

Glycolysis of Poly(ethylene terephthalate) Wastes in Xylene

G. GÜÇLÜ,¹ A. KAŞGÖZ,¹ S. ÖZBUDAK,² S. ÖZGÜMÜŞ,¹ M. ORBAY¹

¹ İstanbul University, Engineering Faculty, Chemical Engineering Department, 34850-Avcılar, İstanbul, Türkiye

² Eczacıbaşı San. ve Tic. A. Ş. Lüleburgaz, Kırklareli, Türkiye

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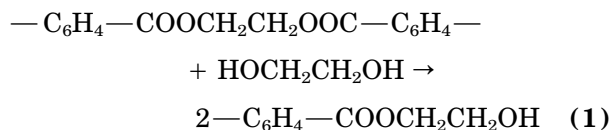
ABSTRACT: To reclaim the monomers or prepare intermediates suitable for other polymers zinc acetate catalyzed glycolysis of waste poly(ethylene terephthalate) (PET) was carried out with ethylene or propylene glycol, with PET/glycol molar ratios of 1 : 0.5–1 : 3, in xylene at 170–245°C. During the multiphase reaction, depolymerization products transferred to the xylene medium from the dispersed PET/glycol droplets, shifting the equilibrium to glycolysis. Best results were obtained from the ethylene glycol (EG) reaction at 220°C, which yielded 80 mol % bis-2-hydroxyethyl terephthalate monomer and 20 mol % dimer fractions in quite pure crystalline form. Other advantages of employment of xylene in glycolysis of PET were improvement of mixing at high PET/EG ratios and recycling possibility of excess glycol, which separates from the xylene phase at low temperatures. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 2311–2319, 1998

Key words: reaction of poly(ethylene terephthalate) (PET); glycolysis of PET; recycling of PET wastes

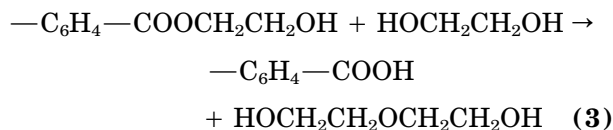
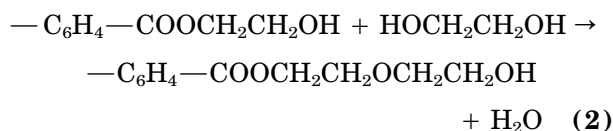
INTRODUCTION

Depolymerization of poly(ethylene terephthalate) (PET) has been widely investigated in recent years. Hydrolysis with an excess of water makes it possible to gain terephthalic acid and ethylene glycol (EG) monomers,^{1–3} where as glycolysis with excess EG yields bis-2-hydroxyethyl terephthalate (BHET) monomer and oligomers.^{4,5} In the case of glycolysis with propylene glycol (PG), depending on the PET/PG molar ratio, diol monomers or oligomers with EG or PG end group dominance could be obtained.^{6,7} These reactions are usually catalyzed with various metal salts, although zinc acetate, giving the highest rate, was preferred.^{2,4,8,9}

The main reaction in case of depolymerization with EG is (1),



where as with some etherification side reactions,¹⁰ water (2) or diethylene glycol (DEG) (3) formation could occur, giving DEG or carboxylic acid end groups, respectively.



Correspondence to: M. Orbay.

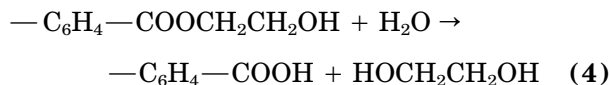
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Another important side reaction is hydrolysis by water formed or present as impurity (4).



These carboxylic acid end groups usually are later esterified with excess glycol.

Recent research on glycolysis of PET was aimed at obtaining intermediates to be used for unsaturated polyesters or polyurethanes. Vaidya and Nadkarni⁵ found 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 the free glycol removed oligomeric products were 374, 402 and 440 mg KOH/g, respectively. These values indicate that with high EG amounts, since the amount required for complete depolymerization to BHET is ~ 32 g EG for 100 g of PET, with a PET/EG molar ratio of $\sim 1 : 5$; almost pure BHET can be obtained. On the other hand, Baliga and Wong⁴ have employed a PET/EG molar ratio of 1 : 4 and have been able to attain a maximal HV of 375 mg KOH/g for the oligomeric products under similar conditions.

