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Simultaneous glycolysis and hydrolysis of polyethylene terephthalate and characterization of products by differential scanning calorimetry

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Abstract

Simultaneous glycolysis and neutral hydrolysis of waste polyethylene terephthalate (PET) has been carried out at 170 and 190 °C with constant amount of ethylene glycol (EG) and increasing amounts of water, in the presence of xylene. The organic solvent made it possible to employ very low amounts of reactants as well as application of lower temperatures and pressures in contrast with previous methods, yielding intermediates suitable for PET or other polymeric materials. These intermediates were characterized by acid value (AV), hydroxyl value (HV) determinations as well as by differential scanning calorimetry (DSC). A water soluble crystallizable fraction with high purity, consisting of mono 2-hydroxy ethyl ester of terephthalic acid (monohydroxyethyl terephthalate, MHT) monomer has been obtained with significant yield and its polymerization tendency has been compared with that of bis(2-hydroxy ethyl) terephthalate (BHET) by application of multiple heating/cooling cycles in DSC.

Keywords: Polyethylene terephthalate; Glycolysis; Hydrolysis

1. Introduction

Ecological concerns provided the drive for research and initial applications of recycling of waste polyethylene terephthalate (PET) as its consumption increased. But the process is also a quite profitable one and some of the physical and chemical recycling plants may be in difficulty of finding enough supply in near future [1] since only 17% of world production was collected for recycling in 1999. Mainly the collection cost and problems limit the reclaimed amounts, although regional differences exist. For example, in Europe, the amount of collected waste PET increased almost 10-fold, from 45,000 tons in 1995 to 449,000 tons in 2003 [2].

The aim of the most chemical recycling procedures is obtaining monomers such as terephthalic acid (TPA), ethylene glycol (EG) and bis(2-hydroxy ethyl) 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 research and applications up to 1997 [3]. Some recent additions are papers on alkaline [4–6] and acidic [7] hydrolysis and glycolysis [8,9] and patents on glycolysis [10–12].

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 the requirement of high temperatures and pressures. For example, in case of neutral hydrolysis, previous researchers found out that large amounts of water (ratios of 5/1 [13] to 20/1 [14] of 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. [15] found that zinc acetate catalysis caused only a modest increase in hydrolysis rate, but they were already applying a very high loading of 5.1 g water/g PET and high 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

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Abbreviations: AV, acid value; BHET, bis(2-hydroxy ethyl) terephthalate; DEG, diethylene glycol; DSC, differential scanning calorimetry; EG, ethylene glycol; HV, hydroxyl value; MHT, monohydroxyethyl terephthalate; $\bar{M}_n$, number average molecular weight; PET, polyethylene terephthalate; TLC, thin layer chromatography; TPA, terephthalic acid; WIF, water insoluble fraction; WSCF, water soluble crystallizable fraction.

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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 [15].

In case of glycolysis, zinc acetate is an efficient catalyst [16] and previous research has shown that after 8 h of reaction at 200 °C with PET/EG (w/w) ratios of 62.5/37.5, 50/50, 37.5/62.5, the hydroxyl value (HV) of EG free oligomeric products rose from 1–2 to 374, 402 and 440 mg KOH/g, respectively [17]. On the other hand, Baliga and Wong have employed a PET/EG molar ratio of 1/4 (w/w ratio of 44/56) and under similar conditions obtained a maximal HV of 375. Chen et al. used PET/EG (w/w) ratio of 33/67 at 190 °C and obtained after 2.5 h of reaction a conversion of 99%, yielding an oligomeric intermediate with a HV of 341.

No mention of simultaneous application of glycolysis and hydrolysis has been found in literature. The nearest applications were patented in 1986 and 1993/1996 [18,19]. One patent claims that if molten PET in extruder is reacted at 280 °C with small amounts of EG prior to hydrolysis, molecular weights can be reduced from 30,000 to 9000–1000 (depending on the amount of EG) which, in turn, reduces the time required for hydrolysis down to EG and TPA from 45 to 12–15 min [18]. The other patent is concerned with an initial glycolysis of PET to BHET, followed by a purification stage of adsorption and filtration and subsequent application of hydrolysis of BHET to yield TPA in a separate, glass-lined reactor at 200 °C [19].

