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Thermal Recycling of Poly(styrene): Temperature Dependence for Depolymerization

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ABSTRACT

The development of polymeric materials in the mid-twentieth century has enhanced the quality of life in advanced societies around the world. However, the ever-increasing accumulation of polymeric waste, particularly plastics, and the depletion of resources has brought sustainability and recycling efforts to prominence. Depolymerization to generate monomers represents a preeminent goal for the recycle of polymer waste. Poly(styrene) is a prominent commercial polymer well-suited for recycling using the approach. However, progress has been hampered by a lack of an understanding of the details of the thermal degradation of poly(styrene). Thermal degradation of poly(styrene) has often been carried out at high temperature or using variable temperature techniques—conditions which mask important features of degradation processes. Most general-purpose poly(styrene) is produced under conditions which lead to polymerization termination by radical coupling. This places a head-to-head unit in the polymer mainchain. This unit is thermally-labile and at modest temperature (280° C), undergoes scission to generate macroradicals which rapidly unzip to liberate styrene monomer. At this temperature styrene monomer is effectively the only volatile species formed. In the presence of an effective hydrogen atom transfer agent, the macroradicals are rapidly trapped and the decomposition to form styrene monomer is suppressed. At higher temperatures (>300° C) random chain scission may occur and a variety of products are formed. If macroradicals are generated by other means, e.g., mechanical milling, depolymerization of poly(styrene) may be achieved at very low temperature (ambient).

Keywords: Poly(styrene) Recycling, Thermal Stability of Poly(styrene), Labile Structures in Poly(styrene), Monomer Production from Waste Poly(styrene), Temperature Profile for Poly(styrene) Decomposition, Mode of Poly(styrene) Degradation.

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Introduction

In the late 1920s Wallace Corothers left academia to become director of research at the DuPont Company. Within a few short years he had put the ideas of Staudinger about the structure of polymeric materials on a firm experimental basis and had begun the development of materials that were used to dramatically improve the well-being of people around the world. The age of modern polymers was born [1-3]. Stockings made from Nylon 6,6 were displayed at the 1939 world's fair in New York City. Parachutes made from the same material enabled the allied landing at Normandy in 1944. The development of poly(styrene) began at the Dow Chemical Company in the late 1930s. During WWII styrene copolymers were developed to replace natural elastomers [4]. After the war the production of polymeric materials and the use of these materials in a myriad of applications which impacted everyday life bloomed. The durability largely responsible for the widespread use of these materials has made satisfactory disposal after a useful lifetime difficult. Large amounts (about 400 Mt/year) of polymeric waste, most notably from polymers formulated as plastics, are generated annually [5]. Disposal of these

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materials has largely been unsatisfactory. Less than 20% of the total is recycled, approximately 25% is incinerated, and the remainder is landfilled or discarded directly into the natural environment. The accumulation of polymeric waste in the environment degrades the quality of human existence and can be devastating to many forms of wildlife. Landfilling of this material represents a convenient but unsuitable method of disposal [5,6].

In a landfill, additives used in the formulation of polymeric materials for the generation of items of commerce may leach into groundwater and ultimately find their way into streams, lakes, oceans where they bioaccumulate and may enter the human food chain. Degradation of the polymeric material is extremely slow and may require decades or longer [7-9]. Physical degradation (embrittlement, cracking) as plasticizing additives are lost may occur first [5]. Chemical degradation (actual cleavage of covalent bonds) occurs much, much more slowly. Physical degradation in the natural environment is facilitated by abradative phenomena and leads to the formation of small particles, the so-called microplastics. These particles are widespread in nature and are readily ingested by a number of organisms including humans [10]. Human exposure to microplastic particles has been correlated with a number of disease states. From an environmental and health perspective alone, better methods for disposal of polymeric waste must be found [11,12]. Further, current methods of disposal are extremely wasteful of raw materials. Consequently, concerns for sustainability, recycling efforts and a circular economy have become prominent. Various recycling schemes have been proposed and several utilized but all are subject to severe limitations. An extremely attractive approach to recycling is depolymerization to generate monomers suitable for the production of new polymer. The ease with which degradation to monomer may be achieved varies widely depending on polymer structure [13-15]. Poly(styrene) is, perhaps, the polymer most amenable to recycling to monomer. General purpose poly(sytrene) produced using current technology undergoes thermal degradation at modest temperature (280° C) to afford styrene monomer as essentially the only volatile product. At higher temperature, random chain scission, hydrogen atom-transfer and cyclization processes lead to the formation of a mixture of products [14].

