UV-INDUCED PET DEPOLYMERIZATION IN CRESOL MONITORED BY TIME-RESOLVED DIFFUSION NMR ON BENCHTOP SPECTROMETER

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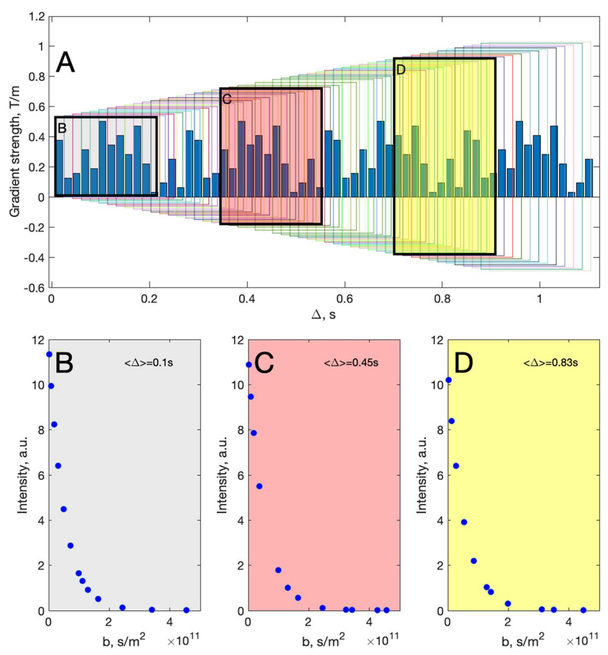
Introduction

Polyethylene terephthalate (PET) is widely used in various applications–from water bottles to the textile industry. However, PET is known for its transparency, durability, and mechanical properties; its use comes at an environmental cost[1]. While PET can gradually break down when exposed to natural UV radiations from the sun, this process is inefficient, leading primarily to microplastics forming, which contribute to pollution[2]. A more efficient method of converting PET into its monomers is photochemical depolymerization using artificial Ultraviolet light (UV)[3]. In this study, PET is depolymerized in m-cresol under 365nm UV radiations, utilizing the solvent ability to dissolve the polymer and facilitate photoactivation. Using Time-Resolved Diffusion Ordered Spectroscopy (DOSY) on a Benchtop Spectrometer, the depolymerization process is monitored, enabling real-time, non-invasive tracking of molecular weight changes to monomer formations. This approach provides insights into the kinetics and mechanistic pathway of UV-driven PET depolymerization under lab-controlled conditions.

Time-Resolved Diffusion NMR



1. TR-DOSY data time resolved diffusion data are collected during dynamic process.[4,5].

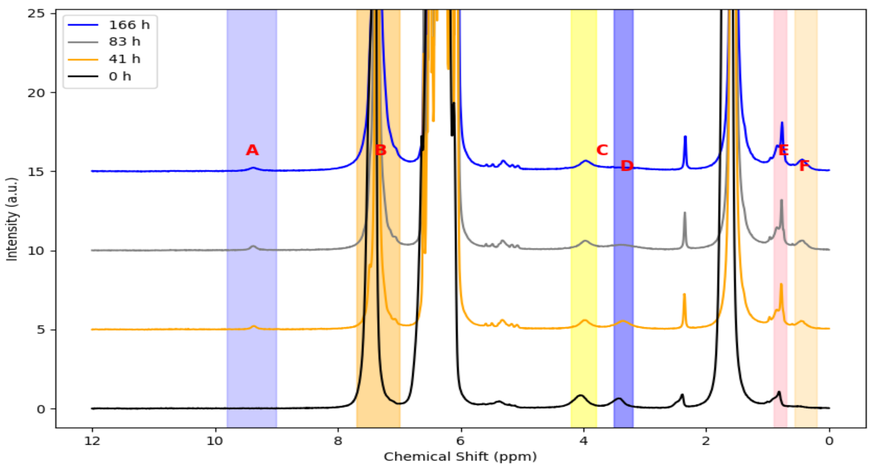
2. The data set were divided into overlapping subsets to construct time resolved diffusion profile. Each frame represents the specific window to track the diffusion changes.

