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Hydrolysis of waste polyethylene terephthalate and characterization of products by differential scanning calorimetry

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Abstract

Neutral hydrolysis of waste polyethylene terephthalate (PET) has been carried out with different amounts of water and different catalysts, in the presence of xylene. The organic solvent made it possible to employ very little amounts of water, lower temperatures and pressures and providing concentrated ethylene glycol (EG) solutions in contrast with previous methods, yielding intermediates suitable for PET preparation. These intermediates were characterized by FTIR spectroscopy, acid value (AV), hydroxyl value (HV), viscosity average molecular weight ($\overline{M}_v$) determinations as well as by DSC. Multiple heating/cooling runs in DSC apparatus were carried out and a deconvolution procedure was applied using Haarhoff–Van der Linde (HVL) function to verify the presence of the same components and also to compare polymerization tendency of these various hydrolysis products.

Keywords: Polyethylene terephthalate; Chemical recycling; Hydrolysis; DSC; Deconvolution; Haarhoff–Van der Linde function

1. Introduction

Ecological and economic considerations increased the research on chemical recycling of waste polyethylene terephthalate (PET) as its consumption increased. The collection problems and cost of many recycling processes limit the reclaimed amounts, but in 1998, 104,000 tonnes of PET were recycled in Europe compared to 36,000 tonnes in 1995 and only 23,000 tonnes in 1993 [1].

The aim of the most processes is obtaining monomers such as terephthalic acid (TPA), ethylene glycol (EG) and bis(2-hydroxyethyl)terephthalate (BHET). The first two can be obtained by hydrolysis under neutral, acidic or alkaline conditions and the last by glycolysis of waste PET. An excellent review summarizes the procedures up to 1997 [2]. Some recent additions are papers on alkaline hydrolysis [3–5] and acidic hydrolysis [6].

The main problems encountered in neutral hydrolysis and glycolysis are either employment of large excess of reactants such as water, or glycols as well as high temperatures and pressures or generation of large amounts of waste salts with acidic and basic conditions. For example, in case of neutral hydrolysis, previous researchers found out that large amounts of water (ratios of 5/1 [7] to 20/1 [8] water/PET (w/w)) were required to depolymerize down to TPA and EG, the latter ratio providing the complete solution of TPA under the reaction conditions. Campanelli et al. [9] found that zinc acetate catalysis caused only a modest increase in hydrolysis rate, since they were applying a very high loading of 5.1 g water/g PET and high

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temperatures of 250–280 °C. Although from reaction stoichiometry only 0.18 g of water/g PET is sufficient to depolymerize PET to TPA and EG, Campanelli et al. have found that below 2 g of water/g PET, an equilibrium is established and no further reaction occurs. The equilibrium point was also confirmed by approaching it from the initial monomer stage, as well [9].

It seems obvious that if the neutral hydrolysis is to be carried out to the TPA + EG stage, large amounts of water and high temperatures must be employed, which means that large reactors which should withstand pressures of 4 MPa or more are required. The other problem is, although solid TPA can be easily separated by filtration after the reaction, a very dilute solution of EG is obtained which should be first concentrated and then purified by distillation under reduced temperature.

One of the aims of our work is to investigate the effect of presence of xylene during the hydrolysis of waste PET. Presence of this solvent during glycolysis of waste PET [10] had provided the advantage of higher conversions at lower temperatures, due to the solubility of oligomeric products in xylene phase during the reaction, which shifted the equilibrium to depolymerization. The other aims were the investigation of the preparation of pyridine soluble oligomers or polymers of low molecular weight, by carrying out the reaction with very low amounts of water, compared to those given in literature and also the testing of polymerization tendency of these products. The hydrolysis products were characterized by hydroxyl and acid value (AV) determinations, pyridine solubility, FTIR spectroscopy and DSC analysis. The polymerization tendency of the obtained intermediates were tested by multiple DSC runs. Deconvolution of the melting endotherms by Haarhoff–Van der Linde (HVL) function made it possible to separate overlapping peak areas.

2. Experimental

2.1. Materials

Waste PET flakes obtained from grinding of post consumer bottles was sieved to obtain a 8–10 mesh fraction. The viscosity average molecular weight ($\overline{M}_v$) was found to be 3.7×10^4. Distilled water was used for reactions and extractions. Tween 60 (polyoxyethylene sorbitan monostearate) was supplied by Sigma Chemical Co. The rest of the materials were Merck synthesis or analytical grade.

2.2. Hydrolysis reactions

The hydrolysis reactions were carried out in a 1L stainless steel pressure reactor equipped with a stirrer, temperature control system, and cooling coil. Temperature was increased to desired value in 1 h and the reaction was continued for three more hours.

The reaction was carried out in presence or absence of xylene and catalyst (KOH or zinc acetate). In one case, the effect of a non-ionic detergent addition (Tween 60) was also investigated. The amount of water used was approximately 0.01 or 1 mol H_2O/g PET, which is either theoretically enough for hydrolysis to TPA and EG or completely dissolving the TPA formed in water under the reaction conditions, respectively. PET (30–100 g) and 250 ml of xylene was loaded to the reactor with predetermined amounts of water. After the reaction, the mixture was filtered and the solid product was extracted three times with one liter of boiling water. A water soluble crystallizable fraction (WSCF) was obtained by cooling to 4 °C and filtration. The water insoluble fraction (WIF) and WSCF were dried under vacuum at 30–40 °C.

