THESIS

MECHANICALLY MEDIATED TRITHIOCARBONATE ADDITION TO COMMODITY POLYMERS FOR A MORE CIRCULAR ECONOMY

Submitted by

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ABSTRACT

MECHANICALLY MEDIATED TRITHIOCARBONATE ADDITION TO COMMODITY POLYMERS FOR A MORE CIRCULAR ECONOMY

Mechanical recycling, while thought of as environmentally conscious, is not nearly as effective as it is lauded to be. Great levels of mechanical force cause chain-scission and lower product value while simultaneously only working once, maybe twice before the material is useless. Studies to harness the chain-scission with functional groups have proved possible but limited. This study shows the effect of adding bis(BTTC) and monomer to a mechanical recycling process to allow for post-recycling reactions with functionalized material. PMMA was shown to decrease in MW from 350 kDa down to ca. 15 kDa, then repolymerized back to 350 kDa. Other post-recycling reactions including block polymer synthesis and depolymerization are also possible and show promise. Expanding the scope outside of PMMA to other common plastics is studied as well, though it needs to be greatly expanded upon.

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Introduction

The first instance of the mechanical recycling of plastics came in 1972 in Conshohocken, Pennsylvania.[1] Since then, it has gradually grown to be a major portion of plastic recycling. However, plastics recycled through this method often lose or have worse physical properties after just one cycle of recycling. This is due to chain-scission that breaks long polymers into shorter polymers. Because of this phenomenon, plastic that is mechanically recycled is often turned from high value products into lower value products and then disposed of entirely (Figure 1A). Chain-scission is an inevitable process in mechanical recycling; thus, it should be taken advantage of rather than allowing products to lose value.

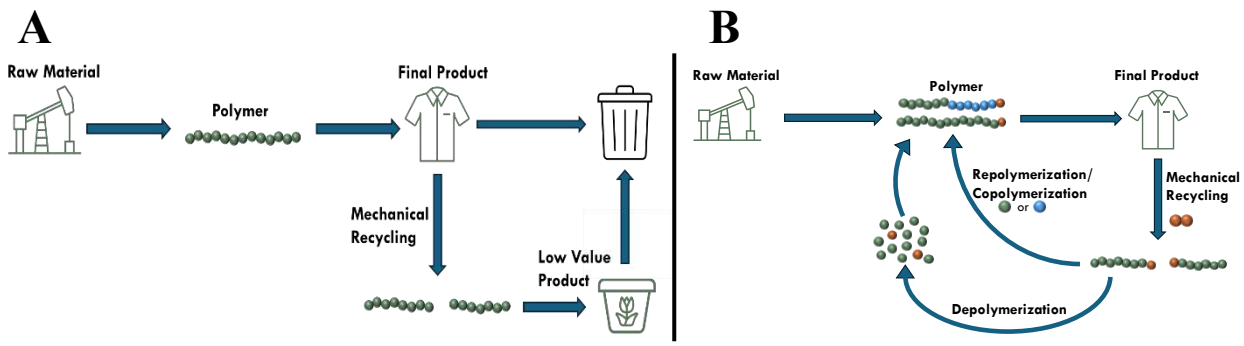


Figure 1: Current mechanical recycling pathway (A) and proposed change pathway (B)

Radicals form at the location of chain-scission and results from Kubota[2] show the ability to capture these radicals with a prefluorescent nitroxide. Once attached, the nitroxide becomes fluorescent and can be measured through light spectroscopy. Other groups have attached functional handles onto polymers during chain-scission, allowing for various post-recycling reactions to be run, though with various limitations. Phthalimide methacrylates attached to poly(methyl methacrylate) (PMMA) allowed for high levels of depolymerization but are not suitable for extending the polymer chain or creating copolymers.[3] Nitroxides attached to PMMA were suitable for extending the polymer chain and creating copolymers but are limited in their scope.[4] Thus, a

widely compatible, radical capture agent was necessary to improve this mechanically mediated radical addition.

The radical capture agent that was chosen was inspired by work by Stache, who used bis(butyl tritihocarbonate) (bis(TTC)) to capture radicals formed on dioxane in solution.[5] We hypothesized that this bis(TTC) could also be used in bulk for the mechanical recycling process. The trithiocarbonate moiety that adds on to the radical would be able to act as a reversible addition fragmentation chain-transfer (RAFT) agent. RAFT agents have a high degree of versatility and are compatible with most polymers used commercially. This work will show how by incorporating bis(TTC) into the mechanical recycling process can create functionalized polymers that can be repolymerized back to their original length, create copolymers, or be depolymerized back into their monomeric form, creating a more circular recycling process (Figure 1B).

Results

Ball milling was used to mimic mechanical recycling as it can be used on industrial scales and shows consistent degradation through multiple cycles. Milling conditions were optimized to be grinding for 2 hours, with 35 grams of beads, and the material of the jars and balls being zirconium ceramic. The basic conditions of the polymers tested were done with virgin PMMA, then with various additions of bis(TTC) and monomer. Through size exclusion chromatography (SEC), the degraded polymers with the new conditions consistently reach molecular weights (MW) between 15-30 kDa, with a fraction of the sample remaining undegraded (Figure 2A). Strong UV absorbance, measured at 310 nm, overlaps with the low MW peaks, indicating successful attachment of the BTTC onto the chains. Bis(TTC) was added in at 5 wt% of the milled polymer, as any more inhibited degradation and any less led to lower degrees of functionalized polymers. The addition of the monomer was used to promote the active species of functionalized polymer,

