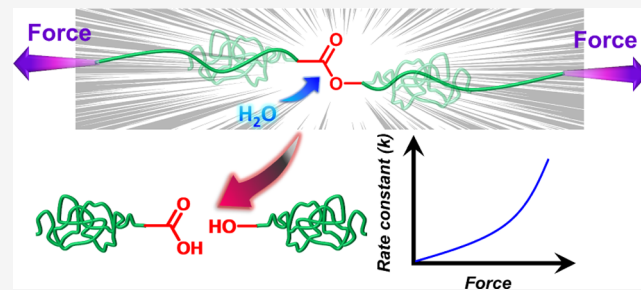


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ABSTRACT: Polymers containing ester bonds are ubiquitous. Often, these materials are mechanically challenged, which impacts their stability and degradation. While the accelerative effect of force on the degradation of polyester polymers is well recognized, little is known about the identity of the bonds that are cleaved, the nature of the cleavage reactions, and the force sensitivity of these processes. To provide molecular-level insights into the force-accelerated degradation of ester bonds, this study has investigated the degradation of ester bond-containing polymers in dilute solution ultrasonication experiments. These experiments revealed that chain degradation proceeds via concomitant homolytic carbon–carbon scission as well as ester bond hydrolysis, and demonstrated that ester bond hydrolysis is force accelerated, both under neutral and basic conditions. Experiments with side chain ester functional polymers, in contrast, did not indicate ester bond hydrolysis, which suggests that the molecular force does not lead to the activation of ester bonds that are orthogonal to the polymer backbone.



INTRODUCTION

It is well established that mechanical force can trigger and accelerate the degradation of polymer materials.^{1–9} In early work, H. Staudinger already reported a decrease in the molecular weight of polystyrene upon mastication.^{10–12} The degradation of all carbon backbone polymers under mechanical load is the consequence of a sequence of multiple homolytic carbon–carbon bond scission events. The impact of mechanical force on the degradation of polymers is ubiquitous and not only limited to macromolecules composed of an all-carbon backbone.

Mechanical force also impacts the stability and degradation of polymers that contain functional groups, such as ester bonds, as part of their main chain.^{13–16} Ester bonds are omnipresent in a wide range of polymer materials. Examples include degradable hydrogels as well as bioresorbable sutures or screws that are used for wound fixation.^{17–20} In many instances, these materials are mechanically challenged in one or several ways during their use.

A large number of studies have been reported, which illustrate the impact of mechanical force on ester containing polymers. One example is the accelerated degradation of poly(lactic acid) under mechanical load.^{21–27} Another example is the environmental stress cracking that is observed when poly(ethylene terephthalate) under tension is exposed to aggressive chemicals.²⁸

While the accelerative effect of force on the degradation of polyester polymers is well recognized, only little is known about the underlying molecular-level chain cleavage events and

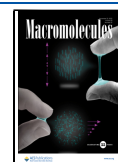
the force sensitivity of these reactions. Important open questions, for example, pertain to the identity of the bonds that are cleaved, the nature of the bond cleavage reactions, and the force sensitivity of these processes. This is in stark contrast to the degradation of all carbon backbone polymers under the influence of force, which, via extensive experiments that have used ultrasonication and flow to apply mechanical load, has been characterized in detail as a mechanochemical process.^{1,2}

This study seeks to provide molecular-level mechanistic insight into the force-accelerated degradation of ester bond-containing polymers. The effect of force on the chain degradation was studied in dilute solution model experiments in which ester bond-containing polymers were subjected to ultrasonication. These experiments were conducted both with model polymers that contain a defined number of main chain ester bonds and polycaprolactone, as a technically relevant polyester, and also included side chain ester-functionalized polymers such as poly(methyl methacrylate) (PMMA) and poly(vinyl acetate) (PVAc).

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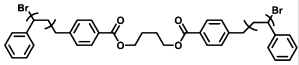
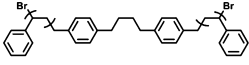
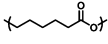


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RESULTS AND DISCUSSION

To decipher the molecular-level scission events that underlie the mechanical degradation of ester bond-containing polymers, this study has investigated the ultrasonication of a variety of different polymers (Table 1). As model polymers that contain

Table 1. Number-Average Molecular Weights (M_n), Number-Average Degrees of Polymerization (DP), and Dispersities (\mathcal{D}), All Determined by GPC Analysis, of the PS(ester), PS(carbon), PCL, PVAc, and PMMA Polymers Investigated in This Study

