Radiation grafting to poly(ethylene terephthalate) fibres

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Polyethylene terephthalate (PET) monofilaments were grafted with styrene in methylene chloride solution using both the mutual and preirradiation methods. Good yields were obtained, the grafted fibres were dissolved and the graft copolymer and both homopolymers separated by various techniques. The graft copolymers were hydrolysed with potassium hydroxide in benzyl alcohol to destroy the PET backbone. The molecular weights were determined by osmometry. The *G* values of grafted side chains were 0.57 and 0.10 per 100 eV for the mutual and preirradiation methods, respectively. The corresponding fractions of PET grafted were 0.24 and 0.11. Less than 4% homopolymer was produced by either method. The yields contrast with radical yields measured by e.s.r. of only 0.025. It is suggested that the high grafting yields are due to the methylene chloride facilitating the accessibility of the monomer to the active sites created by the radiation rather than by the increased yields of radicals by chain transfer. Chlorine, for example, did not lead to increased yields even in the presence of methylene chloride. Presumably, in the mutual grafting system, radicals are available for grafting, which are too labile to be detected by e.s.r. In the case of the preirradiation method, the yields are also higher than the radical yields. This may be due to a regenerative chain transfer mechanism.

INTRODUCTION

Polyethylene terephthalate (PET) is one of the most difficult polymers on which to graft. This is particularly true with PET textile fibres. Yet there is a decided need to graft various monomers to this type of fibre to impart useful properties such as hygroscopicity, soil release, anti-static behaviour and fire retardancy. The reasons for the difficulty in grafting are essentially two-fold: (1) in the case of radiation grafting the yield of free radicals on radiolysis is unusually low and (2) the drawn fibres absorb very little of most organic liquids such as the vinyl monomers and the rates of diffusion into the fibres are extremely low. Previous work has shown, however, that the grafting yield is greatly improved by the judicious use of suitable swelling agents[1–3]. Chlorinated solvents were found to be particularly effective. This finding was confirmed by the publication of parallel work in Japan[4]. In both studies methylene chloride gave optimum swelling and grafting results.

The present paper describes studies aimed at learning more about the role of the swelling agents. In particular how reasonable amounts of grafting are achieved in view of the low *G*(radical) values found with PET. The yields of grafted side chains were determined and the values compared with the *G*(radical) values obtained by e.s.r. measurements. Styrene was chosen as the 'model' monomer since it responds well to both the mutual and preirradiation grafting methods. In addition the polystyrene side chains are not affected by the alkaline hydrolysis necessary to isolate them by destruction of the PET backbone.

The free radical yields and the effects of the swelling agents on the radical buildup and decay were investigated using e.s.r. methods in a parallel study described in a previous paper[5].

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EXPERIMENTAL

Similar polyethyleneterephthalate (PET) monofilaments were used and were treated exactly as in the e.s.r. work described previously[5]. Styrene monomer was purified by washing with 3% NaOH solution, followed by drying over $CaCl_2$ and vacuum distillation while contacting CaH_2. The distilled styrene was stored by refrigeration for a maximum of two weeks. Methylene chloride was of reagent grade and was used without further purification.

Weighted amounts of PET fibre were placed in glass ampoules, contacted with a 1:1 (by volume) mixture of styrene and CH_2Cl_2, degassed by several freeze-thaw cycles, allowed to swell to equilibrium and then irradiated. The weight ratio of solution to fibre was 15.6 to 1.

Other experiments were conducted by the pre-irradiation method. The contact between the irradiated PET and the above mixture was made by breaking a seal after the mixture was outgassed by several freeze-thaw cycles. The samples were then stored in a dark place at room temperature

When the samples were irradiated in the presence of Cl_2, a method which was already described[5] was used for the sample preparation. The irradiations were carried out in a Gamacell ^{60}Co source (Atomic Energy of Canada Ltd.) at a dose rate of 0.38 Mrad/h as determined using Fricke dosimetry modified with $CuSO_4$. The large scale irradiation experiments which involved as much as 30 g fibre were performed in a pool-type ^{60}Co source at a dose rate of 0.5 Mrad/h.