With the use of such high amounts of EG, the oligomeric intermediate can constitute down to only $\sim 40\%$ (w/w) of the reaction product, the rest being EG and side products. It is then reasonable to use it directly as a mixture for new polyesterifications rather than employ tedious procedures to recycle EG, but this would limit the expected contribution of terephthalate backbone to the desired properties of the new polymer.

On the other hand, from our preliminary experiments, it was observed that with low amounts of EG, as with PET/EG (w/w) of 62.5 : 37.5 (w/w) (corresponding to an approximate molar ratio of 1 : 2), until significant depolymerization has occurred, special heavy mixing equipment would be necessary in industrial applications to avoid degradation reactions. With high EG amounts there is no such problem, but if the aim is to obtain high oligomers as intermediates the initial stages of glycolysis proceeds so swiftly that polymerization to mainly BHET and dimer (97% of reaction) occurs in the first hour.⁵

In this work glycolysis of waste PET was attempted with PET/EG or PET/PG molar ratios of 1 : 0.5 to 1 : 3 in xylene, the presence of which improved mixing with low EG amounts as well as reproducibility of desired degrees of depolymer-

ization, and made it possible to reach the same monomer/dimer ratios obtained without xylene at higher PET/EG molar ratios.

EXPERIMENTAL

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 (M_v) was found to be 1.8×10^4 . Distilled water was used for extractions. The rest of the materials were Merck synthesis or analytical grade.

Glycolysis Reactions

High pressure (HP) glycolysis reactions in xylene were carried out in a 1 L stainless reactor equipped with a stirrer, thermocouple well, and cooling coil. A heating collar raised the temperature to desired value in 1 h, and the reaction was continued for 3 h.

A reaction was also carried out with a conventional 4-neck glass reactor, equipped with stirrer and reflux system at ambient pressure (AP) without xylene, for comparison purposes.

All reactions were catalyzed with 1% (w/w) zinc acetate (based on PET). The procedure for high pressure reactions was loading 100 g of PET flakes, 250 mL of xylene, catalyst, and 14.5–87 mL EG (corresponding to PET/EG molar ratios of 1 : 0.5–1 : 3), followed by reacting at 170, 220 and 245°C. The reactor and contents were cooled to ambient temperature in 20 min by circulating water through cooling coils and immersion in running cold water. A series of glycolysis reactions was also conducted with 18.75–112.5 mL PG (corresponding to PET/PG molar ratios of 1 : 0.5–1 : 3) at 220°C.

Filtration of the product separated the liquid xylene phase from the hydrophylic solids which absorbed EG, except at very high molar ratio of 1 : 3. Even in those cases, EG separated from xylene, forming layers, due to its low solubility in xylene. The solid phase, in the case of HP reactions, was extracted by 1 L water at the boiling point $\times 3$. The remaining solid was named water insoluble fraction (WIF). The filtrates were cooled to 4°C and crystallized solids obtained by filtration was named water soluble crystallizable frac-

Table I Effect of PET/EG Molar Ratio on Glycolysis of PET at 170°C with EG in Xylene

Reaction No.	PET/EG Molar Ratio	Analysis of Products							
		Composition (%w/w)		Acid Value (AV)			Hydroxyl Value (HV)		
		WIF ^a	WSCF ^b	WIF	WSCF	AVE ^c	WIF	WSCF	AVE
1	1 : 0.5	92	8	11	10	11	150	422	186
2	1 : 1	83	17	4	2	4	240	369	262
3	1 : 1.5	63	37	7	10	8	234	375	286
4	1 : 3	33	67	8	4	5	197	380	320

^a WIF, water insoluble fraction.

^b WSCF, water soluble crystallizable fraction.

^c AVE, average value obtained from %w/w composition.

tion (WSCF). WIF and WSCF were dried under vacuum at 30–40°C.