Thus, the employment of high reaction temperatures and large excess of reactants is common and considered necessary to reach high conversions and to obtain low molecular weight intermediates or monomers, since hydrolysis and glycolysis are reversible reactions and the equilibrium of polymerization with reverse reaction of polyesterification must be changed. Previous research [8,20] has shown that this equilibrium can be offset by the employment of an inert solvent such as xylene during hydrolysis or glycolysis reactions. Although PET does not dissolve in xylene even at high temperatures, it dissolves in EG readily above 170 °C. In case of glycolysis, the reaction proceeds mainly in PET-EG droplets dispersed in xylene especially during the initial stage. But, since the products have significant solubility in xylene at higher temperatures, part of the oligomers transfer to xylene phase and the (PET + Oligomer)/EG molar ratio decreases, shifting the equilibrium more to depolymerization. Similar effect of xylene in case of hydrolysis was also confirmed and conversion had been further enhanced by use of nonionic surfactant [20]. Another advantage of the process was the precipitation of oligomeric products as a fine powder from the xylene phase as the system is cooled and separation of EG and/or water as a phase from xylene at the end of reaction. Thus the presence of xylene provided the possibility of employment at very small amounts of water or EG and fairly lower reaction temperatures to reach conversions similar to those of previous methods.

This work is concerned with the simultaneous application of glycolysis by EG and neutral hydrolysis by water in the presence of xylene to obtain crystalline low cost products containing both hydroxyl and carboxyl end groups which can be used either as monomers or added to virgin monomers during the production of commercial production of PET. The products were characterized by acid and hydroxyl value determinations and DSC. The polymerization tendency of some of the obtained intermediates was tested by multiple DSC runs.

2. Experimental

2.1. Materials

Waste PET flakes obtained from grinding of post-consumer bottles (containing 0.3% (w) humidity) was sieved to obtain an 8–10 mesh fraction. The viscosity average molecular weight ($\bar{M}_v$) was found to be 3.7×10^4 [20]. 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. EG had a water content of 0.3% (w).

2.2. Reactions

The reactions were carried out in 1 l stainless steel pressure reactor equipped with a stirrer, temperature control system and cooling coil. The temperatures of 170 or 190 °C were attained in 1 h and the reaction was continued for three more hours. The charges consisted of 100 g of PET and 31 g EG (corresponding to a molar ratio of 1/1 based on the molecular weights of the repeating unit of PET and EG), 250 ml xylene, 0.5 g of Tween-60 surfactant, 1 g of zinc acetate catalyst and various amount of water between 5 and 120 ml (corresponding to approximate molar ratios of H_2O/PET of 0.5/1 to 13/1). After the reaction, the reactor was cooled to room temperature in 15–20 min by circulating water through the cooling coils and immersion in running water. The powder product was separated from EG, water and xylene by filtration and was extracted by 1 l water at boiling point three times. The remaining solid was named water insoluble fraction (WIF). The filtrate was cooled to 4 °C and the crystallized solid obtained by filtration was named water soluble crystallizable fraction (WSCF). WIF and WSCF were dried under vacuum at 30–40 °C. All of the samples dissolved in pyridine, indicating the absence of unconverted PET or high molecular weight oligomers.

2.3. Analysis

The acid values (AV) were determined by titration of samples dissolved in pyridine with 0.1N KOH solution [21]. The hydroxyl values (HV) were determined by acetylation of samples dissolved in pyridine by acetic anhydride, followed by back titration of excess reagent with 1N NaOH solution [22]. In all cases, the arithmetic mean of two or more determinations was given for each sample. M_n values were calculated from AV and HV by the known formula of end group analysis method of average molecular weight determination [23].

DSC scans of samples were obtained with Seteram DSC 131 calorimeter with 20 mg samples by heating up to 280 °C and cooling to room temperature with a rate of 5 °C/min, in nitrogen atmosphere. Multiple heating and cooling cycles were applied after the initial DSC run at the same rate in order to compare the polymerization tendency of two of the intermediates.

^{1}H NMR spectra were obtained for the d_6-aceton solutions on a Brucker AC-3000 (250 MHz).

Some of the products were also analyzed by thin layer chromatography (TLC) using chloroform/tetrahydrofuran (2/1, v/v) as the mobile phase and TLC Plates silica 60 F_{254} (Merck, Darmstadt), detecting with ultraviolet light (254 nm). Sample solutions were prepared in methanol.

3. Results and discussion

3.1. Effects of reaction conditions

Glycolysis (1) and hydrolysis (2) of waste PET at the first glance seems to be simple processes, the main problem being the equilibrium between depolymerization by either reagent and the reverse reaction of polycondensation of produced monomer or oligomers. But, some side reactions can yield unexpected oligomers and side products. Simultaneous application of both depolymerization reactions and presence of xylene, which can dissolve partially or completely the reaction products, complicates the situation further, but provides some distinct advantages, which will be discussed below.