Polymer	M_n (kDa)	DP (-)	\mathcal{D} (-)
 PS(ester)	170	1630	1.41
	72	690	1.25
	50	480	1.20
	32	300	1.17
	10.2	100	1.23
 PS(carbon)	190	1820	1.41
	130	1250	1.27
	77	730	1.14
	49	470	1.13
	29	280	1.14
 PCL	120	1050	1.40
	45	400	1.32
 PVAc	84	980	1.45
 PMMA	53	530	1.80

a defined number of ester bonds in the polymer main chain, a series of polystyrene polymers (PS(ester)) that contain two ester linkages in the center of the polymer chain were studied (Table 1). As a control, a second series of polystyrene polymers were investigated that was composed of an all-carbon backbone (PS(carbon), Table 1). PS(ester) and PS(carbon) polymers covering a range of molecular weights were obtained via atom transfer radical polymerization of styrene using butane-1,4-diyl bis(4-(bromomethyl)benzoate) (BDMB) and 1,4-bis(4-bromomethylphenyl)butane (BBPB) as the initiator. Table 1 shows the structures of the two polymers and summarizes the molecular weights of the samples that have been prepared. Details on the synthesis of the PS(ester) and PS(carbon) polymers are provided in Schemes S1 and S2. In addition to experiments on the model polystyrene polymers, ultrasonication studies were also performed on polycaprolactone (PCL) as a representative, technologically relevant ester-containing polymer. For these analyses, PCL samples with two different molecular weights were used, which are listed in Table 1. In addition to being part of the polymer backbone, such as in PCL, ester bonds can also be incorporated in polymers in the form of side chain functional groups. Mechanical force has also been reported to allow the activation and scission of bonds that are not parallel to the direction of force.^{6,29–37} To assess the effect of mechanical force on the cleavage of ester bonds that are orthogonal to the polymer backbone, ultrasonication experiments were also conducted on poly(vinyl acetate) (PVAc) and poly(methyl methacrylate) (PMMA) (Table 1).

One challenge in the study of the effect of mechanical force on ester bond cleavage in polymers is that chain degradation upon activation with, for example, ultrasound may proceed concurrently via homolytic carbon–carbon bond scission as well as ester hydrolysis. When water-soluble polymers are investigated in aqueous solution, these two contributions are hard to distinguish since under these conditions water acts both as the solvent and reagent (for ester bond hydrolysis). This study, therefore, has studied the effect of ultrasonication on the degradation of the ester-containing polymers that are listed in Table 1 in water-miscible organic solvents, such as tetrahydrofuran (THF). In this way, the contributions from homolytic carbon–carbon bond scission and ester hydrolysis can be distinguished by comparing the results of ultrasonication experiments in dry THF, which lacks the water that is necessary for ester hydrolysis, with those of the experiments in which small quantities of water are added to the THF.

In a first series of experiments, the effect of mechanical activation on the degradation of the model PS(ester) polymers was investigated. For these experiments, polymers were dissolved at a concentration of 1.2 mg/mL in either THF or a THF + 5 vol % water mixture. To exclude polymer–polymer interactions and chain entanglements, the sample concentration was selected to be well below the overlap concentration of polystyrene for the range of molecular weights indicated in Table 1.³⁸ Chain degradation during ultrasonication generally occurs at the mid-point of the polymer chain² and continues until the molecular weight of the fragments is below a certain threshold, and no further chain cleavage takes place. To distinguish chain degradation events that are the result of direct homolytic C–C backbone scission from those that are the consequence of ester bond hydrolysis (which requires water), ultrasonication experiments were performed in solutions of the polymer in both THF and THF containing 5 vol % water. Chain degradation was monitored by GPC analysis of samples that were subjected to ultrasonication for different periods of time.

Figure 1A illustrates the decrease in molecular weight that is observed upon exposure of a PS(ester) polymer with an initial number-average molecular weight (M_n) of 170 kDa to pulsed ultrasound at a power density of 2.0 W/cm² for 120 min. From the change in M_n , an apparent rate constant (k') for the chain degradation reaction can be obtained using eq 1:

$$\frac{1}{M_t} = \frac{1}{M_i} + k't \quad (1)$$

where M_t is the number-average molecular weight of the sonicated sample at time t and M_i is the initial number-average molecular weight of the polymer.^{39–43} Rate constants are obtained by least squares linear regression analysis of the slope of plots of $(1/M_t - 1/M_i)$ vs time, as illustrated in Figure 1B for the PS(ester) sample with $M_i = 170$ kDa. To estimate the conversion of the initial PS(ester) polymer, the GPC chromatograms were deconvoluted as illustrated in Figure 1C for a PS(ester) sample with an initial number-average molecular weight of 170 kDa that was subjected to ultrasonication at a power density of 2.0 W/cm² for 120 min in THF with 5 vol % water (deconvoluted GPC traces of this sample at other ultrasonication times are provided in Figure S1). Figure 1D plots the conversion of this PS(ester) sample, that is, the percentage of the polymer that has undergone chain scission, as a function of reaction time.