The grafted fibres were benzene extracted in a Sohxlet

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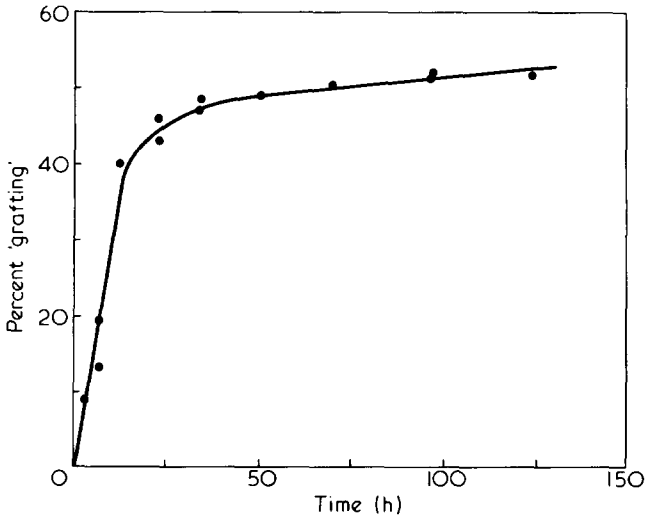

Figure 1 Mutual grafting of styrene to PET at 25°C in 50/50 styrene-methylene chloride solution. Dose rate 0.38 Mrads per hour

for 3 days to remove the homopolymer, then air dried vacuum extracted overnight and weighed. The apparent grafting was determined as the weight increase percentage. The homopolymer from the reaction mixture and from extraction was precipitated with methanol, dried in air and vacuum and stored. Two different ways were used for the separation of occluded homopolymer and the graft copolymer; fractionation by precipitation and column chromatography.

The Soxhlet extracted fibre was dissolved in tetrachloroethane (TCE) and then precipitated with methanol. The precipitate was dried, ground and Soxhlet extracted in benzene for occluded polystyrene (PS) removal. After drying the residue was again dissolved in TCE and precipitated in methanol to give a powder in which other parts of the occluded homopolystyrene were made available for extraction. The procedure was repeated three times and after the third precipitation practically no homopolymer could be extracted. However, an extremely small amount of homopolystyrene could still be isolated by thin layer chromatography.

An attempt was also made to separate the mixture of unreacted PET, occluded homopolystyrene and graft copolymer (PET–*g*–PS) by fractional precipitation. Small volumes of methanol were added under stirring to a solution of 3% of the polymer mixture in TCE. The precipitated fractions were collected after centrifugation. The polymer was dried and its nature determined by thin layer chromatography (t.l.c.).

T.l.c. experiments used Eastman Kodak chromatogram sheets, without preliminary activation, and were conducted in a simple chamber. A glass rod bearing the plate could be pushed through the stopper and after a period of one hour required for chamber saturation, the rod was lowered till the chromatoplate reached the solution.

The chamber presented a big enough evaporation area and just before use was tilted to wet the lateral walls thus insuring rapid evaporation. The polymers were spotted and dissolved in TCE which evaporates quickly in air. The plates were developed in different solutions as will be described later. The chromatograms were examined under u.v. light and were made visible by spraying with a 1.5% iodine solution in methanol when yellowish spots appeared on a blue background.

In some experiments the polymers were separated on a column of 6-inch diameter and 30-inch length filled with silicagel G on which amounts as large as 10 g were separated. The fractions collected (10 ml) were checked by t.l.c. for the identification of the polymer. Fractions containing the same polymer were added together and the polymer isolated by precipitation with methanol.

The grafted polystyrene branches were separated from the backbone polymer by hydrolysis at 50°C in N/Y KOH benzyl alcohol as described by Sakurada *et al.*[6].

RESULTS

The use of methylene chloride as a swelling agent results in very high grafting yields with the mutual method as can be seen from *Figure 1* which presents the apparent grafting as a function of the irradiation time.

Still higher grafting yields are obtained by the preirradiation method as shown in *Figure 2* where the grafting yield is plotted against the reaction time. These highly increased grafting yields are clearly connected with the presence of the methylene chloride as shown in *Table 1* where the grafting yields in the presence and absence of the solvent are presented for the purpose of comparison.

In order to check if the increased grafting yields are due to chlorine atoms released during the radiolysis, some experiments of mutual grafting were conducted in the presence of Cl_2, or mixtures of Cl_2 + CH_2Cl_2 and the results are presented in *Table 2*. As can be seen from *Table 2*, the presence of Cl_2 results in a slight decrease of the grafting yield either