Experimental

Methods and materials have previously been described in detail. Thermal degradation of general-purpose poly(styrene) prepared by standard radical techniques, poly(styrene) of idealized head-to-tail structure prepared by nitroxyl-mediated polymerization followed by reductive removal of reactive chain ends or by anionic techniques, and fully head-to-head poly(styrene) prepared by reduction of poly(2,3-diphenyl-1,3-butadiene), was assessed using thermogravimetry [15,16]. A TA Instruments model 2950 TGA instrument was used. Samples, 5-10 mg, were contained in a platinum sample pan and the cell was subject to a constant nitrogen purge, 50 ml/min., during degradation runs. The temperature was ramped at a rate of 2 or 10°/min. for dynamic analysis. For isothermal kinetic studies the temperature was maintained at a specific temperature between 280 and 350° C. Evolved gas analysis was accomplished using a Thermo Cahn TG-2131 microbalance in conjunction with a Thermo Finnigan TRACE GC/MS instrument. Structures of polymers and pyrolysis products were determined using spectroscopic and chromatographic techniques. Molecular weights were determined using size exclusion chromatography (SEC) and solutions in tetrahydrofuran, microstyrogel columns and linear poly(styrene) calibration.

Results and Discussion

General purpose poly(styrene) is a large-scale commodity polymer useful in a variety of applications. Because it may be processed into a tough, transparent sheet/film it is widely used in disposable packaging. For these applications, the presence of trace amounts of styrene monomer which imparts undesirable taste and aroma to packaged food items must be avoided. This requires careful control of process conditions. The thermal stability of poly(styrene) is lower than would be expected for a fully head-to-tail polymer of ideal structure. The source of this instability may be revealed by comparison of the thermal degradation of general-purpose poly(styrene) with that of a fully head-to-head isomer generated by hydrogenation of poly(2,3-diphenyl-1,3-butadiene). This is illustrated in Figure 1 [16].

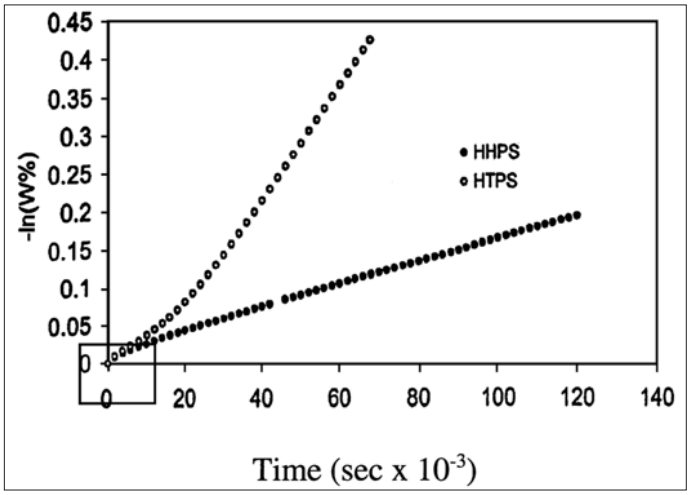


Figure 1: Comparison of the Thermal Degradation of Fully Head-to-head Poly(styrene) [HHPS] with that of General-Purpose Poly(styrene) [HTPS] at 280° C. Reprinted with permission (Elsevier) from B. A. Howell, Y. Cui and D. B. Priddy, "Assessment of the Thermal Degradation Characteristics of Isomeric Poly(styrene)s Using TG, TG/MS and TG/GC/MS," Thermochim. Acta, 2003, 396, 167-177].