2.3. Analysis

The acid values were determined by titration of samples dissolved in pyridine with 0.1 N KOH solution [11]. In case of pyridine insoluble fractions such as high molecular weight oligomers, acid values were determined by potentiometric titration of samples dissolved in dimethylformamide–chloroform mixture with 0.1 N KOH solution [12].

The hydroxyl values (HV) were determined by acetylation of samples dissolved in pyridine by acetic anhydride followed by back titration of excess reagent with 1 N NaOH solution [13]. In all cases, arithmetic mean of two or more determinations was given for each sample.

Viscosity average molecular weight was determined with Cannon IB E541 Ubbelohde Viscometer in tetrachloroethane-phenol mixture at 25 °C according to Huggins [14] and Schulz–Blaschke methods [15].

Pyridine solubility was determined gravimetrically by refluxing 2 g of the product in 20 ml of pyridine for 30 min, followed by filtration of the insoluble fraction after cooling to room temperature and weighing after drying.

DSC scans of WIF was obtained with Setaram DSC 131 calorimeter with 10 mg samples by heating up to 280 °C and cooling to room temperature with a rate of 5 °C/min, in nitrogen atmosphere. A second heating and cooling cycle was applied after the primary DSC run at the same rate, in order to investigate the polymerization tendency of the obtained intermediates.

FTIR spectra were obtained with Perkin-Elmer Spectrum One with ATR attachment.

Deconvolution of the melting endotherms was achieved using Haarhoff–Van der Linde peak fitting algorithms [16] to separate the overlapping peak areas, by an available software. Linear D2 baseline, 3% tolerance, SD type deconvolution with HVL gave an excellent ($r^2 > 0.999$) fit for all cases.

3. Results and discussions

3.1. Effects of the reaction conditions

The effect of reaction conditions on hydrolysis of waste PET can be seen from Table 1. Since some product did not dissolve completely in pyridine, it was not possible to carry out hydroxyl value determinations for these samples. In these cases, the hydroxyl value was assumed to be equal to the acid value of the sample, for $\overline{M}_n$ calculation.

The first three reactions (Experiments 1–3) show the effect of temperature on hydrolysis carried out in the presence of a significant excess of water. Although the amount of water was 100 times the stoichiometric requirement, at 140 °C, almost no hydrolysis took place. At 160 °C, a small amount of hydrolysis occurred, WIF becoming partially soluble in pyridine and at 190 °C, hydrolysis, as expected, was almost complete.

In case of experiments carried out in the presence of xylene (Experiments 4–7), the reactions were carried out with stoichiometric amount of water at 170 °C for three experiments and 160 °C for the last experiment. In the absence of catalysis (Experiment 4) and in case of KOH catalyst (Experiment 5), the products were similar to those obtained from Experiment 2. But, when zinc acetate was used as the catalyst (Experiment 6), significant depolymerization occurred. In order to establish a comparison with the product of Experiment 2, the last reaction (Experiment 7) was carried out at 160 °C, but 0.1% Tween 60 emulsifier was added to improve the dispersion of water in xylene, as well as the wetting of the polymer surface and providing better contact between the solid PET and liquid water. Positive effects of ionic surfactant addition on alkaline hydrolysis of PET has also been previously observed [17]. The xylene system in combination with Tween 60, in this case, provided a definite improvement, where a greater degree of depolymerization was achieved with only 1% of the water used in Experiment 2.

White powder products were obtained from Experiments 3, 6 and 7, in contrast with others, where unchanged or partially changed (on outer layer) PET flakes were still visible. This is confirmed by increases in WSCF from 2 to 8% and in pyridine solubility from 17 to 100%, as well as AV and HV of the products.

Thus, the main advantages of this organic solvent for depolymerization of PET are as follows:

(a) Employment of very small amounts of water compared to literature and much lower reaction temperatures, reducing the production costs.
(b) Ease of recovery of EG, since its mixture with excess water separates as phase from xylene at room temperature and also, since very little amount of water was used initially, the possibility of obtaining a very concentrated solution, in contrast with previous methods.
(c) Obtaining of fine white powdery products in case where depolymerization was high, indicating extraction of degradation products from the oligomers by the organic solvent phase and possibly solution of some of the oligomers during the reaction stage followed by precipitation when cooled to lower temperatures, as observed previously in case of glycolysis reactions [10].

3.2. FTIR spectra

The FTIR spectra the products are given along with those of waste PET and pure TPA in Fig. 1, where the AV of the samples increase from top to the bottom

Table 1
Conditions of hydrolysis reactions and properties of the reaction products

Experiment number	Hydrolysis reaction conditions				Products								
	Temperature (°C)	H_2O[a]	Catalyst	Xylene[b]	WIF					WSCF			
					Yield (%)	AV (mg KOH/g)	HV (mg KOH/g)	$\overline{M}_n$[c]	Pyridine solubility (%)	Yield (%)	AV (mg KOH/g)	HV (mg KOH/g)	Pyridine solubility (%)
1	140	1	ZnAc	−	100	6.4	–	8765[d]	0	0	–	–	–
2	160	1	ZnAc	−	98	42.7	–	1313[d]	17	2	341	175	100
3	190	1	ZnAc	−	80	581	102	165	100	20	308	240	100
4	170	0.01	–	+	99.8	23.9	–	2347[d]	7	0.2	70	–	100
5	170	0.01	KOH	+	99.8	27.4	–	2047[d]	29	0.2	78	–	100
6	170	0.01	ZnAc	+	97.2	145.5	62	540	100	2.8	201	123	100
7[e]	160	0.01	ZnAc	+	92	149	150	375	100	8	285	241	100

[a] Mol H_2O/g PET.

