ELSEVIER

Determination of solid products from the de-polymerization of poly(trimethylene terephthalate) in supercritical methanol

Changming Zhang*, Long Xu, Haohong Zhang, Jianli Yang,
Junmin Du, Zhenyu Liu

State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, PR China

Abstract

A method based on high-resolution size-exclusion chromatography (SEC) was established to analyze the solid products from the de-polymerization of poly(trimethylene terephthalate) (PTT) in supercritical methanol. In the qualitative analysis, four factors (chromatographic retention time, qualitative multi-wavelength ultraviolet spectra, linear internal-insert SEC and qualitative IR spectra) were considered. The main solid products from the process were dimethyl terephthalate (DMT), methyl-(2-hydroxypropyl) terephthalate (MHPT), bis(2-hydroxypropyl) terephthalate (BHPT), methyl-(2-hydroxyethyl) terephthalate (MHET), bis(2-hydroxyethyl) terephthalate (BHET), and hydroxyethyl-(2-hydroxypropyl) terephthalate (HEHPT). It is found that the method is of a high resolution among the solid products and has a fine repeatability. In addition, the solid products from the de-polymerization of poly(ethylene terephthalate) (PET) in similar process were also analyzed by this method. Furthermore, the effects of supercritical conditions on the distribution of the products were also discussed.
© 2004 Elsevier B.V. All rights reserved.

Keywords: Poly(trimethylene terephthalate); Supercritical methanolytic de-polymerization; Dimethyl terephthalate

1. Introduction

With the increasing environmental concerns on the pollution of waste plastics, the consumption and the recycling of it become more and more important, thus many recycling methods of waste plastics have been developed [1–4]. Among such methods, supercritical fluid technologies are considered to be potentially attractive [2–4]. Supercritical fluid has been focused on de-polymerization of plastics, because of its environmental friendly nature of the fluids. Above the critical point, the supercritical fluid has a large density like liquid and a high kinetic energy like gas, and the reaction rate is therefore expected to be faster than that under normal liquid conditions.

Poly(trimethylene terephthalate) (PTT) is a kind of synthetic plastics. In supercritical fluid process, PTT can be de-polymerized mainly into its original monomers (dimethyl terephthalate (DMT)) by solvolysis in supercritical water or methanol [1–5]. Some researchers indicated that the yield of DMT by methanolytic de-polymerization is much higher than that by hydrolysis supercritical water [5].

Characterization of solid products from supercritical fluid technologies has been developed accordingly to evaluate the efficiency of the de-polymerization and to optimize the operation parameters. Some analytical methods were applied in this field, such as size-exclusion chromatography (SEC) [1–4], gradient polymer elution chromatography (GPEC) [6] and reversed-phase liquid chromatography (RPLC) [7]. In Goto

* Corresponding author. Fax: +86 351 404 8571.
E-mail address: zhangcm@sxicc.ac.cn (C. Zhang).

et al.'s work [3], the products from the de-polymerization of poly(ethylene terephthalate) (PET) in supercritical methanol were analyzed by SEC. However, it is too difficult to exactly distinguish such low-molecular-weight product (DMT) by ordinary SEC. In Philipsen et al.'s work [7], the low-molar-mass polystyrenes and polyesters were characterized by RPLC. In literature [7], the mobile phase used was a binary tetrahydrofuran (THF)–water mixture and a C_{18} column was used, but under such conditions the baseline of RP-GPEC was not smooth, which affected the accuracy of final results. These works were important in basic study such as thermodynamic parameters [7] and molecular weight distribution [2]. However, these related analytical methods are not proper for determination of individual component such as DMT, bis(2-hydroxypropyl) terephthalate (BHPT), methyl-(2-hydroxyethyl) terephthalate (MHET), etc. In 1975, Yamanis et al. [8] applied gas–liquid chromatographic analysis to this study, and found that there were some bis(2-hydroxyethyl) terephthalate (BHET) besides DMT in the products. However, the silylation of hydroxyl groups prior to chromatography was essential to obtain reproducible results due to the high boiling points of the compounds. In recent years, Jirong [6] and Yong et al. [9] analyzed the solid products from de-polymerization of PET by RP-HPLC. In this method, the solid samples were separated on a Zorbax-C_8 chromatographic column and with a methanol–water (7:3) mobile phase. Though they obtained high distinguishable and quantitative results, there were still some doubts. Because the solubility of DMT or MHET in methanol is very low, so the solubility of them in methanol–water solution should be much worse, thus it also resulted in some problems in qualitative and quantitative analysis.

