



## Separation and Identification of Cyclic Oligomers in Poly (trimethylene terephthalate)

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**Abstract** : The NMR and MS techniques were applied to identification and quantitative analysis of oligomers in a commercialized poly (trimethylene terephthalate). Oligomers in a commercialized poly (trimethylene terephthalate) were extracted via a dissolving and re-precipitation method. Analysis of the components of the extract using NMR and MS revealed that it contained mainly cyclic oligomers with degrees of polymerization of 2, 4 and 5 (dimer, tetramer and pentamer). Trimer and cyclic oligomers with degrees of polymerization of more than 6 were not found in the extract in the present study. Quantitative analysis of dimer was performed by NMR spectroscopy.

Keywords : poly (trimethylene terephthalate), polymerization, NMR spectroscopy

### INTRODUCTION

Poly (trimethylene terephthalate) (PTT) is a promising polymer that forms fiber having excellent physical properties<sup>1</sup>. However, for a long time, PTT did not draw commercial interest because of the limited production of 1,3-propanediol. It was very recently when several institutes actively began researching the commercialization of the PTT, which means that there might be still several unknown factors in the commercialization of the PTT. Oligomers present in the PTT polymer may be one of these factors. For example, a recent patent from Japan pointed out that the content of cyclic dimer of PTT in PTT fiber had crucial effect on dyeability of the fiber<sup>2</sup>. Besides this fact, consider

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ing well-known negative effects of similar oligomers in homologous poly (ethylene terephthalate) (PET)<sup>3-5</sup>, the control of these oligomers of PTT is considered to be very important. For this purpose, accurate and efficient analysis of these oligomers is indispensable. Previously, the analysis of oligomers in PTT polymer was carried out only in limited studies<sup>6-7</sup>. Even in these studies, they did not present the exact chemical structures of the oligomers on the basis of spectroscopic methods such as NMR and MS. In this study, we tried to identify the exact chemical structures of oligomers in a commercialized PTT using NMR and MS. On the basis of identified structures of the oligomers, we suggested a very efficient way to quantitatively analyze cyclic dimmer, which is most important. For PTT samples, we used the polymer produced by Degussa AG (Germany). For extraction of the oligomers, dissolving and re-precipitation procedures were applied. The same procedures are expected to be used to analyze other PTT polymers from different sources.

## EXPERIMENTAL

### *Materials*

The PTT polymer was provided by Degussa AG (Germany) for the study of physicochemical properties.  $\text{CDCl}_3$  and phenol- $d_6$  were purchased from Aldrich Chemical Company, Inc. (USA). All other chemicals were HPLC grade purchased from Fisher Scientific (USA) and used without purification.

### *Extraction of oligomer*

One gram (1 g) of PTT was dissolved in 50 ml of trifluoroacetic acid (TFA) and thereafter 450 ml of  $\text{CHCl}_3$  was added. To the solution, 250 ml of methanol was added gradually to induce precipitation of the polymer. The polymer was separated by filtration using filter paper, Quantitative ashless, 5C, Toyo Roshi Kaisha (Japan). The solvent of filtrate was evaporated and the remaining precipitation (purified polymer) was dried for further study.

### *NMR spectroscopy*

Bruker Avance-400 NMR spectrometer (Germany) equipped with temperature controller was utilized to acquire all NMR data. For the extract, NMR experiments were made on the solution of  $\text{CDCl}_3$ . For the polymer, phenol- $d_6$ /TCE (50/50 in volume) was used as the NMR solvent. The concentration of polymer solution was adjusted to be 10 % (w/v). For better resolution of the spectra, the temperature was maintained at 80 °C during the experiments for the polymer samples. Detailed experimental conditions were described in other papers<sup>8-9</sup>.

### ***MS spectrometry***

All positive-ion FAB mass spectra were obtained using a JEOL JMS 700 Mstation mass spectrometer (Japan) operating at an accelerating voltage of 10KV with a mass range of 100-1500. The sample was bombarded with a beam of  $\text{Cs}^+$  ion having energy of 20KeV. Spectra were obtained with a magnetic scan rate of 10s/scan. Generally a weighed sample was dissolved with an appropriate amount of methylene chloride. 3-Nitrobenzyl alcohol (1  $\mu\text{L}$ ) and sample solution (1  $\mu\text{L}$ ) were mixed on the FAB probe and introduced into the ion source.

## **RESULTS AND DISCUSSION**

### ***Identification of the oligomers***

$^1\text{H}$  and  $^{13}\text{C}$  spectra of the extract are shown in Fig. 1. In Fig. 1-a, the  $^1\text{H}$  NMR spectrum of the extract was shown. From the examination of both the aliphatic and aromatic regions of the spectrum, it is easy to notice that the sample is the mixture of some compounds. Closer examination of the peaks of the spectrum suggests that the major compounds of the extract are a mixture of cyclic oligomers. In other words, the patterns of the NMR peaks don't match the expected ones of linear oligomers. If linear oligomers were there, more complicated scalar coupling patterns, which were definitely different from Fig. 1-a, had to be visible in the spectrum.  $^{13}\text{C}$  spectrum of the extract supports the above suggestion. In Fig.