In the case of the AP reaction, the contents of the reactor were heated to 195°C in 30 min and the reaction was continued for 6 h at this temperature. WIF and WSCF were obtained similarly, by extraction of the reaction mixture.

Analysis

Since all of the reaction product fractions dissolved in pyridine, the acid values (AV)¹¹ and hydroxyl values (HV)¹² were determined from pyridine solutions.

DSC scans were obtained with Perkin DSC-7 calorimeter with 10 mg samples by heating up to 275°C with a rate of 5°C/min in air.

RESULTS AND DISCUSSION

Glycolysis Reactions

PET was previously depolymerized by glycolysis with EG by various researchers down to monomer and dimer stage.^{4,5} The main goal of the use of xylene in this article was initially to provide mixability to the PET-glycol mixture, especially with high PET/EG molar ratios, such as 1 : 0.5. Preliminary experiments have shown that EG dissolves in xylene sparingly, even at temperatures as high as 225°C. On the other hand, EG dissolves PET quite readily above 170°C. Thus the glycolysis reaction in our case was conducted in PET-EG droplets dispersed in xylene, especially during the initial stage. But, glycolysis products (especially the monomer BHET) have higher solubility in xylene

Table II Effect of PET/EG Molar Ratio on Glycolysis of PET at 220°C with EG in Xylene

Reaction No.	PET/EG Molar Ratio	Analysis of Products							
		Composition (%w/w)		Acid Value (AV)			Hydroxyl Value (HV)		
		WIF ^a	WSCF ^b	WIF	WSCF	AVE ^c	WIF	WSCF	AVE
5	1 : 0.5	97	3	28	144	32	220	200	219
6 ^d	1 : 0.5	99	1	15	97	16	150	187	150
7	1 : 1	83	17	22	11	20	257	425	286
8	1 : 1.5	63	37	10	7	9	250	430	317
9	1 : 3	33	67	5	5	5	235	435	369

^a WIF, water insoluble fraction.

^b WSCF, water soluble crystallizable fraction.

^c AVE, average value obtained from %w/w composition.

^d All reactants and xylene were dried for this experiment.

Table III Effect of PET/EG Molar Ratio on Glycolysis of PET at 245°C with EG in Xylene

No.	Reaction PET/EG Molar Ratio	Analysis of Products							
		Composition (%w/w)		Acid Value (AV)			Hydroxyl Value (HV)		
		WIF ^a	WSCF ^b	WIF	WSCF	AVE ^c	WIF	WSCF	AVE
10	1 : 0.5	98	2	23	230	25	110	177	111
11	1 : 1	81	19	13	20	14	155	387	221
12	1 : 1.5	69	31	10	15	12	280	390	314
13	1 : 3	37	63	5	15	11	177	368	298

^a WIF, water insoluble fraction.

^b WSCF, water soluble crystallizable fraction.

^c AVE, average value obtained from %w/w composition.

at high temperatures. Thus, as the reaction proceeds, part of the product oligomers transfer to xylene phase PET-oligomer/EG ratio decreases, shifting the equilibrium to depolymerization.

Other advantages of xylene were the ease of separation of oligomers and excess EG and purity of the products, since most of the degradation products dissolved in the xylene phase.

All of the intermediates were soluble in pyridine, and extent of depolymerization was followed by HV and AV determinations of two different fractions. Extraction by hot water, followed by crystallization of the product, yielded a WSCF, which was mainly monomer BHET, and WIF, which was mainly dimer and trimer. The results are summarized in Tables I–V.

Glycolysis products, as expected, had low AV and high HV although depending on reaction temperature and PET/glycol ratio, monomer/oligomer molar ratios showed great changes.

Reaction products of 170°C (Table I) had low AV of 2–11 mg KOH/g and the average HV as well as WSCF increased significantly with an increase in the amount of EG employed. The HV of WSCF indicates that some dimer was also extracted. High AV at 220°C at high PET/EG ratios indicate that significant hydrolysis also occurs during the reaction (reaction 5, Table II). This is partly due to humidity of PET and water content of reactants, since AV decreases when the PET, EG, and xylene is dried (reaction 6). Lower WSCF, as well lower HV, in the latter case, show that hydrolysis due to even very low water content contributed to depolymerization. Higher than normal AV also confirms other side reactions, beside hydrolysis, in case of dried reactants. As the PET/EG molar ratio decreased, AV decreased to normal low values and both HV and amount of WSCF increased, similar to 170°C reactions.