By now, there is no suitable method to separate components from supercritical terephthalate products with high-resolution and representative characteristics. So it is needed to further improve the existing methods for such study. In this paper, a determination method using SEC was developed for analyzing the products from de-polymerization of PTT in supercritical methanol. Tetrahydrofuran with high solvency for DMT, BHET, etc. was selected as the mobile phase. And the infrared spectrum (IR) and qualitative multi-wavelength ultraviolet method [10] and internal-insert SEC method also investigated. Moreover, the effects of reaction temperature and residence time in supercritical system on the distribution of components were also discussed.

2. Experimental and analysis methods

2.1. Methanolysis and preparation of sample

Two kinds of synthetic plastics, PTT and PET, were used in the methanolysis processing. The PTT was bought from Shanghai huayuandisi Company (Shanghai, PR China) and the PET resins were commercial chips of fiber grade supplied by Liaoyang Petrol-Chemical Fiber Company (Liaoyang, PR China). Analytical grade methanol produced by Tianjin Chemical Reagent Factory (Tianjin, PR China), was used in the supercritical system after further purification by distillation.

A 150 ml stainless batch-type autoclave equipped with an electromagnetic stirrer, thermometer well, inert gas inlet and outlet valves, was used for the methanolysis. A heating collar controlled by a temperature controller was used to heat the reactor rapidly to the reaction temperature. In each run, the polymer and methanol in a weight ratio (R, raw material/methanol) of 0.1 were charged into the reactor. After the required residence time (t_r) of methanolysis at designed reaction temperature (T_r) and pressure (P_r) above or near the critical point of methanol ($T_c = 512.3$ K, $P_c = 8.09$ MPa), the vessel was removed from the heating collar, and quenched in a water-ice bath till it was cooled below 298 K. Then, the mixed products were taken out. A certain amount of cold methanol was added to the products to dissolve the small amount of propyl-di-alcohol. Subsequently at about 273 K, the mixture was separated into solid and liquid by filtration. Finally, the dried solid products were subjected to following analysis.

In the paper, the analysis data of some samples (solid products), such as #9, #51, #129, etc. would be discussed in the following sections. And the detailed experimental conditions of these samples are all listed in Table 1.

2.2. SEC analysis and corresponding qualitative and quantitative methods

The SEC was performed on a Shimadzu LC-3A high-performance liquid chromatography (Japan) with a UVD-2 UV detector and an SPD-10AUP UV detector. The chromatographic column used was Shimpack GPC-801 (30 cm length, 0.8 cm i.d., polystyrene 6 μm) (Japan Shimpack Company). THF, as mobile phase, was analytical grade pure reagent from Tianjin Chemical Reagent Factory, and it was further purified by distillation before used. In each run, the flow rate of THF was 0.9 ml/min, and the column temperature is kept 19 °C. The wavelength (λ) of UV detector was chosen at 254, 240 and 270 nm. The sample content was prepared with 0.02–0.05 g/l and the injected amount of sample solution was 1–3 μl.

Four kinds of standards were used in qualitative and quantitative analysis. BHET (99.5%) and DMT (>99%) were obtained from Aldrich (USA). MHET and BHPT were synthesized according to literature [8].

2.2.1. Qualitative chromatographic retention time method

By comparing the chromatographic retention time of the standards and the components in samples, the composition of samples can be determined. It should be noted that each and every retention time was obtained by 10 times of tests.

