# Ultrasonic Degradation of Polystyrene for Tailoring Molecular Weight and Polydispersity of Polystyrene Fragments

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*Dedicated to Prof. Dr.-Ing. Matthias Kraume on the occasion of his 65th birthday*

Ultrasonic degradation of polymers attracts more and more attention in the field of chemical recycling of polymers due to the promising opportunity to tailor molecular weight and polydispersity of the gained polymer fragments. In this work, the influence of solvent, gas atmosphere, and ultrasound amplitude on the ultrasonic degradation process of polystyrene is investigated. Therefore, an experimental procedure to perform ultrasonic degradation of polystyrene under homogeneous temperature conditions in the solvents cyclohexane and toluene under the gas atmospheres $CO_2$ and $N_2$ for different ultrasonic amplitudes was designed. It could be shown that a significant effect on the molecular weight and polydispersity of the polymer could only be revealed for $N_2$ and not for $CO_2$ atmosphere.

## 1 Introduction

Today, plastics play an important role in our daily lives. In various sectors, plastic materials are involved and contribute strongly to the product performance, e.g., in construction, medical and pharmaceutical engineering, automotive, aerospace, packaging, electronics, and food science. Growth in terms of economy and in population leads to a higher demand on plastics and, consequently, on their intermediates and feedstocks [1]. Global production of plastics was about 322 million tons in 2015 and 335 million tons in 2016, where fibres of PET, PP, and polyamide are excluded from these values [2]. Approximately 50 % of plastics are made for single-use applications, e.g., packaging products, where the rest is used for long-term infrastructure, e.g., polystyrene and its composites in constructions [3]. This shows the demand on the application and development of plastic recycling processes, which transforms this linear economy more and more into a circular one.

In principal, there are four categories in recycling along the line of ASTM D5033 [3]. The first category is mechanical reprocessing of scrap materials with controlled history into products with equivalent properties, which is termed as primary recycling. Secondary recycling means the mechanical reprocessing of used materials into products with lower properties. The third category is tertiary recycling, which means on principle the recovery of valuable chemical constituents, e.g., monomers, tailored oligomers, or additives. The fourth recycling category represents energy recovery, which is also denoted as quaternary recycling [2, 3].

Recently, tertiary recycling has attracted much attention because it seems that it could be profitable and beneficial in the context that it might reduce the demand for energy and feedstock on the one hand and ensures a cyclic material flow on the other hand [2]. Generally tertiary recycling, also termed as chemical or feedstock recycling, is a process where plastics are decomposed to their building blocks or other valuable and tailored molecular weight fragments [3].

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Several methods for tertiary recycling exist, these are gasification, pyrolysis, liquid-gas hydrogenation, steam and catalytic cracking, hydrolysis, glycolysis, methanolysis, aminolysis, ammonolysis, etc. [4–11]. The application of the listed tertiary recycling methods depends especially on the respective synthesis process of the polymer. Additional interesting chemical recycling methods are photodegradation [12, 13], ultrasound degradation [14–22] as well as microwave degradation [23–25]. These methods are not directly linked to a specific polymer synthesis method.

The reduction of molecular weight of a polymer in solution by applying an ultrasonic field has a long history [16, 26, 27]. First studies with respect to degradation of polymers in ultrasonic fields go back to 1930, where sonication was applied to solutions of natural polymers and, hence, viscosity reduction was observed [28]. Starting to systematically investigate ultrasonic degradation of polymers in solutions dates back to 1950 [26]. A number of different mechanisms for explaining the degradation process were postulated at that time. One explanation for the degradation mechanism was given in [26]. In [26], it is claimed that the degradation is a pure mechanical effect caused by rapid movements of molecules around collapsing bubbles in the liquid mixture. The bubbles are generated by cavitation, which in turn is triggered by alternating compression and rarefaction of the sound wave, which overcomes the intermolecular forces between the components in the liquid phase [26]. However, it has to be mentioned that a fundamental and comprehensive explanation of the degradation process and a thermodynamic framework for analyzing, evaluating, and predicting the ultrasound-based degradation process are still lacking today [20]. This is an ongoing and even debated current research field. In the past, it could be figured out, that an ultrasonic degradation process shows unique features which distinguishes this process from thermal, photochemical, or microwave-based degradation [26]. Especially, non-random degradation behavior and molecular weight dependence of the process leads to the possibility to modify and tailor the molecular weight distribution of the polymer [26].

Several investigations of the ultrasonic degradation of polystyrene have been published [16, 26, 27]. Polystyrene is a polymer, which is used for many application purposes, e.g., construction and packaging, in high volumes. Hence, efficient recycling methods for this polymer are required [29]. In [16, 26, 27], it is shown that the ultrasonic degradation process of polystyrene is strongly dependent on the ultrasonic amplitude, dissolved gases, used solvent as well as solution concentration. These parameters trigger the degradation process and lead to respective molecular weights and polydispersities of the polystyrene after a certain sonication time [16, 26, 27, 30]. It is stated in literature, that, e.g., the polystyrene degradation over time in the solvent toluene, strongly depends on the gas atmosphere set as an experimental boundary condition [16]. It is concluded in the literature that the system polystyrene-toluene-$CO_2$

shows a weaker degradation kinetics compared to the system polystyrene-toluene-$N_2$. Furthermore, the influence of the gases $CH_4$, Ar, CO, and $O_2$ on the polystyrene degradation behavior with toluene as solvent has been investigated. Consequently, the polydispersity as well as the molecular weight which is gained at a certain sonication time are significantly different for these systems. It is also shown in the literature, that CO and $O_2$ indicate a stronger influence on the degradation kinetics than other gaseous components [16]. This was explained by the fact that other gases, i.e., $CH_4$, Ar, $N_2$, and $CO_2$, are more inert and, hence, the radical would have a longer lifetime, which increases the likelihood of these processes and slows the reduction in molecular weight [16].

