EVIDENCE FOR THE FORMATION OF ETHER LINKAGES DURING THE SYNTHESIS OF POLY(ETHYLENE PHTHALATE)

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Abstract—^{13}C-NMR, both solution and solid-state (CP/MAS) and ^{1}H-NMR evidence for the formation of ether linkages during the synthesis and thermal degradation of poly(ethylene phthalate) is presented. The facile elimination of phthalic anhydride is evident during the polymerization of dimethyl phthalate and ethylene glycol and is characterized by FTIR and HPLC. Qualitative analysis of elimination products did not detect acetaldehyde, an expected product of the thermal degradation of polyesters, at the reaction temperature employed.

INTRODUCTION

Poly(ethylene phthalate), PEP, is a non-crystallizable polyester with T_g in the region of 38–40°. It can be synthesized by the condensation polymerization of dimethyl phthalate (DMP) and ethylene glycol (EG) in the presence of small amounts of metal salts which act as transesterification catalysts. In these experiments, a combination of zinc diacetate dihydrate, $Zn(CH_3COO)_2 \cdot 2H_2O$, antimony trioxide, Sb_2O_3, and phosphorous acid was employed.

Under normal procedures, the initial ester exchange reaction takes place at temperatures up to the boiling point of ethylene glycol (197°). The zinc salt is recognized as a very efficient catalyst for the production of low molecular weight polyester [1]. However, at the higher temperatures required for the formation of high polymer by further transesterification, it is known to promote undesirable side-reactions such as the formation of ether linkages [2]. The role of the phosphorus compound added after the first stage is therefore to inactivate the zinc catalyst so that the degree of ether formation is minimized. For the second stage of reaction, Sb_2O_3 is an effective transesterification catalyst which is unaffected by the catalytic inhibitor and is not reported to encourage ether formation [3].

EXPERIMENTAL PROCEDURES

DMP, dimethyl isophthalate (DMI) and EG were purchased from Aldrich. DMP and DMI were used as supplied. EG was predried over activated molecular sieve grades 3B; all glassware in contact with the reagents was flame-dried. The assembled vapour bath apparatus [4] in which the polymerization was performed was purged with N_2 and evacuated three times. Such precautions were considered necessary as it has been reported [5] that the presence

of moisture has a detrimental effect on development of molecular weight.

Synthesis and characterization of PEP and associated elimination products

DMP (50 g, 0.258 mol) and EG (40 g, 0.645 mol excess) were polymerized in a two-stage reaction such as that employed for a standard melt polymerization. $Zn(CH_3COO)_2 \cdot 2H_2O$ (0.05 g) and Sb_2O_3 (0.06 g) were added in accordance with normal procedures. Mixing of reagents was achieved by the use of a dry N_2 bubbler which provided both an inert atmosphere and an effective purge for condensation products. The reagents were heated in the vapours of EG gradually over a period of 2 hr or until no more methanol was collected.

The second stage of the reaction involved heating the low molecular weight polyester in the vapours of DMP (b.p. 282°) for 2 hr and then with full immersion in the hot vapours for a further 1 hr with vacuum application (<0.01 mbar) to remove residual EG and produce high molecular weight polymer. Phosphorus acid (2 drops) was added on commencement of the polycondensation to inactivate $Zn(CH_3COO)_2 \cdot 2H_2O$ for the reasons explained previously. A substantial amount of a white crystalline sublimate formed in the still head/receiver adaptor during the vacuum cycle and continued to form until the termination of the polymerization. The viscous product was cast in a PTFE mould and allowed to cool to room temperature in a desiccator. All products eliminated from the reaction were kept in air tight bottles for analysis. This synthetic procedure was repeated in exactly the same manner with DMI and EG so that the configurations of PEP and poly(ethylene isophthalate) (PEI) could be compared.

Polymer characterization

Solution viscosity was determined in a 60:40 v/v% phenol:1,1,2,2-tetrachloroethane mixture at $25 \pm 0.05°$ using solutions in the concentration range 0.1–0.5 g · dl^{-1}.

Microscopic observations to evaluate softening, flow and decomposition temperatures were carried out using a Stanton-Redcroft Hot Stage (Type TH600) at a heating rate of 10° min^{-1}.