The effect of hydrolysis was again evident at

Table IV Effect of Reaction Time on Glycolysis of PET at 220°C with EG in Xylene at PET/EG Molar Ratio of 1 : 1

No.	Reaction Time (h)	Analysis of Products							
		Composition (%w/w)		Acid Value (AV)			Hydroxyl Value (HV)		
		WIF ^a	WSCF ^b	WIF	WSCF	AVE ^c	WIF	WSCF	AVE
14	1	79	21	17	33	20	278	348	293
15	2	78	22	12	12	12	250	360	274
7	3	83	17	22	11	20	257	425	286

^a WIF, water insoluble fraction.

^b WSCF, water soluble crystallizable fraction.

^c AVE, average value obtained from %w/w composition.

245°C reactions (reaction 10, Table III) although the increased rate of esterification at this temperature provided lower average AV than those found for 220°C oligomers. But at low PET/EG ratios, the AV was higher than 170°C or 220°C reaction oligomers. The effect of equilibrium with reverse reaction, that is, polymerization also decreased the attainable average HV to lower values than those for 170 and 220°C reactions.

The change of AV and HV with reaction time at 220°C (Table IV) again shows that hydrolysis is a competing reaction. Such small fluctuations of average HV has also been observed by Baliga and Wong.⁴ It is interesting that the amount of WSCF decreases but its HV increases with time.

A preliminary experiment¹³ was also carried out at 195°C ambient pressure with PET/EG molar ratio of ~ 1 : 5.2, (37.5 : 62.5, % w/w) in the absence of xylene according to the procedure employed by Vaidya and Nadkarni,⁵ but with 1% zinc acetate instead of 0.5%. Samples obtained at 1, 3, 5, and 6 h had HV of 193, 233, 235, and 239 mg KOH/g for WIF, 394, 415, 423, and 430 for mg KOH/g for WSCF, and 354, 379, 385, and 392 mg KOH/g average, respectively. Although reaction time was ~ 2 h shorter, the catalyst concentration was double and at the end of the reaction, the average HV of 440 found by Vaidya and Nadkarni was unattainable, confirming that it is extremely unlikely to obtain pure BHET as suggested by these authors, since some dimer must exist in equilibrium, even at such high PET/EG molar ratios. Supportingly, Baliga and Wong⁴ reached only a HV of 375 mg KOH/g at the end of 4 h at a PET/EG molar ratio of 1 : 4, which is lower than the ratio used for this ambient pressure depolymerization.

Oligomers obtained from all EG glycolysis reactions were fine powders but the oligomers obtained from PG glycolysis reactions were, except for the highest PET/PG molar ratio, viscous liquids. In those cases, again in contrast with Vaidya and Nadkarni's work,^{6,7} hot water extraction did not yield WSCF, although consecutive concentration and chilling was carried out repeatedly. In the case of WIF, as expected, HV increased with a decrease of PET/PG molar ratio. The theoretical HV of six probable dimers containing EG, PG, or both EG and PG groups are between 234 and 251.5. Thus it is not possible to predict the structure from HV determinations. It is also probable that some monomers have not been extracted from the organic phase by hot water.

DSC Characterization

Glycolysis of PET should yield oligomers with hydroxyl end groups, although the above results show that due to side reactions, some with carboxyl end groups are also formed.

