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STUDIES ON THE THERMAL DEGRADATION OF ACRYLIC POLYMERS BY SIMULTANEOUS AUTOSTEP TG/DTA

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Key Words: TGA; DTA; Thermal characterization

ABSTRACT

Simultaneous autostep technique, a novel methodology in thermal analysis, was employed for the investigation of multiple stage degradation of acrylic polymers in thermogravimetric (TG) and differential thermal analysis (DTA) methods. Heating of the sample was controlled automatically with respect to the rate of mass loss in each degradation step in addition to the control of heating by a given steady heating rate. Three standard samples (polymethyl acrylate, polymethyl methacrylate, and polystyrene) and a newly synthesized polymer (polycinnamoyloxyethyl methacrylate) were taken to study the advantages of this technique for the better understanding of thermal degradation of polymers involving a multiple stage decomposition pattern over the conventional method. Results from this method revealed information about the degradation of acrylic polymers in a more precise and accurate manner and were compared with those of the conventional method.

INTRODUCTION

Studies on the thermal behavior of polymers are of prime importance due to their efficacy of revealing thermal stability, lifetime under particular conditions, degradation mechanism, composition, and molecular structure such as sequence and arrangement of repeating units or monomers in homo- or copolymers [1]. The everwidening complex field of polymer science and technology demands analytical tools that can more fully characterize the polymers investigated. In addition to the traditional way of analysis, new techniques like TGA-FT-IR [2, 3] and modulated DSC [3, 5] have emerged to probe the degradation pathway of polymers and for monitoring chemical reactions so that more detailed quantitative measurements of thermal behavior of synthetic polymers can be achieved.

Multiple degradation stages were reported [6, 7] by several authors, even for homopolymers like PMMA, which depend on various factors like method of preparation and molecular weight distribution. But precision in separating such reported multiple stage decomposition patterns was not good even at low heating rates due to nonstop continuous heating between the temperature limits. This is very important in studying the mechanistic pathway of degradation as it involves whether a particular degradation step is due to thermal unzipping back to a volatile monomeric precursor or to thermal degradation of the polymer.

The Autostep TG/TDA Method

This simultaneous autostep thermal analysis was applied in TG and DTA analyses. It entails heating a sample at a constant rate until a significant weight loss occurs as determined by when the rate of decomposition exceeds a preselected "entrance" threshold level. The TG instrument then automatically holds the sample under the isothermal condition until the rate of reaction decreases to the point where it becomes less than the preselected "exit" threshold level, i.e., the sample was analyzed in isothermal conditions depending upon its rate of mass loss based on the pre-fixed threshold values. The optimum threshold values are selected after carrying out several experiments with representative samples and fixed in terms of micrograms. This approach enhanced the power of resolving closely spaced multiple decomposition events more than did the conventional method [8-10].

In this preliminary study we utilized this technique with three standard samples, polymethyl acrylate (PMA), polymethyl methacrylate (PMMA), polystyrene (PS), and a newly synthesized polycinnamoyloxyethyl methacrylate (PCEMA) to explore the use of this technique over conventional method. All these polymers were analyzed both by the conventional method and by autostep TG/DTA, and the results were compared.

EXPERIMENTAL

Materials

Methyl acrylate (MA), methyl methacrylate (MMA), and styrene were received (Sisco Chem., India) and purified using standard procedures. PMA, PMMA, PS, and PCEMA were prepared by the usual free radical polymerization using

benzoyl peroxide as initiator at 80°C for 12 hours. PS2 is narrow molecular weight polystyrene standard supplied by Waters Inc. USA. PCEMA was prepared from its monomer CEMA which was synthesized by the esterification reaction of hydroxyethyl methacrylate (HEMA) and cinnamoyl chloride. The detailed procedure for the synthesis and characterization of CEMA was reported in an earlier publication [11]. The polymerization of CEMA was carried out in conditions similar to those applied for MA and MMA. Methanol was used as a nonsolvent for the precipitation of PCEMA.