Solution state NMR spectra were obtained on a GEC 300 MHz instrument at room temperature in CDCl$_3$ using TMS as internal standard. Solid state NMR was performed on a Varian VXR 300 MHz instrument with a ^{13}C-resonance

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Table 1. Summary of NMR spectral data

Polymer	Chemical shift (δ) (ppm)(plus splitting)	Assignment
PEP	62.9	C_9,C_{10}
^{13}C-NMR	64.4	C_{11},C_{13}
(CDCl$_3$)	68.5	C_{12},C_{14}
	70.2	C_{15}
[see Fig. 2(a)]	128.7	C_1,C_6
	131.3 (-0.4 to $+0.2$)	C_2,C_3
		C_4,C_5
	167.0 (-0.2 to $+0.1$)	C_7,C_8
PEP	52.9	Methyl
^{13}C-NMR		phthalate
(CP/MAS)		end group*
	66.7, broad with	C_9,C_{10}
	shoulders at	
[see Fig. 3]	70.7 and 77.3	C_{11},C_{13}
		C_{12},C_{14},C_{15}
	129.7, broad	C_2,C_3,C_4,C_5
	132.0, broad with	C_1,C_6
	shoulders at	
	128.7 and 134.0	
	106.7, broad	C_7,C_8
PEP	3.84	H_b
^{1}H-NMR	(0.09)	
(CDCl$_3$)		
	4.49	H_a
	(0.09)	
[see Fig. 4]		
	7.51, 7.72	H
PEI	62.8	C_9,C_{10}
^{13}C-NMR	64.1	C_{11},C_{13}
(CDCl$_3$)	68.9	C_{12},C_{14}
	70.4	C_{15}
[see Fig. 2(b)]	128.6 (-0.1 to $+0.1$)	C_1,C_2,C_3
	130.1 (-0.1 to $+0.2$)	———
	130.8 (-0.05 to —)	
	133.9 (-0.1 to $+0.4$)	———
	165.2	C_4,C_5,C_6
		C_7

*Only in this particular sample.

frequency of 75.4 MHz. Samples were spun at the magic angle at a speed of 5 kHz with a cross-polarization (CP) contact time of 1 msec at room temperature. Use of dephasing experiments [6] offered a means of discriminating between protonated (P) and nonprotonated (or quaternary, Q) carbons.

Characterization of elimination products

The nature of the elimination products was investigated using FTIR and HPLC. All FTIR measurements were made on a Perkin–Elmer 1725X spectrometer at a resolution of 4 cm^{-1} averaged over 20 scans. HPLC was performed on solutions of the elimination products and solvent extracted fractions of the bulk polymer using a Pye–Unicam LC-XPD pump on a normal phase column at a flow rate of 1.3 ml·min^{-1} and a pressure of 630 psi. Eluted fractions were detected on a LC-u.v. detector at $\lambda_{max} = 250$ nm using a 70:30%v/v hexane:dioxane carrier solvent. Blanks were run on pure samples of phthalic anhydride and DMP.

Condensation and elimination products were qualitatively tested for the presence of acetaldehyde, a possible by-product of the thermal degradation of vinyl-ester end-groups [7], by reactions with 2,4-dinitrophenylhydrazine, 2,4-DNPH and Schiff's reagent [8].

RESULTS AND DISCUSSION

Solution viscosity measurements produced values of [η] which ranged from 0.10 to 0.60 depending on the time of reaction, the maximum temperature employed and the degree of vacuum achieved. Although it was difficult to determine exactly the

optimum reaction conditions, it was apparent that the reaction temperature of 282° and an applied vacuum of <0.01 mbar encouraged the elimination of phthalic anhydride in the PEP system. Formation of this stable cyclic during the second stage of reaction was slow up to the point of application of vacuum conditions, whereupon the rate of sublimation was similar to the rate of elimination of EG.

Thermal analysis of PEP which had been stored at room temperature for one week revealed a strong T_g in the region of 38–40° (Fig. 1). Quenching from above T_g to dry-ice temperatures and subsequent reheating altered the pseudo first-order peak to a classical second-order inflection. Such a phenomenon can be attributed to a natural physical ageing process [9]. The absence of further detectable phase transitions up to the point of decomposition, at ca 300°, indicated the amorphous nature of PEP.

Observations on the hot-stage microscope indicated the onset of softening at around 40°, corresponding to the T_g as measured by DSC. No clear melting point was observed and the material displayed a decrease in viscosity as a function of temperature. With crosspolarizers in place, non-birefringence of the soft plastic indicated isotropic characteristics above T_g as would be expected for a non-crystalline material.