[b] 2.5 ml of xylene was used for 1 g of PET.

[c] Calculated from AV and HV.

[d] HV was assumed to be equal to AV since sample did not dissolve completely in pyridine.

[e] Tween 60 was added to the reactor (0.005 g/g PET).

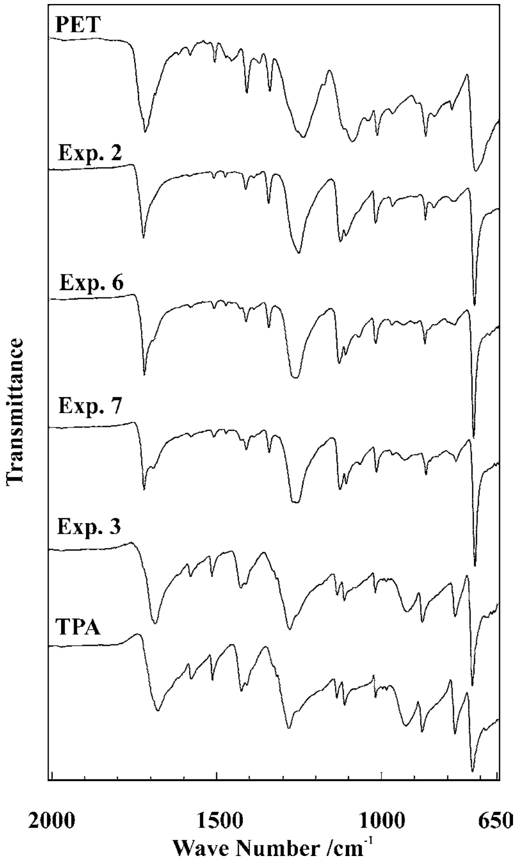

Fig. 1. FTIR spectra of PET, hydrolyzed products and TPA.

of the figure. Although IR spectra was claimed to be inadequate for quantitative estimation of conversion in hydrolysis [7], it confirms the AV determinations.

The main changes were in the intensities or wave numbers at 1713 cm^{-1} C=O, 1238 cm^{-1} C–O, 1043 cm^{-1} –O–(CH$_2$)–O– and 969 cm^{-1} C–O peaks of PET [18]. For example, with increase in AV of the samples, a shoulder at 1688 cm^{-1} develops into a peak, with the disappearance of 1713 cm^{-1} C=O peak. Similarly the ester C–O band peak observed at 1238 cm^{-1} shifts to higher wave numbers as the AV of the samples increase and double peaks at 1257 and 1270 cm^{-1} appear on the spectrum of Experiment 7. For samples with very high AV such as Experiment 3 and TPA, we observe a single peak at 1275 cm^{-1}. The –O–(CH$_2$)–O– peak of 1043 cm^{-1} becomes a shoulder in case of Experiment 2 and disappears completely when AV reaches 149 (Experiment 7). On the other hand, the 969 cm^{-1} C–O peak disappears only incase of Experiment 3 and TPA, where AV is very high. The similarity between the spectra of these confirms that product of Experiment 3 consist of mainly TPA and a little amount of low oligomers with high carboxyl group contents.

3.3. Potential of oligomeric products and DSC results

PET is manufactured either by transesterification of dimethyl terephthalate or more recently direct esterification of TPA by EG. In both cases, the intermediate BHET is obtained. In case of direct esterification, excess EG is used or side-product water is removed. High conversion in industry is obtained by high temperatures to ionize TPA to catalyze the reaction. In order to avoid this, the vapor pressure of the mass may be lowered by addition of PET [19]. Even if no PET is added, the product is never BHET alone, but consist of several oligomers of BHET [20–22]. Also the reaction is carried out in train of stirred tank reactors where TPA is partially dissolved and partially exists as granules which are suspended in EG. With increase in product BHET concentration, more TPA is dissolved, since its solubility in BHET is larger than it is in EG [20,21] and then the reaction transforms into a homogeneous one.

The polyester is manufactured in two or three stages in BHET method. The initial polycondensation reaction at 260–290 °C under high vacuum is followed by removal of residual EG in wiped film reactors and usually a consequent solid state polymerization. BHET formation as well as polycondensation is catalyzed by presence of carboxyl groups as well as the antimony compounds [23].

Now, the above mentioned facts confirm the importance of carrying out a moderate hydrolysis of PET in the presence of xylene. An intermediate with a low to medium molecular weight would be good substitute for TPA in BHET production, since it would have better solubility EG/BHET and depending on its structure may provide a homogeneous reaction in early stages, instead of the heterogeneous one. Another advantage is that below depolymerization conversions of about 30%, very little EG is split-off [7] from the polymer, which will provide great decrease in the amount of EG to be added to the reactor for the BHET production.

Furthermore, the oligomers will decrease the vapor pressure of reaction mass and still contribute to the catalysis of the reaction with their carboxyl groups and the likelihood of side reactions such as diethylene glycol or ether bridge formation [24] would be less. Obviously, it would be even better if oligomers with low melting points could be employed as precursors for high molecular weight PET formation. It was stated that the unfavorable equilibrium constant [23] rarely allows formation of high molecular weight species from direct esterification of TPA with EG. On the other hand, one of the more recent patents claims that BHET stage is not mandatory [22]. The inventors reacted EG and TPA at molar ratios of (1.4–1.1)/1 and not 2/1 as in the conventional method, skipping the BHET stage. They conducted reaction under 0.3 MPa pressure, removed the side-product water and returned escaping EG to the reactor by an attached rectification column. The oligomers obtained were further polymerized under reduced pressure at temperature, up to 290 °C. Thus, some of the oligomers obtained in this work will be very suitable raw materials for the second stage of this process, since most of the side-product water would be absent.