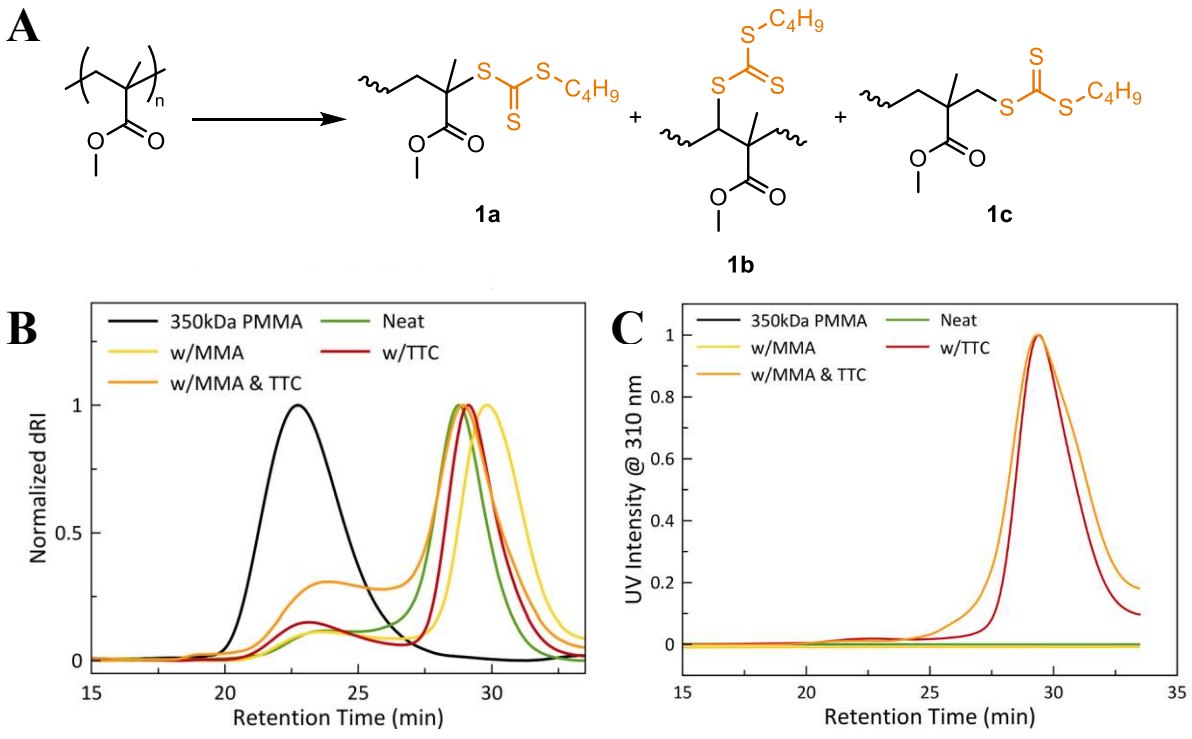


Figure 2: Mechanism of ball milling with potential products (A), dRI traces of PMMA milled under various conditions (B), UV traces of PMMA milled under various conditions (C)

1a. Only **1a** is active for any post-milling processing as it forms the most stable radical. Without monomer, **1b** and **1c** are also produced, limiting the usefulness of the functionalized polymers.

From the now functionalized polymers, the three different methods of post-milling modifications can be started: chain-extension, block polymer synthesis, and depolymerization. Starting with chain-extension, the functionalized PMMA was dissolved and then mixed with methyl methacrylate (MMA) and exposed to blue light. Polymerizations with heat are possible but require extra amounts of initiators that could introduce smaller chains without extending any of the functionalized PMMA. After reacting for three hours, chain-extension was noted on the smaller, functionalized chains. This extension is shown by a shift towards higher MW seen on the SEC in both the differential refractive index (dRI) and the UV traces (Figure 3). The shift in the dRI is seen as a disappearance of the low MW peak, while the UV has a shoulder appear. This indicates that this sample was not perfectly functionalized in the **1a** form.

Once it was confirmed that there were reactive chains that can repolymerize, block polymer synthesis was the next step. For this, functionalized PMMA was dissolved and then mixed with

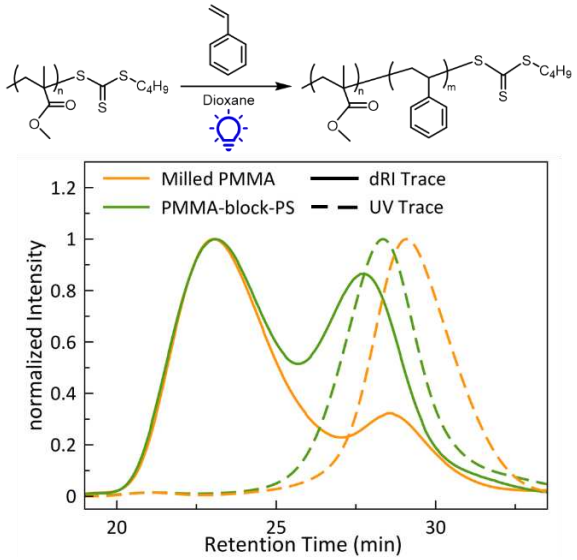


Figure 4: Functionalized PMMA chain-extended with styrene (top) with overlapping dRI and UV traces (bottom)

styrene. Similar reaction conditions were used, though this system needed twice as long to react as styrene has a relatively slow polymerization rate. Styrene was chosen as another portion of this project focused on the degradation of polystyrene (PS) as opposed to this work focused on PMMA. SEC results showed an equal shift in both the dRI and the UV traces, with a uniform shift in the UV unlike the shouldering seen in the chain-extension experiment (Figure 4).

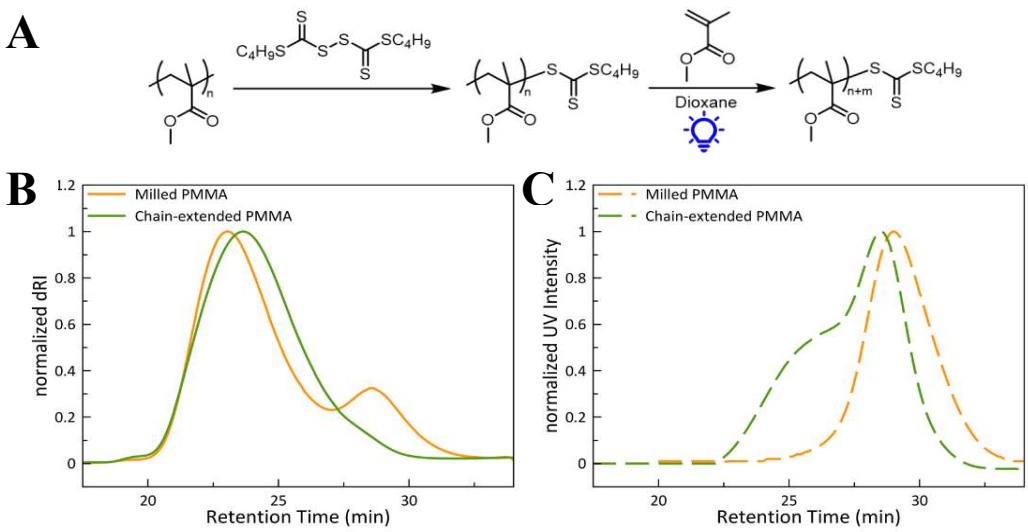


Figure 3: Mechanism of ball milling with polymerization conditions (A), dRI traces of milled PMMA and chain-extended PMMA (B), UV traces of milled PMMA and chain-extended