At the very early stages of decomposition, the process is similar for both polymers. For the fully head-to-head polymer this must reflect cleavage of the mainchain at head-to-head units/ This is also the case for initial degradation of the general-purpose material. A head-to-head unit is incorporated into the mainchain by polymerization termination by radical coupling. For the general-purpose polymer, degradation quickly deviates from that of the fully head-to-head polymer and occurs at a much more rapid rate. What is occurring is evident from evolved gas analysis, thermogravimetry/gas chromatography/mass spectrometry (TG/GC/MS). As illustrated in Figure 2, styrene monomer is the only volatile product evolved from decomposition of the general-purpose polymer. This suggests that the macroradicals initially formed by cleavage of a head-to-head unit rapidly unzip to form styrene monomer [16,17].

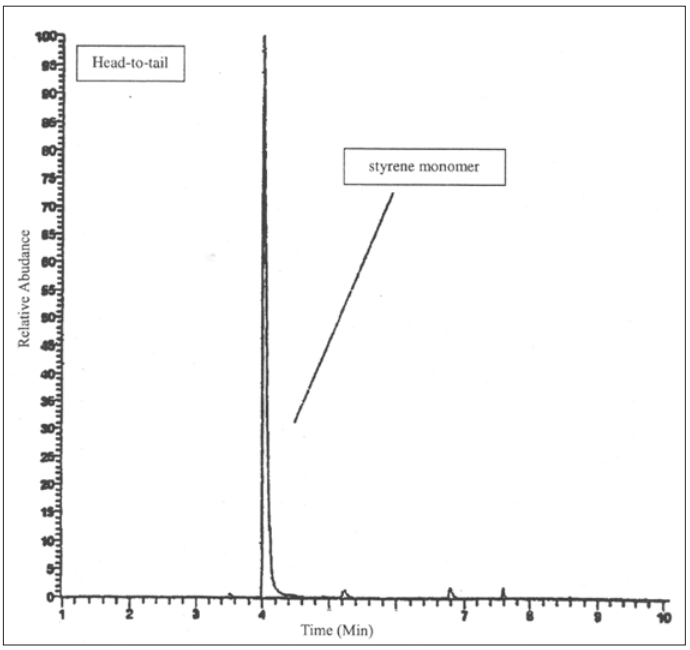
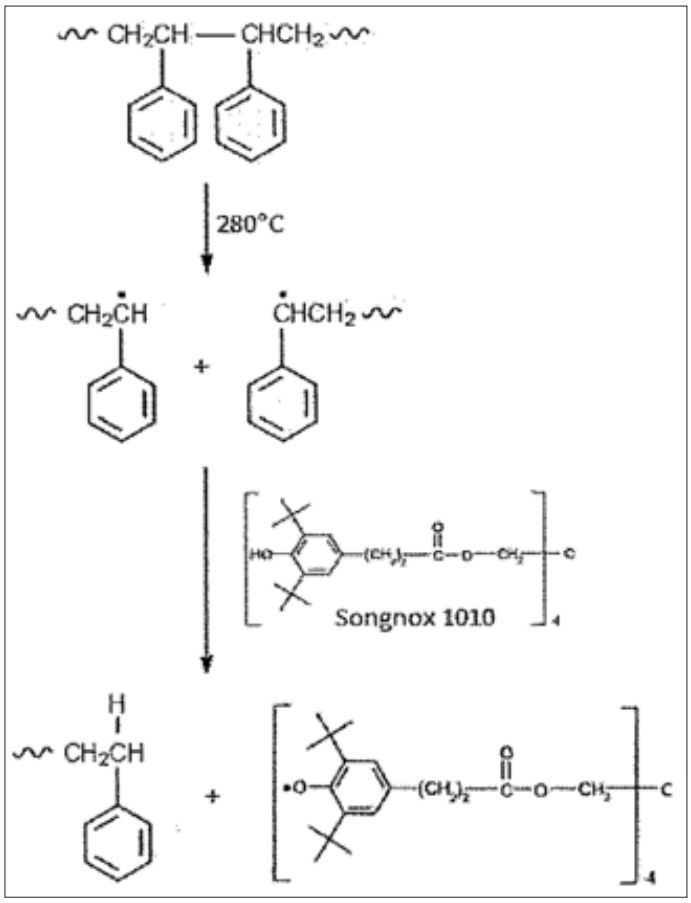