Two consecutive DSC runs with proper deconvolution of the thermograms could be indicative of the medium molecular weight polymer formation potential of these oligomers obtained from hydrolysis of waste PET.

The endotherms of melting of polymer crystals can give an idea of about the structure of polymers. In case of PET depolymerization products, if the reaction has proceeded down to monomer stage, the crystalline monomer and low oligomers give endothermic melting peaks which are well separated from each other. But, for medium depolymerization products, the peaks may be interpenetrating and require a deconvolution application to obtain a secondary plot where the main components can be seen. The maxima of the secondary curves obtained by deconvolution are dependent on their melting points, but they can be affected strongly by their solubility in the molten phase, the composition of which changes continuously as new components are added during the heating stage. This shift was especially observed for samples of glycolysis of waste PET. BHET monomer melting at 110 °C, dissolves crystals of its dimer readily, lowering its maxima by 10 °C. The thermograms of a DSC runs of synthetic mixtures containing up to 25% dimer may show a single melting peak at 108 °C for BHET and none for the dimer. But previous experience has shown that in case of oligomers with carboxyl end groups, mutual solubility is lower. Thus, when deconvolution is applied to the DSC curves of hydrolysis products, the peaks of the main oligomers should be observed at the same or very similar temperatures.

Unfortunately, very little data is available about the melting temperatures of PET oligomers. The melting points or ranges of synthetically prepared and purified samples of some oligomers are given in Table 2 [25]. We see that the melting points of oligomers with carboxyl groups at both ends decrease as the size of the molecule increases. Although the melting point decreases down to 236 °C for $n = 5$, we can expect a “U” turn in melting point temperatures. The increase in this case should approach industrial PET melting points, in case of higher molecular weights. On the other hand, for oligomers with carboxyl groups at one and hydroxyl groups at the other end, the melting points increase with increase in molecular weight, reaching 223 °C for a molecular weight of 594.

In case of high molecular weight polymers, multiple peaks may also be due to different crystalline structures. The melting point of crystalline fractions of industrial PET is quite high, about 260 °C and usually dual melting endotherm maxima are encountered on the DSC curves. These dual peaks have been attributed either to two different structures [26–28] or recently, to partial melting and recrystallization followed again by the melting of this more orderly structure [29]. Qiu et al. have carried out an excellent study of the effect of heating rate, crystallization temperature and solid state polymerization on the crystallization behavior of PET samples [29]. They have developed a mathematical model which predicted the size and shape of the double peaks with high accuracy. At heating rates below 8 °C/min, since enough time was available for the perfection of crystalline structure, double melting peaks were obtained. They have confirmed that when amorphous PET was crystallized at low temperatures, poor quality crystals are formed, which melt at lower temperatures and then recrystallize to yield the other orderly species, which melt at higher temperatures. The same behavior was observed for low crystallization times. For example, a single peak was obtained

Table 2
Properties of some PET oligomers

Formula	*n*	AV (mg KOH/g)	HV (mg KOH/g)	Melting point (°C)	Molecular weight[a]
$HOOCC_6H_4CO(OCH_2CH_2OOCC_6H_4CO)_nOH$	1	313.5	–	>360	358
	2	204	–	280–281	550
	3	151	–	268–270	742
	4	120	–	252–255	934
$H(OCH_2CH_2OOCC_6H_4CO)_nOCH_2CH_2OH$	1	–	442	109–110	254
	2	–	252	173–174	446
	3	–	176	200–205	638
	4	–	135	213–216	830
$H(OCH_2CH_2OOCC_6H_4CO)_nOH$	1	267	267	178	210
	2	139.5	139.5	200–205	402
	3	94.5	94.5	219–223	594
	4	71.5	71.5	–	786

[a] Calculated.

when PET was crystallized for several hours at 220 °C. But they have disregarded effect of molecular weight on the shape or maximum temperature of the peaks, although by this procedure they have practically applied a mild “solid state polymerization” to the sample. One can expect that crystals of lower molecular weight polymers would start to melt at low temperatures and crystalline melting temperature distribution plots are quite similar to polymer molecular weight distribution curves.

For the deconvolution, HVL function was preferred to Gaussian or Lorentzian ones, since it was designed to fit the skewed (tailing or fronting) peaks of chromatographic data and has been successfully applied to capillary zone electrophoresis [30], high resolution gel permeation chromatography [31] and quite recently, to shape analysis of DSC ice melting endotherms. Popa and Segal [32], in this DSC application, mention that symmetrical spectroscopic functions were not suitable, since during the initial partial melting of ice crystals, a liquid interface layer controlling further melting process forms, resulting in skewed peaks [33]. In our case, additional factors such as contaminating small oligomers and different types of crystals caused further deviation of DSC plots from symmetry and HVL provided excellent fits.

Data obtained from DSC and deconvoluted curves are presented in Figs. 2–5 and Table 3. In Figs. 2 and 3, the deconvolution secondary plots are given underneath the DSC primary plots for waste PET and Experiment 1, 2, 4–7 WIF fractions. DSC plot for Experiment 3, where the product was TPA to a great extent, is not given, since the maximum temperature of the DSC run was 280 °C and TPA sublimes over 300 °C and low amount of oligomers could not be seen on the thermogram.