NMR evidence for the formation of ether linkages

^{13}C-NMR provided the most interesting information as to the configurational nature of PEP due to the presence of extra peaks at 68.5 and 70.2 ppm in the solution state spectrum [Fig. 2(a)] not associated with ethylenic ester resonances, —COOCH$_2$CH$_2$COO—, which are normally observed below 66 ppm [10] in the common solvents. In
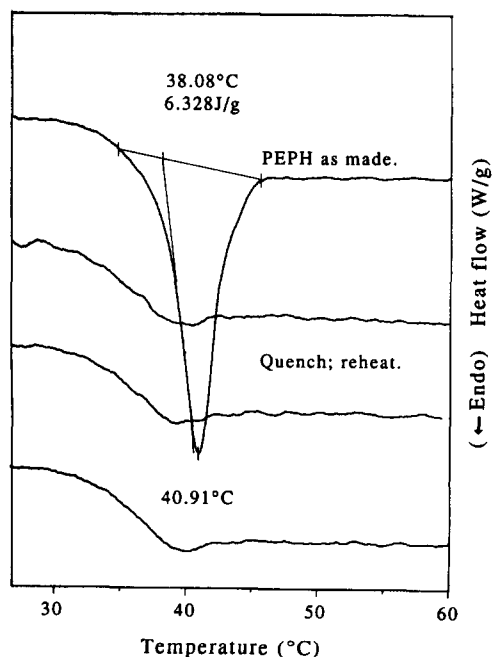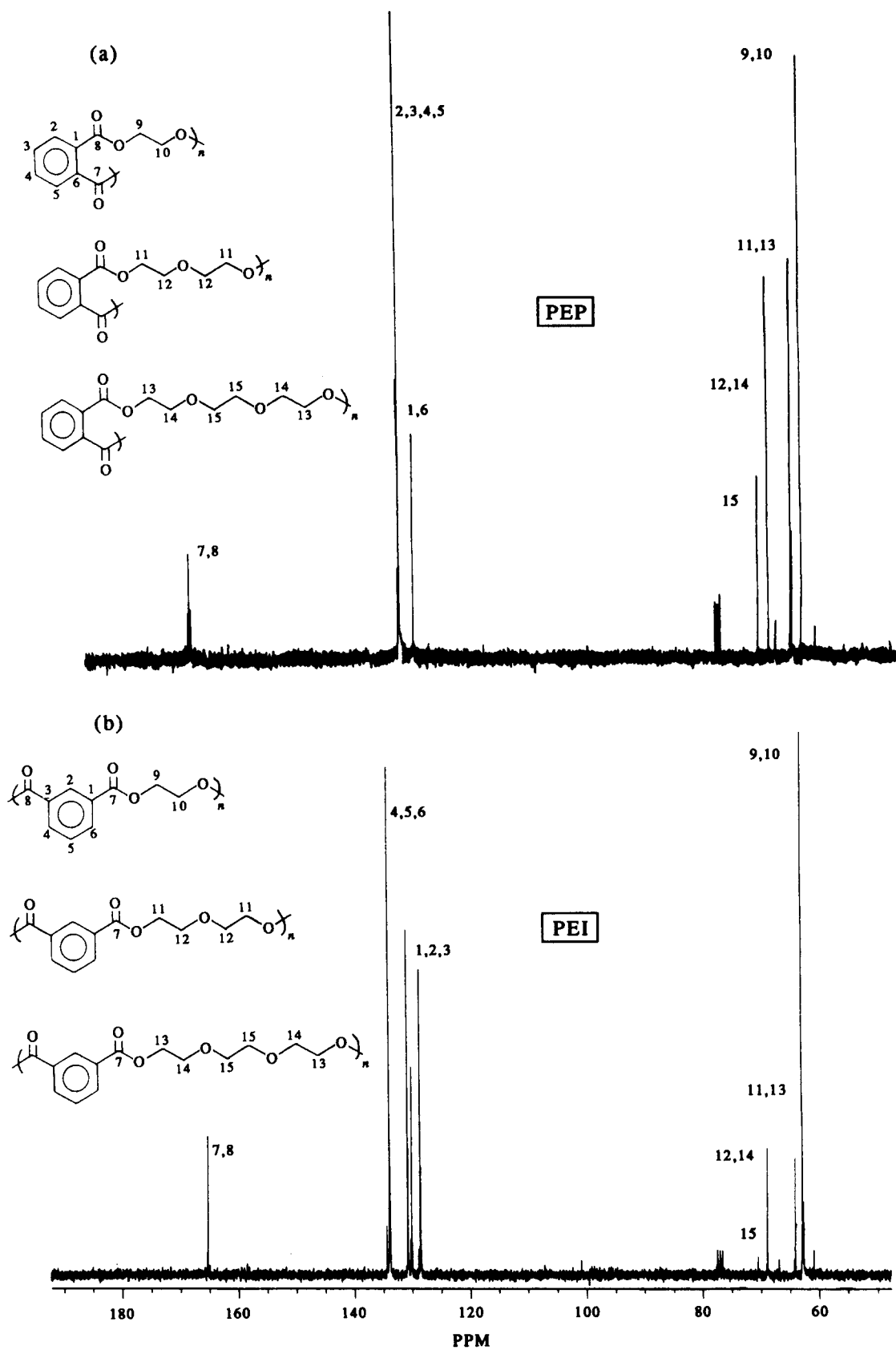

Fig. 1. DSC profile of the T_g of PEP. (a) Preheat, 10° min^{-1}, (b) reheat following a 20 min isothermal soak and quench, (c) second reheat, (d) third reheat.