The melting points of PET oligomers of $H(OCH_2-CH_2OOC C_6H_4CO)_nOCH_2CH_2OH$ structure were previously determined to be 109–110°C, 173–174°C, 200–205°C, 213–216°C, and 218–220°C for $n = 1-5$, respectively. For oligomers of $H(OCH_2-CH_2OOC C_6H_4CO)_nOH$ type, the melting points were higher: 178°C, 200–205°C, and 219–223°C for $n = 1-3$, respectively.^{14,15}

Baliga and Wong,⁴ who prepared similar WSCF and WIF from PET glycolysis, found sharp melting peak maxima of 110.5 and 162°C for monomer (BHET) and its dimer. The glycolysis product, a mixture of these fractions, yielded a

Table V Glycolysis of PET at 220°C with PG in Xylene

No.	Reaction PET/PG Molar Ratio	Analysis of Products							
		Composition (%w/w)		Acid Value (AV)			Hydroxyl Value (HV)		
		WIF ^a	WSCF ^b	WIF	WSCF	AVE ^c	WIF	WSCF	AVE
16	1 : 0.5	98	2	18	165	21	107	110	107
17	1 : 1	— ^d	—	16	—	—	184	—	—
18	1 : 1.5	—	—	4	—	—	245	—	—
19	1 : 3	—	—	4	—	—	245	—	—

^a WIF, water insoluble fraction.

^b WSCF, water soluble crystallizable fraction.

^c AVE, average value obtained from %w/w composition.

^d —, no WSCF was isolated in experiments 17–19.

broader, but reasonably sharp peak with a maximum of 106°C and a very much broader peak centered about a maximum of 148°C. The authors believed that this shift of peak maxima to lower temperatures indicated "some interactions between the monomer and dimer at elevated temperatures."

Figure 1 shows the DSC scans of WSCF of 170°C reactions. Sharp maxima of 104–107°C due to BHET are somewhat in contrast with low hydroxyl values (Table I) in two cases. The exothermic peak ~ 70°C is probably due to a crystalline phase transition and was not observed in other oligomer product DSC scans.

DSC scans given in Figure 2 show multiple peaks for 170°C WIF, indicating the presence of higher oligomers as well as some unextracted monomer or presence of diethylene glycol end groups. Dimer peaks with maxima ~ 150°C in-

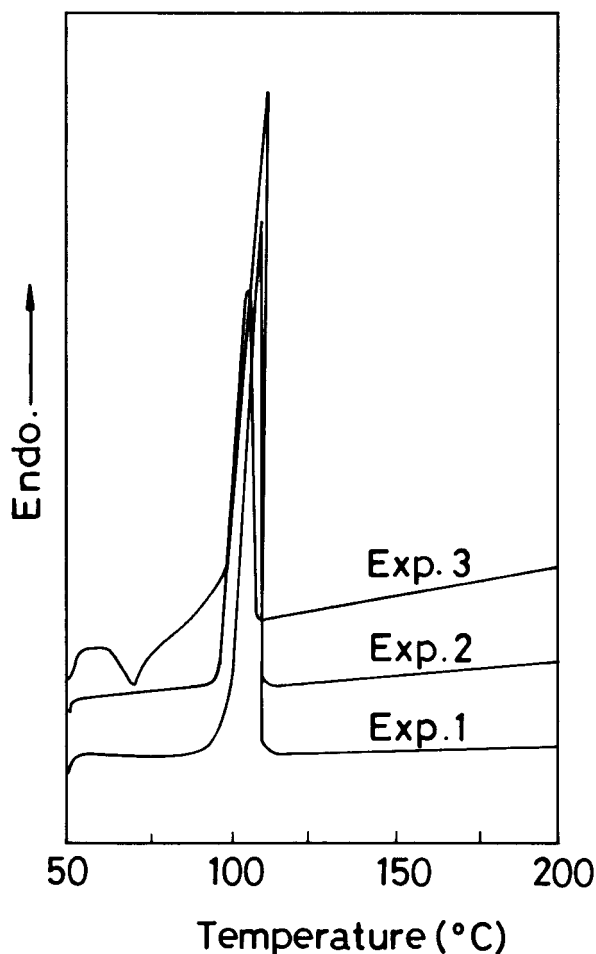


Figure 1 DSC scans of WSCF at 170°C.