$$-C_6H_4-COOCH_2CH_2OOCC_6H_4- + HOCH_2CH_2OH \rightarrow 2\ -C_6H_4-COOCH_2CH_2OH \quad (1)$$

$$-C_6H_4-COOCH_2CH_2OOC-C_6H_4- + H_2O \rightarrow -C_6H_4-COOCH_2CH_2OH + HOOC-C_6H_4- \quad (2)$$

$$-C_6H_4-COOCH_2CH_2OH + HOCH_2CH_2OH \rightarrow -C_6H_4-COOCH_2CH_2OCH_2CH_2OH + H_2O \quad (3)$$

$$-C_6H_4-COOCH_2CH_2OH + HOCH_2CH_2OH \rightarrow -C_6H_4-COOH + HOCH_2CH_2OCH_2CH_2OH \quad (4)$$

$$-C_6H_4-COOCH_2CH_2OH + H_2O \rightarrow -C_6H_4-COOH + HOCH_2CH_2OH \quad (5)$$

According to Yoon et al. [24], the etherification reactions (3) and (4) yield polymers with diethylene glycol (DEG) end groups and water formation or result in DEG formation and polymers with carboxylic end groups, respectively. The evolved water can react further according to reaction (2) or (5) increasing the acid value of the product and DEG can compete with EG in glycolysis and further etherification reactions [24]. These reactions are known to occur during the polycondensation of commercial PET. Analysis of a commercial PET sample has shown that it may contain 1.77% (w) diethylene glycol and 0.92% (w) triethylene glycol [25]. The properties of the products of experiments 1–13 are given in Table 1 and the DSC thermograms are given in Figs. 1–4. Please note that since the melting endotherms of the WIF was significantly lower intensity than those of WSCF, different mW scales have been used in these thermograms.

The analysis results of products of glycolysis reactions 1 and 7 (Table 1) indicate the presence of the above mentioned side reactions, although it seems that at these temperatures neither DEG formation nor hydrolysis by water formed or present as impurity (0.3% in PET, 0.3% in EG) is not significant, since AV's are low. Previous research [8] has shown that in a series of glycolysis reactions and under similar conditions at 170, 190, 220 and 245 °C, the

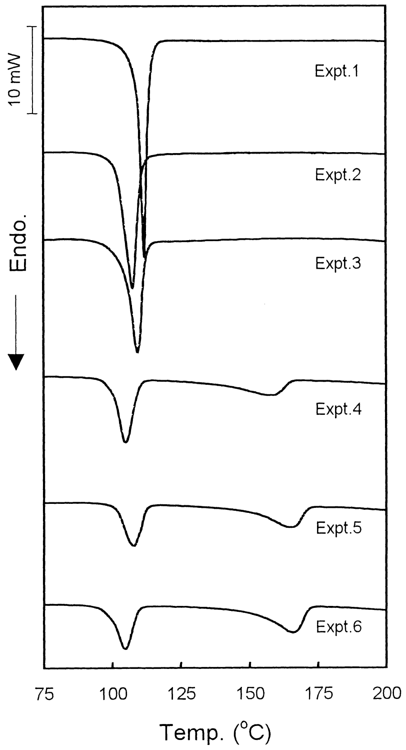

Fig. 1. DSC thermograms of WSCFs of Expt. 1–6.

Table 1

Conditions of simultaneous glycolysis and hydrolysis reactions and properties of reaction products

Expt. no.	Temp. (°C)	H_2O (ml)	WSCF			WIF			AVE[a]			
			HV[b]	AV[b]	Yield (%)	HV[b]	AV[b]	Yield (%)	HV[b]	AV[b]	Molar ratio (–OH/–COOH)	$\bar{M}_n$[c]
1	170	0	369	2	17.0	240	4	83.0	262	4	66.00	422
2	170	5	300	53	6.5	172	18	93.5	180	20	9.00	561
3	170	15	385	15	18.0	210	98	82.0	242	83	2.90	345
4	170	45	301	180	47.0	225	282	53.0	261	234	1.10	227
5	170	90	295	225	40.0	187	361	60.0	230	307	0.75	209
6	170	120	290	226	32.5	118	190	67.5	174	202	0.86	298
7	190	0	445	4	19.0	200	11	81.0	247	10	24.70	437
8	190	5	360	84	16.0	256	24	84.0	273	34	8.03	365
9	190	15	340	112	25.0	224	63	75.0	253	75	3.37	342
10	190	30	297	218	42.0	97	344	58.0	181	291	0.62	238
11	190	60	296	227	43.0	40	509	57.0	150	388	0.39	209
12	190	90	280	265	36.0	45	529	64.0	130	434	0.30	199
13	190	120	266	268	25.0	20	539	75.0	82	471	0.17	203

[a] AVE, average values obtained from wt% composition.

[b] mg KOH/g.

[c] Calculated from HV and AV.

product of 220 °C had an average HV of 286, AV of 20 and $\bar{M}_n$ of 367, but the product of 245 °C had an average HV of 221, AV of 14 and $\bar{M}_n$ of 477. Evidently, side reactions increased the AV of the products as the temperature is increased from 170 to 220 °C but at 245 °C, the reverse reaction of polycondensation was quite effective. The WSCF of 220 and 245 °C reactions was 17 and 19 wt%, respectively, indicating that after 3 h of reaction an equilibrium of products has been attained, yielding very consistent 18 ± 1% WSCF and 82 ± 1 WIF at this temperature range of 170–245 °C.