Fig. 2. ^{13}C-NMR of (a) PEP, (b) PEI, both in CDCl$_3$.

the spectrum of PEI, [Fig. 2(b)] the same peaks were also present but to a much lesser extent. Reference to the model spectrum of triethylene glycol (TEG) in $CDCl_3$ [11] indicated the chemical shifts of ether carbons, —OCH_2CH_2O— at 70.3 ppm which corresponded to the shift at 70.2 ppm in Fig. 2. Presumably the other peaks at 68.5 and 68.9 ppm for PEP and PEI respectively, were ether carbons subject to the shielding effect of vicinal ester groups, —$COOCH_2CH_2OCH_2CH_2OOC$—. Careful analysis of the model spectra of selected ether compounds indicated the chemical shifts of carbon atoms shielded by methyl groups such as those in diethylether [12], $CH_3CH_2OCH_2CH_3$ and 2-ethoxy ethanol [13], $CH_3CH_2OCH_2CH_2OH$, at 66.0 and 66.7 ppm, respectively, and at 72.7 ppm in TEG for carbons
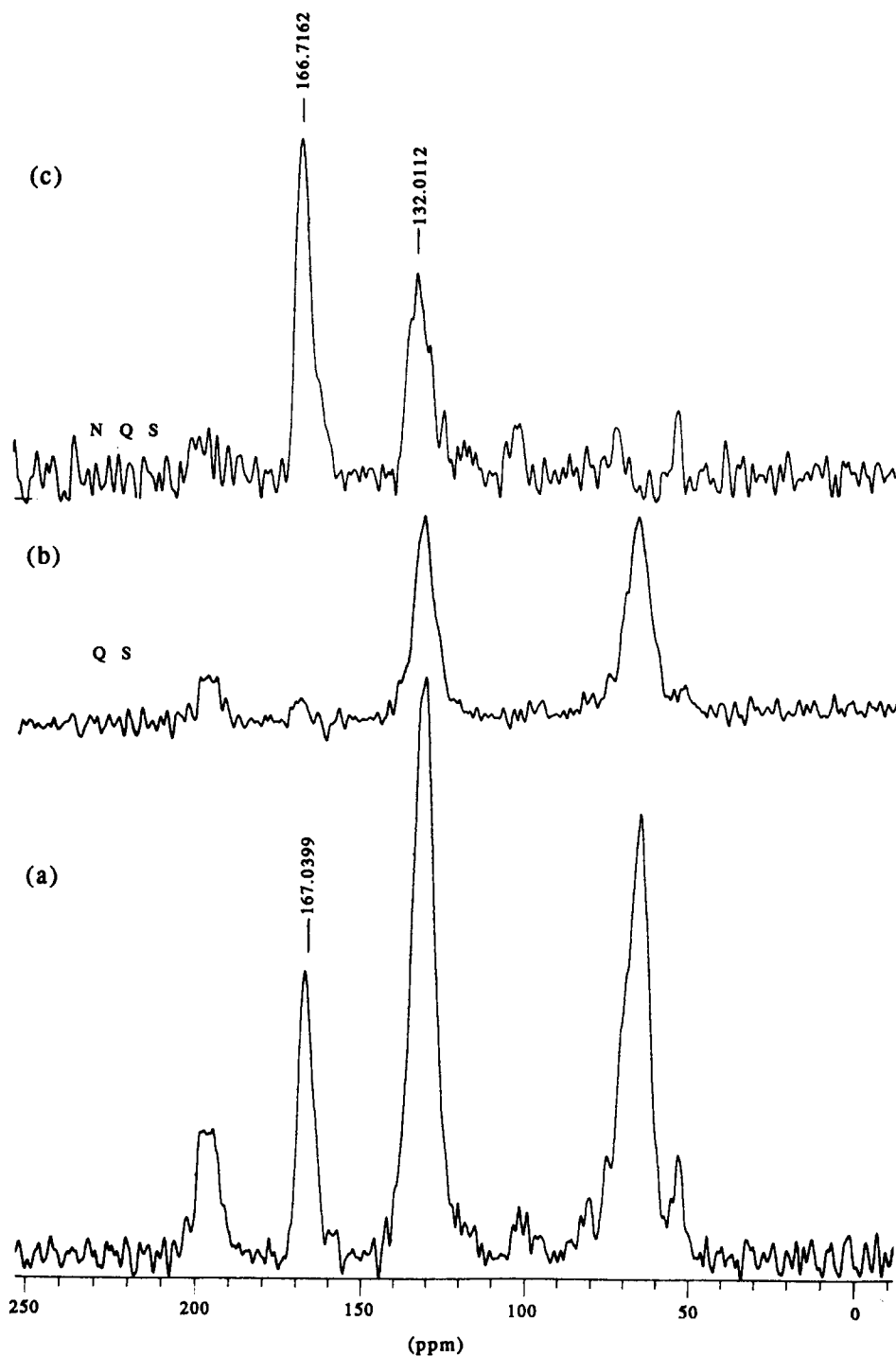

