Polymer Vol. 37 No. 7, pp. 1079–1085, 1996
Copyright © 1996 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0032-3861/96/$15.00+0.00

Determination of the end-group concentration and molecular weight of poly(ethylene naphthalene-2,6-dicarboxylate) using infra-red spectroscopy

H. Zhang, A. Rankin and I. M. Ward*
IRC in Polymer Science and Technology, The University of Leeds, Leeds LS2 9JT, UK
(Received 1 June 1995; revised 14 July 1995)

Infra-red (i.r.) end-group analysis is used to determine the hydroxyl and carboxyl end-group concentrations and therefore the number-average molecular weight of poly(ethylene naphthalene-2,6-dicarboxylate)(PEN) film samples in the solid state. The end-group i.r. spectrum of a sample is obtained by subtracting the i.r. spectrum of a deuterated control sample from the experimental sample i.r. spectrum. We have used integral absorbances obtained from fitted absorption bands in the i.r. spectra of PEN for the calculation of end-group concentrations. Using this method, the limitations of chemical methods of determination of end-group concentrations caused by the poor solubility of PEN are avoided. In addition, corrections can readily be made to allow for difference in crystallinity between the control and the experimental samples. The extinction coefficients for the OH stretching vibration in the hydroxyl and for the carboxyl end-groups have been determined for PEN as well as for poly(ethylene terephthalate). Both the hydroxyl and the carboxyl end-group concentrations, and the number-average molecular weight of the samples, can then be easily determined from the i.r. absorbances.

(Keywords: poly(ethylene naphthalene-2,6-dicarboxylate) (PEN); end-group concentration; infra-red spectroscopy)

INTRODUCTION

End-group analysis is one of the most important absolute methods of obtaining the number-average molecular weight of condensation polymers of known structure. In addition to chemical methods for end-group analysis such as titration, various physical methods have been employed to determine the end-group concentration and hence the molecular weight. These include optical spectroscopy, n.m.r. and dielectric methods[1]. These methods determine the molecular weight of the solid polymer and are specially suitable for polymers with rigid chains that are difficult to dissolve for chemical analysis.

In the late 1950s Patterson and Ward[2,3] developed an infra-red (i.r.) method for the measurement of the end-group concentration of poly(ethylene terephthalate) (PET) in the solid state. This method determines the concentration of both hydroxyl OH end-groups and carboxyl OH, COOH, simultaneously from one spectrum. This was very useful in the study of chemical reaction mechanisms[4] and has been applied to various PET films[5] and also to poly(butylene terephthalate)[6]. The method involves creating a reference spectrum from a deuterated sample of the polymer in which the end-group protons have been quantitatively replaced with deuterons without affecting the protons in the main chain. The deuterated sample thus defines the background absorption for effectively zero OH and COOH end-group content. Subtraction of the sample spectrum from the reference spectrum yields solely the absorption spectrum of the OH and COOH ends. The end-group concentration can then be obtained using the Lambert–Beer law:

$$n_x = \frac{10^3 A_x}{\rho \ell \epsilon_x} \tag{1}$$

where x refers either to the OH or to the COOH ends, n_x is the concentration of the x end-group in mole/(10^6 g equiv.) A_x is the absorbance of the end-groups, ρ is the density of the sample (g cm^{-3}), ℓ is the thickness of the film sample (cm) and ϵ_x is the extinction coefficient (litre mole^{-1} cm^{-1}) of the x end-group.

Polyesters are essentially linear molecular chains terminated by hydroxyl and carboxyl ends. For the linear polymer, the number-average molecular weight, M_n, can be calculated from the concentration of these two end-groups:

$$M_n = \frac{2 \times 10^6}{n_{\mathrm{OH}} + n_{\mathrm{COOH}}} \tag{2}$$

where n_{OH} and n_{COOH} are the numbers of hydroxyl and carboxyl ends, respectively [in mole/(10^6 g equiv.)].

Originally, the absorbance of the end-groups was measured as the absorbance, $\log_{10}(I_0/I)$, at the peak

---

*To whom correspondence should be addressed position. This value was very sensitive to the baseline chosen. Moreover, the change of the vibration energy distribution of the end-groups, due to the different crystallinity and orientation of the samples, can cause a change in the i.r. absorption peak shape which affects the determination of the absorbance[5]. The elimination of moisture from the sample was also vital when measuring the absorbance of the hydroxyl end i.r. absorption, because the free OH group absorption (due to moisture) is more or less superimposed on the hydroxyl OH end-group peak.

In this paper, we report recent results of the measurements of the end-group concentrations of poly(ethylene naphthalene-2,6-dicarboxylate) (PEN), as well as of PET, using i.r. analysis based on Ward's method. PEN is attracting increasing attention as its larger scale commercialization, promoted by a major facility for producing dimethyl naphthalene-2,6-dicarboxylate, is under way. PEN is very similar to PET in its structure but contains 2,6-naphthalene rings which produce much stiffer molecular chains than those of PET, which contains 1,4-phenylene rings. This rigidity of the polymer backbone makes PEN very difficult to dissolve in conventional solvents without extensive heating, making chemical analysis difficult.