Thermogravimetric and Differential Thermal Analyses

Both TGA and DTA were carried out simultaneously in the Seiko Instrument SSC 5200H TG/DTA 220 thermal analysis system from 30 to 600°C. For each polymer sample, conventional TG/DTA was carried out at a heating rate of 15°C/min. The autostep analysis technique was applied to all the polymer samples with an "entrance" threshold value of 175 $\mu\text{g}/\text{min}$ and an "exit" threshold value of 25 $\mu\text{g}/\text{min}$ with the same heating rate. These optimum "entrance" and "exit" threshold values were selected for the analysis after carrying out the experiment for a representative sample (PCEMA) with varying threshold values, as explained later. Samples weighing 5 to 6 mg in platinum pans were taken for all these experiments using α -alumina as a reference. All the thermal analyses were carried out in nitrogen atmosphere at a flow rate of 100 mL/min.

RESULTS AND DISCUSSION

Thermogravimetric Analysis

The thermograms for the polymers are shown in Figs. 1 to 6. It was very clearly noticed that the TGA curves acquired by adopting the autostep method imparted all the multiple stage decompositions precisely and accurately. The onset temperature and percent weight loss of each decomposition were easily determined compared to the conventional TGA method. Variation in heating rate by TGA mostly displaced the thermograms to higher or lower temperatures [12] without much precision in the peak temperatures. The thermograms obtained by using the autostep method are taken into consideration for the explanation.

Polymethyl Acrylate (PMA)

The degradation thermogram of PMA depicted in Fig. 1 shows that the first decomposition involves 80% loss at the temperature range of 300 to 360°C. This is due to random scission of the main chain, leading to the formation of a variety of long chain fragments. The presence of α -H favors various inter- and intramolecular transfer reactions instead of monomer evolution by depolymerization as reported earlier [13, 14]. The rate of formation of various fragments should be very close or almost the same as it was not represented by any multiple stage degradation pattern in this method. The end temperature of the first degradation and the starting temperature of the next stage, 359°C, was distinctly noted by this technique. The percentage loss as determined by using this autostep technique for the first stage was

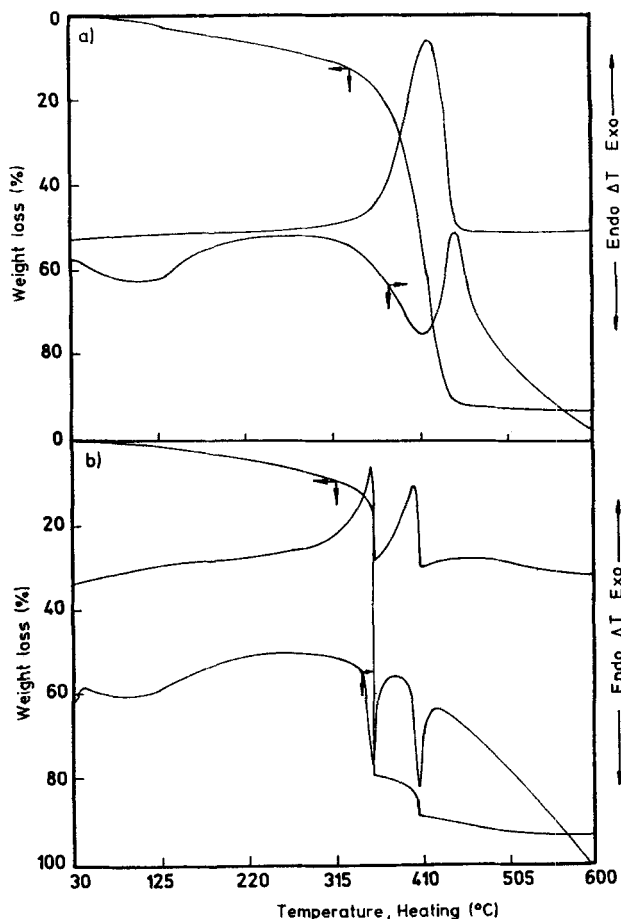


FIG. 1. TG/DTA of PMA by (a) conventional and (b) autostep methods.

80. This is in good agreement with that calculated by thermogravimetric and thermal volatilization analysis [15]. The decomposition products of the second stage may be CO_2 and CH_3OH [16, 17], which consumed 13% of the total weight. These two degradation patterns were well separated by the autostep technique. On the other hand, the conventional method showed a complete single stage decomposition pattern.