Fig. 3. ^{13}C-NMR of PEP in the solid-state. (a) CP/MAS, (b) QS spectrum (carbons with protons attached), (c) NQS spectrum (quaternary carbons).

deshielded by oxygen atoms, —CH$_2$CH$_2$CH$_2$OH. Carbons attached to terminal hydroxyl groups in CDCl$_3$ were more commonly found further upfield at 61.3 ppm for TEG and 63.4 ppm for EG [14]. The absence of precise shift values for free oligomers of EG in Fig. 2 suggested that ether groups may be part of the polymer backbone. Consideration of the aromatic resonances appeared to support this conclusion. Fine splittings of <0.2 ppm associated with the main aromatic carbons in both spectra were thought to be due to variations in the configurational nature of the attached repeat units. We might not expect PEP or PEI consisting entirely of one repeat unit to produce such multiplicities in solution.

The solid state ^{13}C-NMR of PEP [Fig. 3(a)] displayed a broad aromatic resonance centred on 130 ppm. Suppression of all carbons with no attached protons [carbons 1,6,7/8 from Fig. 2(a)] produced the so-called "quaternary suppressed" spectrum [Fig. 3(b)]. Subtraction of this spectrum from the CP/MAS spectrum [Fig. 3(a)] resulted in the NQS spectrum [Fig. 3(c)]. This spectrum revealed only those carbons with no attached protons. The appearance of two shoulders on the main resonance centred on 132.0 ppm could also be explained by variations in the configurational nature of the attached aliphatic chains. However, the overall broadened nature of the solid state spectra of PEP reflects the infinite number
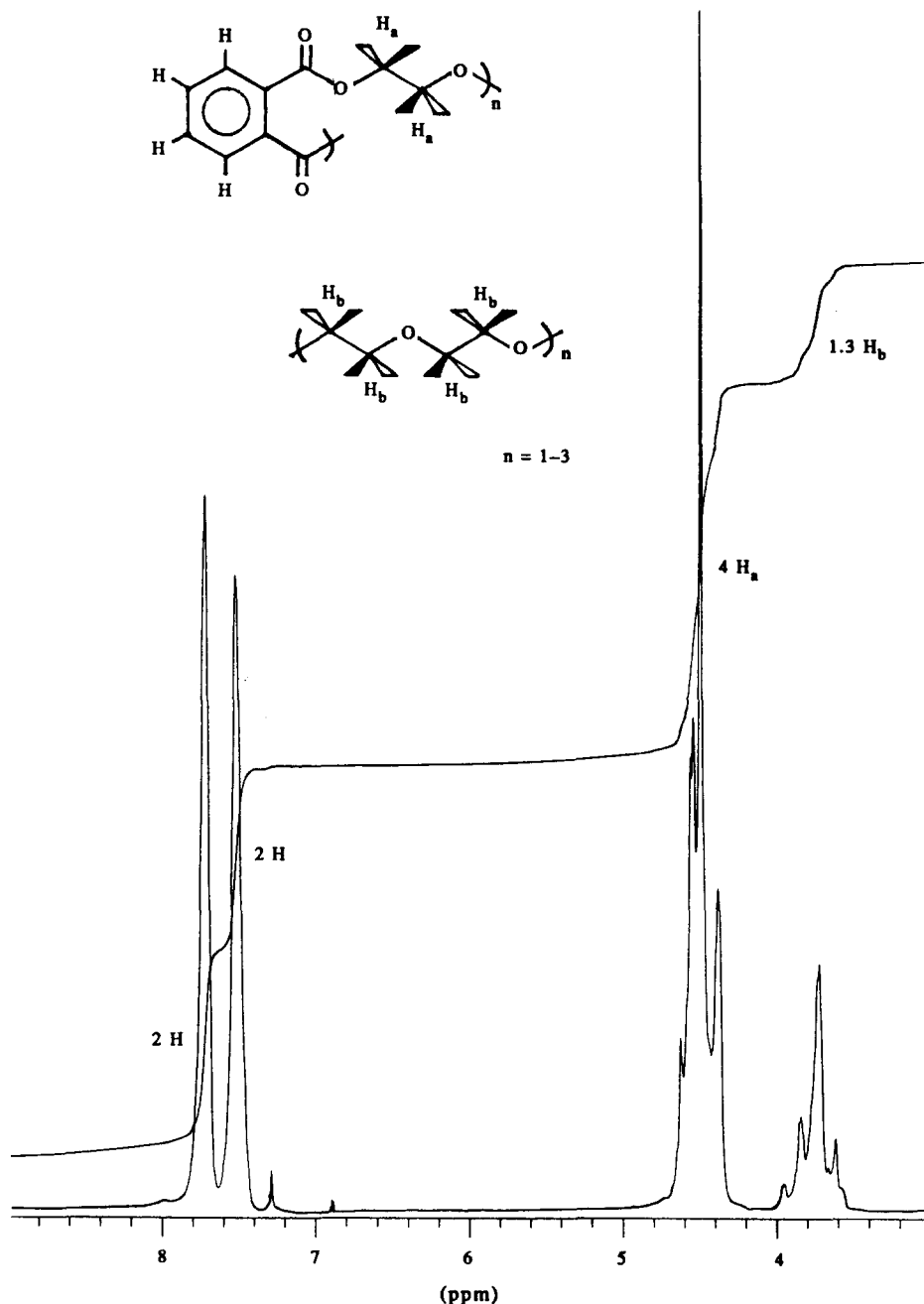