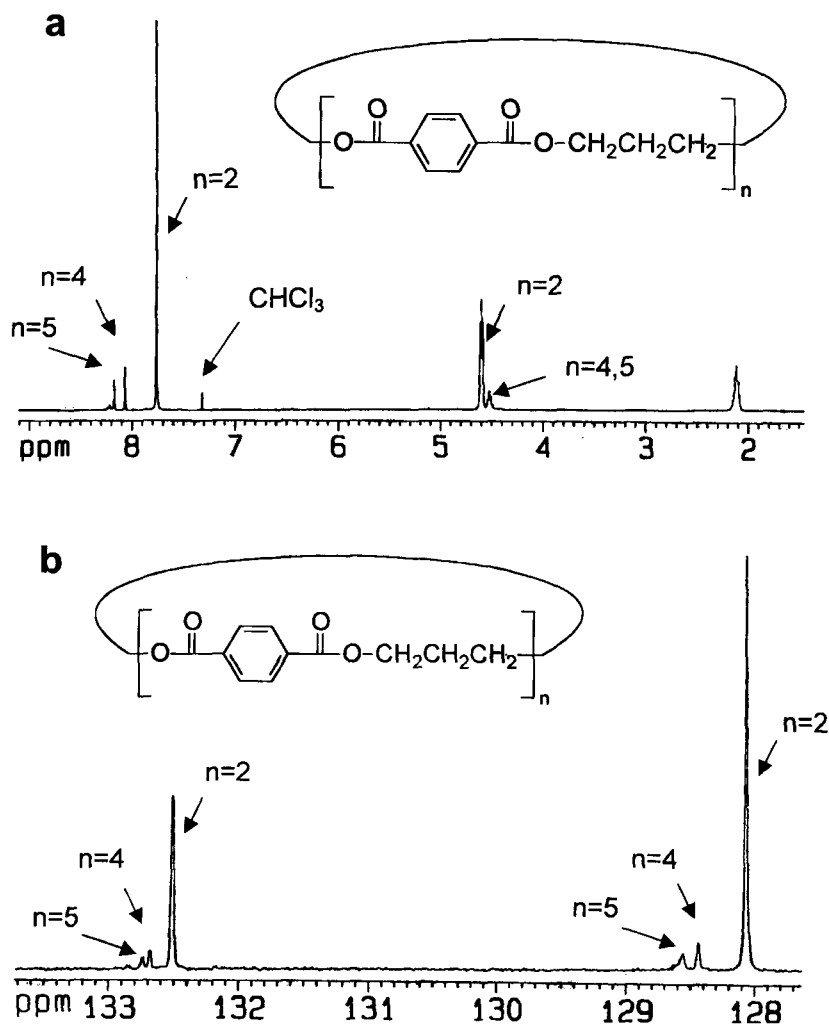


Fig. 1.  $^1H$  (a) and  $^{13}C$  (b) NMR spectra of the extract. For  $^{13}C$  NMR spectrum, selected regions are shown; 128 – 129 ppm for tertiary carbons, 132 – 133 ppm for quaternary carbons in phenyl ring respectively.

1-b, the peaks of aromatic carbons of the extract are shown. In the figure, three clear peaks are visible in each of two spectral regions representing two different aromatic carbons. These three peaks are considered to correspond to the three peaks in the aromatic region of  $^1\text{H}$  NMR, which also indicates that the extract is composed of three cyclic oligomers. For the confirmation of the above suggestion, we performed MS spectrometry that could show the molecular ions of the compounds in the extract. Fig. 2. shows the FAB MS spectrum of the extract. In this spectrum, 413.2, 825.3 and 1031.3 have considerable intensity. Clearly, these match the  $[\text{M}^+\text{H}]^+$  of cyclic oligomers with  $n=2$ , 4 and 5 (dimer, tetramer and pentamer). This result is in agreement with previous  $^1\text{H}$  and  $^{13}\text{C}$  NMR results in terms of existence of three cyclic oligomers. It is noticeable that we can't find molecular ion peak of oligomer with  $n=3$ (trimer). Two possibilities can be suggested as the reasons why we can't see the oligomer with  $n=3$ . First consideration is that the trimer might not be formed or was formed in a very small amount during the polymerization. The other possible reason is that, if there is considerable amount of trimer in the original polymer, the extraction efficiency for this particular oligomer might be very low. Because the procedure of the oligomer extraction is mainly composed of dissolving the original sample and successive re-precipitation of the polymer, the extraction efficiency of each oligomer is related to the solubility of the oligomer in the final solvent; 5/45/25 of trifluoroacetic acid, chloroform and methanol. Considering the chemical structures of the cyclic oligomers which have the same unit structure as well as the same elemental composition, it is very hard to think that only the cyclic trimer have noticeably lower solubility in the same solvent. So above experimental result means that the amount of trimer was very small in the original polymer and not to be detectable, which also means that it was not formed or was formed in a very small amount during the polymerization. At present, we can't suggest any reason of the low production of trimer during PTT polymerization for this particular sample in this study. Molecular models didn't reveal any difference in the stabilities of these PTT oligomers including the cyclic trimer. A more quantitative and systematic study may be needed to elucidate the reason of these observations.