Figure 2: Volatile Products (TG/GC/MS) from Thermal Degradation of General Purpose Atactic Nominally Head-to-tail Poly(styrene) at 280° C. [Reprinted with permission (Elsevier) from B. A. Howell, Y. Cui and D. B. Priddy, "Assessment of the Thermal Degradation Characteristics of Isomeric Poly(styrene)s Using TG, TG/MS, TG/ TG/MS and TG/GC/MS," Thermochim. Acta, 2003, 396, 167-177.]

In fact, when the degradation of this polymer is carried out in the presence of an effective hydrogen atom-transfer agent the macroradicals are trapped as formed and the evolution of styrene monomer is suppressed [see Scheme 1]. The molecular weight of the polymer decreases as a function of time but no monomer is formed [18]. Further, an ideal, fully head-to-tail poly(styrene) produced by mediated radical polymerization followed by reductive removal of labile endgroups or by anionic polymerization is much more thermally stable than general purpose poly(styrene) and undergoes degradation very slowly at 280° C (Figure 3) [19,20].

Polystyrene macroradicals generated by an alternative method, a ball milling mechanical process, rapidly unzip to form styrene monomer, even at room temperature. Pyrolysis to generate styrene monomer may be enhanced by microwave heating [21,22]. Conversion to styrene monomer of greater than 70% and formation of very little residue has been observed [23].

The thermal liability of poly(styrene) may be exploited for the recycle of waste from commercial applications. In general, pyrolysis of waste poly(styrene) is carried out in the temperature range of 300-500° C to generate a liquid oil consisting of a mixture of products reflecting multiple decomposition processes [24]. To maximize conversion to styrene monomer a relatively low temperature should be maintained. Although, the thermal instability of poly(styrene) has long been known and variously studied, an essential feature of the degradation has often been obscured. At relatively low temperature (280° C), the degradation affords styrene as essentially the only product. However, at only slightly higher temperature (300° C) sufficient energy is available to promote a variety of processes and the formation of a variety of products. As illustrated in Figure 4 both general purpose poly(styrene) and that containing no head-to-head units undergo nonuniform degradation at 350° C [25]. Most generally, poly(styrene) degradation has been observed at variable temperature with high heating rates or at high temperatures. In either case, the more productive of styrene monomer low-temperature degradation has been missed. To maximize conversion of styrene monomer, pyrolysis of poly(styrene) should be carried out at relatively low temperatures (<300° C).



Scheme 1: Trapping of Macroradicals from Thermal Degradation of Poly(styrene) by a Hydrogen Atom Transfer Agent.