The final test of the functionalized PMMA was to test its ability to depolymerize. This was done in the bulk, with initial tests being run through thermogravimetric analysis (TGA) and secondary tests being run with a vacuum distillation set-up. Static TGA tests were run with an isothermal hold at 220°C for three hours. This mimicked the tests run by the Sumerlin group to determine the depolymerizability of their phthalimide functionalized PMMA.[3] The results of the static TGA were unexpected, as the PMMA milled neat or with just MMA showed high degrees of depolymerization while any PMMA milled with bis(BTTC) showed low degrees of depolymerization (Table 1). Further examination of the samples showed a presence of unsaturated ends forming where the radical is generated. These unsaturated groups show greater ease of depolymerizing and are being further studied by other members of the group.

Table 1: %Depolymerization of PMMA milled under various conditions

Sample	%Depolymerization
350 kDa PMMA	6.5%
Neat	27%
w/MMA	28%
w/TTC	12%
w/MMA & TTC	8%

To further expand upon this functionalization through ball milling, the scope of milled polymers has been expanded and briefly studied. This includes polyacrylonitrile (PAN) and poly(2-vinyl pyridine) (PVP). Initial milling experiments of the PVP show no change in MW (Figure 6B), though there is an increase in the UV trace with incorporation of bis(BTTC) into the milling process (Figure 6D). This indicates that the TTC may be reacting and adding onto the PVP in a new and unknown way. The PAN, however, shows various degrees of degradation, with no clear

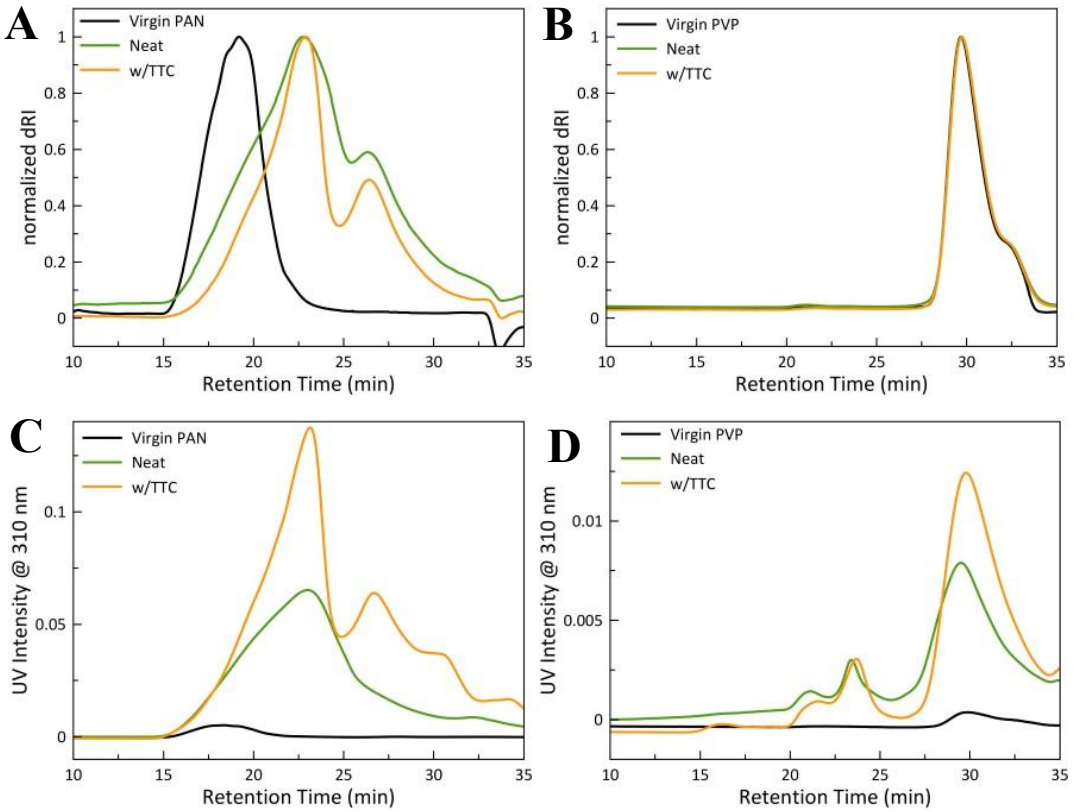


Figure 6: dRI traces of virgin, milled neat, and milled w/TTC for PAN (A) and PVP (B) and UV traces of PAN (C) and PVP (D)

pattern (Figure 6A). UV traces indicate there may be some functionalization onto the polymer, yet there is also an increase in UV absorbance after milling neat (Figure 6C). Further optimization of the milling conditions needs to be examined, as parameters such as the jar and ball material can have a large impact.

Conclusions

In conclusion, the milling of PMMA in the presence of MMA and bis(BTTC) show potential for moving mechanical recycling towards a more circular system. The functionalized PMMA was able to be repolymerized with MMA, polymerized with styrene to make block copolymers, and, while only to a small degree, improve the depolymerization of PMMA while also opening another avenue for depolymerization in the manner of unsaturated chain-ends. Expanding the scope shows some promise with the requirement of further optimization. Future directions of this project include attempting mixed polymer milling, along with incorporation of other monomers being introduced into the milling process, rather than monomer matching the polymer being milled.

References

[1] Polymer, A. A. A. Walk Down Memory Lane: A History of Plastic Recycling. AAA Polymer.

[2] Kubota, K.; Toyoshima, N.; Miura, D.; Jiang, J.; Maeda, S.; Jin, M.; Ito, H. *Angewandte Chemie International Edition* **2021**, 60 (29), 16003–16008.

[3] Young, J. B.; Goodrich, S. L.; Lovely, J. A.; Ross, M. E.; Bowman, J. I.; Hughes, R. W.; Sumerlin, B. S. *Angew Chem Int Ed* **2024**.