The influence of different gases on the ultrasonic degradation process is well studied for the polystyrene-toluene-gas system in [16]. The influence of the solvents, i.e., 2-butanone, tetrahydrofuran, $o$-xylene, benzene, and methyl acrylate on this process under one specific atmosphere is pointed out in [31]. For deeper understanding the ultrasonic degradation process of polystyrene-solvent-gas systems, it is necessary to further investigate the solvent effect in combination with different gas atmospheres, e.g., $CO_2$ and $N_2$. This is important for investigating especially cross influences between solvent and gas on the ultrasound-based degradation process. By studying this influence, the possibilities of generating polydispersities as well as molecular weights after a certain sonication time arise. This should extent the ability to tailor specific polydispersities and molecular weights of polystyrene by employing proper solvent and gas boundaries.

Hence, it is the aim of this work to setup an experimental procedure to perform ultrasonic degradation of polystyrene under homogeneous temperature conditions for the solvent cyclohexane and the gases $CO_2$ and $N_2$. To the best of to the authors' knowledge, these system combinations are investigated for the first time and will contribute to additional possibilities to tailor polystyrene molecular fragments based on ultrasonic degradation. In this work, the kinetics of the degradation process is measured and the respective polydispersities together with the corresponding molecular weights of the polymer at specific sonication times are evaluated. Further, the results are compared with values, which could be achieved when toluene is used as solvent. This is done for the sake of comparison and for embedding the new experimental results into state of the art. Additionally, the new experimental findings could contribute to further consideration and understanding of ultrasound based sonication of polystyrene and help to further lift the potential for recycling based on ultrasound degradation, with the opportunity to tailor the molecular fragments of the polymer regarding molecular weight and polydispersity.

## 2 Experimental and Materials

A cylindrical, double-walled beaker with a volume of 500 mL was selected as ultrasonic reactor. With this reactor, it is ensured that a respective amount of solution can be provided, such that an adequate amount of polystyrene fragments can be gained after the sonication process for post analysis. An advantage of this reactor is the avoidance of strong reflection of the ultrasound at the bottom. The vessel head has four inlets where the sonotrode, the gas pipe, and two thermometers can be inserted for setting up the ultrasonic process. For ultrasonic homogenization purposes, the ultrasonic homogenizer HD 4200 from BANDELIN electronic was applied. This element provides a power input of up to 150 W at a frequency of 20 kHz. The applied sonotrode TS 113 from BANDELIN electronic transmits the energy to the liquid, the sonotrode has a diameter of 12.7 mm. The apparatus which was designed to carry out the experiments is schematically presented in Fig. 1.
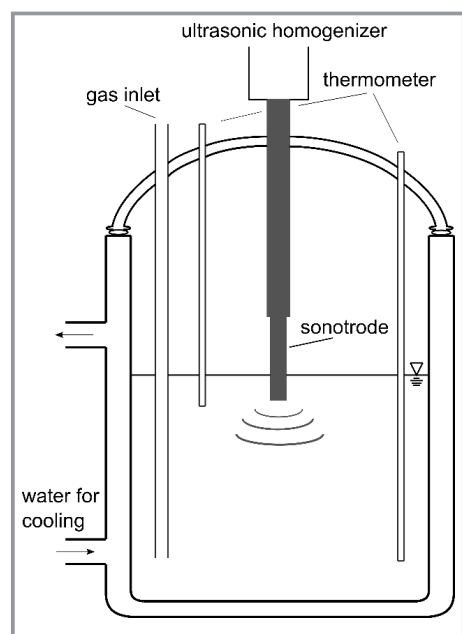


**Figure 1.** Ultrasonic reactor with jacket cooling and four inlets for sonotrode, thermometers, and gas pipe.

The adjustable parameter at the ultrasonic homogenizer is the amplitude rather than the input power. In this paper, amplitudes of 25 and 50 % of the maximum amplitude, 132 µm, were investigated.

Pre-experiments were conducted to investigate the homogeneity of the temperature within the solution. This was tested by using a third thermometer to measure the temperature at different points inside the vessel while the ultrasonic process was ongoing and applied to pure cyclohexane. As thermometers Pt-100 resistance thermometers of class A ($-100\,°C$ to $450\,°C \pm 0.15\,°C$) were used. An intermediate deviation of $\pm 0.15\,°C$ of the temperature between the three thermometers was observed. Hence, it can be concluded that spatial temperature homogeneity is ensured.