We have used integral i.r. absorbance, $\int \log_{10}(I_0/I)\mathrm{d}\tilde{v}$ of the whole absorption band, instead of the absorbance, $\log_{10}(I_0/I)$, at the peak position, for the determination of the end-group concentrations. This makes the analysis more versatile and less affected by possible absorption band shape changes associated with polymer structure changes in the solid state. The effect of the crystallinity of the PEN film samples on the determination of the end-group concentrations is discussed in this report. Initially, it is necessary to determine values of the extinction coefficients of the hydroxyl and the carboxyl end-groups in PET and PEN using polymer samples of known number-average molecular weights determined by dilute solution viscometry measurements. These values are then used in the subsequent i.r. end-group determinations.

Table 1 Density and crystallinity of various samples of PEN used for the study of crystallinity effect on the determination of the end-group absorptions

Sample code	Density ($\mathrm{g\,cm^{-3}}$)	Crystallinity (wt%)
PEN-A	1.3320	9
PEN-B	1.3342	12
PEN-C	1.3365	15
PEN-D	1.3465	27
PEN-E	1.3485	30

EXPERIMENTAL

Sample preparation

Films 200 μm thick were hot-pressed from both PEN pellets (supplied by Amoco Chemical Co.) and PET pellets (from the Eastman Kodak Co.). The pellets were vacuum dried at 120°C overnight before pressing. They were sandwiched between two poly(tetrafluoroethylene) coated glass-fibre fabrics and heated to a temperature of 280°C for PEN or 250°C for PET. A pressure of 200–500 $\mathrm{kg\,cm^{-2}}$ was applied and maintained for approximately 30 s. The sample, together with the fabrics, was then quickly removed from the press and quenched in

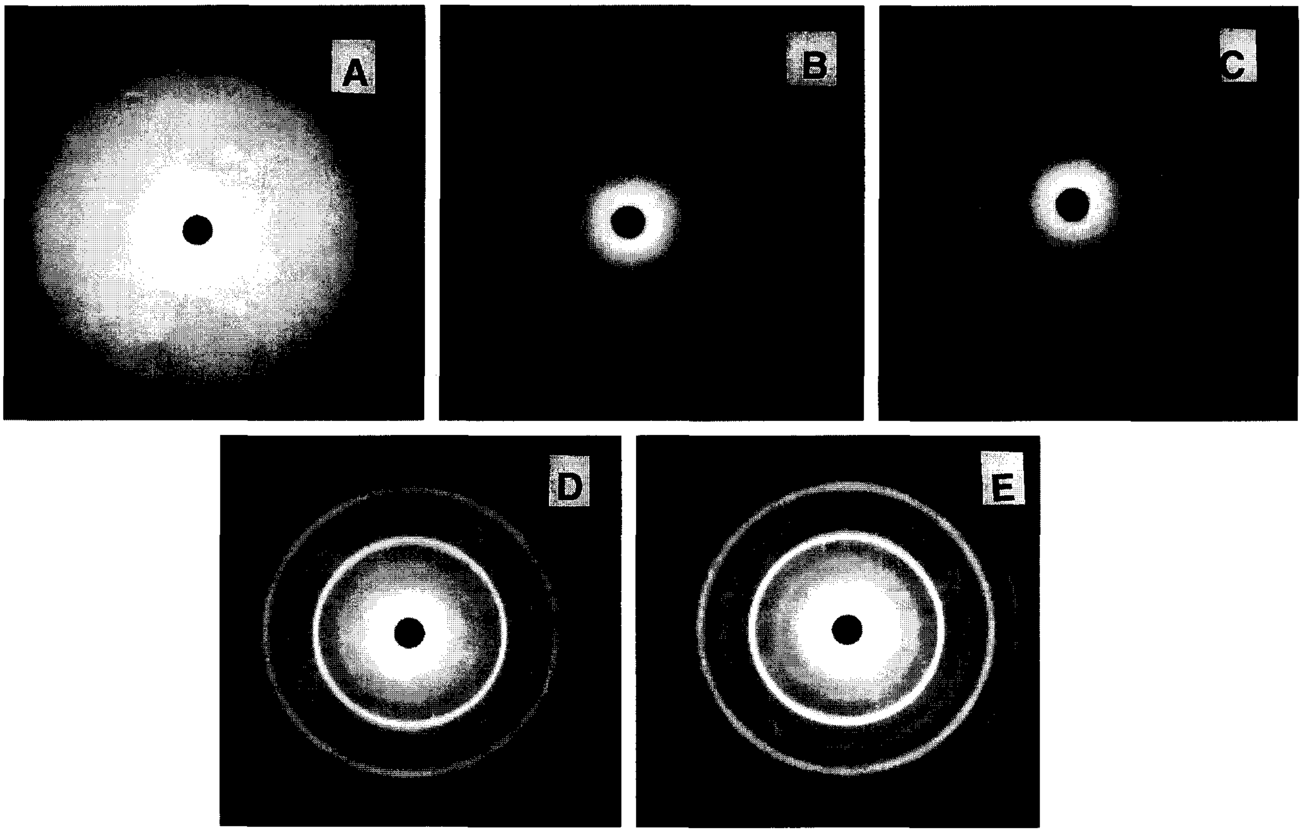

Figure 1 Wide-angle X-ray diffraction photographs of PEN film samples with various crystallinities (see *Table 1*)