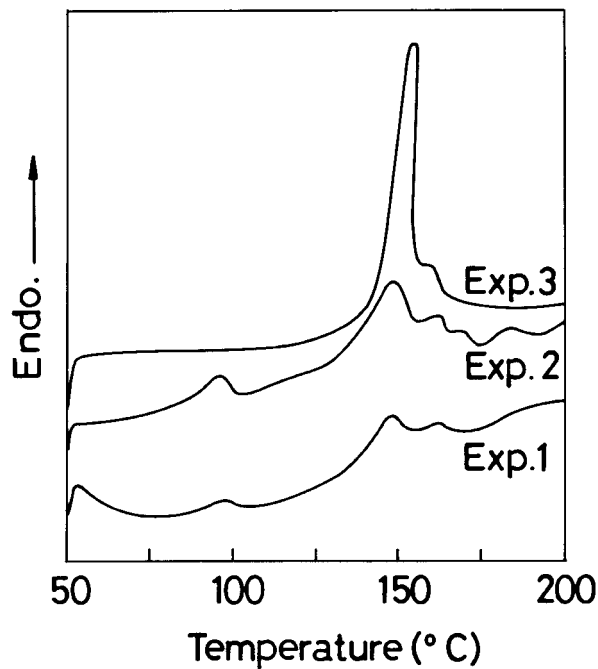


Figure 2 DSC scans of WIF at 170°C.

crease in intensity with higher amounts of EG employed in the reaction. When the fractions were homogenized by grinding at the weight ratios where they were obtained (Fig. 3), even at 8 and

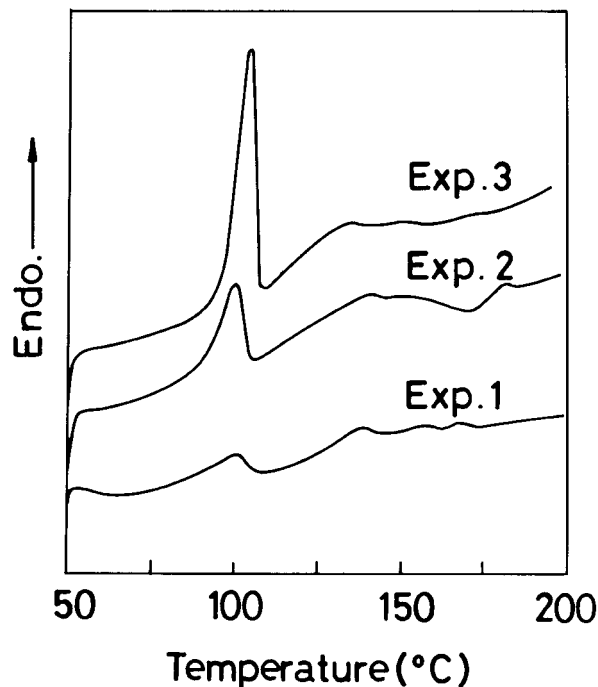


Figure 3 DSC scans of mixture products (WSCF/WIF) (w/w) at 170°C.

17% WSCF, the dominance of BHET peak is significant. Dimer and higher oligomer peaks shift to much lower temperatures and their intensity is also quite less than pure fractions. This must be due to the fact that, as BHET starts to melt, dimer and part of higher oligomers start to dissolve in molten monomer, decreasing the peak maxima to 99–101°C. A further increase in temperature causes more oligomers to dissolve, flattening the dimer peak and lowering the maximum temperatures to 132–138°C. It seems that the solubility of higher oligomers in molten monomer-dimer mixture is quite low, since small peaks or shoulders ~ 145–183°C can still be observed, although their high HV indicate that their amount in the product is small.