Table 1
Sample number and corresponding reaction conditions

Sample number	Material	R (material/methanol)	T_r (K)	P_r (MPa)	t_r (min)
#9	PPT	0.1	773	7.5	10
#51	PPT	0.1	593	7.5	10
#73	PPT	0.1	613	7.5	0
#124	PPT	0.1	553	7.5	0
#126	PPT	0.1	553	7.5	10
#128	PPT	0.1	553	7.5	20
#129	PPT	0.1	553	7.5	30
#132	PPT	0.1	553	7.5	60
#138	PPT	0.1	613	7.5	10
#140	PPT	0.1	613	7.5	20
#141	PPT	0.1	613	7.5	30
#152	PET	0.1	513	7.5	10
#153	PET bottle	0.1	513	7.5	10

2.2.2. Qualitative multi-wavelength UV method

The existence of BHET in samples was further confirmed by qualitative multi-wavelength UV method. The chromatographic peak areas of samples and standards were determined at different wavelength. The ratios of peak areas at different wavelength of each component were compared with that of standards, and thus the composition of samples can be determined.

2.2.3. Qualitative internal-insert SEC method

There were no standards of methyl-(2-hydroxypropyl) terephthalate (MHPT), hydroxyethyl-(2-hydroxypropyl) terephthalate (HEHPT) and di-polymer of DMT in experiments, and it is difficult to synthesize these compounds. Hence, the qualitative analysis of them cannot follow the forenamed methods. Thus, a qualitative internal-insert SEC method was used in determination of MHPT, HEHPT and di-polymer of DMT. The SEC curve expressed as a function of $\log M$ versus retention time was firstly established from the molecular weights of the standards (DMT, MHET, BHET and BHPT) and corresponding retention times. By the SEC curve, the molecular weights of ambiguous components can be calculated once their retention times

are confirmed. With the real theoretical M as standard, M_c (calculated molecular weight) was compared with M and thus the assumed component may be defined. By the way, it is also note that the retention time was also the average of 10 times results.

2.2.4. Quantitative method for DMT and BHET in samples

The components of DMT and BHET were quantified by external standard method, in which the standards DMT and BHET were used, respectively. Because the inject amount of sample solution is the same as that of the standard solution in experiments, the calculation formula of DMT or BHET content (wt.%) in sample can be expressed as the following:

$$C_{sa}\% = \frac{A_{sa}}{A_{st}} \times \frac{C_{st\text{-}pre}\% \times C_{st}\%}{C_{sa\text{-}pre}\%} \tag{1}$$

In which, $C_{sa}\%$ and $C_{st}\%$ represent the content (wt.%) of the component in sample and standard, respectively. A_{sa} and A_{st} represent peak area of the component in the prepared sample solution and the prepared standard solution. $C_{sa\text{-}pre}\%$ and $C_{st\text{-}pre}\%$ are the concentrations prepared of sample and standard in solutions.
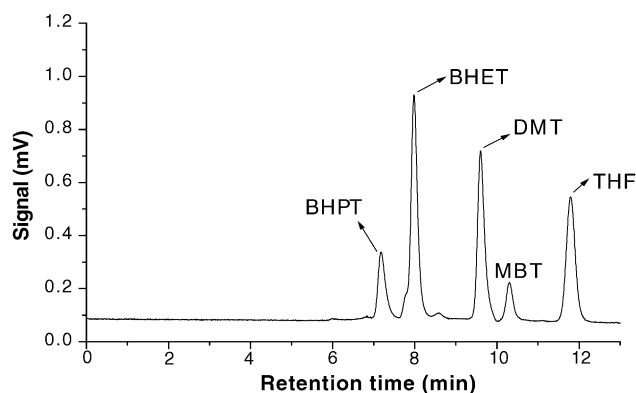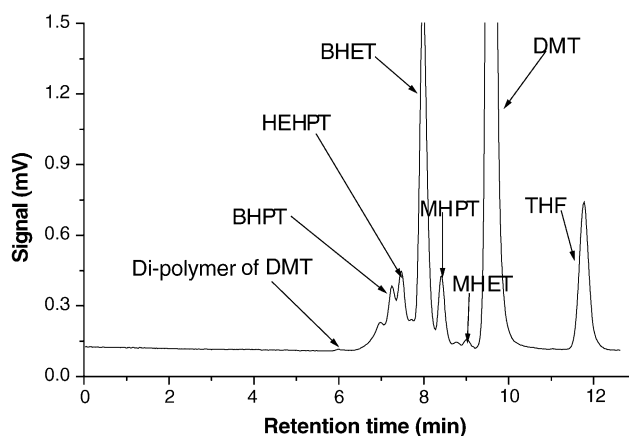

Fig. 1. The chromatogram of mixed standards.