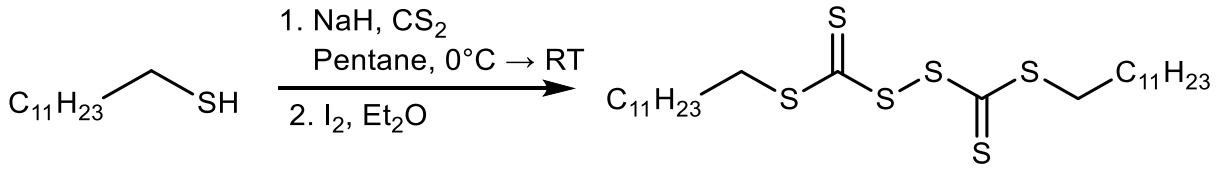
[4] Bartsch, M.; Schmidt-Naake, G. *Macro Chemistry & Physics* **2006**, 207 (2), 209–215.

[5] Stache, E. E.; Kottisch, V.; Fors, B. P. *J. Am. Chem. Soc.* **2020**, 142 (10), 4581–4585.

SUPPORTING INFORMATION

Synthesis of Model Compound 1

Bis(Dodecyl Trithiocarbonate) (Bis(DTTC))



Sodium hydride (60% suspension in mineral oil, 15.4 mmol, 616.5 mg, 1.04 equiv.) was added to a flame-dried round bottom flask and was followed by diethyl ether (27 mL) under N_2 gas. The flask was kept under N_2 for the remainder of the reaction. The flask was cooled to 0 °C, and 1-dodecanethiol (14.8 mmol, 3.55 mL, 1.0 equiv.) was added slowly. The suspension was stirred at 0 °C for 30 min, then warmed to room temperature and stirred for 3 h at room temperature. Then, carbon disulfide (15.4 mmol, 0.9269 mL, 1.04 equiv.) was added slowly at 0 °C and the reaction was allowed to warm to room temperature and stirred an additional 3 h at room temperature. Pentane (25 mL) was added to the reaction mixture and the resulting solid was filtered and washed with pentane. The precipitate was redispersed in diethyl ether (15 mL) under ambient conditions, cooled to 0 °C, followed by the addition of solid I_2 over 5 min (16 mmol, 4.06 g, 1.1 equiv) with vigorous stirring. The reaction was stirred overnight under ambient conditions. The resultant solid, NaI, was removed via filtration, then the filtrate washed with water (20 mL), followed by sat. aq. sodium thiosulfate (3 x 20 mL) at which point the washings became colorless. The organic layer was washed with brine, dried over Na_2SO_4, filtered and concentrated. The product was dried under high vacuum to afford a waxy yellow solid. 88.25% yield.

Figure S3: Picture of final product, model compound **1**

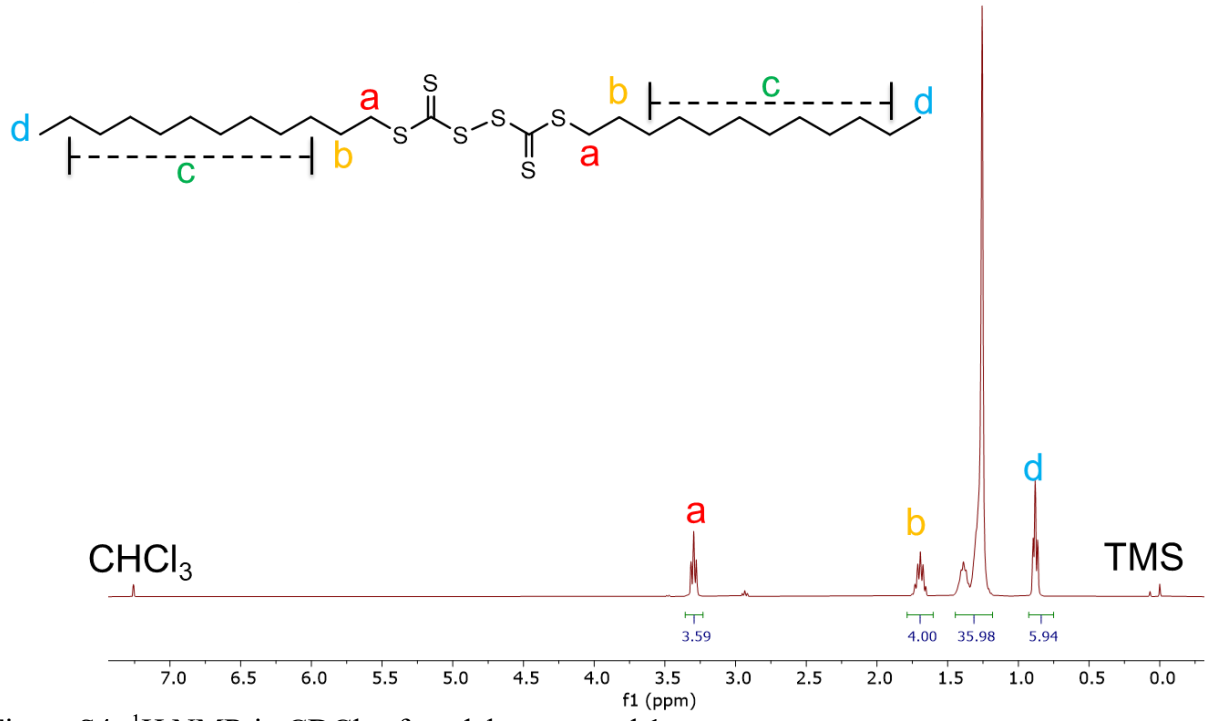
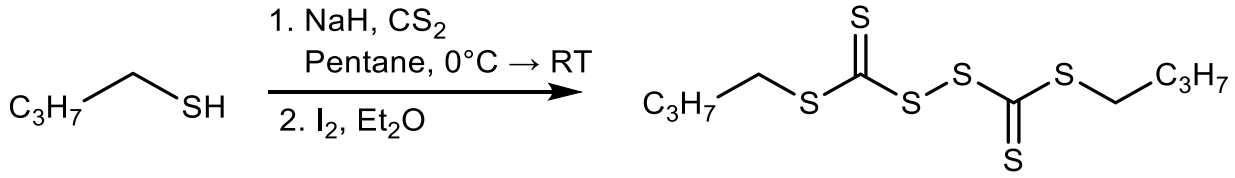


Figure S4**:** ^{1}H NMR in $CDCl_3$ of model compound **1**.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.30 (t, 4 H), 1.70 (p, 4 H), 1.25 (m, 36 H), 0.85 (t, 6 H)