For the reactions carried out at 220°C the DSC scans of WSCF (Fig. 4), due to higher purity of

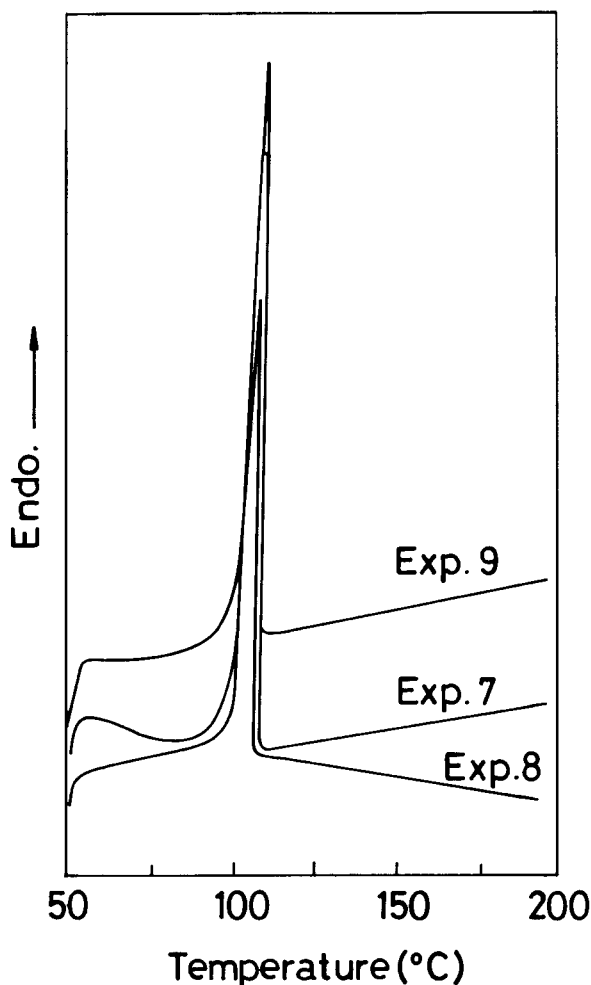


Figure 4 DSC scans of WSCF at 220°C.

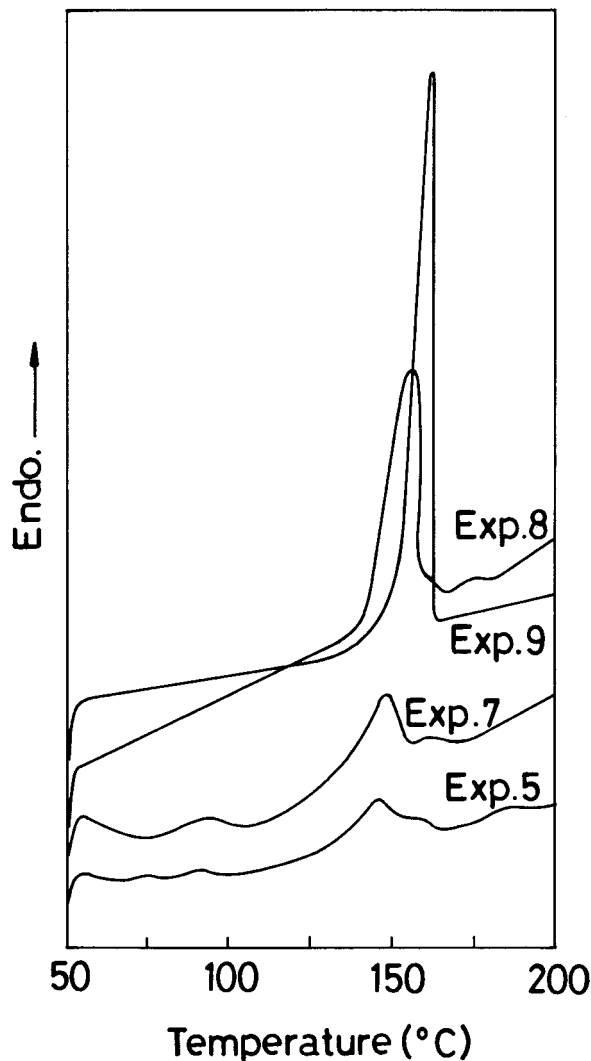


Figure 5 DSC scans of WIF at 220°C.

BHET (HV of 425–435 mg KOH/g), have sharp peaks at 106–108°C, WIF scans (Fig. 5) indicate that the oligomers similar to those obtained at 170°C reactions have been obtained. With lowest PET/EG molar ratio, both the DSC plot and (a single peak with a maximum temperature of 160°C) and HV (235 mg KOH/g) confirm that WIF, in this case, was quite pure dimer. These results show that pure BHET and its dimer can be obtained at a molar ratio of ~ 80 : 20 with a lower amount of EG (at a PET/EG molar ratio of 1 : 3 versus 1 : 4) used in Baliga and Wong's⁴ work.