Polymethyl Methacrylate (PMMA)

The thermal behaviors of PMMA analyzed by conventional and autostep TG/DTA are shown in Figs. 2(a) and 2(b), respectively. It was observed that there are two major decomposition stages. The first step was observed between 275 and 293°C while the second was observed between 295 and 353°C, and the total weight loss was 97.2% (Table 1). Even though the temperatures of these two major decompositions were detected fairly well by the conventional method as shown in Fig. 2(a), the first stage involves the formation of radical fragments due to random

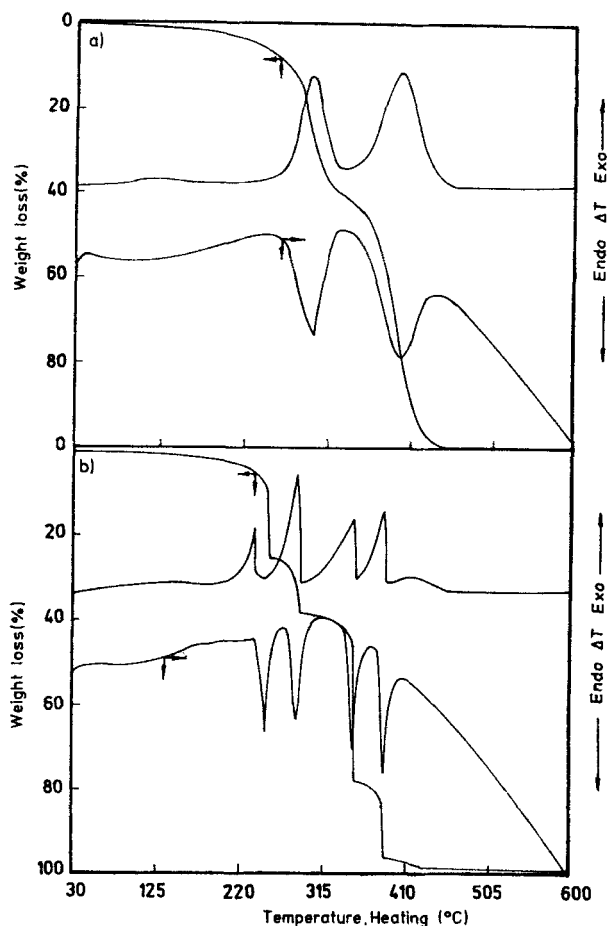


FIG. 2. TG/DTA of PMMA by (a) conventional and (b) autostep methods.

TABLE 1. Percent Weight Loss of Various Degradation Stages of Acrylic Polymers

Polymer	Weight loss in various degradation stages (wt%)				Total
	I	II	III	IV	
PMA	80.0	10.4	—	—	90.4
PMMA	25.5	12.7	40.7	18.3	97.2
PS1	92.1	6.9	—	—	99.0
PS2	98.5	—	—	—	98.5
PCEMA	36.0	42.4	15.2	—	93.6

scission of the polymer chain as reported [6]. The rate of formation of these fragments is not the same as evidenced by the appearance of a multiple stage pattern in the autostep method. As reported in the literature, the first stage should be random scission of the polymer chain to form radicals. These radicals then depropagate or unzip into monomer in a reaction which is the exact reverse of the propagation reaction of polymerization. Similar to the first stage, the second major depropagation step should also have products with different rates of formation as observed in this autostep method. These random scission and depropagation reactions were easily observed by using our technique. Both led to 97.2% monomer production [7, 18, 19]. Unlike PS and PMA, PMMA does not have any α -H atoms which lead to depolymerization. The initial and final temperatures and percent loss of each degradation were precisely determined with the help of the autostep technique.

Polystyrene (PS)

The TG/DTA thermograms of radically polymerized polystyrene (PS1) and the narrow standard (PS2) by both the conventional and autostep methods are depicted in Figs. 3(a), 3(b), and 3(c). PS1 showed its first degradation in the 315 to 395°C temperature range, while for PS2 the range was 370 to 395°C. The sharp degradation pattern observed for PS2 may be due to its narrow molecular weight distribution. The single-stage decomposition observed by utilizing this technique was supported by earlier studies in which this involves 42% of monomer evolution by unzipping of polymer by depolymerization and volatile products due to various transfer reactions (due to the presence of α -H). The formation of products of these transfer reactions, i.e., dimer, trimer, and tetramers, are in direct competition with the monomer-producing depropagation process. It was reported that the probabilities of a polymer radical undergoing depropagation or transfer are roughly equal to the monomer-producing process [20–22]. The single-stage decomposition pattern observed between these temperature ranges in the autostep method confirmed that the rates of the reactions seem to be similar. Here it was noted that PS1 analyzed by the conventional method did not show any second stage which involved the evolution of very small amounts of benzene, toluene, etc. [23].