Synthesis of Model Compound 2

Bis(Butyl Trithiocarbonate) (Bis(BTTC))



A flame-dried round bottom flask was charged with sodium hydride (60% suspension in mineral oil, 10.4 mmol, 417 mg, 1.04 equiv) followed by diethyl ether (24 mL) under N_2. The flask was cooled to 0 °C with an ice bath, and butanethiol (10.0 mmol, 1.1 mL, 1.0 equiv) was added slowly under N_2. The suspension was stirred at 0 °C for 30 min, then warmed to room temperature and stirred for 3 h at room temperature under N_2. Then carbon disulfide (10.4 mmol, 0.63 mL, 1.04 equiv) was added slowly at 0 °C and the reaction was allowed to warm to room temperature and stirred an additional 3 h at room temperature under N_2. Pentane (25 mL) was added to the reaction mixture and the solid was filtered and washed with additional pentane. The solid was redispersed in diethyl ether (15 mL) under ambient conditions, cooled to 0 °C, followed by the addition of solid I_2 over 5 min (5.5 mmol, 1.5 g, 0.55 equiv) with vigorous stirring. The reaction was stirred overnight under ambient conditions. The resultant solid NaI was removed via filtration, then the filtrate washed with water (20 mL), followed by sat. aq. sodium thiosulfate (3 x 20 mL) at which point the washings became colorless. The organic layer was washed with brine, dried over Na_2SO_4, filtered and concentrated. The product was dried under high vacuum to afford an orange oil. To remove excess butanethiol not removed by the separation process, pass the product through a basic alumina plug. Yield: 75%

Figure S5**:** Picture of final product, Bis(BTTC)

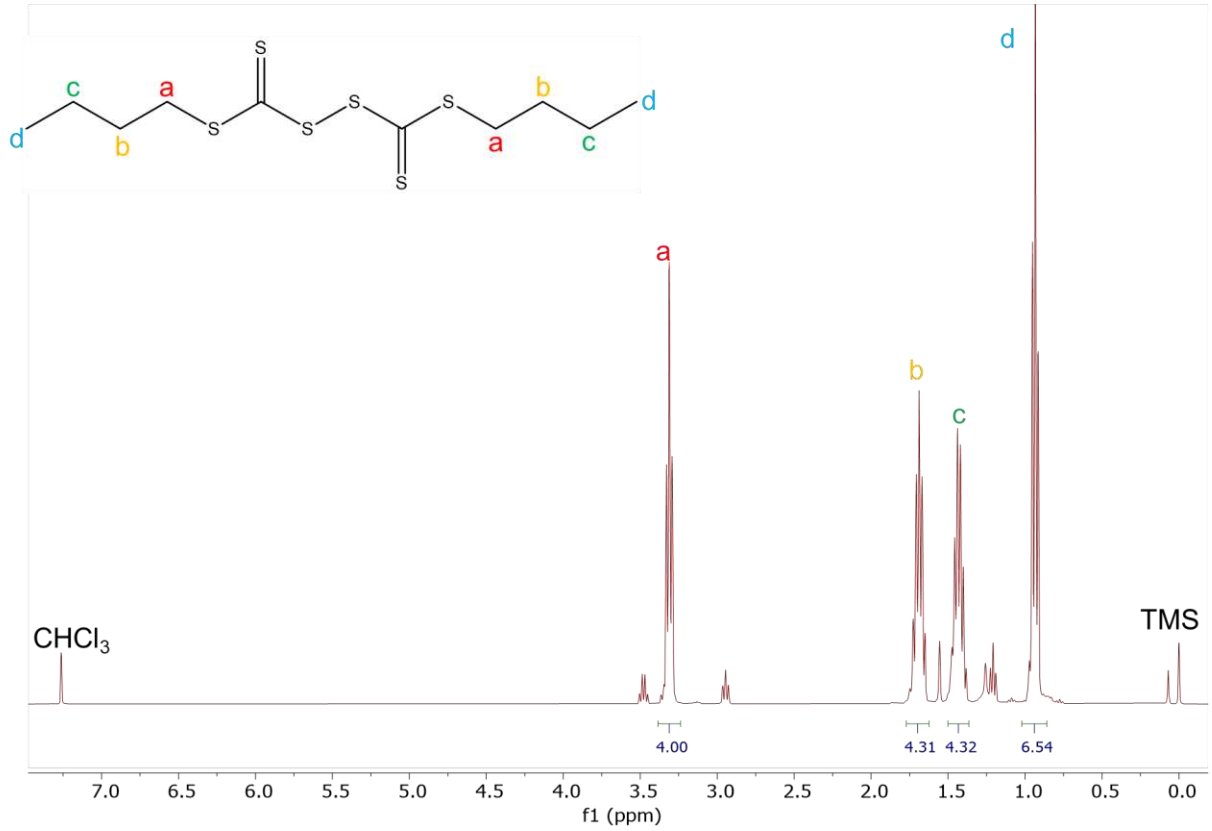


Figure S6**:** ^{1}H NMR in $CDCl_3$ of Bis(DTTC)

^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.30 (t, 4 H), 1.70 (p, 4 H), 1.45 (m, 4 H), 0.90 (t, 6 H)

General Procedure for Ball Mill Grinding for Mechanical Degradation

Two 50 mL ceramic jars are loaded with 35 g of ceramic beads. Next, each jar is loaded with 100-500 mg of sample. The mill is set to a frequency of 50 Hz and runs for 2 hours. Remove the jars and use DCM to wash ground sample out into a 20 mL vial. Dry under vacuum or open to air with kim wipe cover to remove DCM.

General Procedure for Ball Mill Grinding for RAFT Incorporation

Two 50 mL ceramic jars are each loaded with 35 g of ceramic beads. Next, each jar is loaded with 100-500 mg of sample. Then RAFT is added at 10 wt% of the loaded sample. The mill is set to a frequency of 50 Hz and runs for 2 hours. Remove the jars and use DCM to wash ground sample out into a 20 mL vial. Precipitate sample into cold methanol once to remove any unfunctionalized RAFT. Once precipitated, centrifuge and decant off solvent before drying under vacuum overnight. Total mass yield typically ranges from 70-80% of the starting material mass.