Furthermore, $N_2$ and $CO_2$ were the investigated gas atmospheres and since ultrasound has a strong degassing effect, the experiment was designed such that the gas was bubbled through the liquid during the experiments ensured by the gas pipe in Fig. 1.

The solutions under investigation in this work were made from polystyrene (Sigma Aldrich) and cyclohexane (99 %, Sigma Aldrich) and toluene (99 %, Sigma Aldrich) for comparison reasons, with a polymer concentration of 2 wt % under gas atmospheres $N_2$ and $CO_2$. The polystyrene used was delivered in pellet form with a melt index of 2.0–4.0 g/10 min (200 °C/5 kg), a density of 1.04 g mL$^{-1}$ at 25 °C, a glass transition temperature of 95 °C, and mineral oil impurities < 5 %. The initial molecular weight and distribution of the investigated polymer sample was measured in this work to be $M_n = 168.2$ kg mol$^{-1}$ and $M_w = 332.4$ kg mol$^{-1}$.

For performing the experiments, the polymer solution was initially temperature-controlled such that the temperature was 30 °C while the respective gas was injected in the solution for saturating the solution. When the ultrasound source is turned on, the temperature of the solution increases due to the high energy input. Analyzing the temperature profile, a temperature ramp was observed converging to a constant temperature under which the experiment was performed. Since the degradation rate decreases with the molecular weight, long-time experiments of 450 min were conducted for different solutions to determine the target sonication time window. It was found that the generated number average after 450 min is comparable with the number average after 180 min only. For this reason, the sonication time window was set to the interval [0; 180] min. The experiments were performed for this time window along the experimental design stated in Tab. 1.

The obtained samples according to experimental design were taken and the solvent was evaporated. Hence, the obtained polystyrene samples were analyzed via size exclusion chromatography (SEC). An SEC system consisting of a

**Table 1.** Experimental design of the ultrasound degradation experiments for polystyrene.

| Gas | Solvent | Amplitude [%] | Samples taken at [min] |
|-----|---------|---------------|------------------------|
| CO$_2$ | cyclohexane | 25 | 45, 90, 135, 180 |
| | cyclohexane | 50 | 45, 90, 135, 180 |
| | toluene | 25 | 180 |
| | toluene | 50 | 180 |
| N$_2$ | cyclohexane | 25 | 45, 90, 135, 180 |
| | cyclohexane | 50 | 45, 90, 135, 180 |
| | toluene | 25 | 180 |
| | toluene | 50 | 180 |

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Waters 515 HPLC pump, an autosampler from Knauer Marathon, and a Knauer Smartline refractive index detector was used. Tetrahydrofurane (THF) was used as mobile phase with a flow rate of $1.0\,mL\,min^{-1}$. The SEC setup was calibrated with polystyrene standards ranging from 162 to $3\,053\,000\,g\,mol^{-1}$ from PSS.

## 3  Results and Discussion

This section is structured as follows: first, ultrasound effects on the molecular weight are presented in dependence on different influencing parameters. Second, the influence of ultrasound degradation on the polydispersity is shown under specific influencing parameters, and third, the main findings are summarized in tabular form and are further discussed.

In Fig. 2a, the influence of ultrasound degradation on the molecular weight distribution of polystyrene in cyclohexane under the gas atmosphere $N_2$ for an amplitude amount of 25 % (see further information regarding amplitude variations in Sect. 2) is presented for different sonication times in the interval [0; 180] min. These results clearly show that already in the very beginning of the sonication process, the molecular weight distribution changes strongly. The longer the sonication process continues, the less pronounced are changes in the molecular weight distribution. These findings for the system under consideration correspond to already performed experiments in the literature [26]. Additional experiments are performed to study the influence of the amplitude on the polymer degradation behavior as shown in Fig. 2b. Starting with the same initial molecular weight distribution the resulting distribution after a sonication time of 180 min is different between an amplitude of 25 and 50 % for the system polystyrene-cyclohexane-$N_2$.

In analogy to the results presented above, the influence of ultrasound on the molecular weight distribution of polystyrene in cyclohexane under the gas atmosphere of $CO_2$ was investigated and the results are presented in Figs. 3a and b. As already observed for the system polystyrene-cyclohexane-$N_2$, the effect of accelerated degradation at low sonication times holds true for the system polystyrene-cyclohexane-$CO_2$. However, it was observed that the effect of the amplitude is significantly less pronounced for this system (Fig. 3b) where $CO_2$ was chosen as gas atmosphere. Based on these findings it can be concluded that the variation of amplitude from lower to higher values does not necessarily mean that the degradation process with respect to the molecular weight is strongly influenced by the amplitude. Rather the influence of the amplitude couples with the respective gas atmosphere under which the experiment is performed. This effect has not yet been addressed in the literature because either experiments were performed with one solvent, i.e., toluene, under different gas atmospheres or with different solvents under air conditions [16, 26, 27].

This further leads to the fact, that for tailoring the molecular weight distribution by ultrasound on the one hand and for process optimization as well as for scalability on the other hand, it is required that especially the coupling effect between the used gas atmosphere and the ultrasound amplitude is known.