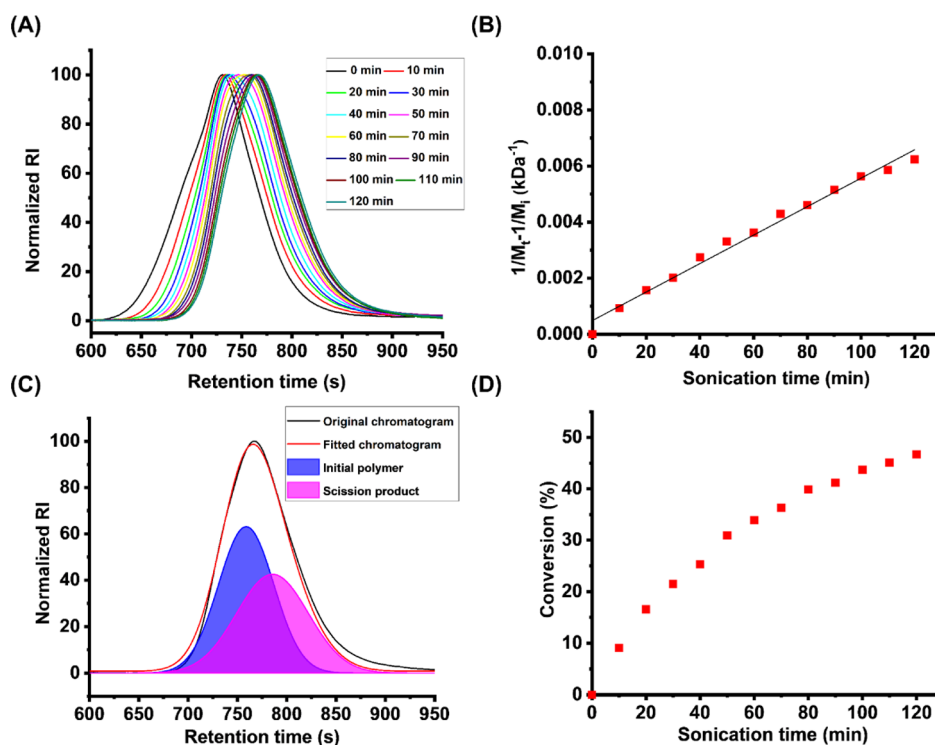


Figure 1. (A) GPC traces of a PS(ester) sample with an initial number-average molecular weight (M_n) of 170 kDa upon ultrasonication in THF + 5 vol % water at a power density of 2.0 W/cm²; (B) plot of $(1/M_t - 1/M_i)$ for a PS(ester) sample with $M_n = 170$ kDa as a function of sonication time in THF + 5 vol % water at a power density of 2.0 W/cm²; and (C) deconvolution of the GPC trace of a PS(ester) sample with initial $M_n = 170$ kDa in THF + 5 vol % H₂O after ultrasonication for 120 min at 2.0 W/cm². Original normalized GPC curve (black), fitted GPC curve (red), initial, non-degraded polymer (blue), and scission product (pink). $r^2 = 0.994$; (D) conversion of the PS(ester) sample with initial $M_n = 170$ kDa as a function of sonication time in THF + 5 vol % water at a power density of 2.0 W/cm².