General Procedure for Ball Mill Grinding for RAFT Incorporation with Monomer

Two 50 mL ceramic jars are each loaded with 35 g of ceramic beads. Next, each jar is loaded with 100-500 mg of sample. Then RAFT is added at 10 wt% of the loaded sample. Finally, monomer is added at 200 equivalences compared to the polymer. The mill is set to a frequency of 50 Hz and runs for 2 hours. Remove the jars and use DCM to wash ground sample out into a 20 mL vial. Precipitate sample into cold methanol once to remove any unfunctionalized RAFT. Once precipitated, centrifuge and decant off solvent before drying under vacuum overnight. Total mass yield typically ranges from 70-80% of the starting material mass.

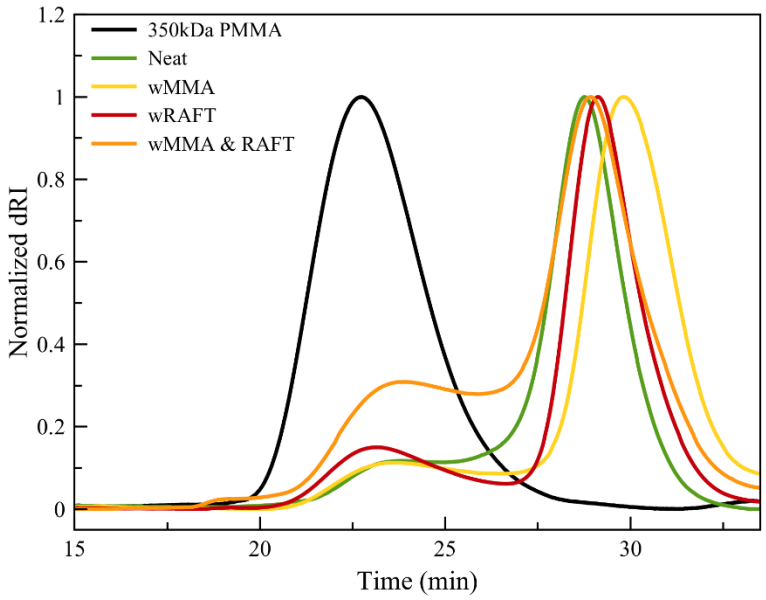


Figure S7: SEC trace comparison of various ball mill conditions

General Method for Thermogravimetric Analysis Mass Spectrometry (TGA-MS)

TGA experiments were performed on a TGA-55 analyzer (TA Instruments) which uses an evolved gas analysis furnace (TA Instruments). This is also coupled with a Cirrus 3 electrospray ionization mass spectrometer (MKS Instruments) to obtain TGA-MS measurements. Data was processed using TRIOS (TGA) and ProcessEye Professional (MS). Methods were run with either dynamically, for determining optimal degradation temperatures, or isothermally, for determining

extent of depolymerization. The dynamic method increases at 10°C /min from 25°C to 500°C. The isothermal method holds at 220°C for 180 minutes.

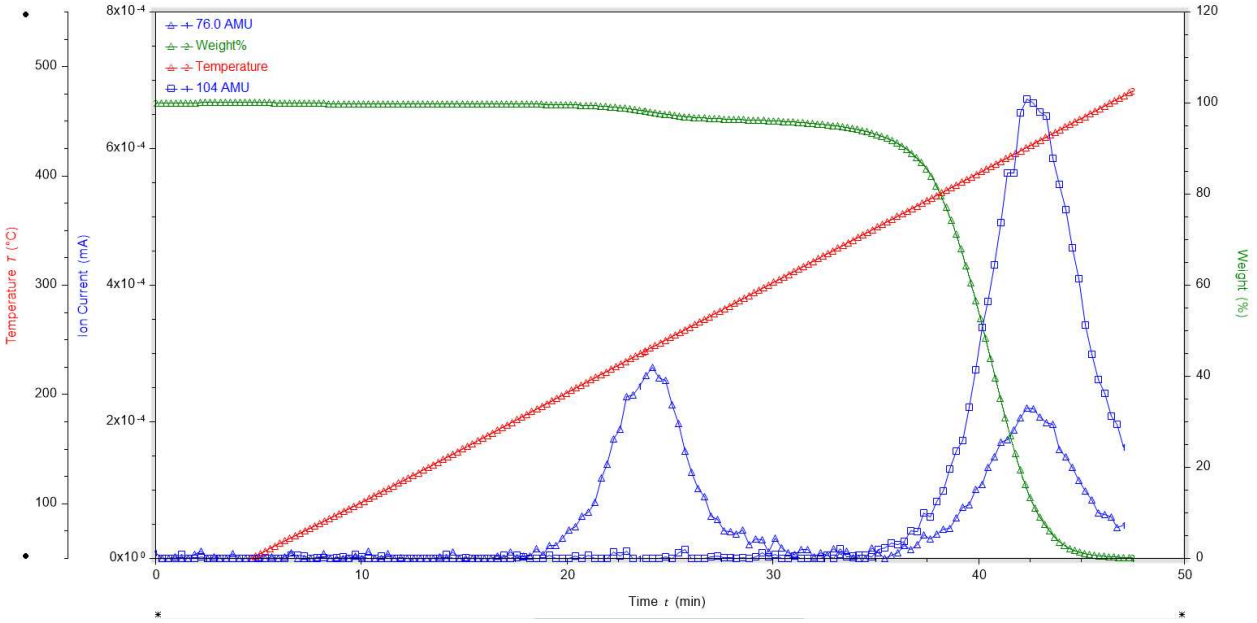


Figure S8: Standard TGA-MS trace of model PS with the major recordings shown: weight% (green), temperature (red), and ion intensity of important fragments (blue)

General Method for Differential Scanning Calorimetry (DSC)

DSC experiments were conducted on a Discovery 2500 DSC (TA Instruments) with a RCS 90 refrigerator. Data was processed using TRIOS. DSC methods were run dynamically to determine the glass transition temperature (T_g) of the sample. The sample was subjected to two cycles of

heating from 25°C to 250°C and then cooled from 250°C to 25°C. The first cycle is to remove any thermal history from the sample to obtain a more accurate T_g in the second cycle.