3. subset overlap ensures high temporal resolution and continuity of kinetics.

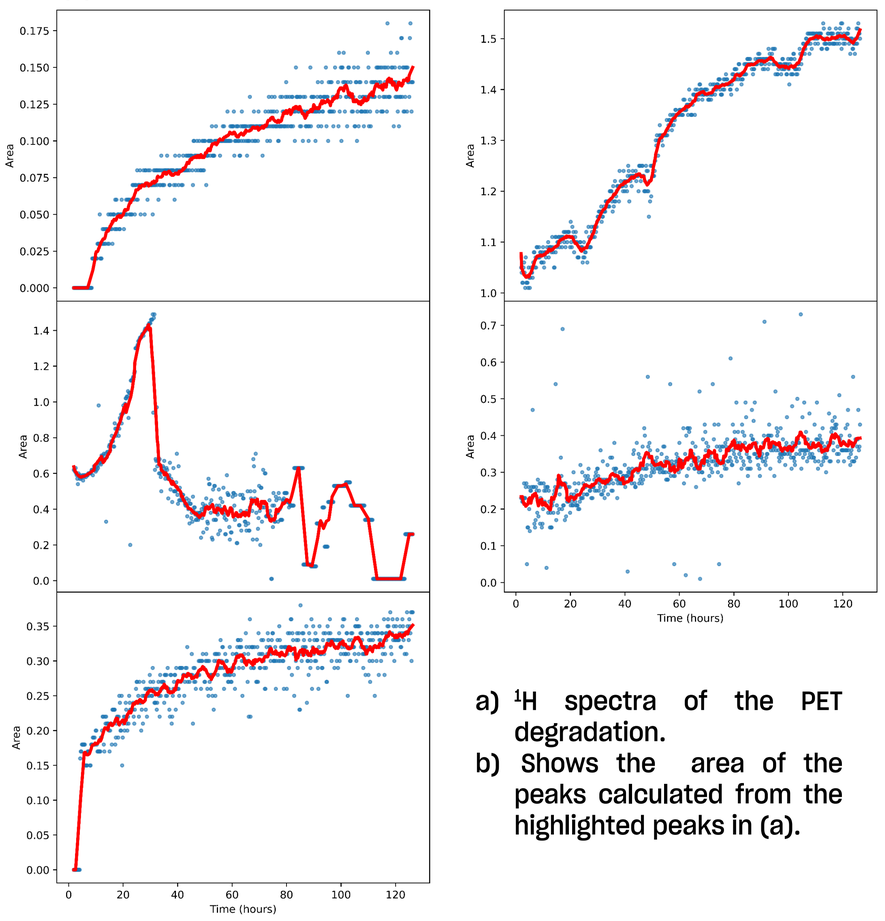
4. The figure is taken from[4].

Photo Depolymerization of PET under 365nm UV light

(a)



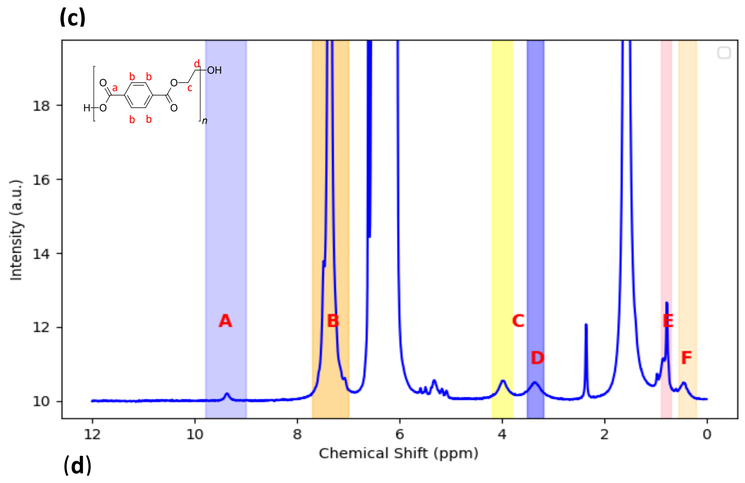
(b)