Two of the compounds which can be obtained in depolymerization of PET dissolve easily in hot water and crystallize out completely when cooled down to 4 °C. These are bis(2-hydroxyethyl) terephthalate (BHET) and mono-hydroxyethyl terephthalate (MHT), but larger oligomers may dissolve partially in hot water and pass into the WSCF. This seems to be case for glycolysis at 170 °C. The original

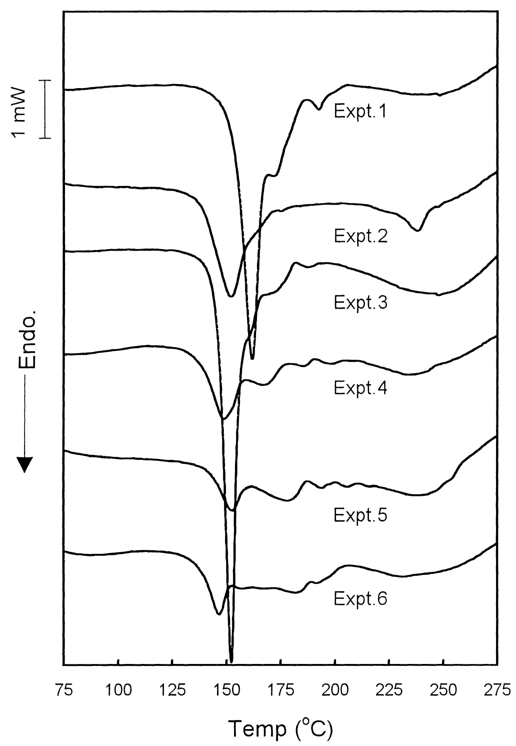

Fig. 2. DSC thermograms of WIFs of Expt. 1–6.

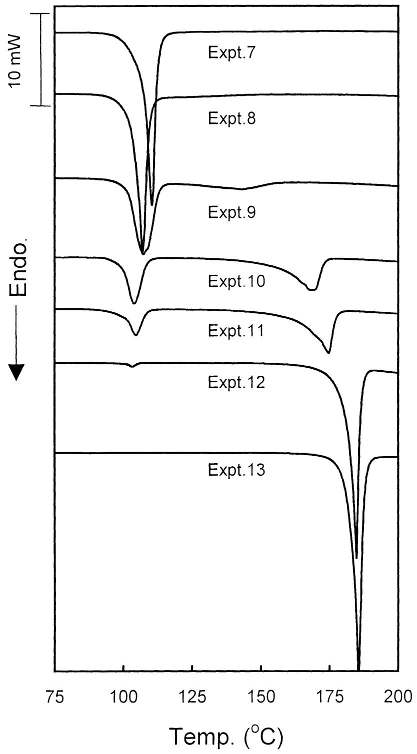

Fig. 3. DSC thermograms of WSCFs of Expt. 7–13.

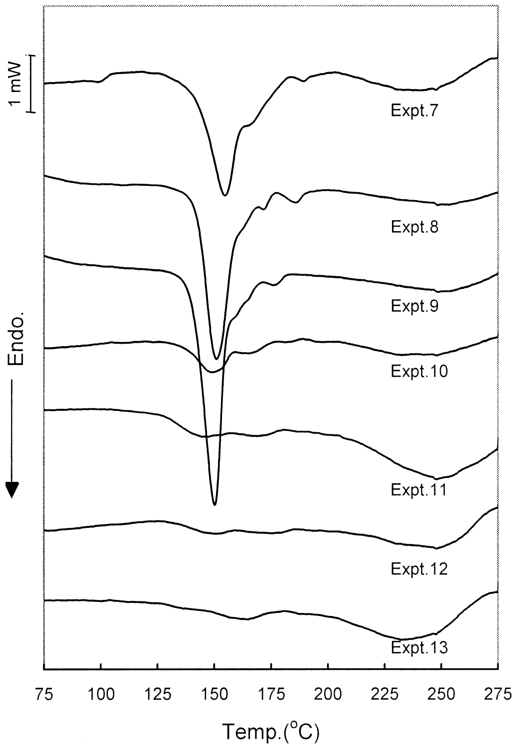

Fig. 4. DSC thermograms of WIFs of Expt. 7–13.

DSC thermogram indicates the presence of some higher molecular weight species along with BHET (which is not seen in Fig. 1 due to figure's temperature limit of 200 °C). The WIF fraction is mainly the primary condensation product of BHET, the 'dimer' H–[OCH_2CH_2O–CO–C_6H_4–CO]$_2$–OCH_2CH_2OH (the verifying HV of 252 mg KOH/g and melting point of 173 °C was reported in literature [8,16]).