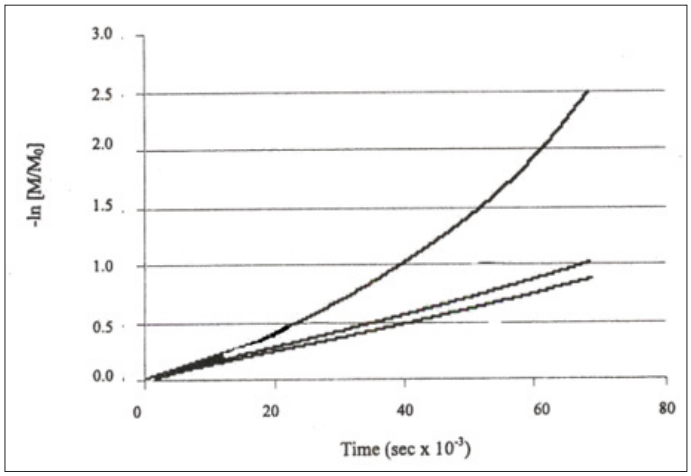


Figure 3: Thermal Degradation of General-Purpose Poly(styrene) [top], Fully Head-to-tail Poly(styrene) Produced by Anionic Techniques [middle] and Fully Head-to-tail Poly(styrene) Produced by Mediated Radical Polymerization [bottom].

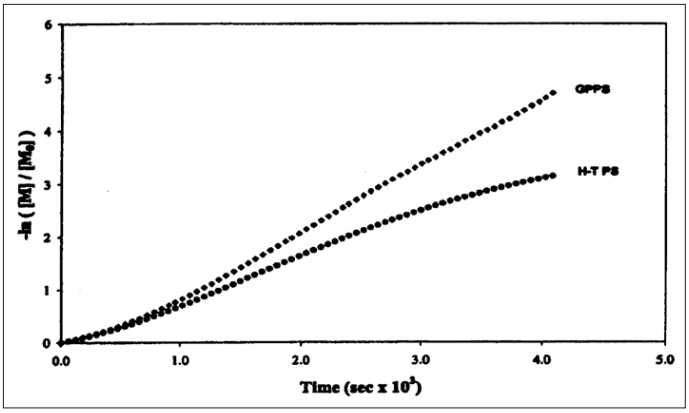


Figure 4: Thermal Degradation of General-Purpose Poly(styrene) [GPPS] and Poly(styrene) Containing no Head-to-head units [HTPS] at 350° C.

Conclusions

General purpose poly(styrene) is a widely-used and valuable commodity polymer. For food packaging applications process conditions must be carefully maintained to avoid the generation of styrene monomer which may impart undesirable taste and aroma. The origin of this contaminant is a head-to-head unit present in the polymer mainchain as a consequence of polymerization termination by radical coupling. At 280° C, chain scission at this unit generates macro styryl radicals which rapidly unzip to form styrene monomer. Styrene monomer is effectively the only volatile product formed at this temperature. At somewhat higher temperature (>300° C) other processes, including radon chain scission, become prominent and a mixture of products is produced. This low-temperature degradation may be exploited for the efficient pyrolytic conversion of waste poly(styrene) to styrene monomer.

Conflicts of Interest

The author declares no conflict of interest.