Figure 2 summarizes the results of all the ultrasonication experiments that were carried out with the PS(ester) samples and the PS(carbon) control polymers. First, the effect of polymer molecular weight on the degradation of the PS(ester) samples at a power density of 2.0 W/cm² was studied. For the PS(ester) sample with an initial M_n of 10.3 kDa, no degradation was observed in THF and THF + 5 vol % water under these conditions (Figure S2). This reflects that a certain threshold polymer molecular weight is required for the polymer main chain to experience a force that is sufficient for chain degradation to occur.^{44–47} For all the other polymers, chain degradation was observed. Figure 2A plots the rate constants of degradation for the PS(ester) polymers that were determined from ultrasonication experiments performed in THF and THF + 5 vol % water. As is commonly observed upon the ultrasonication of polymers in solution, the rate constants for the degradation reaction increase with increasing initial polymer molecular weight.^{16,40,44,46,48–52} Furthermore, for a given initial polymer molecular weight, Figure 2A indicates an increase in the rate constant of degradation in THF + 5 vol % water as compared to that determined in THF for the same sample, which is consistent with a contribution of ester bond hydrolysis to chain degradation in the water-containing medium. GPC analysis of ultrasonication experiments on a PS(ester) sample with an initial M_n of 170 kDa in THF, THF + 2.5 vol % water, and THF + 5 vol % water revealed an increase in the rate constant for degradation with increasing water concentration in the THF solution (Figure S3). In Figure 2B, the degradation rate constants determined for 3 PS(carbon) samples in THF and THF + 5 vol % water

solutions are shown and compared with those measured for PS(ester) samples of similar molecular weight in (dry) THF. PS(carbon) polymers with initial number-average molecular weights of 10.9 and 29 kDa were not found to undergo chain degradation under these conditions. Figure 2B reveals no significant difference between the degradation rate constants for PS(carbon) and PS(ester) samples of comparable molecular weight in THF. Since degradation of the PS(carbon) polymers can only proceed via homolytic scission of backbone carbon–carbon bonds, this indicates that the degradation of the PS(ester) polymers in THF also involves homolytic carbon–carbon bond scission. Figure 2B further shows that the degradation rate constants for the PS(carbon) samples do not change in the presence of 5 vol % water. There is further evidence indicating that the increase in the degradation rate constants that is observed for the PS(ester) samples upon addition of 5 vol % water (Figure 2A) can be attributed to the contribution of ester bond hydrolysis to the chain degradation process. Figure 2C presents the apparent rate constants for ester bond hydrolysis, which were obtained by subtracting the degradation rate constants in THF + 5 vol % water and those measured in THF for the PS(ester) samples reported in Figure 2A. The data in Figure 2C indicate an increase in the apparent rate constant for ester hydrolysis with increasing polymer molecular weight.^{16,40,44,46,48–52} The apparent rate constants for ester hydrolysis increase not only with increasing initial polymer molecular weight but also with increasing ultrasonication power, that is, mechanical force,^{2,49,53–56} as illustrated in Figure 2D. Figure 2D compares the apparent rate constants for ester hydrolysis that were