The DSC curve of waste PET after deconvolution shows four secondary endothermic peaks instead of the expected two. In case of Experiment 1, the primary endothermic peak is somewhat sharper due to further crystallization of unconverted PET during the hydrolysis attempt at 140 °C for 3 h. The other change is the appearance of small secondary peak about 226 °C, indicating the presence of some hydroxyl–carboxyl ended oligomers where $n = 3$ or 4. The secondary DSC curve of Experiment 2 shows three main and two small peaks. This reaction was carried out at 160 °C, where rate of crystallization is greater than 140 °C. The shift in maxima to lower temperatures in comparison with Experiment 1 is significant. The 235 °C peak indicates the increase in hydroxyl–carboxyl ended oligomer content where $n = 4$.

Experiment 4 was carried out in the presence of xylene and absence of catalyst. Maxima of secondary DSC curves confirm its AV, which is between those of Experiments 1 and 2. It can also be seen from Fig. 3 that presence of KOH did not have great effect. Most of the maxima of secondary curves are same or very similar (258, 253, 245, 235, 220 °C) for Experiments 4 and 5.

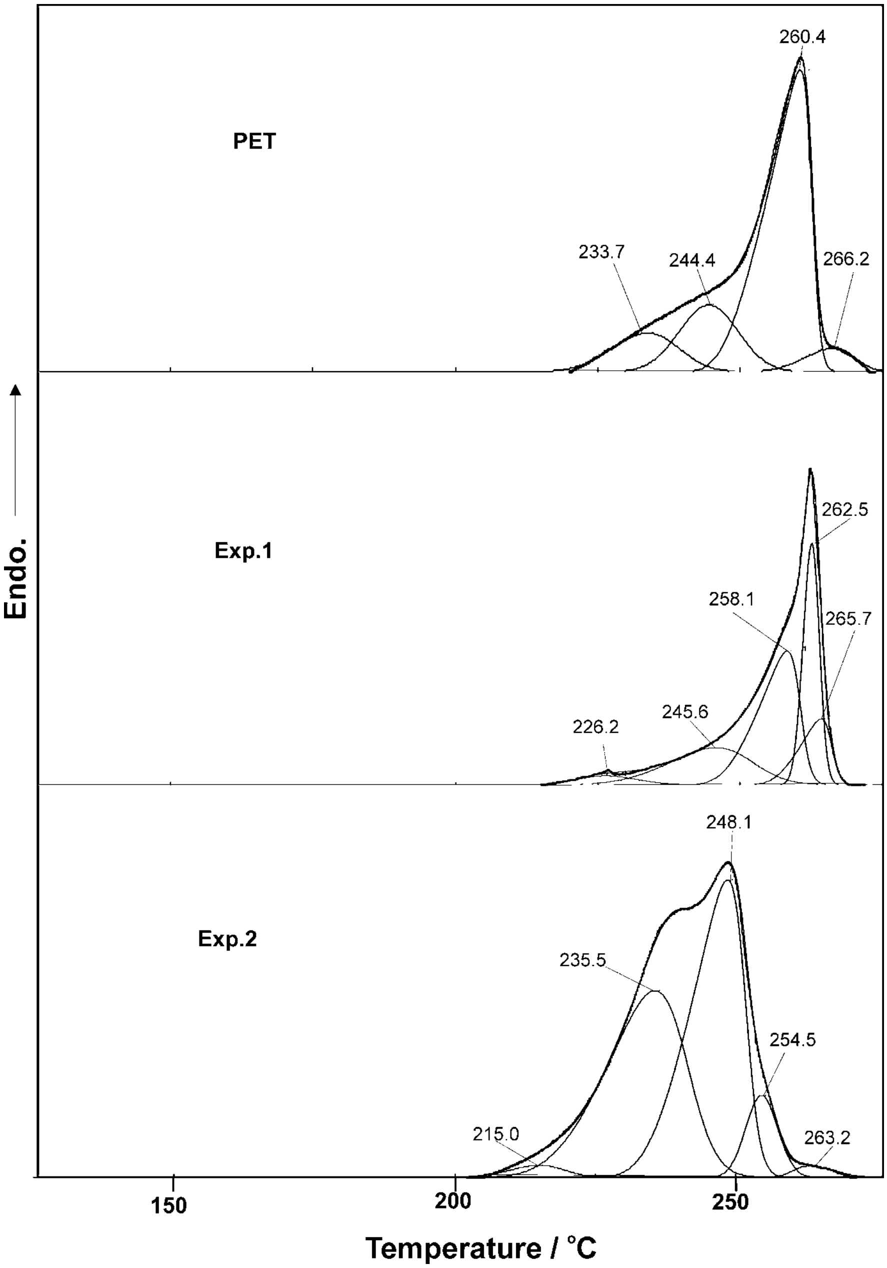

Fig. 2. DSC and deconvolution peaks of PET and Experiments 1 and 2.

DSC curves of Experiment 6 confirm the extent of depolymerization is clearly greater. Presence of both hydroxyl–carboxyl ended $n = 1, 3$ as well as carboxyl–carboxyl ended $n = 4$ oligomers given in Table 2 may account partially for the 176, 210 and 252 °C secondary peaks, respectively. This is supported by the high AV and relatively low HV of the product, although the 254 °C peak is still present in DSC curves of Experiments 4 and 5.