Addition of 5 ml of water (Expt. 2) had an adverse effect on depolymerization, since compared with Expt. 1, WSCF decreased, $\bar{M}_n$ increased and the decrease of HV was not compensated by increase of AV (Table 1 and Fig. 5). The DSC thermogram of WIF (Fig. 2) has a peak at the high temperature range with a maximum about 240 °C, which is not present on any other DSC curve. This hampering of depolymerization reaction may be due to the negative effect of water on the solubility of the products in the xylene phase at this temperature.

Assuming that the WSCFs of Expt. 2–13 are a mixture of BHET and MHT to a very large extent, it is possible to calculate their wt% in total product from the AV and HV of these compounds and thus from the equations ($442x + 267y = \text{HV}$) and ($267y = \text{AV}$), where x is fraction of BHET and y is fraction of MHT. If the total of these fractions calculated from these equations are between 0.9–1, the amounts of BHET and MHT can be accepted to be reliable enough for an approximate estimation of the WSCF composition. Since this was not available for WSCF of Experiments 2 and 3, a plot for 170 °C is not given.

Positive effect of hydrolysis is observed by increasing the amount of water to 15 ml (Expt. 3). It is seen that %WSCF (therefore predominantly the content of BHET and MHT) as well as HV and AV of the products increase. This indicates that hydrolysis occurs mainly on the backbone of the polyester according to reaction (2) rather than splitting of EG from chain end according to reaction (5). DSC curve of WSCF does not show the presence of MHT, although AV indicates that it may constitute up to approximately 15% of WSCF. This is due to solution of MHT during the eutectic-forming melting of BHET during the DSC run, lowering the melting peak maximum only slightly from 110 to 109 °C. Further addition of water up to 90 ml (Expt. 4 and 5) produces similar results. MHT becomes visible as a peak in DSC plots of WSCF and the intensity of peak of dimer of BHET in WIF diminishes. Hydrolysis of BHET to MHT provides a dominance of this compound in WSCF, but since some of it hydrolyses to TPA, amount of WSCF in total product decreases. At 120 ml of water (Expt. 6), the amount of WSCF in total product decreases further, although the composition remains about the same as Expt. 5. The main change is in WIF composition, indicating at this level of water addition the depolymerization reaction is again out of the optimal range, if water soluble products are preferred.

At 190 °C, the reactions are similar, though the effect of hydrolysis is more dominant (Table 1 and Fig. 6). Since

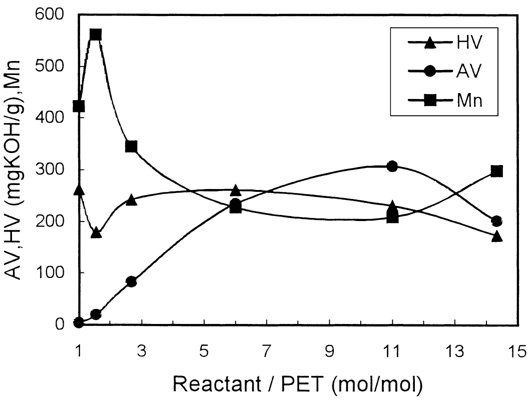

Fig. 5. Effect of the reactant/PET ratio on the HV, AV, and $\bar{M}_n$ for Expt. 1–6.

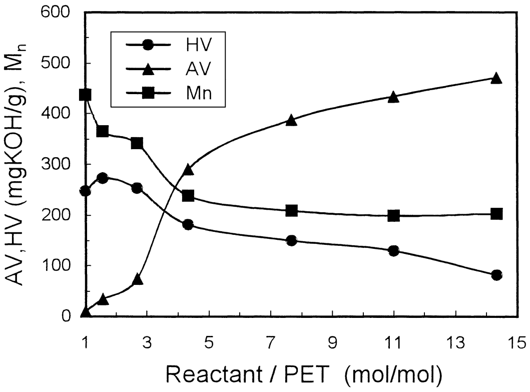

Fig. 6. Effect of the reactant/PET ratio on the HV, AV, and $\bar{M}_n$ for Expt. 7–13.