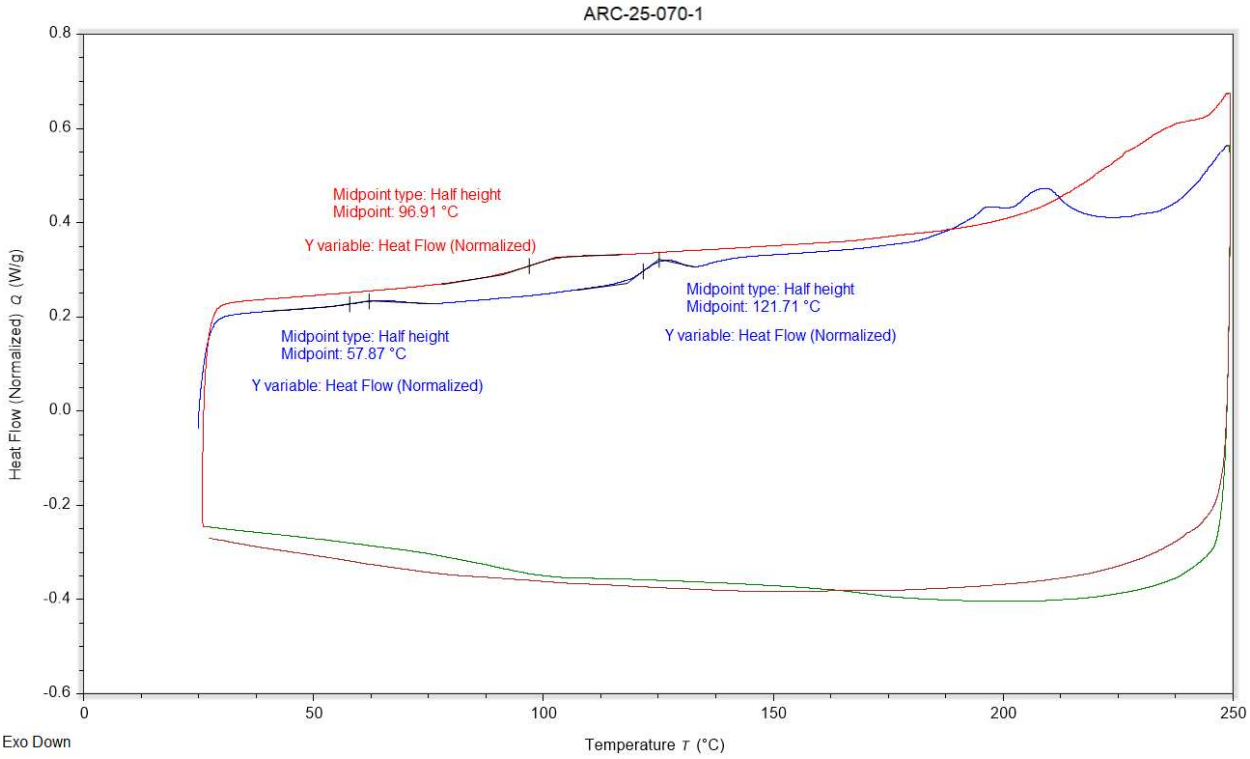


Figure S9: Standard DSC curve of PS shown with analyzed T_g's with both heating and both cooling cycles shown. First heating cycle (blue), first cooling cycle (green), second heating cycle (red), and second cooling cycle (brown).

Creating a Calibration Curve for Determining %Functionalization of RAFT onto Degraded Polymer

This calibration curve was created by using data obtained from the TGA-MS. This was done by integrating the derivative weight loss curve where the first instance of mass loss overlaps with an MS signal at 76 AMU. These overlapping curves are chosen as 76 AMU corresponds to CS_2, which is released from TTC end-groups before any other chemical species. An example of this is shown below in Figure S6. To create the points for the curve, varying ratios of stock PMMA and model PMMA were mixed. Shown in Figure S6 is a mixture of 41 wt% model PMMA, with the remaining being stock PMMA. The blue line shows the weight loss of the polymer mix over time, with the orange line being the derivative of this weight loss. The green line shows the intensity of the CS_2 as it is released from the model PMMA and overlaps with the derivative weight loss curve. This was repeated for a spread of differing wt%'s of model to stock PMMA.

The log of these peak areas was then graphed against the molar ratio of TTC:PMMA to get the calibration curve.

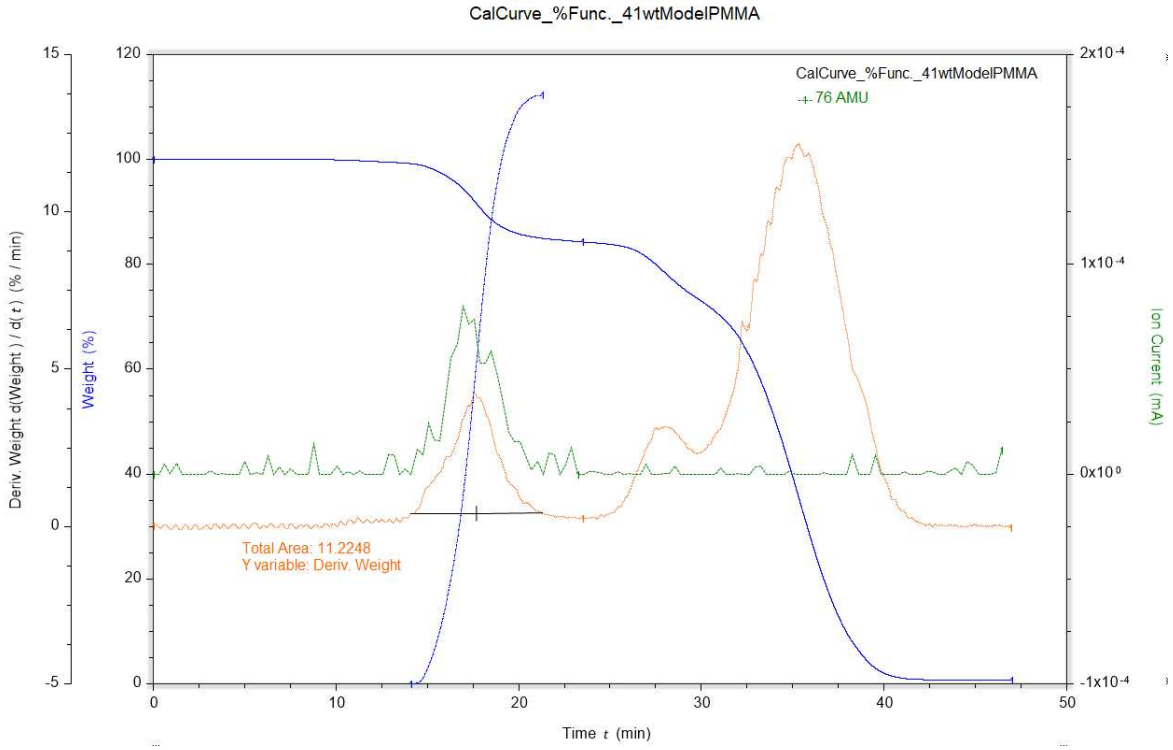


Figure S10**:** Example of TGA-MS used in the creation of the calibration curve with this example showing the trace of a blend of 41 wt% model PMMA