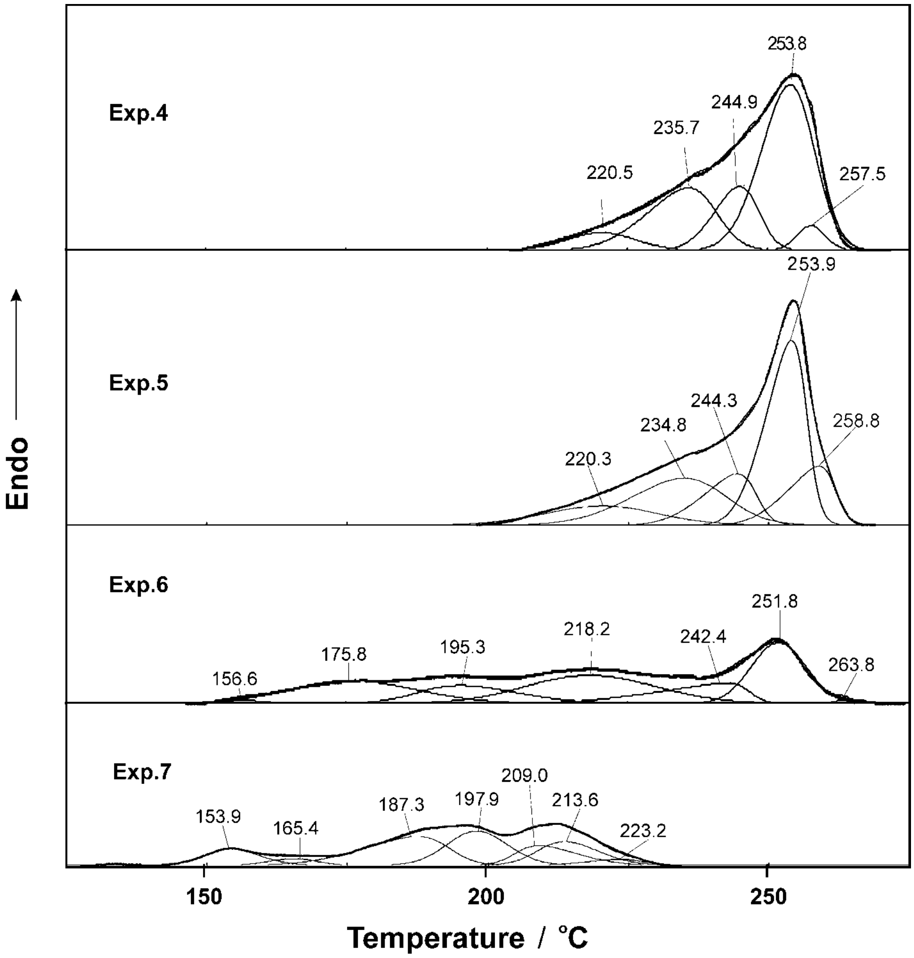

Fig. 3. DSC and deconvolution peaks of Experiments 4–7.

DSC curve of Experiment 7 confirms that a better stage of depolymerization has been achieved in the presence of Tween 60. Since the HV and AV of the product are about the same, some of the secondary peaks must be due to the presence of hydroxyl–carboxyl ended oligomers where $n = 2$ or 3. $n = 1$ oligomer is unlikely, since it is water soluble and should have been removed during the extraction of WIF.

As mentioned above, in order to test high molecular weight polymer formation potential of the products, they were subjected to a second cycle of heating and cooling after the first run. $\overline{M}_\text{v}$ determinations have also been carried out for some samples and the results are given in Table 4.

The deconvoluted DSC curve of the second run for waste PET (Fig. 4) when compared with that of the original waste PET indicates that some rearrangement of molecular weight distribution may have occurred along with a slight decrease of molecular weight (Table 4). This decrease in the molecular weight is expected, since the sample was not dried and contained some humidity and hydrolytic chain scission occurs when PET is heated [34]. For the change in the shape of the melting endotherm, the other and more likely suggestion would be that the industrial sample, which has probably gone through a solid state polymerization stage, attained a better crystalline structure which was not possible to obtain during the cooling cycle in the DSC cell. In this case, 249 °C