liquid nitrogen. The film was peeled off the fabric and kept in a desiccator. From density measurements and wide-angle X-ray diffraction photographs, films prepared from the hot press were amorphous. Samples with various degrees of crystallinity were prepared by annealing the above hot-pressed films under vacuum at 140°C for various times. The crystallinity of the samples, w_c, in wt%, was calculated from their densities, measured at 23°C in a density column (potassium iodide solution) using the following equation.

$$w_c = \frac{\rho_c}{\rho}\left(\frac{\rho - \rho_a}{\rho_c - \rho_a}\right) \times 100 \qquad (3)$$

where ρ is the measured density value ($\mathrm{g\,cm^{-3}}$), $\rho_a = 1.3250\,\mathrm{g\,cm^{-3}}$, the density of amorphous PEN, and $\rho_c = 1.4007\,\mathrm{g\,cm^{-3}}$, the density of crystalline PEN[7]. The results are summarized in *Table 1*. Wide-angle X-ray diffraction photographs were taken of these samples to confirm the development of the crystallinity with annealing. These are shown in *Figure 1*.

Deuteration of PET and PEN films

Deuteration of the PET and PEN films was carried out by immersing the vacuum-dried films (~0.3 g) in a flask containing heavy water (20 g, 99.9% D_2O) at 90°C for several hours. Nitrogen was constantly blown through and around the liquid to prevent the formation of a static HOD vapour layer on the samples and possible rehydrogenation of D_2O, which can be caused by moisture in the atmosphere. Samples were occasionally taken from the flask to record the i.r. spectrum. As judged by the disappearance of the hydroxyl OH i.r. absorption band, immersion for 6 h in deuterium oxide seemed to have completed the replacement of all the end-group hydrogen atoms with deuterium atoms. The final spectra of the fully deuterated samples (deuterated spectra) were taken immediately after the samples were removed from the heavy water to prevent any possible rehydrogenation during handling.

Infra-red spectrometry

I.r. spectra of the samples were recorded directly using a Bomem FT–IR spectrophotometer over the range 2500–4000 $\mathrm{cm^{-1}}$ with a resolution of 2 $\mathrm{cm^{-1}}$. The sample thickness was measured using an electronic micrometer; this thickness was taken as the path length.

Each difference spectrum was obtained by subtracting the deuterated spectrum from a sample spectrum of similar crystallinity. The difference spectrum was then computer fitted using several Gaussian bands (which were found to give the best fit) and a linear baseline between 3100 and 3800 $\mathrm{cm^{-1}}$. The band area of the i.r. absorption (integral absorbance) of the functional groups was then determined.

Solution viscosity measurement

Dilute solution viscometry was undertaken on samples of PEN and PET in order to determine the number-average molecular weight of the polymer, and to correlate these results with those obtained by i.r. spectroscopy. In the studies of polymer dilute solution viscosity, the Mark–Houwink equation is often used to relate the polymer intrinsic viscosity, $[\eta]$, to its viscosity-average molecular weight[8]. However, a similar relationship has been reported for polyesters[3,6] to relate the intrinsic viscosity to the number-average molecular weight, M_n, i.e.:

$$[\eta] = kM_n^{\alpha} \qquad (4)$$

where k and α are empirical constants for a particular polymer solvent system at a particular temperature, and M_n is the number-average molecular weight of the polymer. For PEN, a Mark–Houwink relationship was found for the mixed solvent pentafluorophenol and hexafluoropropan-2-ol (PFP/HFP), 50 : 50% by weight at 30°C. The empirical constants are $k = 4.7458 \times 10^{-4}\,\mathrm{dl\,g^{-1}}$, and $\alpha = 0.747$ (ref. 9).

Viscosity measurements were carried out on a series of polymers of different molecular weights over a range of concentrations, c, between about 1.0 and 0.3 $\mathrm{dl\,g^{-1}}$. Concentrations were changed by dilution using an Ubbelohde suspended level viscometer. Viscosity values were calculated on the basis of comparisons between the flow time of the solution, t, and that of the pure solvent, t_0. A double plot of reduced viscosity, $(t - t_0)/t_0c$, and inherent viscosity, $\{\ln(t/t_0)\}/c$, against the concentration was drawn. The two lines thus obtained were extrapolated back to zero concentration where they intercepted each other.This gave the value for $[\eta]$. Using equation (4), the corresponding values of M_n were determined.