For the sake of comparison, Figs. 4a and b present the weight and number average values of the measured molecular weight distributions for the systems polystyrene-cyclohexane-$CO_2$ (Fig. 4a) and polystyrene-cyclohexane-$N_2$ (Fig. 4b) for amplitudes of 25 and 50 %.

The results presented in Figs. 4a and b show that for both configurations the number and weight average values which are reached after certain sonication times strongly depend on the gas atmosphere. Additionally, for both systems it is shown that the number average value is not significantly
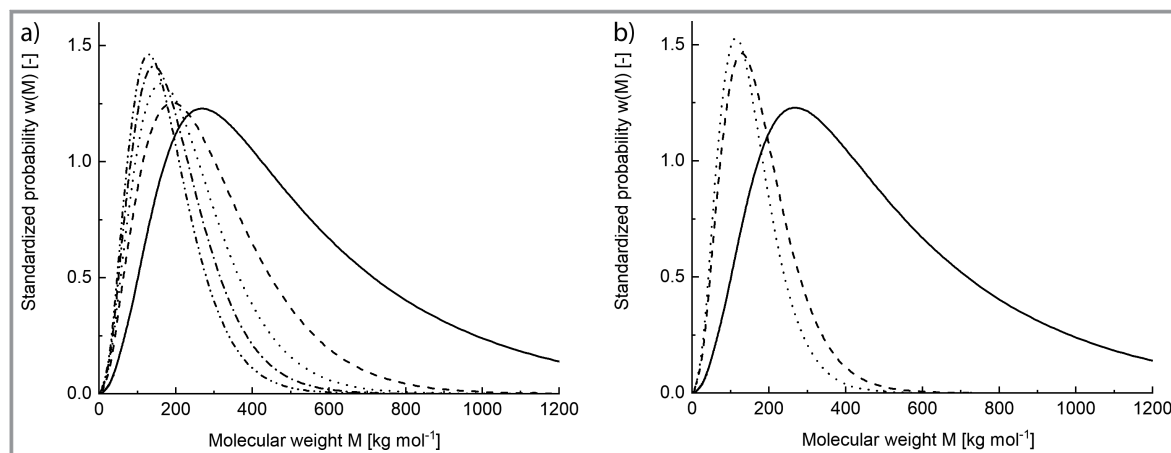


**Figure 2.** Effect of ultrasound on the molecular weight distribution of polystyrene in cyclohexane under $N_2$ at 25 % amplitude after 45 min (dashed line), 90 min (dotted line), 135 min (dash-dotted line), and 180 min (dash-dot-dotted line) (a); 180 min at amplitude of 25 % (dashed line) and 180 min at amplitude of 50 % (dotted line) (b). The solid line corresponds to initial molecular weight distribution.
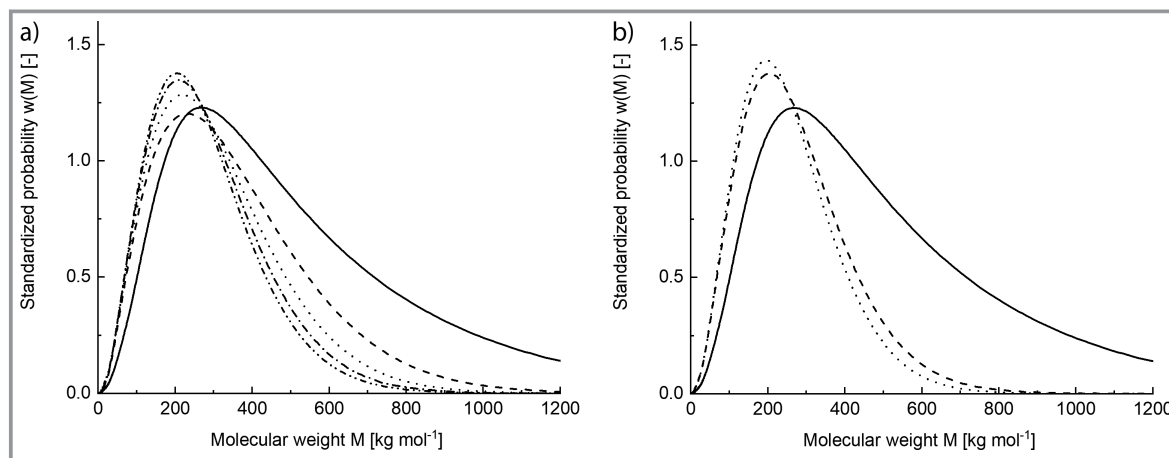
**Figure 3.** Effect of ultrasound on the molecular weight distribution of polystyrene in cyclohexane under $CO_2$ at 25 % amplitude after 45 min (dashed line), 90 min (dotted line), 135 min (dash-dotted line) and 180 min (dash-dot-dotted line) (a); 180 min at amplitude of 25 % (dashed line) and 180 min at amplitude of 50 % (dotted line) (b). The solid line corresponds to initial molecular weight distribution.
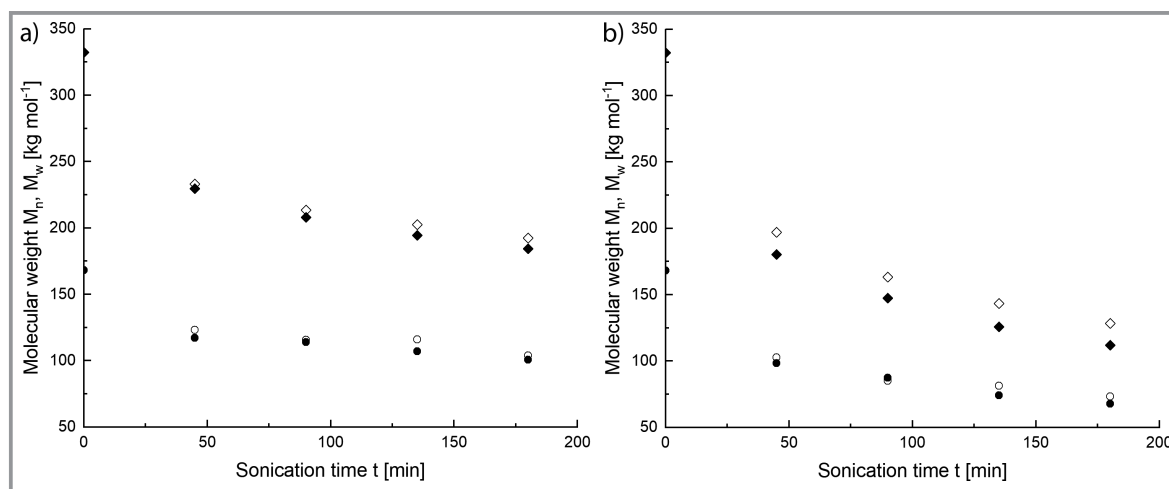