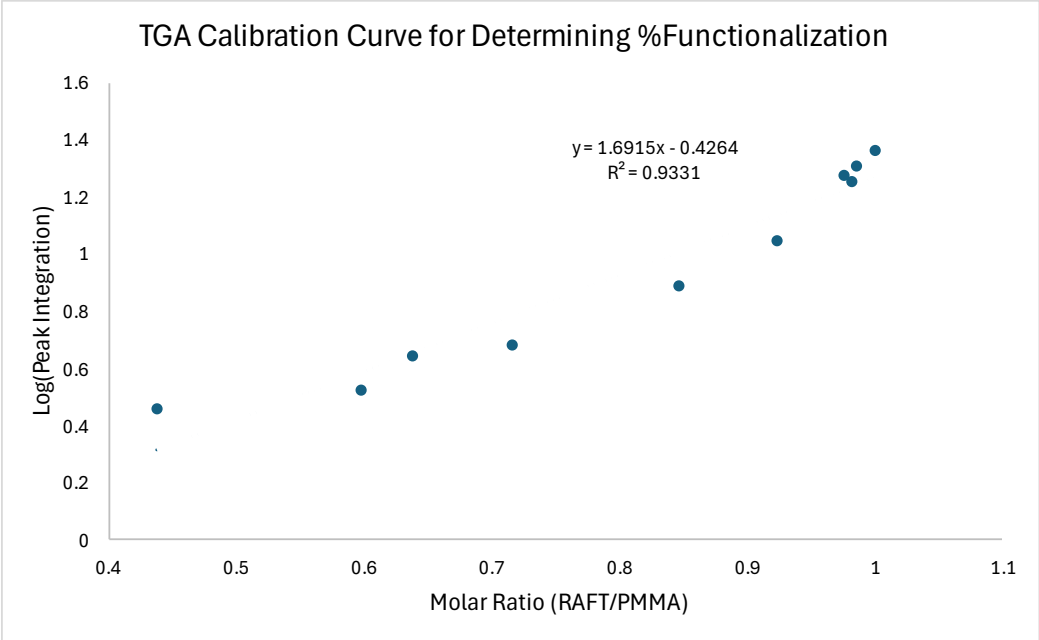


Figure S11: Calibration curve for determining functionalization of Bis(BTTC) onto degraded polymers using peak integration of derivative weight loss on the TGA

Synthesis of PMMA-block-PS

Styrene was removed from the fridge and allowed to reach room temperature. The styrene was then passed through a basic alumina plug to remove any inhibitor (place a small piece of glass wool in the pipette then fill at least 1 inch with alumina, use a pipette bulb to push the styrene through). PMMA milled with bisTTC and MMA (0.05 g) and styrene (1.0724 g) were added to a Schlenk flask along with a small stir bar. Let the mixture stir for 15 minutes to dissolve the PMMA in the styrene to avoid the need for solvent. The flask is then capped and the mixture degassed with N_2 for 10 minutes. Then place the flask into a blue LED light reactor and cover it to prevent eye damage. To take the time points, insert the long needle into the septa with the stopcock closed and the nitrogen on. Flush a syringe 3-4 times with nitrogen using this needle. Open the stopcock, and uptake the sample. Once finished, close the stopcock and turn off the nitrogen. Let the reaction run for 24 hours and then stop by turning off the lights and exposing the mixture to air. Precipitate the mixture into cold methanol 3x to remove any unreacted styrene. Finally, dry the product under vacuum to remove any remaining solvent.

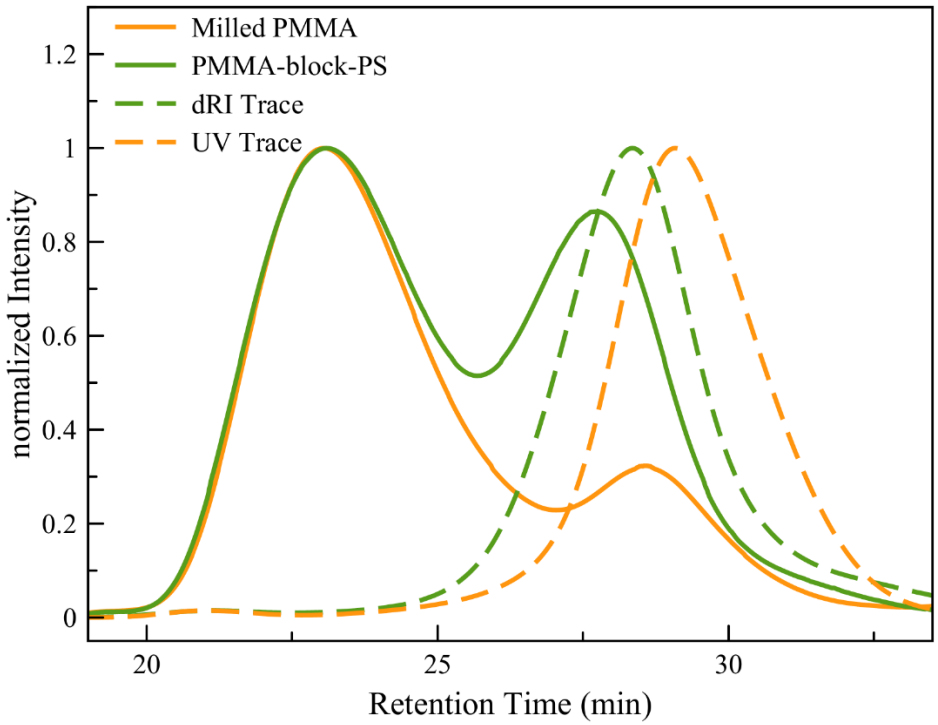


Figure S1012**:** GPC trace of the increase in MW of the functionalized PMMA when polymerized with styrene.