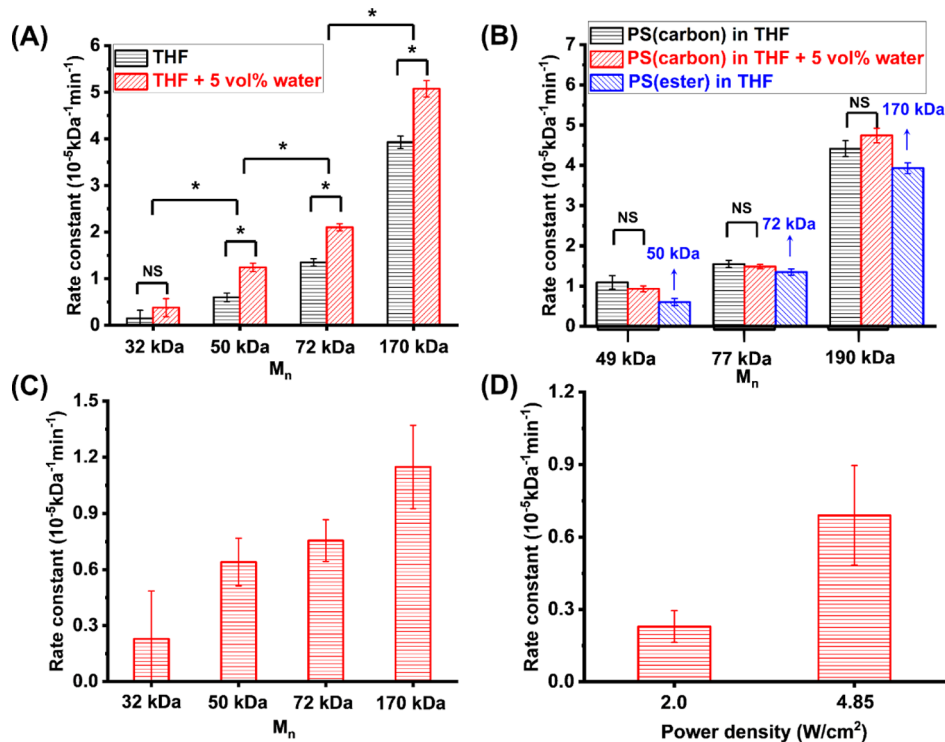


Figure 2. (A) Rate constants of degradation determined for PS(ester) samples with initial M_n = 32, 50, 72, and 170 kDa upon ultrasonication in THF (black) and THF + 5 vol % water (red) at a power density of 2.0 W/cm^2 ; (B) rate constants of degradation determined for PS(carbon) polymers with an initial M_n of 49, 77, and 190 kDa ultrasonicated in THF (black) and THF + 5 vol % water (red) as well as for PS(ester) samples with an initial M_n of 50, 72, and 170 kDa ultrasonicated in THF (blue) at a power density of 2.0 W/cm^2 ; (C) apparent rate constants of ester hydrolysis determined for PS(ester) polymers with initial M_n = 32, 50, 72, and 170 kDa at a power density of 2.0 W/cm^2 ; and (D) rate constants of ester hydrolysis determined for a PS(ester) polymer with an initial M_n of 32 kDa at power densities of 2.0 and 4.85 W/cm^2 . Error bars represent standard deviations from least square linear regression analysis. Asterisks indicate statistically significant differences, whereas NS represent not significant difference between the two conditions. Significant at $*p < 0.05$.

measured for a PS(ester) polymer with an initial molecular weight of 32 kDa at power densities of 2.0 and 4.85 W/cm^2 . The molecular weight and power density dependence of the hydrolysis rate constants are characteristic for ultrasonication-mediated polymer degradation processes.^{49,53–56} The observed increase in the degradation rate constant upon the addition of 5 vol % water (Figure 2A) and the increase in the apparent rate constant of hydrolysis with increasing polymer molecular weight (Figure 2C) and power density (Figure 2D) are strong indications that point toward a mechanical acceleration of ester bond hydrolysis.

To identify the nature of the bond cleavage reactions that contribute to the observed ultrasound degradation of the polystyrene model polymers, a number of further experiments were performed. In a first experiment, ultrasonication of PS(ester) polymer samples was conducted in the presence of 1,1-diphenyl-2-picrylhydrazyl (DPPH). DPPH is a radical scavenger with a UV–vis absorption maximum at 520 nm, which becomes colorless upon reaction with a radical species. Ultrasonication experiments were performed with a PS(ester) sample with an initial M_n of 170 kDa in THF and THF + 5 vol % water in the presence of DPPH at 2.0 W/cm^2 for a period of 120 min. At regular time intervals, samples were withdrawn from the reaction solution and analyzed with UV–vis spectroscopy to monitor the DPPH conversion. For the experiments performed in both THF and THF + 5 vol % water, the spectra shown in Figure S4 illustrate a gradual decrease in the intensity of the UV–vis absorbance at 520 nm, which is consistent with the generation of radicals due to

homolytic carbon–carbon scission. Comparison of the results of the experiments performed in THF and THF + 5 vol % water reveals similar rates of DPPH consumption in both media [$(5.09 \pm 0.14) \times 10^{-4} \text{ mM} \cdot \text{min}^{-1}$ in THF and $(4.54 \pm 0.25) \times 10^{-4} \text{ mM} \cdot \text{min}^{-1}$ in THF + 5 vol % water]. In contrast, in DPPH solutions that did not contain a polymer, no significant decrease in the DPPH concentration was observed, both in the presence and absence of ultrasonication (see Figure S5). This indicates (as also suggested by the results in Figure 2B) that the rate of homolytic carbon–carbon backbone scission is independent of the reaction medium and highlights the contribution of ester bond hydrolysis to backbone scission for experiments performed in THF + 5 vol % water.

Ultrasonication of the PS(ester) polymers was further analyzed by FTIR and ^1H NMR spectroscopy. Figure S6A compares the FTIR spectra of a PS(ester) sample with an initial M_n = 32 kDa before and after ultrasonication at a power density of 4.85 W/cm^2 for 4 h. While end-group analysis on high-molecular-weight polymers is not straightforward, the spectra indicate the appearance of a broad peak at 3400 cm^{-1} upon ultrasonication that can be assigned to O–H stretching vibrations of carboxylic acid residues, which indicates that the ester bond hydrolysis contributes to the observed decrease in molecular weight.