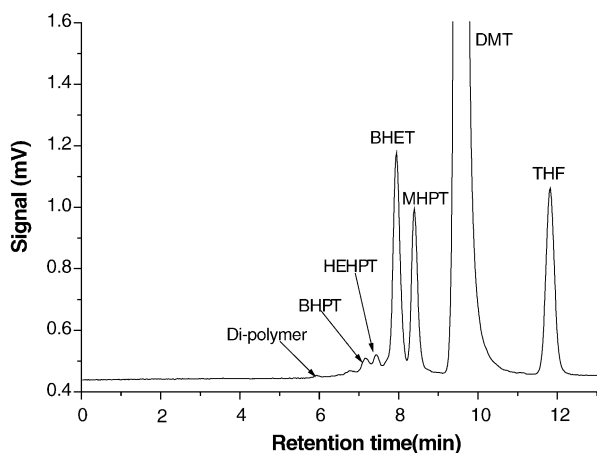Fig. 2. The chromatogram of #51 sample.

Fig. 3. The chromatogram of #9 sample.

2.2.5. Quantitative method for other components

Because the contents of the other components were much lower than that of DMT or BHET, thus it can be approximately calculated as the following on the assumption that the quantitative correction factors of other components were the same as that of DMT:

$$C_{other}\% = \frac{A_{other}}{A_{DMT}} \times C_{DMT}\% \qquad (2)$$

In which, $C_{other}\%$ and $C_{DMT}\%$ represent the contents (wt.%) of other component and DMT (wt.%) in sample, respectively; A_{other} and A_{DMT} represent peak area of other component and DMT in sample, respectively.

2.3. FT-IR analysis and corresponding qualitative method

Fourier transform infrared (FT-IR) was recorded on an Excalibur Series spectrometer (Digilab America Company). The spectra were acquired in the transmission mode as 64 scans in the IR range from 4000 to $500 \, cm^{-1}$ at a resolution of $4 \, cm^{-1}$. KBr standard pellets were used, and the samples were dried and then mixed with KBr, ground, and palletized. The weight ratio of the sample to KBr is 1:200. As the major
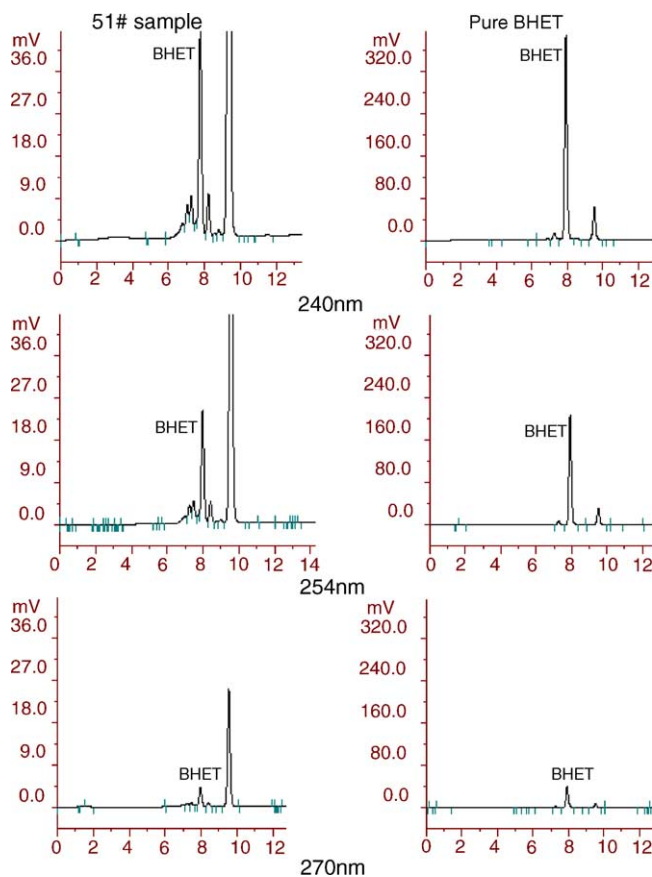

Fig. 4. The multi-wavelength ultraviolet chromatograms of #51 sample.

de-polymerization product, DMT was also further confirmed by its characteristic peaks in FT-IR spectra.