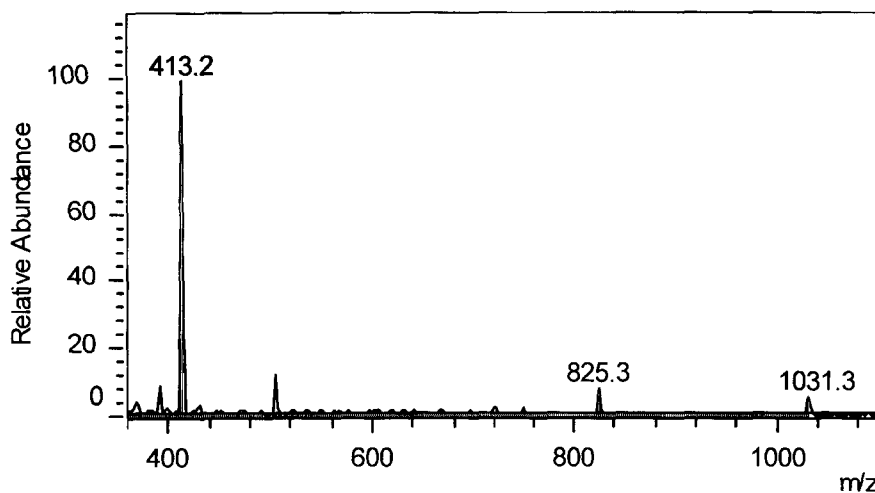


Fig. 2. FAB MS spectrum of the extract. The peaks at 413.2, 825.3 and 1031.3 match the  $[M+H]^+$  of cyclic oligomers with  $n=2, 4$  and  $5$  (dimer, tetramer and pentamer).

### ***Quantitative analysis***

In this study, along with the identification, quantitative analysis of an oligomer was also performed using NMR spectroscopy. For this purpose, in the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of original polymer, the isolated peaks of phenyl group of cyclic oligomers were compared with those of PTT polymer (Fig. 3).

Because  $^1\text{H}$  NMR peaks of tetramer and pentamer were severely overlapped with that of polymer, only the quantification of dimer was possible, which was probably most important. As the result of direct comparison of the integration values, the amount of cyclic dimer was calculated to be 2.5 wt % for this sample. Though the amount of cyclic oligomers in the PTT polymer have been analyzed by GPC previously<sup>6-7</sup>, we think that this NMR analysis in this study is much easier as well of the produced polymer as more accurate to quantify the amount of dimer in PTT. In practical point of view, the control of the amount of cyclic dimer can be important for quality control as denoted in the introduction. So, the accurate and easy analysis of the dimer polymer using present method would greatly help the quality controls in production of PTT.

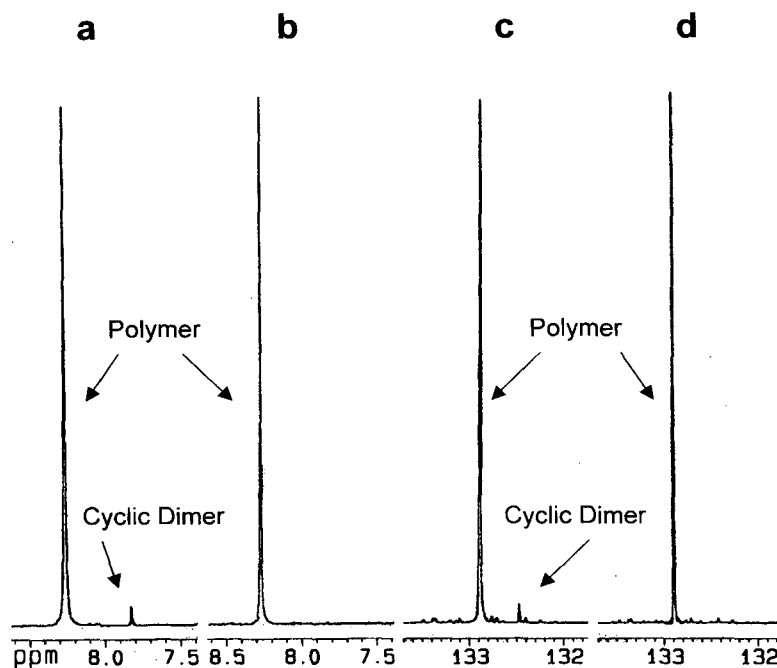


Fig. 3. Comparison of aromatic regions of  $^1\text{H}$  (phenyl proton) and  $^{13}\text{C}$  (phenyl quaternary carbon) NMR spectra of original and purified polymer (a:  $^1\text{H}$  NMR spectrum of original polymer, b:  $^1\text{H}$  NMR spectrum of purified polymer, c:  $^{13}\text{C}$  NMR spectrum of original polymer, d:  $^{13}\text{C}$  NMR spectrum of purified polymer).

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