BHET/MHT balance calculations fulfilled the above-mentioned criteria, a plot of composition has been given in Fig. 7. For example, in case of addition of 5 ml of water (Expt. 8), although the HV increases with AV, BHET decreases. DSC of WSCF again does not show a peak for MHT and WIF has no peaks in high temperature range. Addition of 15 and 30 ml of water (Expt. 9 and 10) increases depolymerization and WSCF. MHT peak can be seen and BHET dimer peak in DSC thermogram of WIF diminishes in intensity. The high AV of WIF (Expt. 10) indicates significant conversion to low molecular weight intermediates and TPA. Addition of further water (60–120 ml) (Expt. 11–13) gave products (total) with lower HV, higher AV with stable $\bar{M}_n$ (Fig. 6). DSC thermograms of WSCF (Fig. 3) and Figs. 7 and 8 show the total conversion of BHET to MHT. Absence of any dominant peaks in WIF DSC thermograms as well as their low HV, show that WIF is composed of mainly TPA and carboxylated low oligomers. Another important point is that in 30–90 ml of water addition range, 35 wt% of the whole product is MHT (Fig. 7) and at 120 ml of water addition although the yield is down to 25 wt%, purity reaches nearly 100% (Fig. 8), as confirmed by AV and HV of 267 ± 1 and further by TLC and NMR of selected samples (Figs. 9–11).

TLC of WSCF of experiments 7, 11 and 13 are given in Fig. 9, where BHET appears as a fainter spot with R_f of 0.67 and MHT as a darker spot with R_f of 0.22. TLC confirms that WSCF of Experiments 7, 11 and 13 are composed BHET, BHET-MHT mixture and MHT, respectively. Likewise, the ^{1}H NMR spectra of WSCF of Expts. 7 and 13 given in Figs. 10 and 11 verify the purity of the products.

In order to confirm that the WSCFs of Expt. 7 and 13 are BHET and MHT respectively, ^{1}H NMR spectra were performed. In Figs. 10 and 11, ^{1}H NMR spectra of WSCFs of Expt. 7 and 13 in acetone-d_6 are presented. The signal at 8.14 ppm indicates the presence of the four phenyl protons. The two triplets between 4.4 and 3.8 ppm are characteristic of the methylene protons of $-COO-CH_2-$ and $-CH_2-OH$ groups.

Integrated curve intensities showed the total number of phenyl protons to be equal to number of methylene protons from the $-COO-CH_2-$ and also $-CH_2-OH$ groups of BHET as shown in Fig. 10, while the number of phenyl protons to be twice that of methylene protons from the same groups of MHT as shown in Fig. 11. TLC and NMR results confirm that the WSCFs of Expt. 7 and 13 consist mainly of BHET and MHT, respectively.

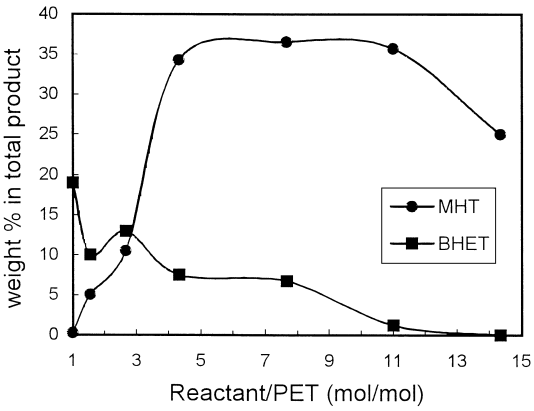

Fig. 7. Effect of reactant/PET ratio on BHET and MHT contents in total product for Expt. 7–13.

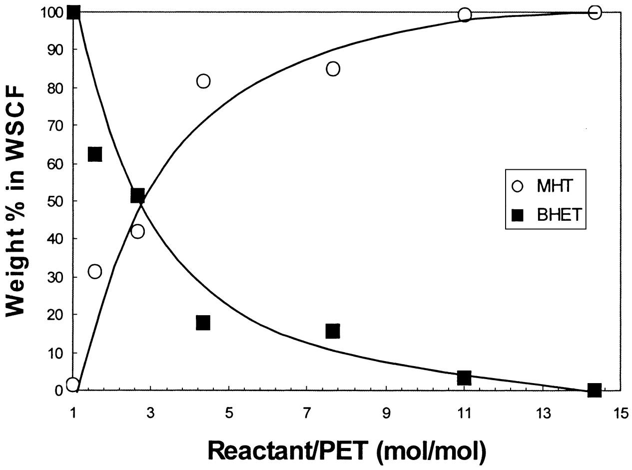

Fig. 8. Effect of reactant/PET ratio on BHET and MHT contents in WSCFs for Expt. 7–13.

None of previous research papers or patents mentions the production of MHT from waste PET with such high purity. We have also compared the polymerization tendency of the BHET (WSCF of Expt. 7) with MHT (WSCF of Expt. 13) by subjecting them to multiple heating and cooling runs at 5 °C/min under nitrogen flow (Figs. 12 and 13). It is seen that catalytic effect of carboxyl group of MHT provides a greater rate of polymerization than BHET and PET with higher melting points (indicating greater molecular weights) [20] can be obtained under the same conditions.