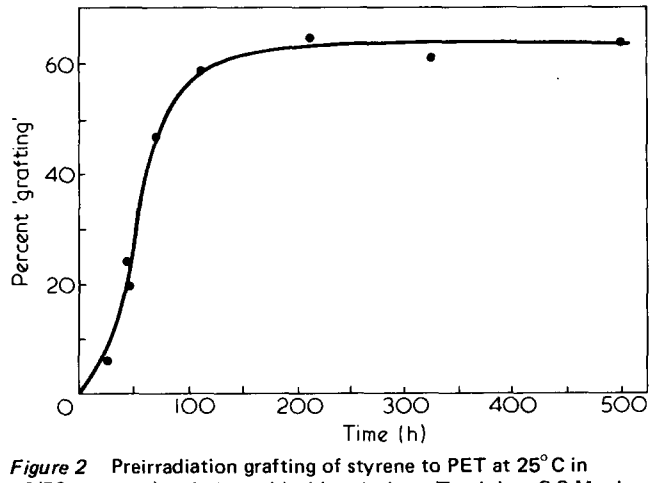

Figure 2 Preirradiation grafting of styrene to PET at 25°C in 50/50 styrene–methylene chloride solution. Total dose 8.9 Mrad at 0.38 Mrad/h

Table 1 The influence of methylene chloride on the grafting yield

Method	Swelling agent	Apparent grafting (%)	Atmosphere
Mutual grafting	None	5.6	Vacuum
Mutual grafting	CH_2Cl_2	28.0	Vacuum
Preirradiation*	None	5.0	Vacuum
Preirradiation*	CH_2Cl_2	64.0	Vacuum
Preirradiation*	None	2.6	Air
Preirradiation*	CH_2Cl_2	6.0	Air

* Time of reaction 14.5 days. Dose = 8.9 Mrad

Table 2 The influence of Cl_2 on the grafting yield in the mutual grafting method

Conditions	–	Cl_2	CH_2Cl_2	$CH_2Cl_2 + Cl_2$
Grafting yield (%)	5.6	5.1	49.0	32.3
		Dose = 18.8 Mrad		

Table 3 Grafting experiments which supplied the polymers for separation and analysis

Method	Dose (Mrad)	Apparent grafting (%)	True grafting (%)	% PS occluded (extractable)
Mutual grafting	3.8	25.4	21.8	3.6
Preirradiation*	9	64	60.5	3.5

* Time of reaction = 29 days. Dose rate = 0.5 Mrad/h

in the presence of the swelling agent or in its absence. At the same time, it was noticed that the amount of homopolymer was considerably increased.

Once the optimum conditions for grafting were established, large scale irradiations were carried out in order to supply enough material for analysis. The separation and analysis of the polymers for molecular weight was performed on the samples described in *Table 3*.

Polymer identification and separation

Thin layer chromatography (t.l.c.) as applied for the separation of the components of a polymeric mixture according to their chemical nature, stereoisomerism and molecular weight is a method still at its beginning. The main problem is to find a suitable developer and eliminate the tailing off phenomena apparently present to a higher extent in polymers than in other materials.

The mixture of PET, PET–*g*–PS and PS was analysed from the point of view of developer and it was found that pure TCE can act as a developer for PS only. Different mixtures of TCE and CH_3OH or CH_3COCH_3 were tested and it was found that although the separation was achievable, the tailing off prevented it. The concentration gradient technique was not of help in eliminating this phenomenon. Different mixtures of PhOH and TCE were tested and it was found that 2.0–2.5:25 PhOH:TCE (by volume) brought the complete separation and eliminated the tailing off. *Figure 3* presents a chromatogram where PS, the Sohxlet extracted fibre and PET were spotted as dissolved in TCE. As can be seen, the graft copolymer remains as a spot on the starting line, a behaviour which has already been described for other graft copolymers[7].

The tailing off phenomena were found to be highly dependent on the concentration of the initial spot, chamber saturation and temperature; the importance of these conditions has already been reviewed in the literature[8].

To check the possibility that the spot remaining at the starting line is due to crosslinked PET, a sample was irradiated at the same dose and a chromatogram carried out. No spot at the starting line was observed.

After establishing the conditions for t.l.c. the separation of the polymers on a silicagel column was performed and the collected fractions were checked by t.l.c. The graft copolymer which remained adsorbed on silicagel was extracted after all other fractions were eluted. It was found that only a mixture of 1:1 PhOH:TCE (by volume) could extract it. TCE alone could not extract the adsorbed graft copolymer.

The separation of occluded homopolymer by an apparently thorough method of alternating steps of precipitation and extraction is not complete; nor was fractionation of the polymeric mixture by precipitation perfect. Using the technique described in the experimental section, the result can be described as follows. The first fraction contained PET, followed by fractions containing PET and graft copolymer, and finally pure PS could be isolated in the last fractions. The graft copolymer could not be obtained by this method and this has been explained by its emulsifying behaviour[6].

Structure of the graft copolymers

The isolated polymers and the grafted PS branches separated by hydrolysis were analysed from the point of view of the molecular weight and the results are presented in *Table 4* together with other pertinent data.