For routine analysis, dichloroacetic acid (DCA) was also used. The Mark–Houwink equation for PEN in DCA at 25°C was obtained by measuring the intrinsic viscosity of the same samples dissolved in DCA for 2 h at 80°C, again over a concentration range between about 1.0 and 0.3 $\mathrm{dl\,g^{-1}}$. Once a set of values of M_n and $[\eta]$ had been obtained, a plot of $\ln(M_n)$ against $\ln[\eta]$ was constructed. The slope of the line, α, was calculated as 0.523 and the intercept, k, to be $3.307 \times 10^{-3}\,\mathrm{dl\,g^{-1}}$. Hence, the Mark–Houwink equation for PEN in DCA at 25°C can be written as:

$$[\eta] = 3.307 \times 10^{-3} M_n^{0.523} \qquad (5)$$

Viscosity measurements were also carried out on a series of PET samples with different molecular weights. For PET in dichloroacetic acid (DCA) at 25°C the corresponding values are $k = 67 \times 10^{-4}\,\mathrm{dl\,g^{-1}}$ and $\alpha = 0.471$ (ref.10).

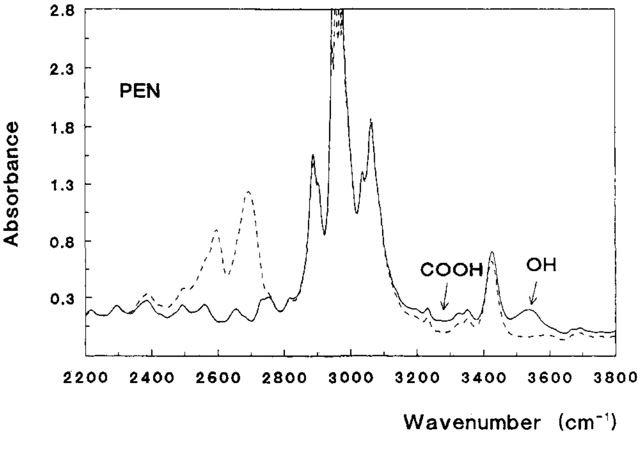

Figure 2 *FT* i.r. spectra of an amorphous PEN film sample before and after deuteration. The hydroxyl, OH, and carboxyl, COOH, end-groups are replaced by OD and COOD ends, respectively. Solid line: original sample; dashed line: deuterated sample

RESULTS AND DISCUSSION

Assignment of the i.r. absorption band of OH and COOH end-groups

The spectra from the original and the deuterated samples of amorphous PEN films are shown in *Figure 2*, and those of PET in *Figure 3*. The difference spectra for both PEN and PET samples are shown in *Figure 4*. The disappearance of the O–H peaks and the appearance of the O–D vibration peaks in these spectra were used to assign the end-group vibrations[11].

In *Figure 2*, two bands, centred at 3290 and 3550 cm^{-1}, respectively, disappeared after deuteration. These are assigned to the O–H stretching vibrations of the carboxyl (COOH) ends and of the hydroxyl (OH) ends, respectively. The corresponding O–D vibrations appear in the deuterated sample at 2400 cm^{-1} (COOD end) and 2600 cm^{-1} (OD end). Note that the COOD peak is very small. A sharp band at 2700 cm^{-1} is ascribed to HOD vapour[11]. The ratios of the wave numbers of the COOH and COOD peaks, and the OH and OD peaks, are both about 1.36, which is expected from simple harmonic theory.

In *Figure 5*, the difference spectrum of PEN in the region 3100–3800cm^{-1}, which shows COOH and OH absorptions, was computer-fitted using three Gaussian bands[12]. Peak 1, at around 3290 cm^{-1}, is the absorption due to the OH stretching vibration of the carboxyl ends, and peak 2, about 3550 cm^{-1}, is that of the hydroxyl ends. Peak 3, centred at about 3650 cm^{-1}, if present, is related to the free O–H vibration associated with moisture residue. A linear baseline from 3800 to 3100 cm^{-1} was found to give consistent fitting results. The areas of peaks 1 and 2, calculated from this fit, are taken as the integral absorbances of these two end-groups.

Effect of the crystallinity of the PEN samples on the FT *i.r. analysis of end group concentrations*

The analysis of the end-group concentrations reported here is based on a difference spectrum to obtain the net OH and COOH absorptions. The difference spectrum is obtained by subtracting a reference spectrum of a deuterated sample from the spectrum of the experimental sample. We have investigated the effect of differences in crystallinity between the deuterated sample and the experimental sample on the determination of the end-group absorbances, which is an important consideration for the samples in the solid state.