Fig. 4. ^{1}H-NMR (high field) of PEP in CDCl$_3$.

of conformational possibilities of a non-crystalline polymer.

Analysis of the integral intensities in the ¹H-NMR spectrum of PEP (Fig. 4) produced the most convincing evidence for the formation of ether linkages. It indicated that there were 33% more ethylenic protons in the polymer configuration than would be expected for a pure sample of PEP. Considering the shift differences between both sets of methylene resonances and the assignment [15] of these peaks to methylene groups flanked by both ether and ester moieties, the substantial imbalance in the compositional ratio was attributed to loss of phthalate segments as phthalic anhydride. The calculated value of 33% was an accurate gauge of the extent to which the elimination of phthalic anhydride, during the synthesis of PEP alone, had resulted in an excess of ether linkages in the final material. When taken into consideration with the ¹³C-NMR spectra [Figs 2(a) and (b)] especially with regard to the absence of precise shift values for EG, DEG or TEG, then it could only be concluded that the ether linkages were incorporated into the main polymer backbone. The amount present was considerably greater than might have been expected as a result of catalytic side reactions.

FTIR and HPLC analyses of PEP

The i.r. spectrum of PEP after the first stage of the polymerization [Fig. 5(a)] showed a strong ester absorption at $1729\,cm^{-1}$, indicative of low molecular weight polyester which resulted from the initial ester exchange reaction, catalysed by $Zn(CH_3COO)_2 \cdot 2H_2O$. Also evident was a strong hydrogen-bonded OH stretch absorption typical of ethylene glycol present in excess. Presumably, this band contained contributions from unreacted —$COOCH_2CH_2OH$ end-groups. Ether C—Ostr absorptions are normally found in the $1040–1160\,cm^{-1}$ region [16], however, the band present at $1131\,cm^{-1}$ was also typical of the CO—O deformation mode of phthalate ester groups hence no conclusions as to the occurrence of ether groups could be made from the FTIR spectrum. The spectrum of the distillates collected in the final stages of the transesterification at 282°, after all the EG had been removed under vacuum [Fig. 5(b)], showed the presence of both phthalic anhydride and low molecular weight oligomers of PEP. The definitive bands for phthalic anhydride are presented in Table 2, and marked as indicated in Fig. 5(b). Most notable are those at 1853, 1789 and $1776\,cm^{-1}$ removed to higher energy than the ester carbonyl stretching mode of PEP at $1729\,cm^{-1}$. No single band could be attributed to ether groups.