**Figure 4.** Effect of the sonication time on the molecular weight averages of polystyrene in cyclohexane under $CO_2$: ◇) $M_w$ at 25 % amplitude), ◆) $M_w$ at 50 % amplitude, ○) $M_n$ at 25 % amplitude, ●) $M_n$ at 50 % amplitude (a); the same under $N_2$ (b).

affected by the ultrasound amplitude. This is contrary to the weight average molecular weight, which is affected by the amplitude in the system polystyrene-cyclohexane-$N_2$. Also, the different slope of the weight and number average molecular weight is changing with sonication time which in turn indicates a change in polydispersity of polystyrene.

The behavior of the polydispersity over sonication time is presented in Fig. 5 for both systems polystyrene-cyclohexane-$N_2$ and polystyrene-cyclohexane-$CO_2$. Based on this result, it can be concluded that significantly different polydispersities of polystyrene can be achieved already after 90 min of sonication time due to application of different gas atmospheres.

Compared to $N_2$, the influence of $CO_2$ on the polydispersity reduction is significantly weaker. Therefore, the polydispersity evolution of the polymer during the ultra-sound degradation process can be tailored by the respective gas atmosphere used as it is presented in Fig. 5.

In Fig. 6a, comparison of the polymer degradation between the solvents cyclohexane and toluene is performed under both gas atmospheres, $CO_2$ and $N_2$. These graphs show that the solvent influences the polydispersity stronger under $CO_2$ atmosphere, where the peak of the molecular weight distribution after 180 min sonication time is shifted to lower values due to the solvent effect of toluene under $N_2$ atmosphere. The results shown in Fig. 6 correspond to an amplitude of 25 %.

For the sake of comparison, the results of the cross effects of solvent and gas on the polystyrene degradation behavior are presented for an amplitude value of 50 % in Fig. 7.

Summarized findings of the solvent and gas influence on the ultrasonic degradation process of polystyrene in
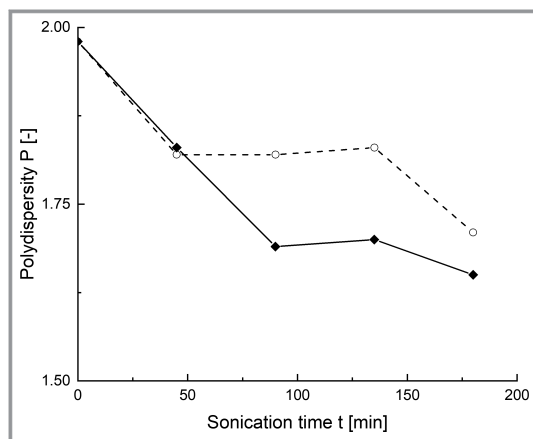
**Figure 5.** Effect of the sonication time on the polydispersity of polystyrene in cyclohexane under $N_2$ (◆, solid line) and $CO_2$ (○, dashed line) at 50 % amplitude.

the systems polystyrene-cyclohexane-$N_2$, polystyrene-cyclohexane-$CO_2$, polystyrene-toluene-$N_2$, polystyrene-toluene-$CO_2$, are presented for the limiting sonication time of 180 min in Tab. 2.

In Tab. 2, it is demonstrated that the degradation effect is stronger under $N_2$ atmosphere compared to $CO_2$ atmosphere for both solvents and approaches significantly lower values of the molecular weight. This holds true for both number and average molecular weight. Additionally, the solvent effect is much more pronounced under $N_2$ conditions where polystyrene in cyclohexane is degraded less than in toluene. This difference is not observable under $CO_2$ conditions.