PCEMA

PCEMA has a slightly more complex structure than PMA, PMMA, or PS. Apart from the main chain, it has a relatively long pendant chain in the backbone. The TG/DTAs of PCEMA analyzed by both methods are shown in Figs. 4–7. It showed four degradations, of which the first two are major and involve 36.0 and 42.4% (Table 1). They may be attributed to chain scission of the polymer backbone and the pendant chain, respectively. The higher amount of loss in the second stage may be attributed to the possibility of obtaining a larger amount of scission fragments from the pendant chain because its structural contribution is greater compared with that of the backbone for a single polymer unit. Further degradations may be due to the decomposition of ester functionality, which led to the evolution of products like CO₂. It is not completely possible at this time to confirm the product evolution in each stage unless other techniques like IR and GC are used.

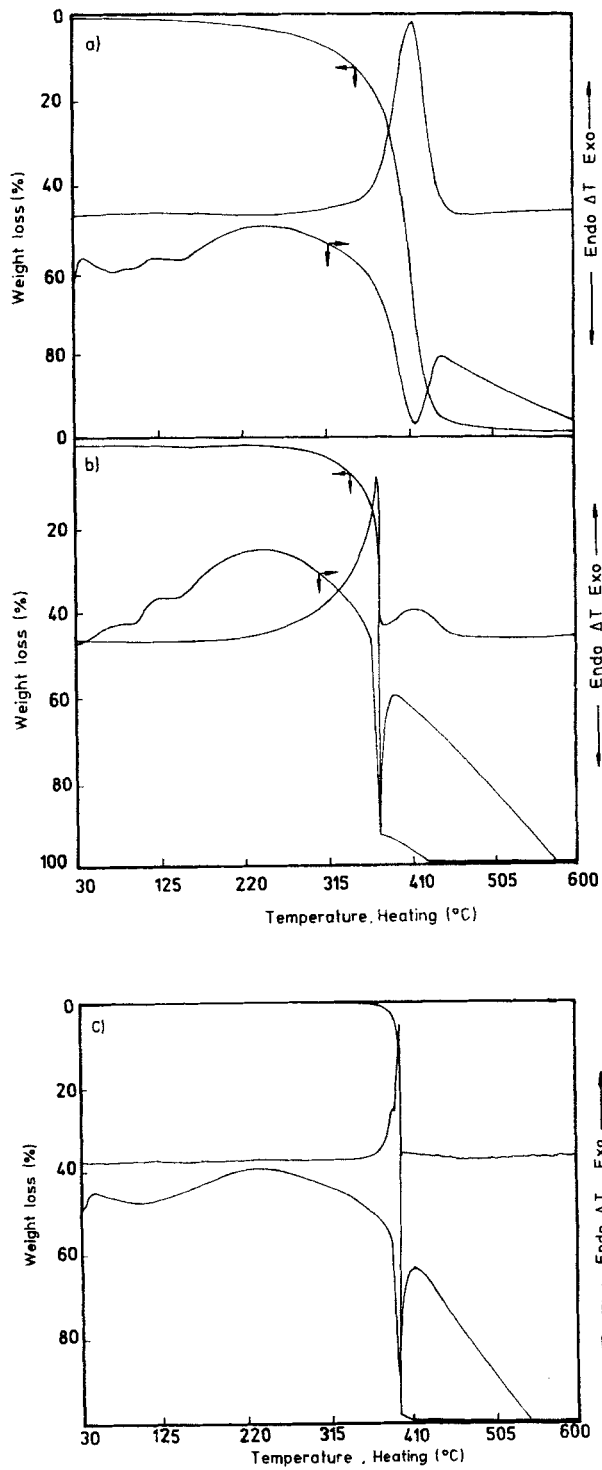


FIG. 3. TG/DTA of PS by (a) conventional, (b) autostep, and (c) autostep (narrow standard) methods.