The contribution of ester hydrolysis to the degradation of the PS(ester) samples was also studied by ^1H NMR spectroscopy. To this end, ultrasonication experiments were performed in 2-butanone (MEK) and MEK + 2 vol % water solutions instead of THF. MEK was chosen as the solvent

since trace amounts of THF that were found difficult to remove resulted in NMR signals that overlap with key NMR resonances of the PS(ester) polymer samples. First, chain degradation of a 50 kDa PS(ester) sample upon ultrasound irradiation at 2.0 W/cm² in MEK and MEK + 2 vol % water for 200 min was monitored by GPC. The degradation rate constants obtained from these experiments are summarized in Figure S6B. These rate constants are comparable to those obtained in THF and THF + 5 vol % water solutions (Figure 2A), indicating that changing the solvent to MEK does not significantly alter the chain degradation. The results in Figure S6B also confirm the earlier observed increase in the rate constant of degradation in the presence of water, which reflects the contribution of ester hydrolysis to chain degradation in the presence of water. Figure S7 presents ¹H NMR spectra of a PS(ester) sample (initial M_n = 50 kDa) and the BDMB initiator and highlights the key resonances that were used to monitor polymer degradation. To assess the contribution of ester hydrolysis to chain degradation, the ratio of the integrals of a signal, which is due to the aromatic protons of the styrene repeat units of the polymer, was compared with that of a key resonance of the BDMB initiator. Figures S8 and S9 show the ¹H NMR spectra of this polymer both before and after ultrasonication for 200 min at 2.0 W/cm². The ¹H NMR spectrum in Figure S9 suggests a small change in the ratio of the integrals of these two sets of characteristic resonances when PS(ester) samples were ultrasonicated in MEK + 2% water, which is consistent with a contribution of ester hydrolysis to chain degradation. Deconvolution of the GPC trace of this PS(ester) sample (initial M_n = 50 kDa) reveals that ~5.6% of the polymer chains have undergone backbone degradation after ultrasonication in MEK + 2 vol % water for 200 min at 2.0 W/cm² (Figure S10). From the ¹H NMR spectra presented in Figure S9, it is seen that an estimated 2.6% of the ester bonds are cleaved via hydrolysis, which indicates that roughly half of the chain degradation events involves homolytic carbon–carbon bond scission and half proceeds by ester hydrolysis. This is in good agreement with the results presented in Figure 2, which indicate comparable rate constants for chain degradation for a PS(carbon) sample of 49 kDa and ester hydrolysis for a PS(ester) polymer with M_n = 50 kDa.

The experiments discussed so far were conducted using water at neutral pH. To further corroborate that ester hydrolysis contributes to the ultrasound-induced degradation of the PS(ester) samples, an experiment was performed, in which a 170 kDa PS(ester) sample was subjected to 2.0 W/cm² ultrasound irradiation in the presence of imidazole, which is a catalyst known to accelerate ester hydrolysis.⁵⁷ Figure 3 presents the degradation rate constants determined for the ultrasonication of a 170 kDa PS(ester) sample in THF, THF + 5 vol % water, as well as THF + 5 vol % water with 0.1 M imidazole. For comparison, Figure 3 also shows the rate constants of degradation determined for ultrasonication of a PS(carbon) sample of M_n = 130 kDa in the same three media. The results in Figure 3 reveal a significant increase in the rate constant of degradation of the PS(ester) sample upon the addition of 0.1 M imidazole, which is further evidence that ester hydrolysis contributes to the observed chain degradation. In contrast, no significant differences between the degradation rate constants for PS(carbon) were observed when a 130 kDa sample was subjected to 2.0 W/cm² ultrasonication in the same three media. As a control experiment, the PS(ester)

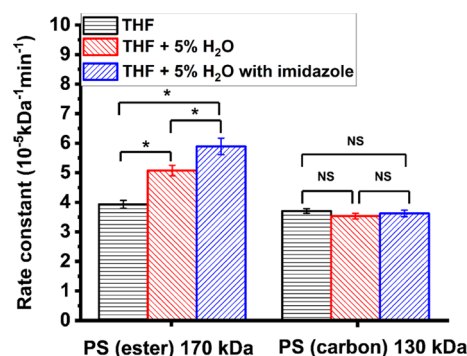


Figure 3. Rate constants of degradation of a PS(ester) sample with an initial M_n of 170 kDa upon ultrasonication at a power density of 2.0 W/cm² in THF (black), THF + 5 vol % water (red), and THF + 5 vol % water with 0.1 M imidazole (blue) as well as for a PS(carbon) polymer with an M_n of 130 kDa in THF, THF + 5 vol % water, and THF + 5 vol % water with 0.1 M imidazole. Error bars represent standard deviations from least square linear regression analysis. Asterisks indicate statistically significant differences, whereas NS represents no significant differences between the two conditions. Significant at $*p < 0.05$.

