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An Attempt to Evaluate Hydroxyl End-Groups in Polybutyleneterephthalate by Spin-Labelling Technique

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SUMMARY

Polybutyleneterephthalate (PBTP) has been labelled both in solution and in solid state with 3-chloroformyl-2,2,5,5-tetramethylpyrroline-1-oxyl . The reaction with PBTP in solution can be used to determine the hydroxyl end-groups . The differences observed in the spin-labelling of the polymer in solution and in solid state are discussed .

Introduction

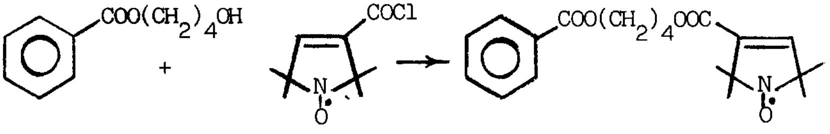
The spin-labelling technique is a simple way to extend the application of e.s.r. spectroscopy to diamagnetic polymer systems which do not contain unpaired electrons .

Many nitroxide radicals have been bounded to natural and synthetic polymers by weak intermolecular forces and by the formation of chemical bonds in the reaction of a polymer functional group with a suitable group in the nitroxide radical molecule (RANBY et al. 1977) .

The main interest in spin-labelled polymers has been in relaxation times (RÅNBY et al. 1977) . However , since e.s.r. spectroscopy is very sensitive to the concentration of free radicals , it may be conveniently used for polymer samples to evaluate functional groups which react quantitatively . In the present paper we describe a study of the spin-labelling of PBTP by reacting 3-chloroformyl-2,2,5,5-tetramethylpyrroline-1-oxyl <u>2</u> (ROZANTSEV 1970) with OH end-groups of the polymer . This reaction and e.s.r. spectroscopy may be employed as an alternative method to the usual ones for evaluating the OH end-groups , especially when their concentration is very low .

Results and discussion

To check the efficiency of the esterification of acyl chloride group of nitroxide <u>2</u> with OH end-groups , we reacted <u>2</u> with 4-hydroxy-1-butyl benzoate <u>1</u> (PILATI et al.1981) , chosen as a model for OH end-groups of PBTP , in benzene under reflux , using a slight excess of <u>2</u> . The ester was obtained in quantitative yield and identified by its elemental analysis and mass and e.s.r. spectra . This result led us to suppose we could determine the free OH end-groups in PBTP by the spin-labelling technique . In fact a 1,1,2,2-tetrachloroethane (TCE) solution of PBTP was treated with a large excess of <u>2</u> at 100 °C . The PBTP , precipitated in the reaction solvent by cooling , was collected , washed with benzene until no trace of radical was present in the washing benzene , and dried at 60 °C for one hour under vacuum . When we compared the areas of the e.s.r.



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signal of a solution of this polymer with that for 3-carbamide-2,2,5,5-tetramethylpirroline-1-oxyl solution (ROZANTSEV et al. 1965), the labelled PBTP showed 8.3 mmol/Kg for OH end-groups (see experimental) . The mean value of the OH groups obtained by the traditional method based on titration was 11.1 mmol/Kg , i.e. ca. 30% higher than that found by the spin-labelling tecnique .

Since the titration method cannot be used for cross-linked polyesters , owing to their insolubility , we also tried to label PBTP in the solid state . For this purpose two 150 μm thick films (A and B) with different crystallinities (A: ρ = 1.318 ; B : ρ = 1.300 g/cc) were refluxed for different times in benzene with an excess of 2 . These films , after the treatement described in the experimental section , were dissolved in phenol/TCE 60:40 (w/w) and the areas of the e.s.r. signal measured. From the results reported in Fig. 1 we can deduce that the concentration of the spin-probe after 5 h is still far from the expected value,and, furthermore , we can observe that the less crystalline film reacted slightly more than the more crystalline one . On the basis of these findings we reacted a 75 μm - thick film of PBTP (ρ = 1.306 g/cc) with nitroxide 2 for 45.5 h , taking samples at different times . The results of this experiment , reported in Fig.2 , show that the concentration of OH end-groups which reacted with nitroxide 2 was 5.8 mmol/Kg after 45.5 h , and that the concentration of reacted OH groups was still increasing and seems to tend to the limit obtained in the reaction performed in solution.