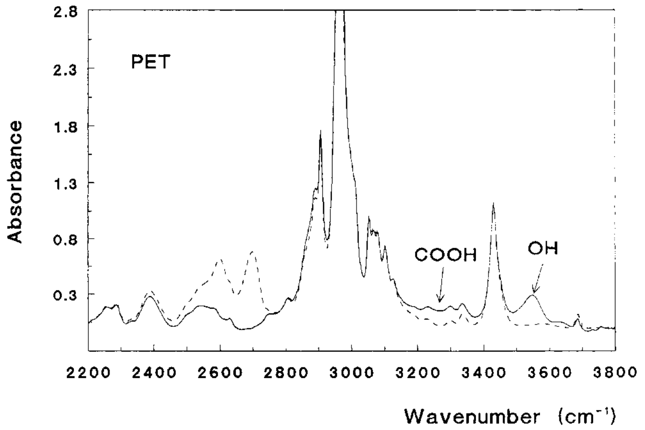

Figure 3 *FT* i.r. spectra of an amorphous PET film sample before and after deuteration. Solid line: original sample; dashed line: deuterated sample

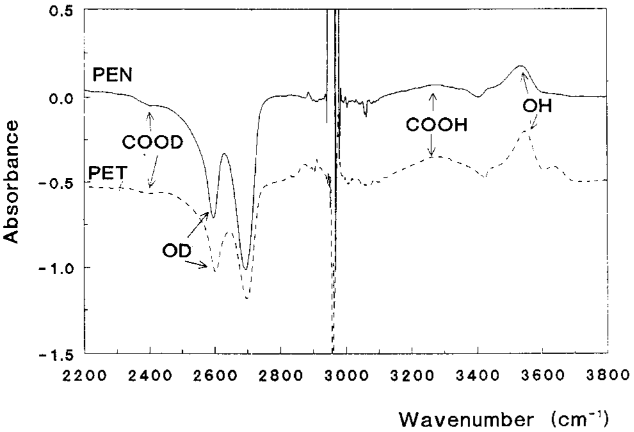

Figure 4. Difference spectra of PEN and PET samples showing hydroxyl and carboxyl end-group absorbances. Solid line: PEN; dashed line: PET (the spectrum is shifted to the lower scale)

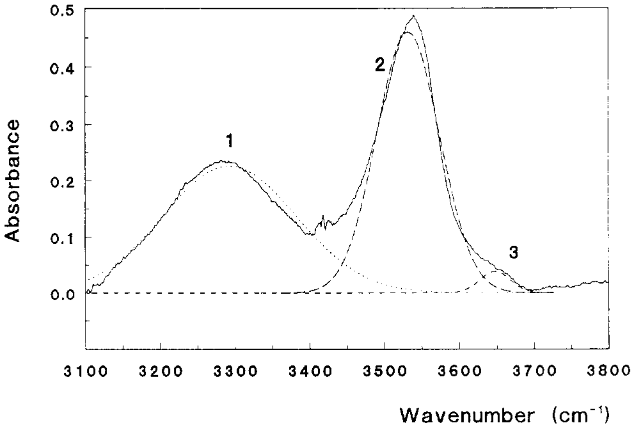

Figure 5 Gaussian band fitting of the end-group absorbances. Peak 1 is related to the carboxyl end-group absorption, peak 2 is the hydroxyl end-group absorption and peak 3 the free OH absorption due to moisture residue

Figure 6 shows the i.r. spectra of the end-group absorption region of deuterated PEN samples with different crystallinities (COOH and OH peaks are removed). The most obvious change due to higher crystallinity of the samples is that the C=O overtone peak at 3420 cm^{-1} shifts to a lower frequency and becomes sharper as the crystallinity increases[13]. This is possibly due to the increase in the intermolecular forces between the molecular chains with increasing crystallinity. The peak becomes sharper because of the reduction in spatial disordering which causes the vibration frequency to be spread over a smaller range[14].

The position of the C=O overtone peak is between the two end-group absorptions, slightly overlapping the COOH band. Therefore, shifts of the C=O peak due to changes in the crystallinity of the samples will affect the determination of the absorbances of the end-groups, especially that of the COOH absorbance as shown in *Figure 7*. The difference spectrum of PEN samples in which the crystallinity of the samples matches that of the

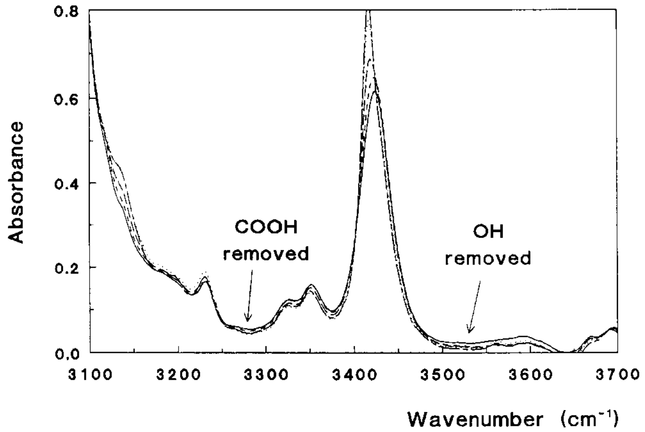

Figure 6 *FT* i.r. spectra of deuterated PEN samples with different crystallanities: A: 9; B: 12, C: 15; D: 27 and E: 30 wt% crystallinity. ———: Sample A; - - - : sample B; — —: sample C; ......: sample D; and — -: sample E

