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The Radiation-Induced Grafting of Vinyl Monomers to Polyethylene Terephthalate Fibers. Part I. Styrene

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The Radiation-Induced Grafting of Vinyl Monomers to Polyethylene Terephthalate Fibers.

Part I. Styrene

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ABSTRACT

Some kinetic features of the mutual radiation grafting of styrene to polyethylene terephthalate fibers have been investigated. The effects of type of swelling agent, monomer concentration, and temperature have been determined. In general a maximum in the grafting rate was found to occur both with the concentration of swelling agent and with temperature. Undrawn fibers were found to graft at higher rates and maximum yield than drawn fibers. These and other features are discussed in terms of a simple grafting scheme coupled with diffusion controlled kinetics.

INTRODUCTION

The modification of textile fibers with ionizing radiation is interesting from the theoretical and practical points of view. Grafting to fibers is particularly interesting since it enables the superposition

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of the group of properties of the grafted side chains onto the fiber without necessarily disturbing the properties of the parent fiber. The whole field of the radiation modification of textile fibers has been reviewed in detail by Stannett and Hoffman [1] and more recently by Hoffman [2, 3].

Studies of the radiation grafting of styrene to polyethylene terephthalate film have been reported by Ballentine and Glines [4]. The radiation grafting of itaconic acid, acrylamide, and vinyl pyridine has been discussed by Hoigne and Schamberg [5, 6] together with the chemical grafting of styrene. The radiation grafting of acrylic acid and other monomers to polyester fibers has been studied in detail by Zielinski [7, 8], Blin [9], and Sakurada [10-16] and their co-workers, and, more recently, by Bonnefis and Puig [17].

In this paper the effects of temperature and of dimethyl sulfoxide and water as swelling agents on the radiation induced grafting of styrene to polyethylene terephthalate fibers will be discussed. A brief report of our initial work was presented in a special dedication volume of the Revue Roumaine de Chimie [18].

EXPERIMENTAL

Materials

Monsanto Chemical Co., U.S.A., polyethylene terephthalate fibers in the form of monofilaments and of drawn and undrawn multifilament tire cord yarn were used. The characteristic of these are given in Table 1. The fibers were treated in a.Soxhlet with methanol and acetone and dried under vacuum to constant weight before use. The styrene, dimethylsulfoxide, dimethylformamide, pyridine, and other reagents were obtained from the Fisher Scientific Co. and purified by distillation before use.

TABLE 1. Polyethylene Terephthalate Fibers Used[a]

Sample No.	666F	30 A undrawn	30 A drawn
Form	Monofilaments	Tire yarns ·	Tire yarns
Denier	297	200 × 30	200 × 5
Molecular weight	33,000	33,000	33,000
Density	-	1.340	1.404
% Crystallinity	~58	~0	~58
COOH end groups μ equiv 1 g	21	21	21
Draw ratio	Highly drawn	0	5.3

[a] All fibers were unfinished. Monsanto Chemical Co.

Procedures

Fibers (0.5-1.0 g) were placed in glass ampoules together with the monomer and solvents and degassed by several freeze-thaw cycles at 10^{-5} Torr and sealed under vacuum. The irradiations were carried out at 0.73 Mrads/hr in a ^{60}Co radiation source. The grafted fibers were washed with benzene and dried to constant weight. The increase in weight was recorded as the grafting yield.

RESULTS

Kinetics in Dimethylsulfoxide Solution

Effect of Dose

The percent of graft was found to increase linearly with dose (time) after only very short induction periods as shown, for example, in Fig. 1.