3. Results and discussion

3.1. Results of separation of solid sample

Due to applying high-resolution chromatographic column under a series of optimal chromatographic conditions, a fine separation of solid sample was shown. The typical chromatograms are shown in Figs. 1–3, in which λ of the detector used was 254 nm. Fig. 1 is the chromatogram of mixed standards, and the chromatograms of #51 and #9 samples are shown in Figs. 2 and 3, respectively. From Figs. 1–3, it can be seen that the distinguished peak of each component was very legible.

3.2. SEC qualitative results

3.2.1. Qualitative results by chromatographic retention time method

The retention times of the components in sample and four kinds of standards (DMT, MHET, BHET and BHPT) are all listed in Table 2. From this table, it is found that the retention

Table 2
Composition of samples and the corresponding retention time

	Retention time (min)			
	DMT	MHET	BHET	BHPT
Standard 1	9.5407	8.7335	7.9350	7.1234
Standard 2	9.5279	8.7625	7.9500	7.1300
Average of 1 and 2	9.5343	8.7480	7.9425	7.1267
Sample 1	9.5473	8.7625	7.9186	7.0250
Sample 2	9.5478	8.7370	7.9458	7.1439
Average of 1 and 2	9.5476	8.7498	7.9322	7.0845
S.D.% (standard and sample)	−0.1389	−0.0201	0.1298	0.5946

Table 3
Multi-wavelength ultraviolet qualitative results of BHET

	BHET standard	BHET in sample
$R_{270/240}$	0.0978, 0.1000	0.0925, 0.0911
$R_{254/240}$	0.5300, 0.5230	0.5270, 0.5320

$R_{x/y}$ represents the ratio of the peak area at x nm to that at y nm from ultraviolet spectrophotometer.

time of each component in sample was very close to that of corresponding standard. Furthermore, S.D.% between the standards and components in sample was very small, and the maximum of S.D.% is only 0.5946%. Hence, the existence of DMT, BHET, MHET and MHPT in sample were be proved by this qualitative method.

Although S.D is small, there is still need to further confirm the results by other qualitative method.

3.2.2. Qualitative multi-wavelength UV method

With #51 sample as example, the chromatographic peak areas of BHET at 240, 254 and 270 nm with the same injection amounts were determined according to the chromatograms of #51 sample (in Fig. 4). Then, the ratios of peak areas at different wavelength were calculated, which was the key for the qualitative multi-wavelength ultraviolet method. Table 3 shows the ratios of peak areas from #51 sample and BHEP standard. From Table 3, it can be seen that the ratio of BHET in sample at different wavelengths basically was in agreement with that of BHET standard. Hence, the presence of BHET in sample was also proved by this way.

3.2.3. Qualitative insert SEC analysis results

The relationship between the $\log M$ and the retention time (min) of the standards (DMT, MHET, BHET and BHPT) is plotted in Fig. 5, and a good linear function between $\log M$ and the retention time was observed. The linear regression equation is expressed as the following:

$$\log M = 2.9413 - 0.06801t \tag{3}$$

where r is 0.99737, and S.D is 0.00512.

According to Eq. (3), the MHET, HEHPT and di-polymer of DMT without corresponding standards can be confirmed. The comparison of M_c of MHET, HEHPT or di-polymer of DMT with M is summarized in Table 4. And the comparison of other components besides MHET, HEHPT and di-polymer of DMT is also listed in Table 4 as reference.
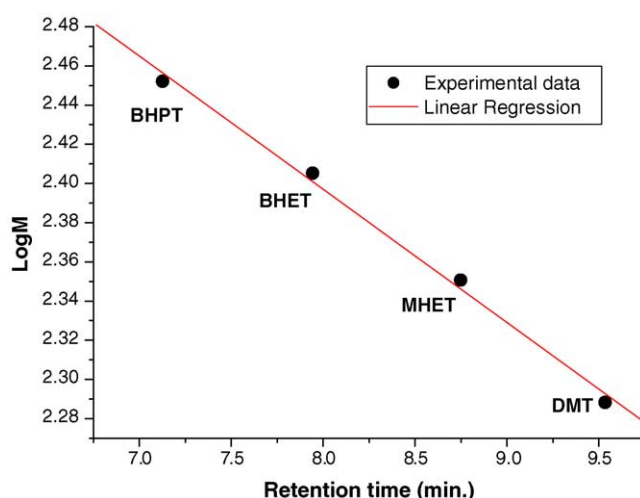

Fig. 5. The relationship between $\log M$ and the retention time.