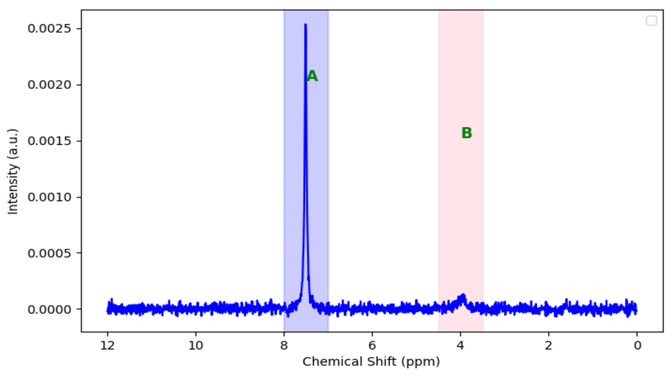
a) ^{1}H spectra of the PET degradation.
b) Shows the area of the peaks calculated from the highlighted peaks in (a).

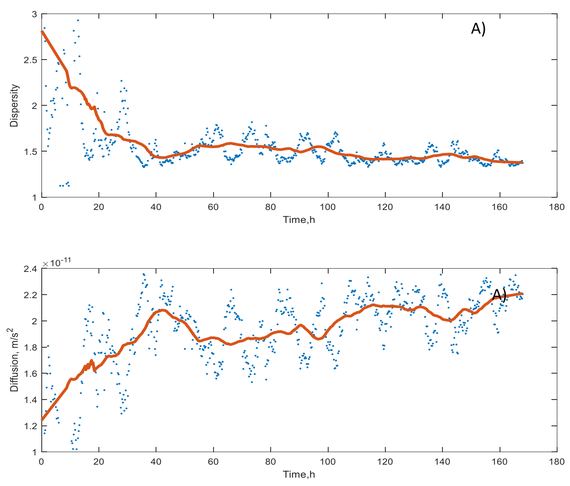
The proton NMR spectra reveal the progressive degradation of the polymer over time. Initially, polymer peaks show an increase in intensity, followed by stabilization, indicating early structural changes and eventual equilibrium. New peaks at 3.35, 0.44, 0.85 ppm and 9.37 ppm correspond to PET monomer degradation products, highlighting the breakdown process. The peak at 3.35 ppm shows a transient behavior, with intensity increasing initially and then decreasing, suggesting secondary reactions or consumption of this product while the other peaks intensity increase and getting stabilized shown in(b). These observations illustrate the kinetics and pathways involved in PET polymer degradation.

(c)

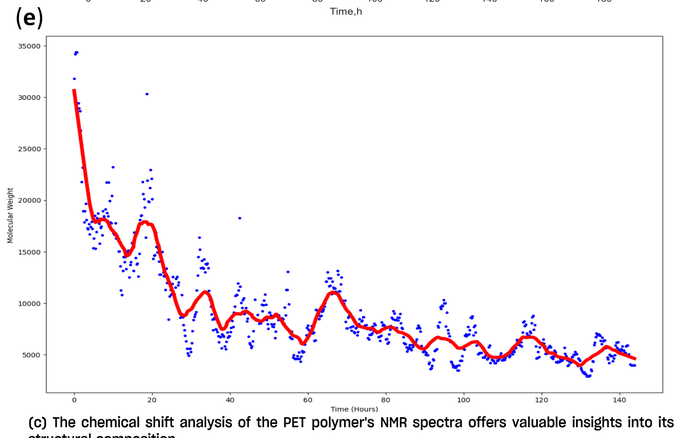


(d)