4. Conclusion

Simultaneous glycolysis and neutral hydrolysis of waste PET with constant amount of EG and increasing amounts of water (1 mol EG, 0–13.34 mol H_2O per mole PET) was

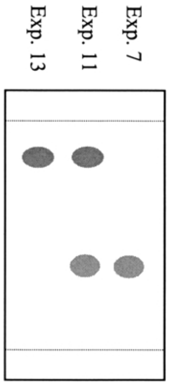

Fig. 9. Schematic TCL chromatogram of WSCFs of Expt. 7, 11, 13.

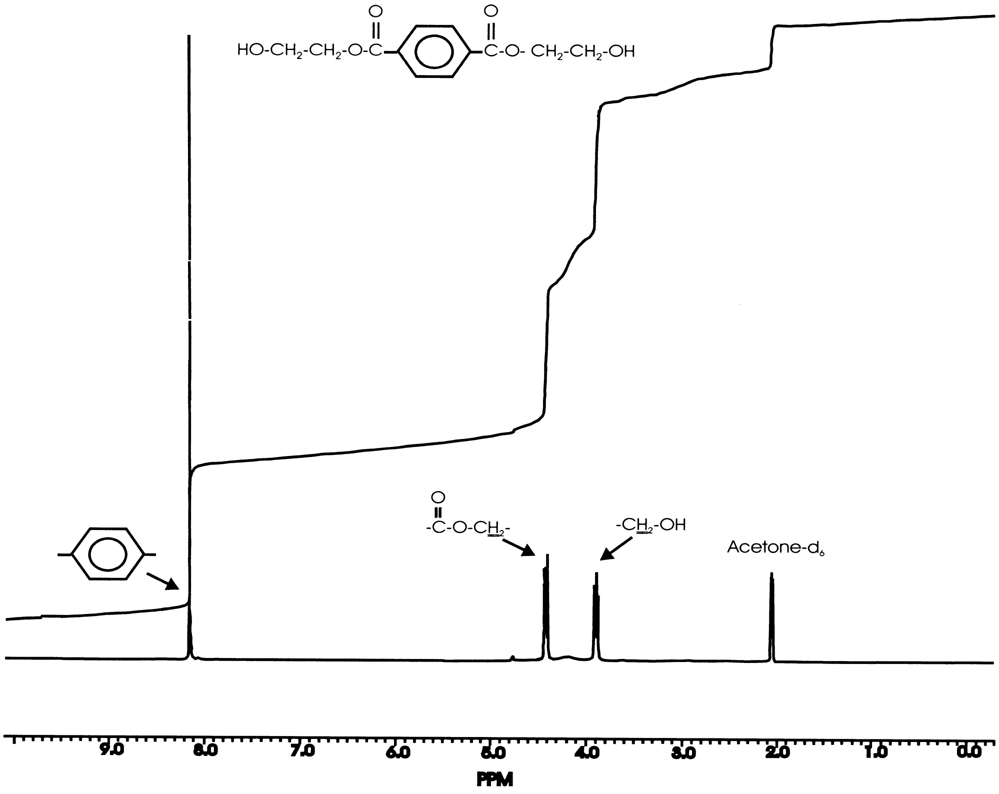

Fig. 10. ^{1}H NMR spectrum of WSCF of Expt. 7.