References

1. Hounshell DA, Smith JK (1988) Jr Science and Corporate Strategy: DuPont R&D, 1920-1980, Cambridge University Press New York NY.
2. Hermes ME (1996) Enough for One Lifetime: Wallace Carothers, Inventor of Nylon. Chemical Heritage Foundation Philadelphia PA.
3. Furukawa Y (1998) Inventing Polymer Science. University of Pennsylvania Press Philadelphia PA.
4. Scheirs J, Priddy D (2003) Modern Styrenic Polymers: Polystyrenes and Styrenic Copolymers. John Wiley and Sons Ltd Chichester UK.
5. Chamas A, Moon H, Zheng J, Qiu Y, Tabassum T, et al. (2020) Degradation Rates of Plastics in the Environment. ACS Sustainable Chem Eng 8: 3494-3511.
6. Baudena A, Kiko R, Jalon-Rojas I, Redrotti ML (2023) Low-Density Plastic Debris Dispersion Beneath the Mediterranean Sea Surface. Environ Sci Technol 57: 7503-7515.
7. Cristale J, Bele TGA, Larcorte S, de Marchi MRR (2019) Occurence of Flame Retardants in Landfills: A Case Study in Brazil. Environ Res 168: 420-427.
8. Hahladakis JN, Velis CA, Weber R, Iacovidou E, Purnell P (2018) An Overview of Chemical Additives Present in Plastics: Migration, Release, Fate and Environmental Impact During their Use, Disposal and Recycling. J Hazard Mater 344: 779-799.
9. Wiesinger H, Wang Z, Hellweg S (2021) Deep Dive into Plastic Monomers, Additives, and Processing Aids. Environ Sci Technol 55: 9339-9351.
10. Isobe A, Azuma T, coworkers (2021) A Multilevel Dataset of Microplastic Abundance in the World's Upper Ocean and the Laurentian Great Lakes. Micropl Nanopl 1: 16.
11. Danopoulos E, Twiddy M, West R, Rotchell JM (2022) A Rapid Review and Meta-regression Analysis of the Toxicological Impacts of Microplastic Exposure in Human Cells. J Hazard Mater 427: 127861.
12. Wu P, Lin S, Cao G, Wu J, Jin H, et al. (2022) Absorption, Distribution, Metabolism, Excretion and Toxicity of Microplastics in the Human Body and Health Implications. J Hazard Mater 437: 129361.
13. Laviolette JP, Leclerc P, Kerenkan AE, Eslarni A, Doucet J (2021) Monomer Recycling of Addition Polymers. D. I. Collias, M. I. James and J. M. Layman, Eds., Circular Economy of Polymers: Topics in Recycling Technologies (Symposium Series 1391), American Chemical Society Washington DC 6: 105-128.
14. Coates GW, Getzler YDYL (2020) Chemical Recycling to Monomer for an Ideal, Circular Polymer Economy. Nat Rev Mater 5: 501-516.
15. Jones GR, Wang HS, Parkatzidis K, Whitfield R, Truong NP, et al. (2023) Reversed Controlled Polymerization (RCP): Depolymerization from Well-defined Polymers to Monomers. J Am Chem Soc 145: 9898-9915.
16. Howell BA, Cui Y, Priddy DB (2003) Assessment of the Thermal Degradation Characteristics of Isomeric Poly(styrene)s Using TG, TG/MS and TG/GC/MS. Thermochim Acta 396: 167-177.
17. Howell BA (2007) The Utilization of TG/GC/MS in the Establishment of the Mechanism of Poly(styrene) Degradation. J Therm Anal Calorim 89: 393-398.
18. Lazar ST, Howell BA, Daniel YG, Li KJ (2017) Thermal Decomposition of Poly(styrene) in the Presence of a Hydrogen Atom Transfer Agent. J Therm Anal Calorim 127: 969-974.
19. Howell BA, Cui Y, Chiawong K, Zhao H (2006) Polymerization as a Means of Stabilization of Poly(styrene). J Vinyl Addit Technol 12: 198-203.
20. Howell BA, Chaiwong K (2009) Thermal Stability of Poly(styrene) Containing No Head-to-head Units. J Therm Anal Calorim 96: 219-223.
21. Balema VP, Hlova IZ, Carnahan SL, Seyedi M, Dolotko O, et al. (2021) Depolymerization of Polystyrene Under Ambient Conditions. New J Chem 45 2935-2938.
22. Jung E, Yim D, Kiru H, Peterson GI, Choi TL (2023) Depolymerization of Poly(α-methylstyrene) with Ball-mill Grinding. J Polym Sci 61: 553-560.
23. Bartoli M, Rosi L, Frediani M, Undri A, Frediani P (2015) Depolymerization of Polystyrene at Reduced Pressure Through a Microwave Assisted Pyrolysis. J Anal Appl Pyrolysis 113: 281-287.

24. Maafa IM (2021) Pyrolysis of Polystyrene Waste: A Review. Polymers 13: 225.
25. Howell BA (2015) The Mechanism of Poly(styrene) Degradation. A Tiwai and B Raj, Eds Reactions and Mechanisms in Thermal Analysis of Advanced Materials, Scrivener Publishing LLC Beverly MA 11: 259-268.