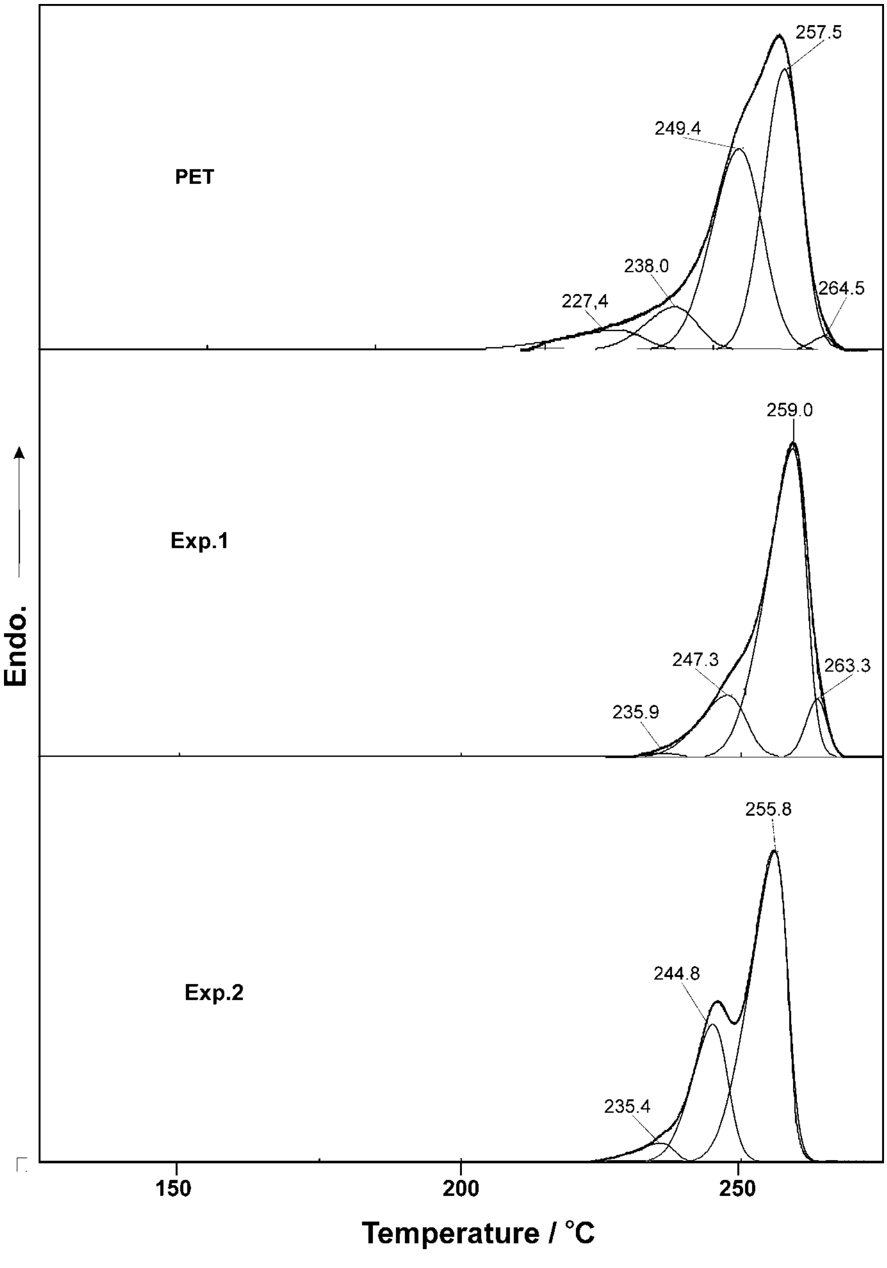

Fig. 4. Second DSC runs and deconvolution peaks of PET and Experiments 1 and 2.

peak and the 257 °C peak should be due to inferior and superior order crystalline formations, respectively (Fig. 4).

Product of Experiment 1, on the other hand, indicates the formation of a more homogenous crystal structure after the second heating/cooling cycle where a peak with a maximum of 259 °C is very dominant. The disappearance of 215 °C peak and the decrease in intensities of 235 and 245 °C peaks, along with increase in intensity of 255 °C peak for Experiment 2