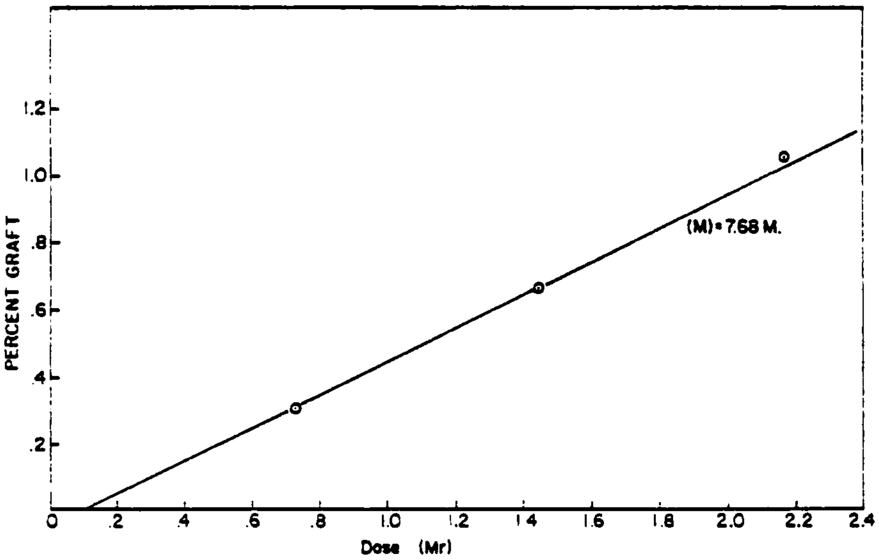

FIG. 1. Effect of dose on radiation grafting yield. Dose rate, 0.72 Mrad/hr; temperature, 30°C. Solvent, dimethylsulfoxide. (Monofilaments).

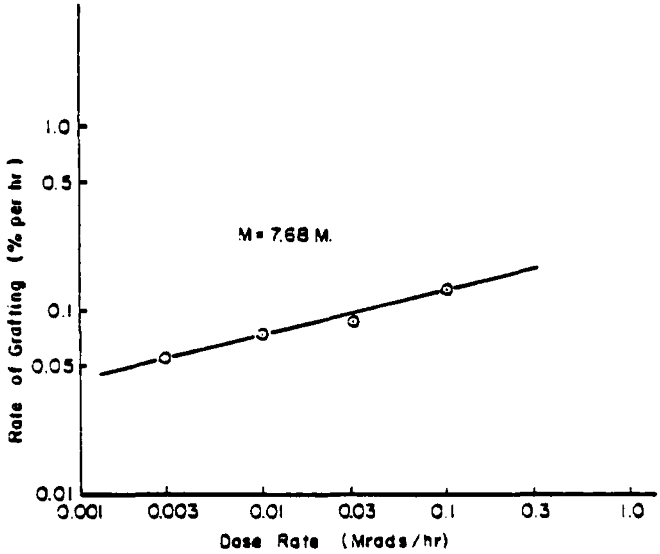

FIG. 2. Effect of dose rate on grafting rate at 30°C. Solvent, dimethylsulfoxide. (Monofilaments).

Effect of Dose Rate

The effect of dose rate on the rate of grafting in styrene-dimethylsulfoxide solution is shown as a log-log plot in Fig. 2. A dose rate dependence of the rate of 0.48 was found.

Effect of Dimethylsulfoxide Concentration

The effect of the concentration of dimethylsulfoxide on the rate of grafting for all three types of fiber is illustrated in Fig. 3. In all cases the addition of small amounts of dimethylsulfoxide to the styrene increased the rate of grafting considerably, followed by a gradual decline in the rate. It is also clear that the undrawn small denier fibers graft much faster than the drawn fibers, the higher denier, drawn monofilaments grafting the least. The dependence of the rate on the monomer concentration after the initial maximum has been reached is shown for the drawn tire cord in Fig. 4. A 1.5 order was found for the dependence of grafting rate on the monomer concentration.

Effect of Temperature

The effect of temperature on the grafting rate with the styrene-dimethylsulfoxide system solutions is illustrated in Fig. 5. It can be