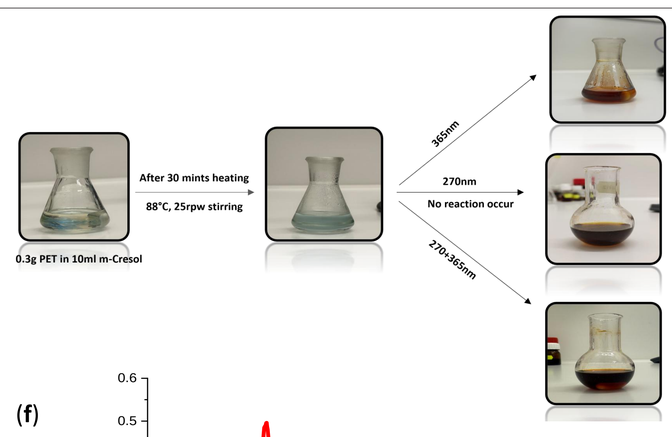




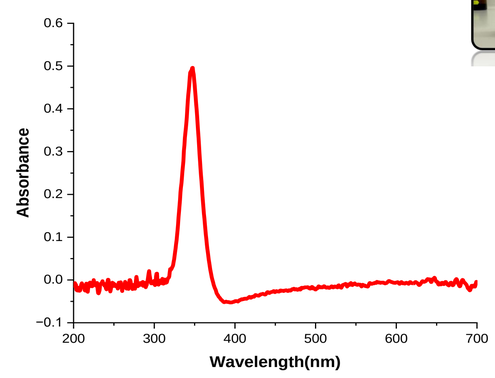
(e)



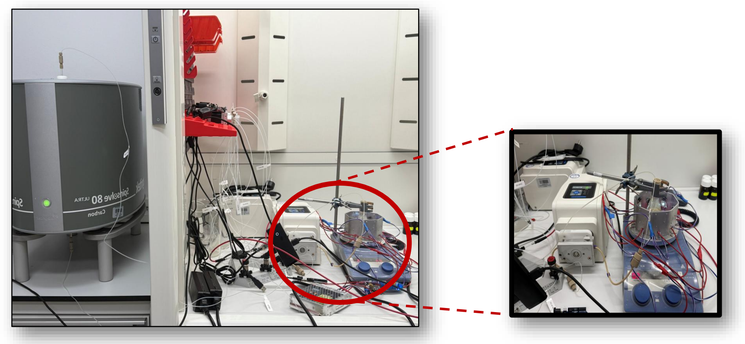
(c) The chemical shift analysis of the PET polymer's NMR spectra offers valuable insights into its structural composition.
(d) The PGSTE NMR spectra of PET polymer peaks ,with peak A showing a decreasing polydispersity index (PDI) over time, indicating improved chain uniformity. The diffusion coefficient reflects dynamic changes, suggesting structural changes.
(e) The molecular weight of peak A decreases, correlating with the narrowing PDI and confirming chain scission and degradation. This process results in shorter, more uniform polymer chains.



(f)



PET (0.3 g in 10 mL m-cresol) was heated at 88 °C for 30 min to form a clear solution. UV irradiation at 365 nm and 270 + 365 nm induced significant color change, indicating photochemical transformation. No reaction occurred under 270 nm alone, highlighting the key role of 365 nm light as shown (f).



A continuous flow setup was designed to study PET degradation under 365 nm UV light. The UV light surrounds the sample reactor for uniform exposure. The degraded sample then flows to the NMR for analysis via a peristaltic pump. This design enables real-time monitoring of photodegradation pathways.

Literature:

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[5] 4. MacDonald, T. S. C., Price, W. S., & Beves, J. E. (2019). Time-Resolved Diffusion NMR Measurements for Transient Processes., ChemPhysChem 20(7), 926-930. https://doi.org/10.1002/cphc.201900150

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