The molecular structures of these products are shown in Fig. 6.

From this table, it is can be seen that S.D.% is very small except di-polymer of DMT. And the problem is still need to be further investigated.

3.2.4. Qualitative analysis results by FT-IR

Because DMT was the majority among the de-polymerization products, it was also qualitatively analyzed with the aid of FT-IR. For example, #129 sample generated from PTT methanolysis under some conditions, contained 99.644% DMT, which was proved by later quantitative analysis (Table 5). The FT-IR spectra of #129 sample and DMT standard are both shown in Fig. 7. From this figure, the characteristic peaks (−CO−O−, 1724 cm^{-1}; C−O−C, 1283 cm^{-1} and so on) of DMT standard and #129 sample are coincident, which suggests that the majority component of #129 sample was DMT. Thereby, the presence of DMT in samples was further confirmed by FT-IR.

3.3. Quantitative results of compositions in solid sample

3.3.1. DMT content in samples and effects of reaction conditions on DMT yield

Nine samples were taken as examples, the DMT content (wt.%) in sample and the corresponding supercritical condi-

Table 4
The comparison of M_c with M

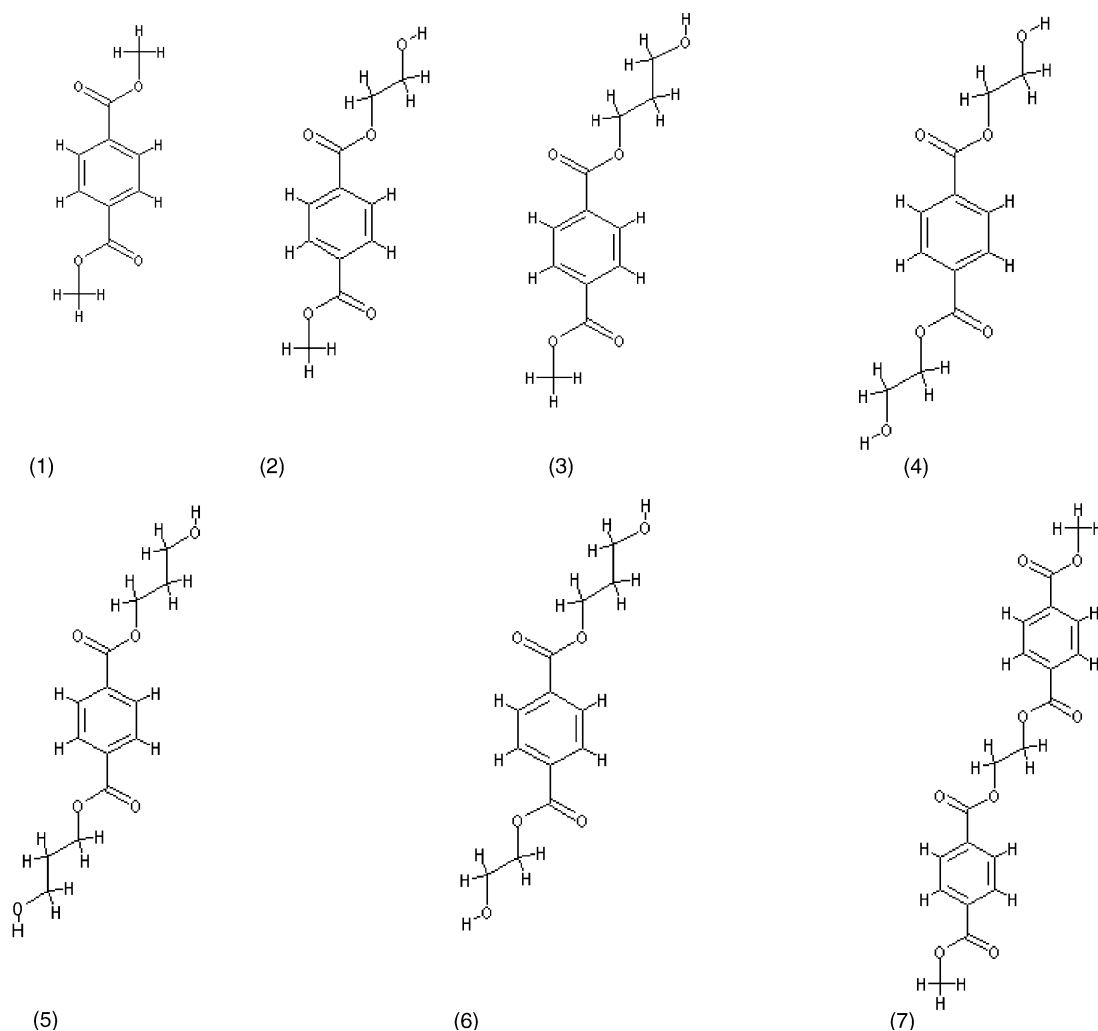| Composition	Retention time (t, min)	M_c	M	S.D.%
Di-polymer ($C_{20}H_{18}O_8$)	5.6599	359.979	386.357	−6.8274
BHPT ($C_{13}H_{16}O_6$)	7.0845	287.979	283.801	1.4723
HEHPT ($C_{14}H_{19}O_6$)	7.4355	272.574	268.286	1.5983
BHET ($C_{12}H_{14}O_6$)	7.9322	252.169	254.230	−0.8107
MHPT ($C_{12}H_{14}O_5$)	8.3798	235.094	238.240	−1.3204
MHET ($C_{11}H_{12}O_5$)	8.7496	221.866	224.212	−1.0463
DMT ($C_{20}H_{18}O_8$)	9.5476	196.793	194.187	1.3420