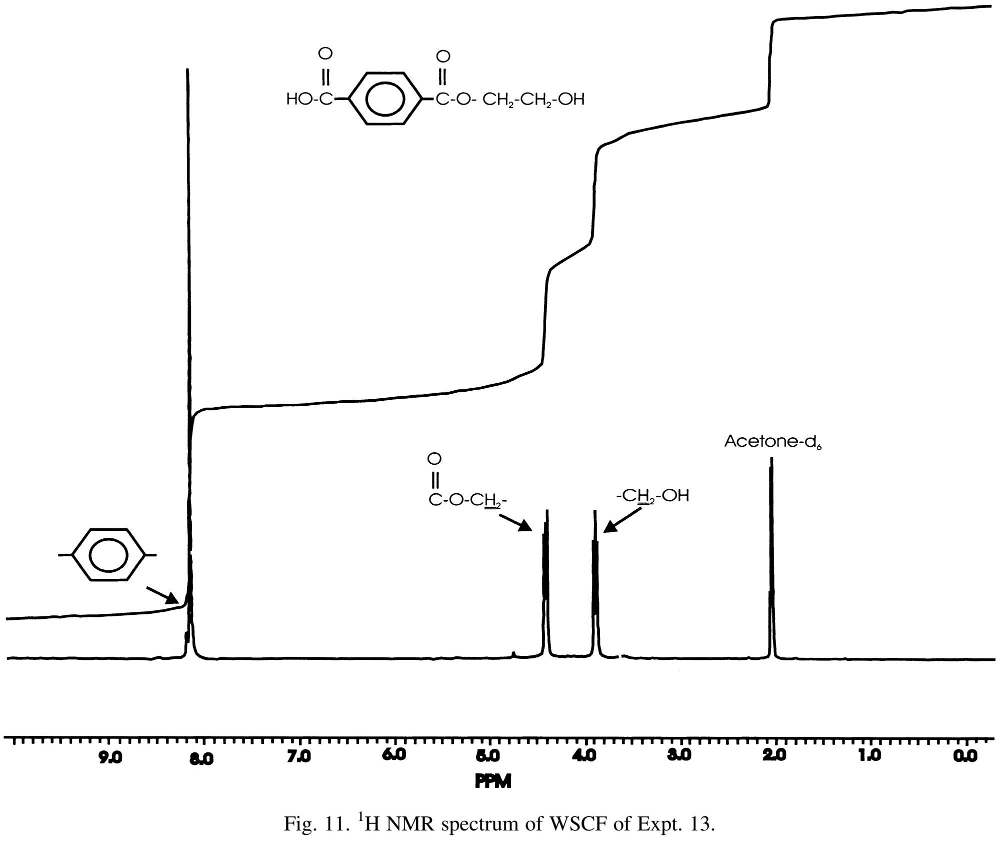

Fig. 11. ^{1}H NMR spectrum of WSCF of Expt. 13.

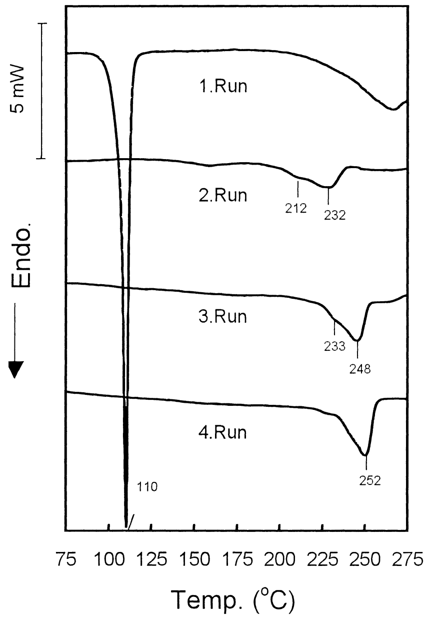

Fig. 12. Multiple DSC runs of WSCF of Expt. 7.

carried out in the presence of xylene and an emulsifier at 170 and 190 °C. The presence of this inert solvent again provided the greater degrees of polymerization at lower temperatures and pressures in comparison with previous methods.

The reaction products, when extracted with boiling water, yielded a WSCF and a WIF. These fractions were characterized by AV, HV determinations and DSC analysis. In case of pure glycolysis, WSCF was composed of mainly BHET and WIF, mainly the dimer. With application of simultaneous glycolysis and hydrolysis, WSCF was found to be mainly composed of BHET and MHT, the amount of the latter increasing with higher content of water in reactant and at higher temperature, as expected.

In case of WIF, hydrolysis decreased the amount of the dimer of BHET and increased the amount of carboxyl ended oligomers, the AV indicating the dominance of TPA in the product at 190 °C. With higher content of water in reactant providing dominance of hydrolysis in the depolymerization reaction, there was a consequent beneficial increase in WSCF yield, which reached a previously unavailable 47% at 170 °C and 43% at 190 °C. Some decrease in WSCF yield in case of very high contents of water is due to conversion BHET and MHT to water insoluble TPA, which remains in WIF fraction. But, in this case, with still a quite significant yield of 25%, the monomer MHT could be obtained with high purity, as confirmed by various analytical determinations. Multiple applications of DSC cycle indicated the superiority of MHT to conventional BHET in polymer formation, due to the catalytic effect of presence of carboxyl groups.

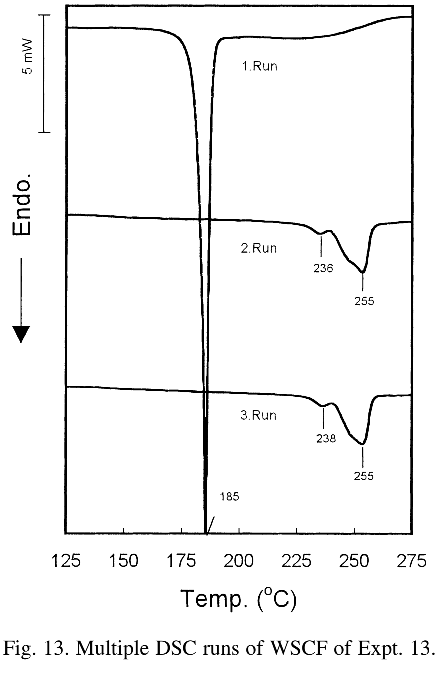

Fig. 13. Multiple DSC runs of WSCF of Expt. 13.

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