polymer was dissolved in THF + 5 vol % water together with 0.1 M imidazole and analyzed by GPC after 24 h (without the application of ultrasound). Supporting Information Figure S11 compares the GPC trace of this sample with that of the original polymer as well as that of the same polymer after 120 min ultrasonication at 2.0 W/cm² in the same medium. While ultrasonication in THF + 5 vol % water in the presence of 0.1 M imidazole results in chain degradation, no changes in polymer molecular weight were observed when the sample was incubated in this same medium without the application of ultrasound. This illustrates that mechanical activation accelerates ester hydrolysis under both neutral and basic conditions.

Next, to explore whether force-accelerated ester hydrolysis also contributes to the degradation of commercially available main chain ester polymers, two polycaprolactone (PCL) polymers with molecular weights of 45 and 120 kDa were studied in the same way as the PS(ester) polymers described above. Figure 4 summarizes the results of these experiments and presents the rate constants of degradation that were obtained from ultrasonication experiments in THF and THF +

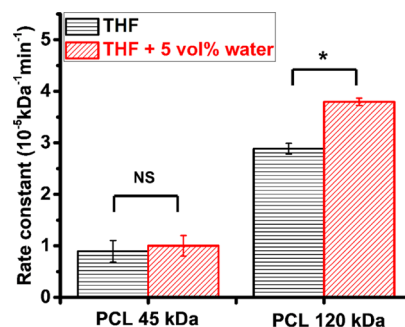


Figure 4. Rate constants of degradation for PCL polymers with an initial M_n of 45 and 120 kDa upon ultrasonication in THF and THF + 5 vol % water at a power density of 2.0 W/cm². Error bars represent standard deviations from least square linear regression analysis. Asterisks indicate statistically significant differences, whereas NS represents no significant difference between the two conditions. Significant at $*p < 0.05$.

5 vol % water. While there is no difference between the rate constants for the degradation of the 45 kDa PCL sample in THF and THF + 5% water, ultrasonication of the 120 kDa PCL polymer in THF + 5% water results in a significant increase in the rate constant of degradation as compared to the experiments with the same polymer in THF. These results resemble those obtained on the PS(ester) polymers, which are summarized in Figure 2, and indicate the existence of a minimal, threshold polymer molecular weight for mechanical acceleration of ester hydrolysis to be observed. Since the rates of polymer chain degradation upon ultrasonication depend on a number of variables, which also include polymer molecular weight, structure, and composition,² a direct comparison of the rate constants in Figure 4 with those in Figure 2 is not trivial.

The experiments presented so far have exclusively concentrated on main chain ester polymers. The mechanochemical response of a bond, however, is not necessarily correlated with the direct mechanical load of a bond. This can be harnessed, for example, to design mechanophores that release a payload upon mechanical activation.^{6,29} To investigate whether mechanical activation does not only accelerate the hydrolysis of main chain but also of side chain ester bonds, two side chain ester-functionalized polymers (PMMA and PVAc, see Table 1) were dissolved at a concentration of 1.2 mg/mL in THF + 5 vol % water, subjected to ultrasonication (2.0 W/cm²) for 120 min, and analyzed by NMR spectroscopy. Figures S12–S15 present ¹H and ¹³C NMR spectra of the PVAc and PMMA samples before and after ultrasonication in THF with 5 vol % water. Analyses of these spectra do not reveal any changes that point toward hydrolysis of the side chain ester groups in these polymers. As a consequence, these experiments indicate that, under the ultrasonication conditions used in this study, mechanical activation of ester-containing polymers does not induce side chain ester hydrolysis.

To understand the mechanistic origin of the observed force-accelerated ester hydrolysis, density functional theory (DFT) energy profiles of a model reaction were analyzed. Ester hydrolysis under neutral conditions was analyzed, both in water and in THF, by considering a molecular complex that is composed of one methyl acetate molecule microsolvated with four water molecules and implicitly solvated with either THF or water (Figure 5). These computations were able to

recapitulate the two-step reaction mechanism characterized by a first transition state (TS1) associated with the attack performed by a water molecule on the ester carbonyl moiety (via concerted proton transfer involving two neighboring water molecules all the way to the carbonyl oxygen atom), followed by ester hydrolysis (i.e., dissociation of the covalent C–O bond, TS2). As shown in Figure 5, the electronic energy profiles computed using water and THF as solvent under neutral conditions are comparable with TS2 being the highest energy transition state (the corresponding free energies are provided in Figure S16). As it is TS2 that is most force sensitive,^{58,59} these subtle differences in the free energies of TS1 and TS2 can help to account for the observed rate acceleration upon the application of ultrasound. It is, however, worth noting that the computed relative energies of the two transition states are very sensitive to both the microsolvated environment and the reaction conditions (basic or neutral).⁵⁸