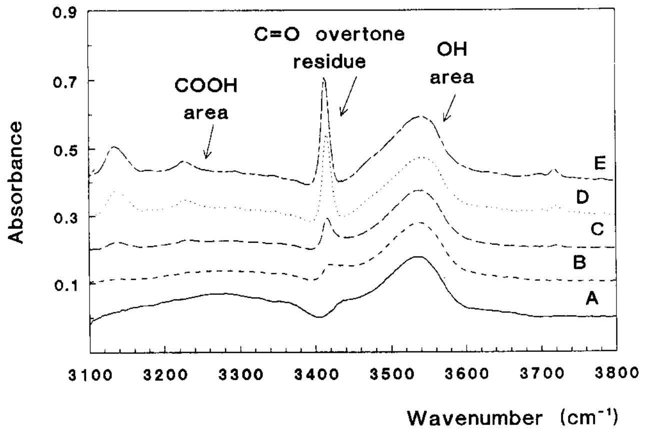

Figure 7 Difference spectra of PEN, showing effective end-group absorptions, with matched crystallinity between the deuterated and experimental samples (the bottom spectrum) and those without matched crystallinities (the top four spectra)

deuterated sample is seen at the bottom as curve A. Curves B, C, D and E are the difference spectra of the samples with higher and higher crystallinity than that of the reference spectrum. It is clear that, in order to obtain the difference spectrum with undistorted OH and COOH absorbance, the deuterated sample must have a similar crystallinity to that of the sample under study and therefore the effect of the C=O overtone residue can be reduced to the minimum. We have noticed that the residual C=O overtone cannot be removed completely, which may be due to an imperfect phase correction in the Fourier transform for a strong, narrow absorption like the C=O overtone[14].

It is worth noting that the deuteration of the samples with different crystallinities showed very similar background absorptions for the end-groups (*Figure 6*). This suggests that all the end-groups are accessible by the heavy water and can be deuterated and that the ends of the PEN polymer chains are all in the amorphous region.

We have taken a series of reference spectra from deuterated samples with a wide range of crystallinities. A suitable reference spectrum could then be chosen which matched the crystallinity of the sample studied. This is a prerequisite for the quantitative analysis of sample end-group concentrations.

Calibration of the FT i.r. absorption extinction coefficients of OH and COOH end-groups

For the quantitative determination of the end-group concentration, the extinction coefficients of the hydroxyl and carboxyl end-groups must be determined. In this study we have adopted a method which uses samples with known M_n determined by solution viscometry for the calibration of these two parameters.

Equation (1) can be rewritten explicitly as:

$$n_{\mathrm{total}} = n_{\mathrm{OH}} + n_{\mathrm{COOH}} = \frac{10^3}{\rho l}\left(\frac{A_{\mathrm{OH}}}{\epsilon_{\mathrm{OH}}} + \frac{A_{\mathrm{COOH^+}}}{\epsilon_{\mathrm{COOH}}}\right) \quad (6)$$

where n_{total} is the total end-group concentration in mole/ (10^6g equiv.) and A_{OH} and A_{COOH} are the measured absorbances of the OH and COOH end-groups, respectively. The relationship between the total end-group concentration and M_n is given in equation (2). Therefore, by solving equation (2) in pairs using two samples of different M_n:

$$\begin{aligned} \frac{2\times10^6}{M_n} &= \frac{10^3}{\rho l}\left(\frac{A_{\mathrm{OH}}}{\epsilon_{\mathrm{OH}}} + \frac{A_{\mathrm{COOH}}}{\epsilon_{\mathrm{COOH}}}\right) \\ \frac{2\times10^6}{M_n'} &= \frac{10^3}{\rho l}\left(\frac{A_{\mathrm{OH}}'}{\epsilon_{\mathrm{OH}}} + \frac{A_{\mathrm{COOH}}'}{\epsilon_{\mathrm{COOH}}}\right) \end{aligned} \quad (7)$$

the values of ϵ_{OH} and ϵ_{COOH} can be calculated.

The measured intrinsic viscosities of the PEN samples used for such calculations and their number-average molecular weights calculated from equation (4) are shown in *Figure 8*. These samples covered a wide molecular weight range of 3000–30 000.

I.r. spectra were taken of the above samples and the integrated absorbances of the end-group absorptions, A_{OH} for the OH ends and A_{COOH} for the COOH ends, were obtained. The number-average molecular weights and the integral absorbance values were then fitted into equation pairs [equation (7)] to calculate the extinction coefficients of the hydroxyl and carboxyl ends. The values obtained were:

$$\frac{1}{\epsilon_{\mathrm{OH}}} = (9.2 \pm 0.4) \times 10^{-5};$$

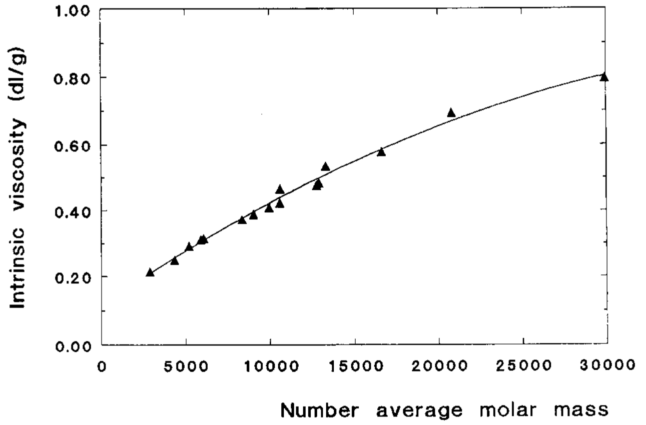

Figure 8 Intrinsic viscosity and the corresponding number-average molecular weight of the PEN samples used in the calibration of i.r. extinction coefficients of the end-groups

and

$$\frac{1}{\epsilon_{\mathrm{COOH}}} = (4.8 \pm 0.4) \times 10^{-5}\ [(\mathrm{litre/mole\,cm})^{-1}]$$

or

$$\epsilon_{\mathrm{OH}} = (10.9 \pm 0.5) \times 10^{4}$$

and

$$\epsilon_{\mathrm{COOH}} = (21.0 \pm 1.7) \times 10^{4} \qquad (8)$$

Similar procedures were applied to PET film samples with M_n ranging from 10000 to 16000. The extinction coefficients of the end-group i.r. absorptions, calculated from equation (7), had very similar values to those obtained from the PEN samples, i.e.:

$$\frac{1}{\epsilon_{\mathrm{OH}}} = (9.4 \pm 0.4) \times 10^{5}$$

and

$$\frac{1}{\epsilon_{\mathrm{COOH}}} = (4.6 \pm 0.4) \times 10^{-5}[(\mathrm{litre/mole\,cm})^{-1}]$$

or

$$\epsilon_{\mathrm{OH}} = (10.6 \pm 0.5) \times 10^{4},$$

and

$$\epsilon_{\mathrm{COOH}} = (21.7 \pm 1.7) \times 10^{4} \qquad (9)$$

It was noticed, however, that for the low-molecular-weight samples, the calculated extinction coefficient values were not consistent. This implies that the Mark–Houwink relationship relating the intrinsic viscosity to the number-average molecular weight, equation (4), is not applicable to low-molecular-weight samples. Only when M_n was greater than 5000 did the calculated extinction coefficients from various equation pairs agree closely with each other.

It has to be noted also that the extinction coefficients obtained above for the PEN and PET were values calibrated against the number-average molecular weight predicted from the intrinsic viscosity. These values, however, were compared with those obtained by Ravens and Ward by absolute methods[4] and ones worked out by infra-red spectroscopy on a model system consisting of a series of solutions of *p*-cresoxyacetic acid in di-*n*-butyl phthalate[5]. As all the extinction coefficients quoted from the previous work in the references were based on absorbance measurements, a simple conversion is needed to relate the extinction coefficient, ϵ_x, from integral absorbance to ϵ'_x from peak absorbance as:

$$\frac{1}{\epsilon_x} = 2\sqrt{\frac{\ln 2}{\pi}}\,\frac{1}{W_{1/2}}\,\frac{1}{\epsilon'_x} \qquad (10)$$

where x can be either OH or COOH and $W_{1/2}$ is the half width of the corresponding absorption band. Given the half width of the absorbance of the end-groups, the extinction coefficients for the integral absorbances can be estimated from those for the absorbance. The values for absorbance have been obtained by Ward as $1/\epsilon'_{\mathrm{OH}} = 1/127.4$ for OH in the hydroxyl end and $1/\epsilon'_{\mathrm{COOH}} = 154.2$ for the OH in the carboxyl end[4]. The half width of the absorption bands can be obtained from Gaussian band fitting of the OH and COOH absorption bands.

Table 2 shows values of $1/\epsilon_{\mathrm{OH}}$ and $1/\epsilon_{\mathrm{COOH}}$ calculated for integral absorbance using Ward's extinction coefficients for absorbance, and the half width, $W_{1/2}$, used for such calculation for four PEN samples and four PET samples. It can be seen that the calculated $1/\epsilon_{\mathrm{OH}}$ and $1/\epsilon_{\mathrm{COOH}}$ from equation (10) are in reasonable agreement with our calibration figures in equation (7). The difference may be due to the difference in the baselines chosen in the two cases. Rather, scattered data for the calculated values of $1/\epsilon_{\mathrm{OH}}$ may be related to the effect of free OH absorption from moisture in the sample and the effect of possible band shape changes caused by differences in the sample crystallinity, both of which affect the determination of the absorbance in the original work.

The calculated end-group concentrations for the hydroxyl ends, n_{OH}, and carboxyl ends, n_{COOH}, of the above PEN samples, as well as the above PET samples, are also listed in *Table 2*. The calculated number of carboxyl end-groups based on the above calibrated extinction coefficients was in good agreement with the number quoted by the PEN supplier, Amoco Chemicals.