Figure 6 shows the above-mentioned dissolving of oligomers in molten BHET with similar shifts of peak maxima to lower temperatures.

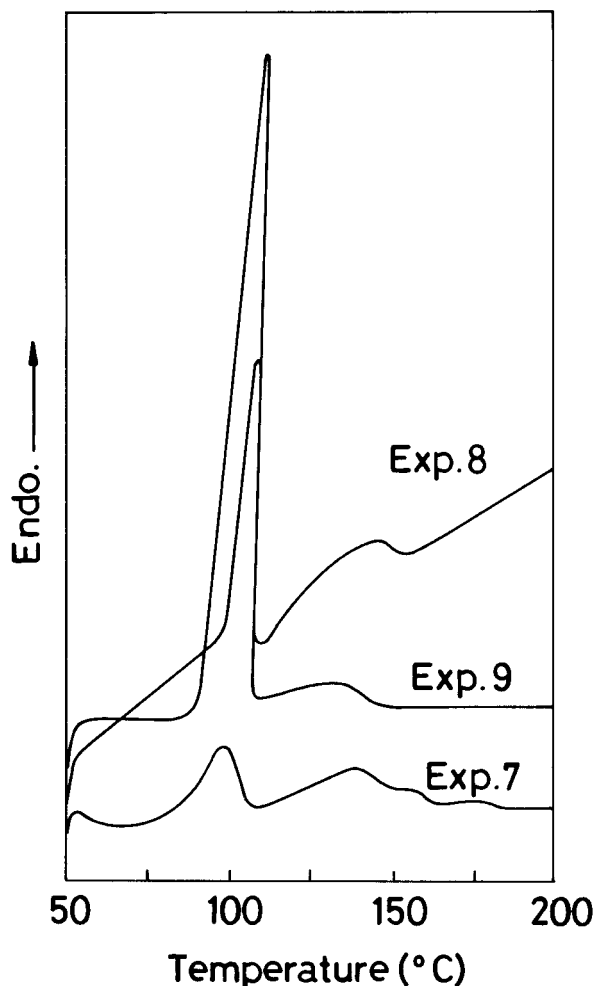


Figure 6 DSC scans of mixture products (WSCF/WIF) (w/w) at 220°C.

The absence of significant amounts of oligomers greater than dimers was again evident for a PET/EG molar ratio of 1 : 3, since no additional peaks at higher temperatures can be observed.

CONCLUSIONS

Glycolysis of PET in xylene was a multiphase reaction, where transfer of oligomers formed from dispersion of PET/glycol droplets to xylene medium at elevated temperatures was possible. This, in turn, provided a shift of the equilibrium to depolymerization due to removal of the monomer and, in part, the dimer, lowering the amount of

EG necessary to provide the desired degree of depolymerization. The solubility of lower oligomers changed with temperature and purified products could be obtained by precipitation at low temperatures.

During the glycolysis reaction, water present as impurity or formed by side reactions caused a significant amount of hydrolysis, especially at higher temperatures and low amounts of glycol.

In case of EG, the ratio of water soluble crystallizable fraction of mainly monomer BHET and water insoluble fraction of dimer and higher oligomers were dependent mainly on PET/glycol ratio rather than temperature. Of the three temperatures employed, 220°C gave the best monomer/dimer ratio. At 170°C, amount of higher oligomers were significant due to low degree of glycolysis, whereas at 245°C reverse reaction of polymerization was effective.

PG glycolysis was not as successful as EG, since no water soluble crystallizable fraction was obtainable with higher amounts of PG, in contrast with previous literature.

Other advantages of xylene were improved stirring of reaction medium at high PET/EG ratios and separation of excess glycol in concentrated form and ready for reuse in the case of a high amount of glycol employment, whereas with homogeneous depolymerization in glycol this is not possible.

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