Fig. 6. The structures of the components: (1) DMT; (2) MHET; (3) MHPT; (4) BHET; (5) BHPT; (6) HEHPT; (7) di-polymer of DMT.

tions are summarized in Table 5. From Table 5, it is observed that the repeatability of the quantitative results was very good and the S.D.% of sample ranged from 0.012% to 0.294%. Therefore, the method established was proper to analyze the solid products from the de-polymerization of PTT in supercritical methanol system. And it is obviously shown that the optimal supercritical reaction conditions were at 553 K and

kept for 30 min, under which the content of DMT achieved 99.644% in solid products.

3.3.2. Quantitative determination of DMT and other components

With #51, #9, #152 and #153 sample as examples, the quantitative results of all components are summarized in

Table 5
Effects of supercritical conditions on DMT content (wt.%) in sample

Sample number	Reaction temperature (T_r, K)	Residence time (t_r, min)	Content of 1 (wt.%)	Content of 2 (wt.%)	Average content of 1 and 2 (wt.%)	S.D.%
#124	553	0	91.178	90.909	91.043	0.148
#126	553	10	98.183	98.206	98.195	0.012
#128	553	20	97.899	97.230	97.565	0.343
#129	553	30	99.320	99.968	99.644	0.325
#132	553	60	68.758	68.516	68.637	0.176
#73	613	0	80.594	80.121	80.357	0.294
#138	613	10	96.808	96.556	96.682	0.131
#140	613	20	98.612	98.206	98.709	0.206
#141	613	30	98.662	98.232	98.447	0.219

In supercritical processes, the weight ratio (R) of PTT to methanol was 0.1 and the pressure was 7.5 MPa.