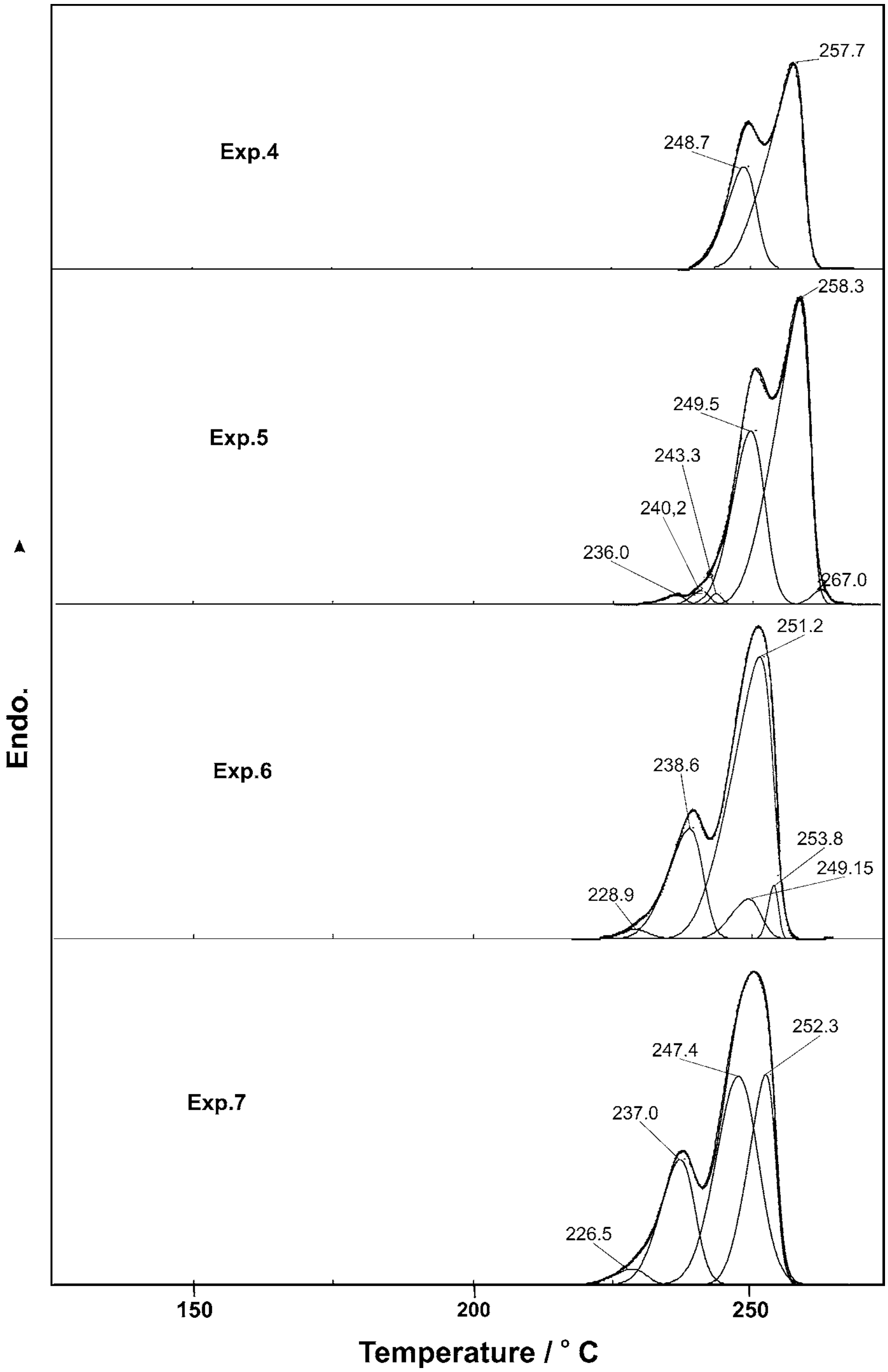

Fig. 5. Second DSC runs and deconvolution peaks of Experiments 4–7.

Table 3
Maxima of the peaks and peak areas of deconvolution peaks

Sample	Maxima of the peaks (°C)		Peak area (%)	
	1st run	2nd run	1st run	2nd run
PET	233.7	227.4	12.2	6.1
	244.4	237.9	18.9	9.0
	260.4	249.4	63.2	41.1
	266.2	257.5	5.6	42.6
	–	264.5	–	1.1
Experiment 1	226.2	235.9	3.5	0.7
	245.6	247.3	20.5	17.6
	258.1	259.0	36.1	74.3
	262.5	263.3	26.3	7.4
	264.1	–	13.7	–
Experiment 2	218.1	235.4	3.5	3.3
	236.1	244.8	47.9	28.4
	248.6	255.8	39.8	68.3
	254.6	–	6.7	–
	264.1	–	2.2	–
Experiment 4	220.3	248.7	6.7	30.0
	235.7	257.7	24.1	70.0
	244.9	–	15.9	–
	253.8	–	49.3	–
	257.6	–	3.9	–
Experiment 5	220.3	236.0	10.7	1.3
	234.8	240.6	22.7	1.5
	244.3	243.3	13.6	0.7
	253.9	249.5	38.8	33.1
	258.8	258.3	14.2	61.9
	–	262.0	–	1.4
Experiment 6	156.6	228.9	0.9	1.6
	175.6	238.6	21.2	22.2
	195.3	249.1	13.2	6.9
	218.2	251.2	26.9	66.0
	242.4	253.8	13.3	3.2
	251.8	–	24.1	–
	263.8	–	0.4	–
Experiment 7	133.2	228.5	0.5	2.6
	153.9	237.0	10.2	22.3
	165.4	247.4	3.5	45.5
	187.3	252.3	27.6	29.5
	197.9	–	27.0	–
	209.0	–	13.8	–
	213.6	–	16.6	–
	223.4	–	3.6	–

after the same treatment shows the increase in molecular weight due to polycondensation.

Table 4
Change in viscosity average molecular weights ($\overline{M}_v$) of after heat treatment for samples of waste PET and Experiments 6 and 7

Sample	Viscosity average molecular weights ($\overline{M}_v$)		
	Original sample	After the 1st run	After the 2nd run
PET	37300	34900	35700
Experiment 6	1350	3400	8300
Experiment 7	550	1400	9600

The same effect of polycondensation after heating to 280 °C can be seen from comparison of the first and second run DSC curves of Experiments 4 and 5, where lower molecular weight tails which appear at low temperatures in original products disappear. The lower AV and thus the higher initial molecular weight of these products gave endotherms with higher maximum temperatures than those of Experiment 2 (Fig. 5).

The DSC plots and data in Table 1 for the last two experiments (Experiments 6 and 7) show that although the bimodal character of distribution is distinct like Experiments 4 and 5, the maximal temperatures of the endotherms are lower. This is caused by the lower molecular weight of the initial products. It is interesting that both oligomers could easily give high molecular weight polymers although their AV/HV ratios are not the same. Since no catalyst was added, this should be due to their initial high carboxyl contents which has a catalytic effect on polycondensation. It also shows that with proper catalysis and under reduced pressure industrially acceptable molecular weights could be attained.

4. Conclusion

Neutral hydrolysis of waste PET has been carried out with high (1 mol H_2O/g PET) or low amount of water (0.01 mol H_2O/g PET) and in the presence of xylene. The presence of this inert solvent provided grater degrees of depolymerization at lower temperatures and pressures, to give oligomers suitable for polycondensation and more concentrated EG solutions compared to previous methods.

The obtained oligomers were characterized by FTIR, AV and HV determinations as well as multiple runs on the DSC apparatus. After a HVL deconvolution process, main peaks of the oligomers were separated and found to be recurring in the thermograms.

Polycondensation of lower oligomers due to the dynamic heating component of DSC cycle was apparent by the decrease in intensity or disappearance of peaks in the low temperature region. The effect of molecular weight on the peaks of high temperature region was smaller and the shape and maximum temperatures of the peaks were more affected by crystalline formations. Viscosity average molecular weights of 7000–8000 were obtainable after two cycles in DSC apparatus although it was carried out under atmospheric pressure, indicating that much higher molecular weights can be obtained in an industrial reactor, under reduced pressure. Thus, these oligomers were suitable as intermediates for PET production either as additives or as the main raw material, saving polymerization time. The second part of this work shall be concerned with the simultaneous glycolysis/hydrolysis of waste PET to obtain various pure monomers of known structure instead of mixture of oligomers.

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