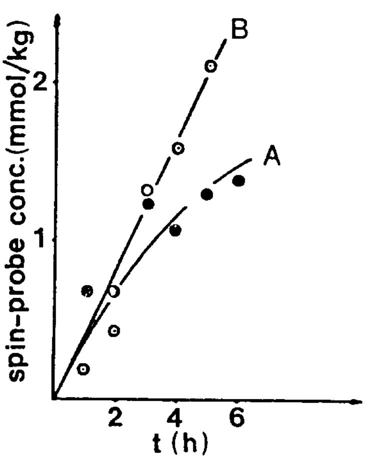

Fig.1 Spin-probe concentration versus time for two films (150 μm thick) with different cristallinities :
ρ_A = 1.318 ; ρ_B = 1.300 g/cc

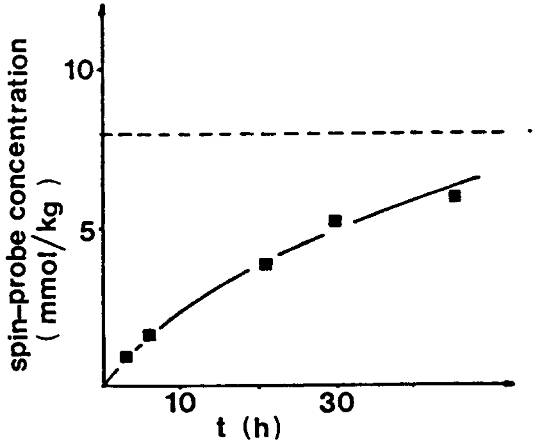

Fig.2 Spin-probe concentration versus time for a film (75 μm thick), ρ = 1.306 g/cc . Dashed line refers to the value obtained for PBTP labelled in solution.

The behaviour of the reaction carried out in solution and the results reported in Fig.s 1 and 2 clearly show that the reaction is diffusion-controlled in solid state . In fact , film samples of PBTP of different thicknesses (ρ = 1.318 g/cc) , when reacted with 2 for 2 h , gave results (see Fig.3) which confirm the diffusion effect in the reaction performed in solid state and show that the relative specific intensity decrease linearly with sample thickness .

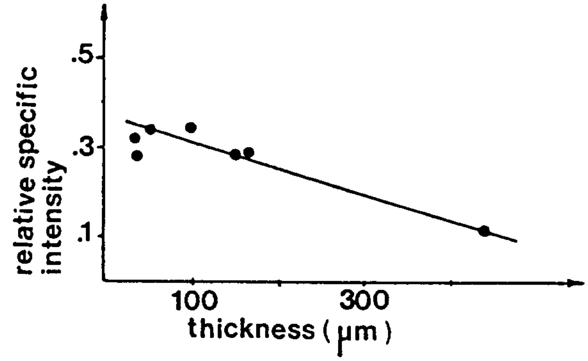

Fig.3 Film thickness effect in spin-labelling reaction.The relative specific intensity is the signal area of a solid sample divided by the signal area of a film obtained from TCE solution of a sample labelled in solution.

The signal recorded for solid films differ from those recorded in solution (see Fig.4) , and look like that obtained for solid spin-labelled cellulose (SUNDHOLM et al. 1980) .

Conclusions

Since each sample , after the spin-labelling reaction , was washed with benzene under reflux until no trace of nitroxide was present in the benzene solution , we can assume that the spin-probe was bounded to the chain by a covalent bond . Furthermore , if one considers that the evaluation of OH end-groups in polyesters by titration (BORMAN 1978) is prone to uncertainty , we can conclude that the proposed method could be considered an efficient alternative when the spin-labelling reaction is carried out on a polymer solution . The reaction performed in solid state can be used to partially label the polymer for relaxation time studies .

Work is now in progress to optimize this method for the quantitative evaluation of the end-groups in solid state , especially for cross-linked polyesters .

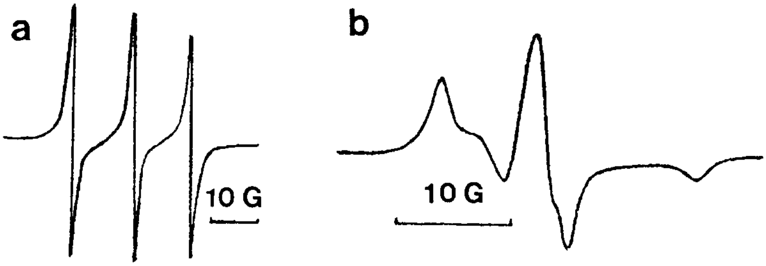

Fig.4 E.s.r. spectra of 3 for $CHCl_3$ solution (a) and of solid labelled PBTP film (b) .

Experimental

E.s.r. spectra were recorded on a Varian E4 spectrometer . The mass spectrum was recorded on a Varian 112 S apparatus . 4-Hydroxy-1-butyl benzoate 1 (PILATI et al. 1981) , and 3-chloroformyl-2,2,5,5-tetramethylpyrroline-1-oxyl (ROZANTSEV 1970) were prepared as described in the literature .