Table 6
Quantitative results of all components (wt.%)

	Content (wt.%)			
	#51[a] (593 K)	#9[a] (773 K)	#152[a] (513 K)	#153[a] (513 K)
Polymer	0.0563	0.0326	0.3090	0.0150
BHPT	2.2720	0.3150	0.0570	–
HEHPT	3.3830	0.3240	–	–
BHET	15.7470	3.2840	0.8770	0.2560
MHPT	2.4730	2.2240	0.4010	0.1970
MHET	0.2540	–	0.1890	–
DMT	70.5060	90.5010	97.8090	93.6110
Total	94.6910	96.6810	99.6420	94.0790

The supercritical conditions were the weight ratio (R) of raw material to methanol was 0.1, the pressure was 7.5 MPa and the reaction time was 10 min.
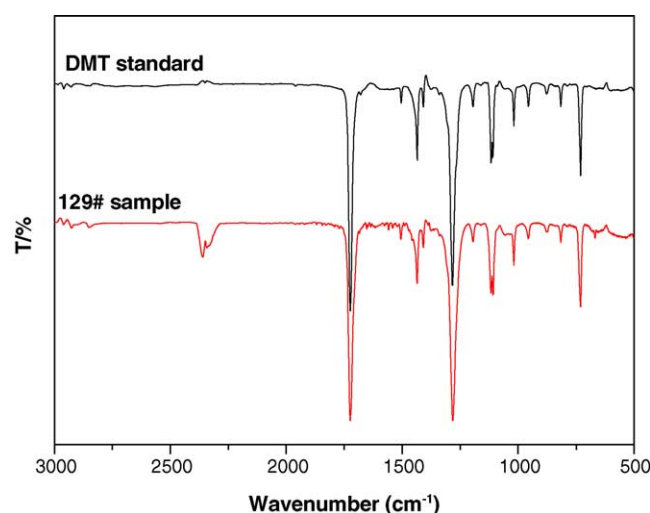
[a] Sample number.

Fig. 7. The IR spectra of DMT standard and #129 sample.

Table 6. The raw materials of #51, #9, #152 and #153 were PTT, PTT, PET and its bottle, respectively. The detected total amount of all products by present method was from 94% to 99%, in which the yield of DMT ranged from 70% to 97%, BHET from 0.3% to 16%, respectively. From the results, it is clearly found that the supercritical methanolytic de-polymerization of PET also shows a high selectivity for the yield of DMT under such conditions. Moreover, it also observed that the products from supercritical de-polymerization of PTT at a high temperature (593 K) were the most complex, therefore it needed better and more practical analysis method to distinguish such complex mixture.

4. Conclusions

(1) A valuable method to analysis the degradation of PTT is presented. A method, which can effectively analyze solid products from supercritical methanolytic de-polymerization of PTT, was established mainly by SEC. The method is of a high resolution among the complex products and a good repeatability for both qualitative and quantitative analysis. The method finely cooperated with the development of supercritical methanolytic de-polymerization. By SEC analysis, it is found that the solid products included DMT, MHET, BHET, BHPT, MHPT, HEHPT, di-polymer of DMT and so on.

(2) Although the method is better than former studies in some characteristics, there are still some problems to be improved, such as the qualitative analysis of di-polymer of DMT, etc.

References

[1] M. Shibata, T. Masuda, R. Yosomiya, M. Ling-hui, J. Appl. Polym. Sci. 77 (2000) 3228.
[2] M. Goto, The Fourth National Symposium on Supercritical Fluid, 2002, p. 17.
[3] M. Goto, H. Koyamoto, A. Kodama, T. Hirose, AIChE J. 48 (2002) 136.
[4] Y. Yang, Y. Lu, H. Xiang, Y. Xu, Y. Li, Polym. Degrad. Stab. 75 (2002) 185–191.
[5] T. Sako, T. Sugeta, K. Otaka, K.N. Nakazawa, M. Sato, J. Chem. Eng. Jpn. 30 (1997) 342.
[6] S. Jirong, Chin. J. Chromatogr. 77 (1989) 118.
[7] H.J.A. Philipsen, H.A. Claessens, H. Lind, B. Klumperman, A.L. German, J. Chromatogr. A 790 (1997) 101.
[8] J. Yamanis, R. Vilenhich, M. Adelman, J. Chromatogr. 108 (1975) 79.
[9] Y. Yong, Z. Changming, X. Yuanyung, L. Yongwang, X. Hongwei, Chin. J. Anal. Chem. 29 (2001) 676.
[10] D. Xiuyun, Z. Changming, J. Fuel Chem. Technol. 10 (1982) 221.