HPLC analysis of the fractions collected in the final stages of the synthesis gave a chromatogram containing a total of eight peaks (Fig. 6). The predominant fraction was that of phthalic anhydride (peak No. 1).
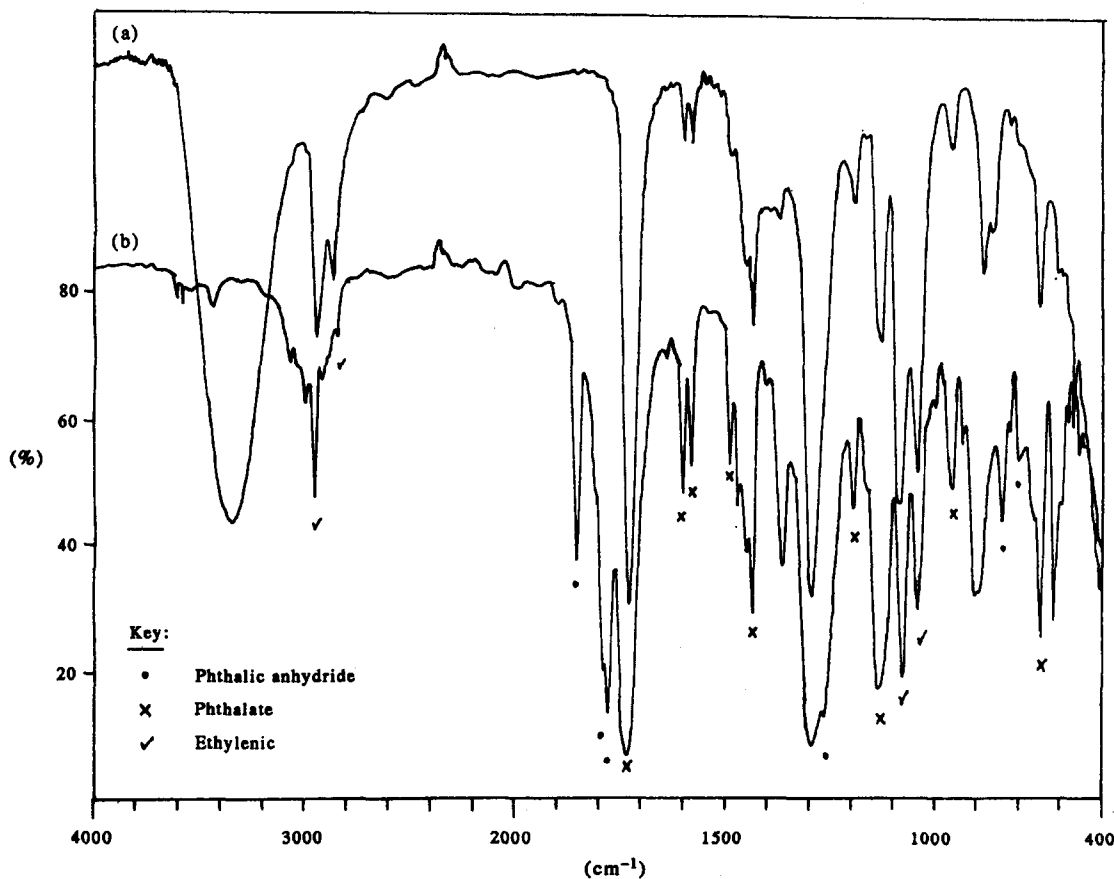

Fig. 5. FTIR absorption spectra of (a) the reaction mixture after the first stage of reaction and (b) the distillates collected in the final stages of the reaction.

Table 2. Characteristic i.r. absorptions of the major components found in the reaction medium after the first stage of reaction (a) and in the distillates from the final stages of reaction (b) in Fig. 5

Component	$\tau(cm^{-1})$	Assignment
PEP (includes cyclic oligomers)	3071w; 3001w.	C—Hstr (arom)
	2955m; 2911w; 2845vw.	C—Hstr (aliph)
(see Fig. 5, spectra a and b)	1729vs;	CO—Ostr (ester)
	1601w; 1580w.	C—Cstr (arom) o-disubstituted
	1489w; 1470w; 1450m; 1435m.	C—Hdef (aliph)
	1293vs; 1131s	CO—Odef phthalates
	821w; 748w.	C—Cdef (arom)
EG	3368vs, broad.	O—Hstr (b)
	2952m; 2878m.	C—Hstr
(see Fig. 5, spectrum a)	1400w; 883w; 865w; 773.	Characteristic of EG
Phthalic anhydride	1853m; 1789s; 1776vs.	CO—O—COstr cyclic anhydride
	1260s; 1040s;	Characteristic
(see Fig. 5, spectrum b)	1075s; 839w; 798	of phthalic anhydride

vs = very strong, s = strong, m = medium, w = weak, vw = very weak, arom = aromatic, aliph = aliphatic, str = stretching mode, def = deformation mode, b = hydrogen bonded.

This assignment was made as a result of measuring the retention time of a pure sample of phthalic anhydride under the same HPLC conditions as the collected fractions. When the log (retention time) was plotted vs fraction number (Fig. 7) and the best linear correlation calculated, it was clear that not all the detected fractions could be attributed to cyclic oligomers of PEP. Cyclic oligomers related by integral molecular weights are known to exhibit a linear relationship in such a plot [17]. A good correlation between peaks Nos 2, 4, 6 and 8 suggested that they may indeed be the monomer, dimer, trimer and tetramer of PEP, however the other peaks were not assigned. Possible assignments may include linear, low molecular weight polyester fractions or possibly cyclics containing ether linkages as appears possible from the bulk evidence of this study. As ethylene diols do not absorb at $\lambda_{max} = 250$ nm, the spurious fractions which deviate from the linear correlation cannot be assigned to free EG, DEG or TEG.