CONCLUSION

Infra-red spectroscopy has been used to determine the hydroxyl and carboxyl end-group concentration, and therefore the number-average molecular weight, of PEN film samples in the solid state. The effect of different crystallinities of the samples on the determination of the end-group concentration can be allowed for by matching

Table 2 Calculated extinction coefficients of the OH stretching vibration in the hydroxyl ends, ϵ_{OH}, and that in the carboxyl ends ϵ_{COOH}, from absorbance measurements (ref. 4) are compared with the calibrated values in equation (8) for PEN and values in equation (9) for PET. $W_{1/2}$ is the half width of the absorption band obtained from Gaussian shape fittings. The concentrations of hydroxyl ends, n_{OH}, and that of the carboxyl ends, n_{COOH}, for these samples are calculated using the extinction coefficients for the integral absorbances

Sample	$1/\epsilon_{\mathrm{OH}}$ (10^{-5}) (calibrated)	$W_{1/2}$ of A_{OH}	$1/\epsilon_{\mathrm{OH}}$ (10^{-5}) (calculated)	$1/\epsilon_{\mathrm{COOH}}$ (10^{-5}) (calibrated)	$W_{1/2}$ of A_{COOH}	$1/\epsilon_{\mathrm{COOH}}$ (10^{-5}) (calculated)	n_{OH} (mole/10^6g equiv.)	n_{COOH} (mole/10^6g equiv.)
PEN-C1		82	8.99		151	4.03	73	27
PEN-C2	9.2 ± 0.4	58	12.7	4.8 ± 0.4	180	3.38	96	45
PEN-C3		120	6.14		200	3.05	151	100
PEN-C4		100	7.37		211	2.89	208	128
PET-A1		80	9.22		160	3.81	63	61
PET-A2	9.4 ± 0.4	70	10.5	4.6 ± 0.4	190	3.21	78	61
PET-A3		80	9.22		200	3.05	91	55
PEN-A4		60	12.3		190	3.21	113	59

the crystallinity between the sample to be analysed and the sample for deuteration (to generate baselines corresponding to zero end-group absorptions). The difference spectrum (sample spectrum – deuterated spectrum) gives accurate hydroxyl and carboxyl end-group absorptions and can be fitted by Gaussian bands and a linear baseline from 3100 to 3800 cm^{-1}, from which the integral absorbances of the OH stretching vibration from the hydroxyl and the carboxyl ends are obtained. The i.r. extinction coefficients of the OH stretching vibration in the hydyroxyl and the carboxyl ends derived from the integrated absorbance in this investigation are $\epsilon_{\mathrm{OH}} = (10.9 \pm 0.5) \times 10^4$ and $\epsilon_{\mathrm{COOH}} = (21.0 \pm 1.7) \times 10^4$ litre $\mathrm{mole}^{-1}\,\mathrm{cm}^{-1}$.

ACKNOWLEDGEMENTS

The authors wish to thank the SERC and SCAPA Group plc for supporting the project. They thank Hoechst Celanese Research Co., at Summit, NJ, USA for supplying the equation relating intrinsic viscosity to the number-average molecular weight of PEN. They also thank RAPRA Technology Ltd, Shawsbury, UK for the g.p.c. measurements on various PEN samples used in this study. They thank Professor J. E. McIntyre in particular for his many valuable suggestions during the course of the work. They are grateful to Mr P. L. Carr for helpful discussions about this paper and Mr G. P. Thompson for excellent technical help.

REFERENCES

1 Garmon, R.G., in 'Polymer Molecular Weights', Part I (Ed. P. E. Slade Jr) Marcel Dekker, New York, 1975, ch. 1
2 Patterson, D. and Ward, I. M. *Trans. Faraday Soc.*, 1957, **57**, 291
3 Ward, I. M. *Trans. Faraday Soc.*, 1957, **53**, 1406
4 Ravens, D. A. S. and Ward, I. M. *Trans. Faraday Soc.*, 1961, **57**, 150
5 Addleman, R. L. H. and Zichy, V. J. I. *Polymer* 1972, **13**, 391
6 Kosky, P. G., McDonald, R. S. and Guggenheim, E. J. *Polym. Eng. Sci.*, 1985, **25**, 389
7 Buchuer, W., Wiswe, D. and Zachmann, H. G. *Polymer* 1989, **30**, 480
8 Elias, H. G., 'Macromolecules', John Wiley, London, 1977, Vol. 1, p. 362
9 Choe, E. W. private communication
10 Moore, W. R. and Sanderson, D. *Polymer* 1968, **9**, 153
11 Szymanski, H. A. 'Interpreted Infrared Spectra', Plenum Press, New York, 1964, Vol. I
12 Siesler, H. W. and Holand-Moritz, K., 'Infrared-Raman Spectroscopy of Polymers', Marcel Dekker, New York, 1980
13 Ouchi, I. Hosoi, M. and Shimotsume, S. *J. Appl. Polym. Sci.* 1977, **21**, 3445
14 Ferraro, J. R. and Basile, L. J. 'Fourier Transform Infrared Spectroscopy', Academic Press, London, 1985, Vol. 3