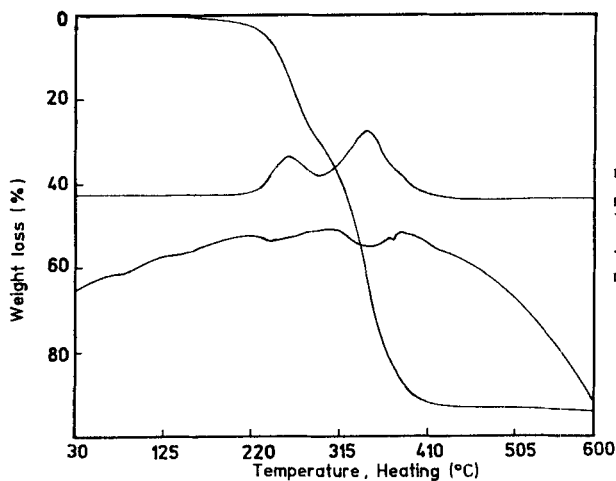


FIG. 4. TG/DTA of PCEMA by conventional method.

It was noted in all polymers that DTA gave very good endothermic peaks for the corresponding degradations. Quantitative analysis from the area of DTA peaks is possible with the help of the autostep technique. Moreover, the determination of peak temperature for any degradation step is quite easy with the help of DTG provided by this autostep technique.

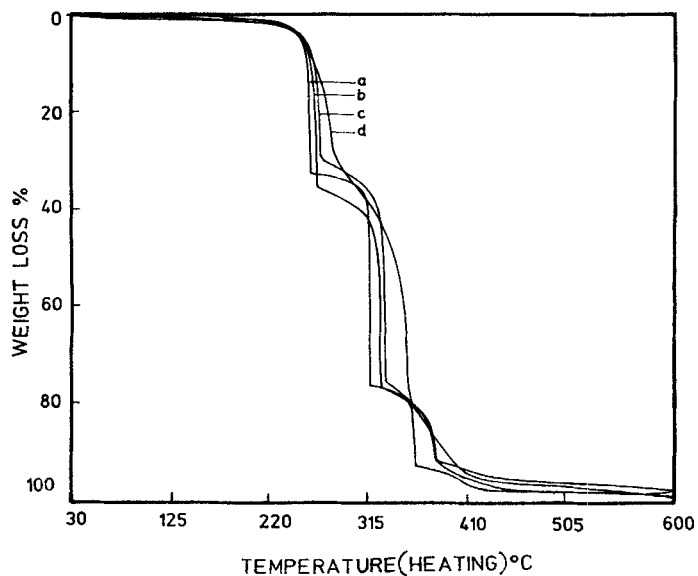


FIG. 5. Effect of change of threshold values on TGA curves of PCEMA: (a) 15:90, (b) 25:125, (c) 75:225, (d) 200:400 $\mu\text{g}/\text{min}$.

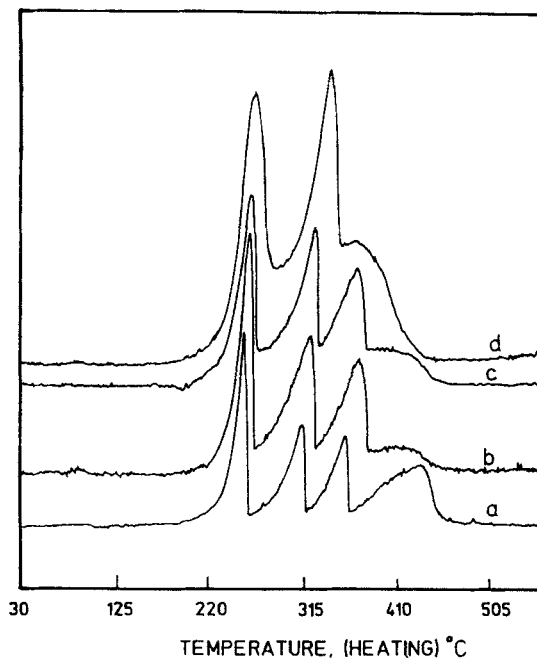


FIG. 6. Effect of change of threshold values on DTA curves of PCEMA: (a) 15:90, (b) 25:125, (c) 75:225, (d) 200:400 $\mu\text{g}/\text{min}$.