The use of CH_2Cl_2 as a swelling agent results in a very high true grafting yield for this polymer, known from the literature to give poor grafting. According to our experimental data using sorbed chlorine it is not the Cl atoms released by radiolysis of CH_2Cl_2 that increase the grafting yield, but the plasticizing action of CH_2Cl_2 itself which results in a higher mobility of the macroradials and an increased rate of diffusion of monomer inside the fibre. The amount of occluded PS is only about 3.5% irrespective of the method of grafting. This is the maximum which was obtained.

The molecular weight of the homo PS formed in the liquid phase is lower than that of occluded PS, both in mutual and preirradiation grafting, which has been already explained by the gel effect being easily attained inside the plasticized fibre.

The molecular weights of the homo PS and the grafted branches are quite similar; this can be explained by the radicals growing in the same conditions inside the fibre. We do not have any direct evidence regarding the molecular weight distribution of the polymers formed inside the fibre, but the spot obtained in the t.l. chromatogram (*Figure 3*) for the homopolymer formed in the bulk of the solution could be regarded as due to a large molecular weight distri-

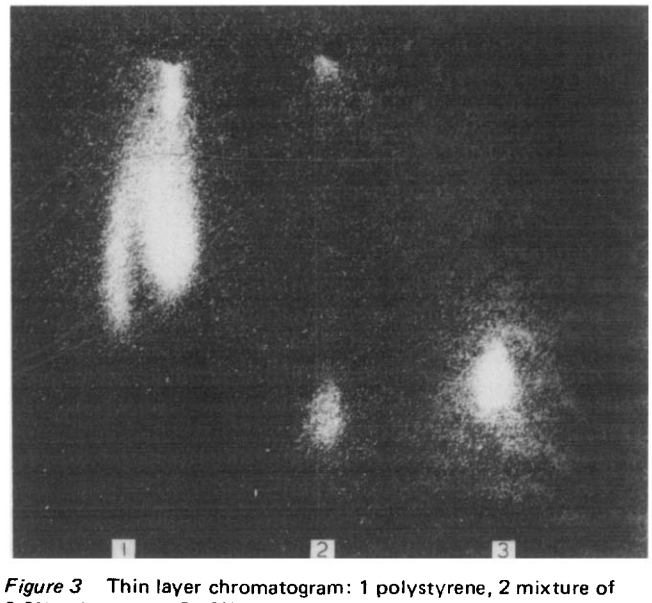

Figure 3 Thin layer chromatogram: 1 polystyrene, 2 mixture of 3.6% polystyrene, 21.8% graft copolymer and 74.6% PET, 3 PET

Table 4 The molecular weight of the isolated polymers

Method	Initial PET	Homo PS	Occluded PS	PET-*g*-PS	Grafted branch	No. branches* per PET-*g*-PS molecule	$\frac{\bar{M}_B}{\bar{M}_{BO}}$†	*G* (branches/ 100 eV)	Fraction of PET grafted
Mutual grafting	51.700	1400	78 800	165 400	63 600	1.40	1.50	0.57	0.24
Preirradiation	51 700	50 100	661 600	870 600	661 660	1.18	1.75	0.10	0.11

* cf. 1.15 and 1.06 theoretical
† cf. 1.60 and 1.84 theoretical

bution by comparison with the spot obtained for the occluded homo PS.

The molecular weights of the homo PS, occluded PS and grafted branches are higher in the preirradiation method and this is easy to understand in view of the continuous initiation in the case of mutual grafting. A calculation of the number of grafted PS branches per backbone chain, Ng, using the method of Ikada and Horii[9] for the case of a most probable molecular weight distribution gave somewhat lower values compared with the actual experimental results. The ratio of the number average molecular weights of the grafted backbones $\bar{M}_B$ and the original PET substrate $\bar{M}_{BO}$, on the other hand, showed rather good agreement. These values are included in *Table 4*. It is probable that the molecular weight distribution of the PET is somewhat narrower than the most probable value.

The *G* (branches) values are also included in *Table 4* and are much higher than the *G* (radical) values found with e.s.r. It is probable that, with the mutual method, a proportion of the radicals formed by the radiolysis are captured by styrene before they can terminate by recombination. This cannot be the explanation for preirradiation grafting when lower, but still high, values are obtained. A reasonable explanation which is also valid for part of the mutual grafting *G* value is that the growing chains transfer to the PET molecules leading to new branches. This explanation is strongly supported by the extremely low yields, less than 3.5%, of occluded homopolymer found with both methods of grafting.

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