Hence, as it was already stated for the amplitude influence, it also holds true for the solvent influence on the degradation process that the knowledge of cross effect with the respective gas atmosphere is strongly required to tailor
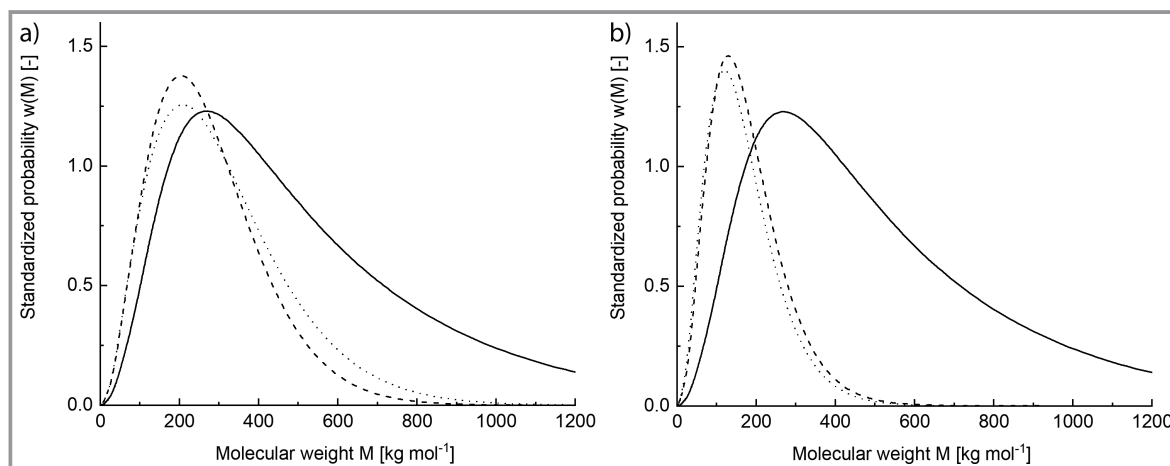
**Figure 6.** Effect of ultrasound on the molecular mass distribution evolution of polystyrene in the system polystyrene-cyclohexane-$CO_2$ (dashed line) and polystyrene-toluene-$CO_2$ (dotted line) (a); in the system polystyrene-cyclohexane-$N_2$ (dashed line) and polystyrene-toluene-$N_2$ (dotted line) (b); both lines correspond to a sonication time of 180 min, the amplitude was 25 %; the solid line represents the initial molar weight distribution.
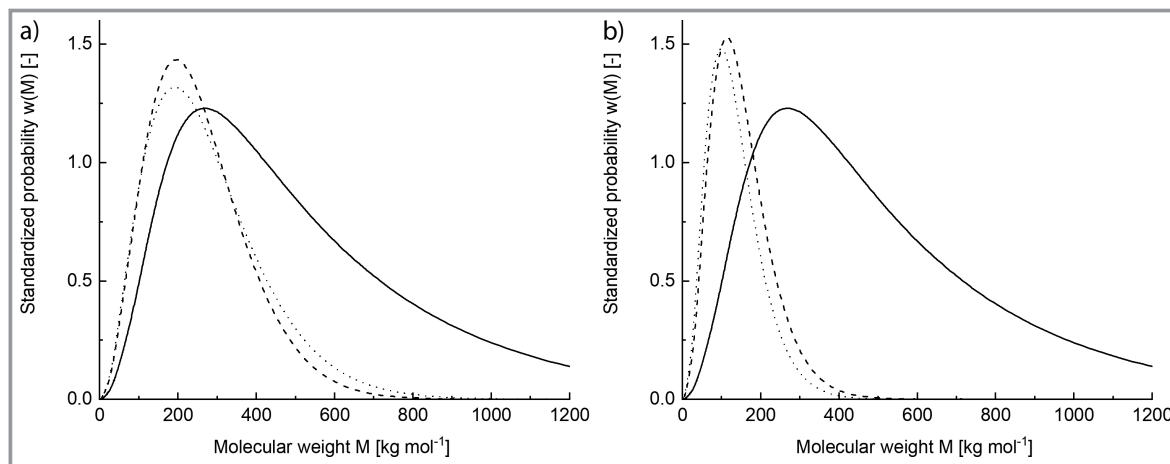
**Figure 7.** Effect of ultrasound on the molecular mass distribution evolution of polystyrene in the system polystyrene-cyclohexane-$CO_2$ (dashed line) and polystyrene-toluene-$CO_2$ (dotted line) (a); in the system polystyrene-cyclohexane-$N_2$ (dashed line) and polystyrene-toluene-$N_2$ (dotted line) (b); both lines correspond to a sonication time of 180 min, the amplitude was 50 %; the solid line represents the initial molar weight distribution.