Effect of Change in Threshold Values

The TG/DTA experiments were repeated with varying threshold values in order to ascertain the reproducibility from run to run and to study the effect of change in threshold values on the nature of decomposition patterns. The PCEMA samples were taken as representative. TG/DTA runs were carried out with "entrance": "exit" values of 15:90, 25:125, 75:225, and 200:400 $\mu\text{g}/\text{min}$ while keeping the heating rate constant at 15°C/min. The results of these experiments are illustrated in Figs. 5, 6, and 7.

On increasing the threshold values, i.e., increasing the difference between "entrance" and "exit" values, it was observed that the overall pattern of a thermogram moves toward the conventional thermogram. Of the threshold values studied, it was noticed that an increase in threshold values shifts the peak temperature values in DTG and DTA toward higher temperatures and lowers the precision in determining the starting and final temperatures of a particular decomposition step. For instance, the peak temperature of the first stage decomposition increases from 240 to 245, 257, and 264°C when the differences in threshold values are raised from 75 to 100, 150, and 200 $\mu\text{g}/\text{min}$. In the case of a relatively higher threshold values, 200:400 $\mu\text{g}/\text{min}$, the third decomposition step almost merges with the fourth one, giving rise to a three-stage pattern and in DTA one endothermic peak vanishes. This clearly indicates that the rate of mass loss is less than that of the given values in terms of threshold values. The same trend was observed on changing the threshold while otherwise keeping the difference between the threshold values constant.

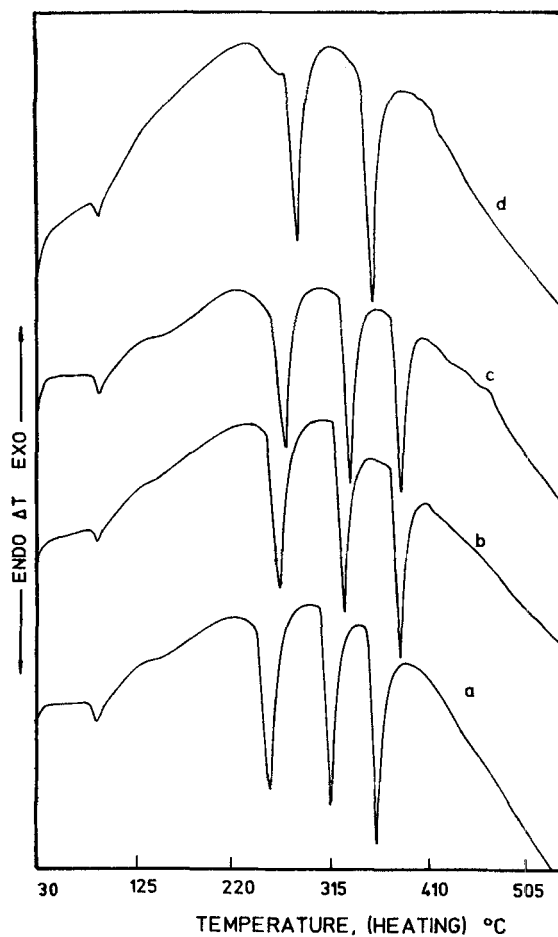


FIG. 7. Effect of change of threshold values on DTG curves of PCEMA: (a) 15:90, (b) 25:125, (c) 75:225, (d) 200:400 $\mu\text{g}/\text{min}$.

Importantly, it was noted that there was almost no change in the melting temperature of PCEMA (90.5°C), a transition showing no change in weight, even when the high threshold values showed good reproducibility. The percentages of total mass loss are 99.1, 97.8, 98.3, and 98.7 for the increases in difference between threshold values of 75, 100, 150, and 200, respectively, indicating that there was not much change in total mass loss when the threshold values were altered.

CONCLUSION

The autostep TG/DTA applied in this work revealed an ability to improve the resolution of closely spaced decomposition events even in homopolymers. The efficiency of this technique was studied with the help of acrylic and methacrylic polymers. The percent weight loss, the peak temperature, and the endothermic

nature of each degradation in acrylic polymers were determined precisely and accurately over the conventional method. The results obtained from this technique confirmed and agree well with earlier findings. The most effective utilization of this technique should be for product analysis of each decomposition stage after coupling with some other spectroscopic technique like FT-IR or GC. Such studies will be published in a future publication.

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