Preparation of PBTP samples

The PBTP used to obtain the films was prepared from dimethylterephthalate and 1,4-butanediol with $Ti(OBu)_4$ as catalyst by the usual method .
PBTP films with different thicknesses and/or different degrees of cristallinity were prepared by hot pressing PBTP between Teflon foils at 240°C in a hydraulic press . The films were either cooled at 100°C between the heated plates (films A) or were taken off while still melted and immidiatly quenched in an ice-water bath (film B) .

Density and intrinsic viscosity measurements

The film densities were measured by the floating method in CCl_4/Chlorobenzene.
The intrinsic viscosities of the films were measured with a Ubbelohde viscometer in phenol/TCE 60:40 (w/w) at 30.0 °C . All films had $[\eta]$ =

0.886 ± 0.006 dl/g .

Titration of end-groups

Total end-groups (OH + COOH) were evaluated according to Borman (BORMAN 1978) by dissolving ca. 0.5 g of sample in 40 ml of nitrobenzene/pyridine 95:5 at 150°C in an oil bath . Succinic anhydride (ca. 0.6 g) was added and the reaction was allowed to proceed for 100 min . The precipitated obtained , after several washings with acetone , was dried , weighed , dissolved in hot benzyl alcohol and titrated with 0.02 N KOH in methanol against a phenol-red indicator . Carboxyl end-groups were evaluated by dissolving a weighed portion of film in hot benzyl alcohol and titrating as described above . Five different samples were titrated for COOH end-groups and five for total end-groups . We obtained 70.6 ± 1.5 and 81.7 ± 7.3 mmol/Kg for COOH and total end-groups respectively . By difference the OH end-groups were 11.1 ± 1.2 mmol/Kg .

Synthesys of 4-(3-carbonyloxyl-2,2,5,5-tetramethylpyrroline-1-oxyl)-1-butyl benzoate 3

4-hydroxy-1-butyl benzoate (1.6 mmol in 25 ml of dried benzene) and 3-(chloroformyl-2,2,5,5-tetramethylpyrroline-1-oxyl (2.0 mmol in 30 ml of dried benzene) were mixed and refluxed for 1 h under nitrogen . The reaction mixture was than poured into water (100 ml) . The benzene layer was dried on Na_2SO_4 and chromatographed on silica-gel column eluting with benzene/acetone 9:1 . Compound 3 was isolated as an oil in 95% yield . Analysis : found; C , 66.7;H,7.3;N,4.0 ; calcd.for $C_{20}H_{26}NO_5$; C,66.64;H,7.27;N,3.89 . M^+/e : found 360 ; calcd.for $C_{20}H_{26}NO_5$ 360.42 . E.s.r. :a^N=13.75 G for $CHCl_3$ soln.

Reaction of PBTP with 3-chloroformyl-2,2,5,5-tetramethylpyrroline-1-oxyl in solution

3-chloroformyl-2,2,5,5-tetramethylpyrroline-1-oxyl (2 mmol in 30 ml of benzene) was added to a solution of PBTP (500 mg in 50 ml of TCE) at 100°C . After the addition , the reaction mixture was left to cool at room temperature . The precipitated labelled polymer was collected by filtration under vacuum , washed with boiling benzene until there was no trace of nitroxide in the washing benzene and then dried at 60°C under vacuum (3 mm Hg).

Spin-labelling of PBTP in film

a) Two films of PBTP (A , ρ = 1.318 ; B , ρ = 1.300 g/cc ; 150 μm thick; total amount 300 mg) were refluxed in 50 ml of benzene with 2 mmol of 2 . Samples were taken after 1,2,3,4,5 and 6 h . Each sample was washed with boiling benzene and then dried at 60°C under vacuum .

b) A 75 μm -thick film of PBTP (500 mg) was refluxed in 50 ml of benzene for 45.5 h with 2 mmol of 2 . Five samples were taken off after 3,6,21,30 and 45.5 h respectively and treated as described in (a) .

c) films of different thicknesses (total amount 315 mg) were refluxed for 2 h with 2 mmol of 2 in 30 ml of benzene . The samples were then treated as described above .

Spin-probe concentration in labelled polymer

E.s.r. signal areas of phenol/TCE 60:40 (w/w) solutions of spin labelled PBTP (ca. 5 g/l) and 3-carbamide-2,2,5,5-tetramethylpyrroline-1-oxyl (ca. $3 \cdot 10^{-3}$ M) were compared using as reference a signal of a ruby located into the e.s.r. cavity . The concentration of the spin-probe bounded on polymer was calculated from the concentration of the nitroxide radical 2 , assuming that this compound had one unpaired electron per molecule . The areas were calculated both with a planimeter and by the double integration method described by WYARD (WYARD 1965) .

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