**Table 2.** Summarized experimental findings for number and weight average of ultrasound-degraded polystyrene in cyclohexane and toluene under the gas atmospheres $CO_2$ and $N_2$ for 180 min sonication time and different amplitudes.

| Gas | Solvent | Amplitude [%] | $M_{n,180}$ [kg mol$^{-1}$] | $M_{w,180}$ [kg mol$^{-1}$] | Polydispersity $P$ [–] |
|---|---|---|---|---|---|
| $CO_2$ | cyclohexane | 25 | 104.0 | 192.5 | 1.85 |
| | cyclohexane | 50 | 100.6 | 184.4 | 1.83 |
| | toluene | 25 | 104.6 | 207.4 | 1.98 |
| | toluene | 50 | 102.1 | 189.4 | 1.86 |
| $N_2$ | cyclohexane | 25 | 73.2 | 128.4 | 1.75 |
| | cyclohexane | 50 | 67.8 | 112.0 | 1.65 |
| | toluene | 25 | 62.7 | 118.2 | 1.88 |
| | toluene | 50 | 56.5 | 97.7 | 1.73 |

respective molecular weights and polydispersities of the polymer by ultrasound degradation.

## 4 Conclusions

In this contribution, an ultrasonic reactor for polymer degradation under spatial homogenous temperature conditions and defined gas injection was designed to investigate the degradation behavior of polystyrene under certain boundary conditions with the focus on clarifying cross influence effects on the one hand and investigate the ability of tailoring polymer molecular weight and polydispersity on the other hand. As influence factors on the ultrasonic degradation effect on polystyrene, the solvent, the gas atmosphere, and the ultrasound amplitude are considered and studied for the systems polystyrene-cyclohexane-$N_2$, polystyrene-cyclohexane-$CO_2$, polystyrene-toluene-$N_2$, and polystyrene-toluene-$CO_2$. It could be revealed that the influence of ultrasound amplitude as well as solvent influence are strongly related to the gas atmosphere used. Significantly different molecular weights and polydispersities could be achieved by applying cyclohexane and toluene as solvents. This result, however, holds only true by using $N_2$ as gas atmosphere. As shown in Tab. 2, substituting $N_2$ by $CO_2$ leads to no significant difference of the degraded molecular weights and polydispersities after 180 min sonication time in dependence on the solvent toluene and cyclohexane. Hence, the solvent effect on the degradation behavior is strongly related to the respective gas atmosphere which is applied in the process. The same result holds true for the ultrasound amplitude influence for the respective investigation interval, where a stronger influence on the molecular weight distribution degradation of polystyrene was observed under $N_2$ atmosphere compared to $CO_2$ atmosphere. These experiments clearly show the potential concerning the possibility of tailoring molecular weight and polydispersity of polymers by ultrasound degradation and, hence, contribute to the development of tailored recycling methods of

polymers. However, it is also shown that the process strongly depends on the influencing factors and it is not sufficient that they are investigated without considering mutual influencing effects between them.

These findings contribute to the additional understanding of mutual influence factors on the ultrasound degradation process of polymers in solution. Furthermore, thermodynamic models which are able to consider these influencing factors are required to further understand and apply this process in the field of polymer recycling.

## Symbols used

| | | |
|---|---|---|
| $M$ | [g mol$^{-1}$] | molecular weight |
| $P$ | [–] | polydispersity |
| $t$ | [min] | sonication time |
| $w(M)$ | [–] | standardized probability of molecular weight distribution |

## Subscripts

| | |
|---|---|
| n | number-averaged |
| w | weight-averaged |
| 180 | after 180 min of sonication time |

## Abbreviation

| | |
|---|---|
| SEC | size exclusion chromatography |

## References

[1] S. M. Al-Salem, A. Antelava, A. Constantinou, G. Manos, A. Dutta, *J. Environ. Manage.* **2017**, *197*, 177–198. DOI: https://doi.org/10.1016/j.jenvman.2017.03.084

[2] M. Okan, H. M. Aydin, M. Barsbay, *J. Chem. Technol. Biotechnol.* **2019**, *94*, 8–21. DOI: https://doi.org/10.1002/jctb.5778

[3] J. Hopewell, R. Dvorak, E. Kosir, *Philos. Trans. R. Soc., B* **2009**, *364*, 2115–2126. DOI: https://doi.org/10.1098/rstb.2008.0311

[4] M. D. Jagtap, *Int. J. Recent Technol. Mech. Electr. Eng.* **2015**, *2*, 120–122.

[5] M. S. Abbas-Abadi, M. N. Haghighi, H. Yeganeh, *Fuel Process Technol.* **2013**, *109*, 90–95. DOI: https://doi.org/10.1016/j.fuproc.2012.09.042

[6] A. Demirbas, *J. Anal. Appl. Pyrolysis* **2004**, *72*, 97–102. DOI: https://doi.org/10.1016/j.jaap.2004.03.001

[7] A. Aboulkas, K. Makayssi, L. Bilali, K. El Harfi, M. Nadifiyine, M. Benchanaa, *Fuel Process Technol.* **2012**, *96*, 209–213. DOI: https://doi.org/10.1016/j.fuproc.2011.12.001

[8] S. Singh, C. Wu, P. T. Williams, *J. Anal. Appl. Pyrolysis* **2012**, *94*, 99–107. DOI: https://doi.org/10.1016/j.jaap.2011.11.011

[9] R. Miandad, M. A. Barakat, A. S. Aburiazaiza, M. Rehan, A. S. Nizami, *Process Saf. Environ. Prot.* **2016**, *102*, 822–838. DOI: https://doi.org/10.1016/j.psep.2016.06.022