CONCLUSIONS

This study has sought to provide molecular-level mechanistic insights into the force-accelerated degradation of ester bond-containing polymers. Dilute solution ultrasonication experiments that were performed both on model polymers containing a defined number of ester bonds and on common ester bond-containing polymers such as poly(caprolactone) indicated that chain degradation of these polymers proceeds via concomitant homolytic carbon–carbon bond scission as well as ester bond hydrolysis. The experimental results together with DFT calculations demonstrated that ester bond hydrolysis is force accelerated, both under neutral and basic conditions. Solution ultrasonication experiments that were performed with side chain ester functional polymers in contrast did not indicate ester bond hydrolysis, which suggests that the molecular force does not lead to the activation of ester bonds that are orthogonal to the polymer backbone.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.macromol.2c01789>.

Detailed descriptions of synthetic procedures and ultrasonication experiments; synthesis of BDMB, BBPB, PS(ester), and PS(carbon); NMR and MS spectra of BDMB, BBPB, PS(ester), and PS(carbon); NMR spectra of PMMA and PVAc; GPC chromatograms of the PS(ester) and PS(carbon) polymers and deconvoluted GPC traces of PS(ester); images of the ultrasonication setup and calibration curves of the ultrasonication experiments; UV–vis spectroscopy of DPPH and PS(ester) and DPPH mixture; FTIR of PS(ester) before and after ultrasonication; rate constants of the degradation of PS(ester) in THF with different amounts of water; and detailed methods and data of computed free energies of model reagent, TS1, Int, TS2, and products (PDF)

AUTHOR INFORMATION

Corresponding Author

Harm-Anton Klok – Institut des Matériaux and Institut des Sciences et Ingénierie Chimiques, Laboratoire des Polymères, École Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland; orcid.org/0000-0003-3365-

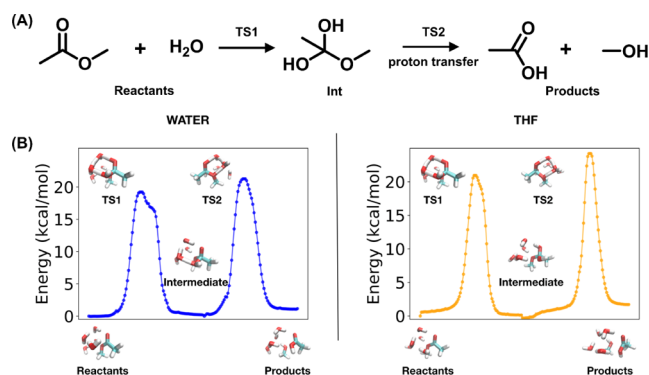


Figure 5. (A) Ester hydrolysis under neutral conditions; (B) electronic energy profiles of the hydrolysis of methyl acetate microsolvated with four water molecules computed at the M06-2X/Def2-M06-2X/Def2-SVPD level with THF and water as implicit solvent (with the SMD model).

6543; Phone: + 41 21 693 4866; Email: harm-anton.klok@epfl.ch

Authors

Jian Wang – Institut des Matériaux and Institut des Sciences et Ingénierie Chimiques, Laboratoire des Polymères, École Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland; orcid.org/0000-0003-0459-5833

Xiaobin Gao – Institut des Matériaux and Institut des Sciences et Ingénierie Chimiques, Laboratoire des Polymères, École Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland

Alice Boarino – Institut des Matériaux and Institut des Sciences et Ingénierie Chimiques, Laboratoire des Polymères, École Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland

Frédéric Célerse – Institute of Chemical Sciences and Engineering and National Centre for Computational Design and Discovery of Novel Materials (MARVEL), Laboratory for Computational Molecular Design, 1015 Lausanne, Switzerland; orcid.org/0000-0001-8584-6547

Clémence Corminboeuf – Institute of Chemical Sciences and Engineering and National Centre for Computational Design and Discovery of Novel Materials (MARVEL), Laboratory for Computational Molecular Design, 1015 Lausanne, Switzerland; orcid.org/0000-0001-7993-2879

Complete contact information is available at:

<https://pubs.acs.org/10.1021/acs.macromol.2c01789>

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