Qualitative analysis of elimination products

The formation of ether linkages during ester interchange was known to occur as a consequence of the oligomerization of EG [18]. Oligomerized glycols could possibly take part in the transesterification in the manner of EG. This process would of course give rise to ether segments in the polyester chain. It might then be expected that the participation of glycol ethers would be common to both the polyesters PEI
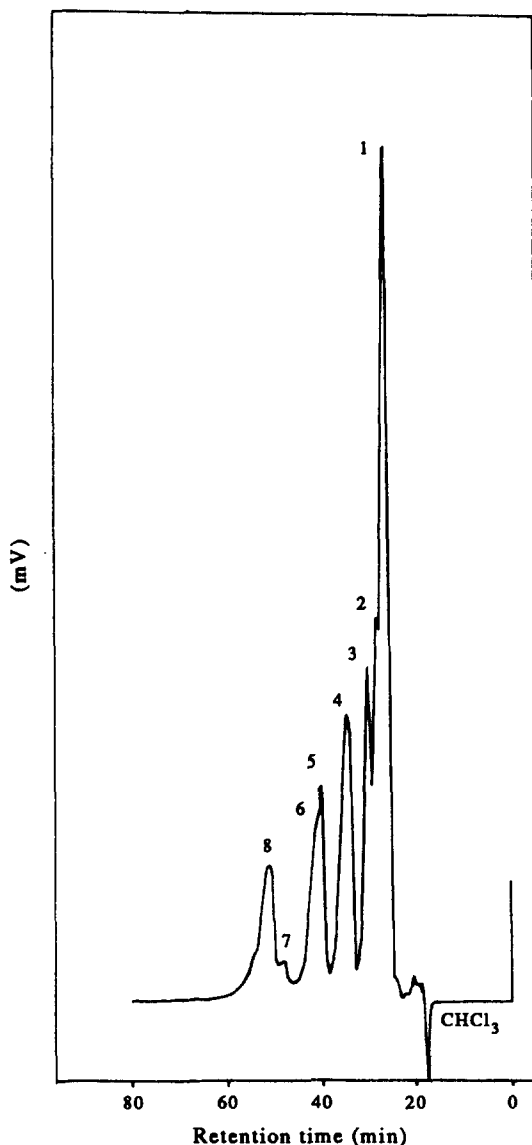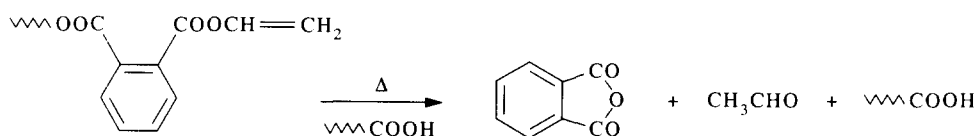

Fig. 6. HPLC chromatogram of the distillates collected in the final stages of the reaction.

and PEP which were synthesized under the same reaction conditions. This effect should give rise to approximately equivalent amounts of ether segments in the synthesized polymers. The NMR measurements (Fig. 2) clearly indicated that this was not the case. In this study, PEP contained substantially more ether linkages than PEI.

Earlier studies on the thermal degradation of PET [19] suggested that vinyl ester end groups could also form and be eliminated as acetaldehyde. When this reaction was applied to PEP, the formation of phthalic anhydride also appeared likely:
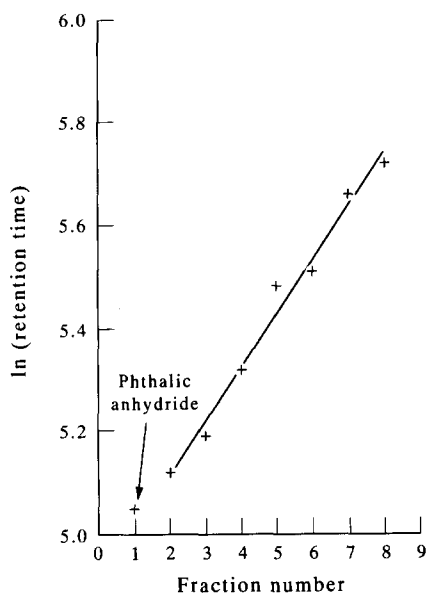
Fig. 7. Plot of *ln* (retention time) as a function of fraction number.

However, qualitative tests for the presence of acetaldehyde in the distillates collected from the polymerizations provided mainly negative results. The few positive results which were obtained from higher temperature polymerizations carried out in the vapours of benzophenone (b.p. 305°) over longer periods, up to a maximum of 12 hr, were common to both PEP and PEI as might have been expected. At such temperatures, degradation was unavoidable.

CONCLUSIONS

Considering all the evidence, it was concluded that the formation of ether linkages during the synthesis of PEP was *primarily* associated with the facile formation of phthalic anhydride and that they were part of the polymer backbone. It was acknowledged that participation of polyether glycols or catalytic side-reactions, resulting in the formation of ether linkages, was possible and probably accounted

for a small proportion of those found. However, it was believed that some other reaction mechanism specific to the ortho-substituted system was the main reason for the unexpectedly large number of ether linkages encountered in the synthesis of PEP.

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