[10] S. H. Shaha, Z. M. Khana, I. A. Rajaa, Q. Mahmooda, Z. A. Bhattia, J. Khana, A. Farooqa, N. Rashida, D. Wub, *J. Hazard. Mater.* **2010**, *179*, 15–20. DOI: https://doi.org/10.1016/j.jhazmat.2010.01.134

[11] M. Stelmachowski, K. Slowinski, *Chem. Process Eng.* **2012**, *33*, 185–198. DOI: https://doi.org/10.2478/v10176-012-0016-z

[12] B. C. Daglen, D. R. Tyler, *Green Chem. Lett. Rev.* **2010**, *3*, 69–82. DOI: https://doi.org/10.1080/17518250903506723

[13] J. Shang, M. Chai, Y. Zhu, *Environ. Sci. Technol.* **2003**, *37*, 4494–4499. DOI: https://doi.org/10.1021/es0209464

[14] S. P. Vijayalakshmi, G. Madras, *Polym. Degrad. Stab.* **2004**, *84*, 341–344. DOI: https://doi.org/10.1016/j.polymdegradstab.2004.02.00

[15] G. Sivalingam, S. P. Vijayalakshmi, G. Madras, *Ind. Eng. Chem. Res.* **2004**, *43*, 7702–7709. DOI: https://doi.org/10.1021/ie049589r

[16] G. J. Price, P. F. Smith, *Polymer* **1993**, *34*, 4111–4117. DOI: https://doi.org/10.1016/0032-3861(93)90675-Z

[17] G. Madras, S. Chattopadhyay, *Polym. Degrad. Stab.* **2001**, *73*, 33–38. DOI: https://doi.org/10.1016/S0141-3910(01)00064-7

[18] A. Grönroos, P. Pirkonen, O. Ruppert, *Ultrason. Sonochem.* **2004**, *11*, 9–12. DOI: https://doi.org/10.1016/S1350-4177(03)00129-9

[19] J. Chakraborty, J. Sarkar, R. Kumar, G. Madras, *Polym. Degrad. Stab.* **2004**, *85*, 555–558. DOI: https://doi.org/10.1016/j.polymdegradstab.2003.09.021

[20] A. Akyüz, H. Catalgil-Giz, A. T. Giz, *Macromol. Chem. Phys.* **2008**, *209*, 801–809. DOI: https://doi.org/10.1002/macp.200700533

[21] M. T. Thaghizadeh, H. Rad, R. Abdollahi, *J. Appl. Polym. Sci.* **2012**, *123*, 1896–1904. DOI: https://doi.org/10.1002/app.34717

[22] V. Desai, M. A. Shenoy, P. R. Gogate, *Chem. Eng. J.* **2008**, *140*, 483–487. DOI: https://doi.org/10.1016/j.cej.2007.11.030

[23] K. N. Aishwarya, N. Sindhu, *Procedia Technol.* **2016**, *25*, 990–997. DOI: https://doi.org/10.1016/j.protcy.2016.08.197

[24] M. M. A. Nikje, M. Askarzadeh, *Prog. Rubber, Plast. Recycl. Technol.* **2013**, *29*, 169–176. DOI: https://doi.org/10.1177/147776061302900303

[25] E. Bäckström, K. Odelius, M. Hakkarainen, *Ind. Eng. Chem. Res.* **2017**, *56*, 14814–14821. DOI: https://doi.org/10.1021/acs.iecr.7b04091

[26] G. J. Price, P. F. Smith, *Polym. Int.* **1991**, *24*, 159–164. DOI: https://doi.org/10.1002/pi.4990240306

[27] G. J. Price, P. F. Smith, *Eur. Polym. J.* **1993**, *29*, 419–424. DOI: https://doi.org/10.1016/0014-3057(93)90114-U

[28] E. W. Flosdorf, L. A. Chambers, *J. Am. Chem. Soc.* **1933**, *55*, 3051–3052. DOI: https://doi.org/10.1021/ja01334a509

[29] T. Maharana, Y. S. Negi, B. Mohanty, *Polym.-Plast. Technol. Eng.* **2007**, *46*, 729–736. DOI: https://doi.org/10.1080/03602550701273963

[30] F. Kanwal, J. J. Liggat, R. A. Pethrik, *Polym. Degrad. Stab.* **2000**, *68*, 445–449. DOI: https://doi.org/10.1016/S0141-3910(00)00034-3

[31] G. J. Price, P. J. West, P. F. Smith, *Ultrason. Sonochem.* **1994**, *1*, S51–S57. DOI: https://doi.org/10.1016/1350-4177(94)90028-0

# Ultrasonic Degradation of Polystyrene for Tailoring Molecular Weight and Polydispersity of Polystyrene Fragments

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**Research Article:** Ultrasonic degradation is a suitable method for the chemical recycling of polymers, due to the promising opportunity to tailor molecular mass and polydispersity of the polymer fragments. The paper reports experimental results of the ultrasonic degradation of polystyrene in different solvents (cyclohexane and toluene) under different gas atmospheres (CO2 and N2) for different ultrasonic amplitudes. ................................. ■