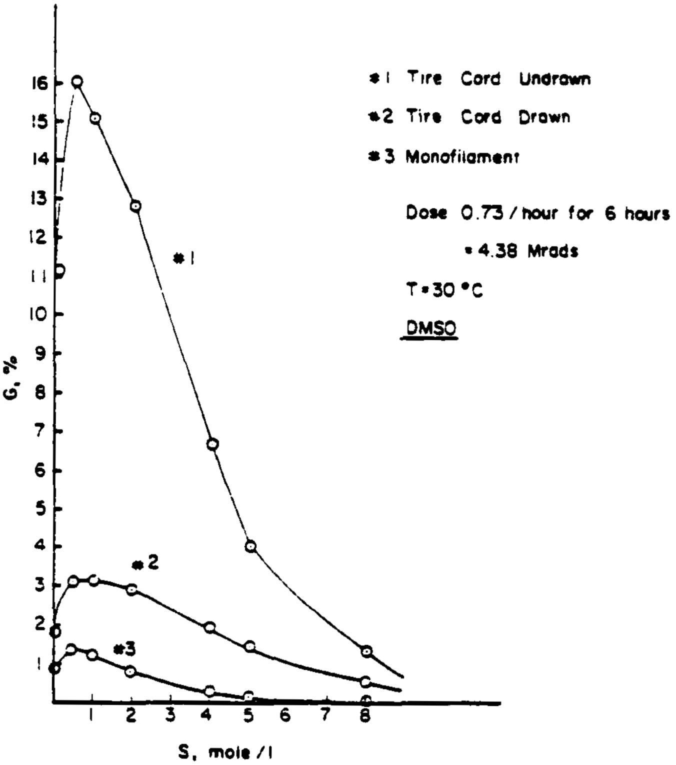

FIG. 3. Effect of dimethylsulfoxide concentration on the grafting yield for three different types of fibers.

seen that, in agreement with the results of Hoigne and Schamberg [5, 6], a maximum is reached in the vicinity of the glass temperature. Below the glass temperature an overall activation energy of 13.7 kcal/mole is found in the absence of water and 12.4 kcal/mole in the presence of water. The decrease in the activation energy presumably reflects the slight plasticizing effect of the water.

Grafting Rates in Other Solvents

A similar series of experiments were conducted in pyridine and in dimethylformamide-styrene mixtures. The results, illustrated in Figs. 6, 7, and 8, are very similar to those found with dimethylsulfoxide.

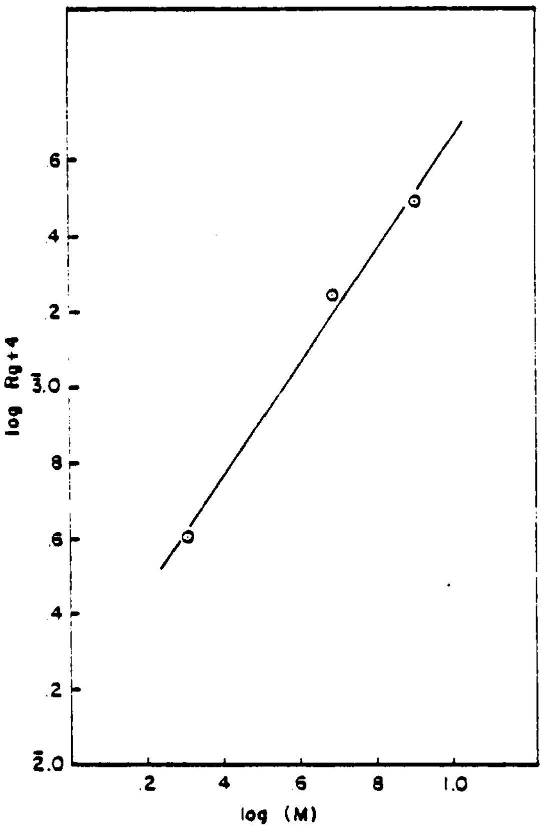

FIG. 4. Effect of monomer concentration on the rate of grafting, drawn tire cord at 30°C. Dose rate, 0.73 Mrad/hr. Solvent, dimethylsulfoxide.

From 50-80°C the rates were in the order DMSO > pyridine > DMF but were of a similar order of magnitude for all three solvents. Similar maxima were also found for all three solvents and there were also similar temperature effects as shown in Fig. 8. The three different types of fibers grafted in the same order for all three solvents.

DISCUSSION

The overall radiation grafting and homopolymerization process can be expressed in the following steps:

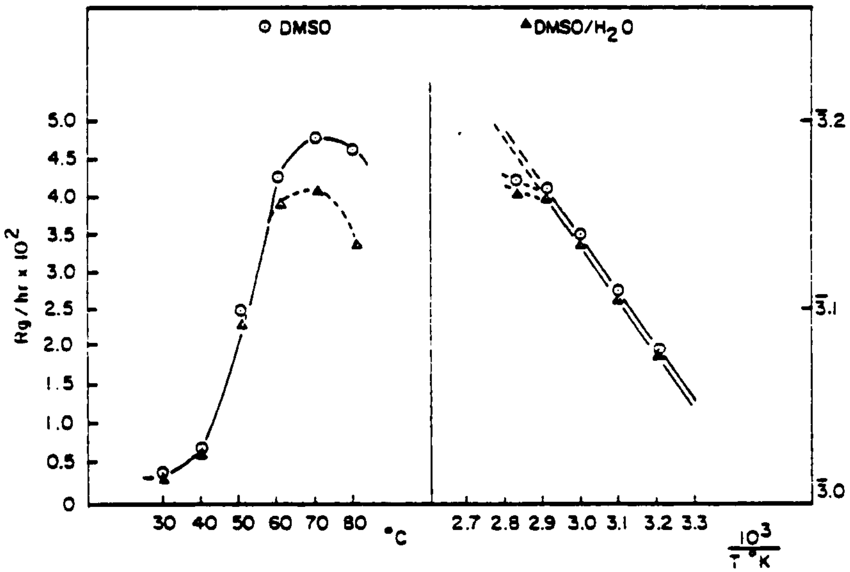

FIG. 5. Effect of temperature on the rate of grafting, drawn tire cord. Dimethylsulfoxide concentration, 2.55 moles/liter H_2O and 0.92 mole/liter. Dose rate, 0.73 Mrad/hr.

Formation of Radicals

Monomer $M \rightsquigarrow M'\cdot \qquad R_{11} = G_R(M)I$ (1)

Solvent $S \rightsquigarrow S\cdot \qquad R_{12} = G_{RS}(S)I$ (2)

Polymer $P \rightsquigarrow P\cdot \qquad R_{13} = G_{RP}(P)I$ (3)

Chain Initiation

$M'\cdot + M \rightarrow M'M\cdot$ (4)

$S\cdot + M \rightarrow SM\cdot$ (5)

$P\cdot + M \rightarrow PM\cdot$ (6)

Chain Growth

$M'M\cdot + M \rightarrow M'M_2\cdot$ homopolymer (7)

$SM\cdot + M \rightarrow SM_2\cdot$ homopolymer (8)

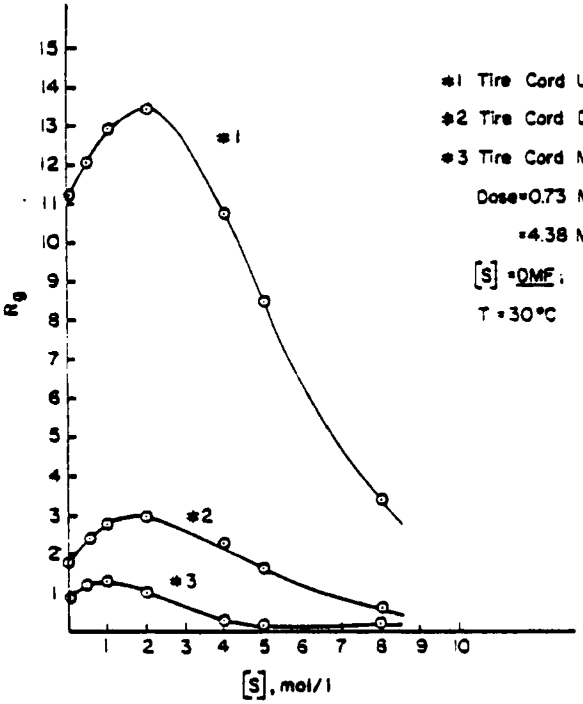

FIG. 6. Effect of dimethylformamide concentration on the rates of grafting for three types of fibers.

$$PM\cdot + M \rightarrow PM_2\cdot \quad \text{graft copolymer} \tag{9}$$

$$\text{Rate} = K_p(M\cdot)(M)$$

Chain Transfer

$$M\cdot + M \rightarrow MH + M\cdot \tag{10}$$

$$\rightarrow \text{homopolymer}$$

$$M\cdot + S \rightarrow MH + S \tag{11}$$

$$M\cdot + P \rightarrow MH + P\cdot \rightarrow \text{graft copolymer} \tag{12}$$

Termination

$$M\cdot + M\cdot \rightarrow M{-}M \tag{13}$$

The overall rate of grafting is given by the reactions

$P\cdot + M \rightarrow PM\cdot$

$PM\cdot + M \rightarrow PM_2\cdot$ etc.

Whereas homopolymer is produced by

$M'\cdot + M \rightarrow M'M\cdot$

$M'M\cdot + M \rightarrow M'M_2\cdot$ etc.

$S\cdot + M \rightarrow SM\cdot$

$SM\cdot + M \rightarrow SM_2\cdot$ etc.

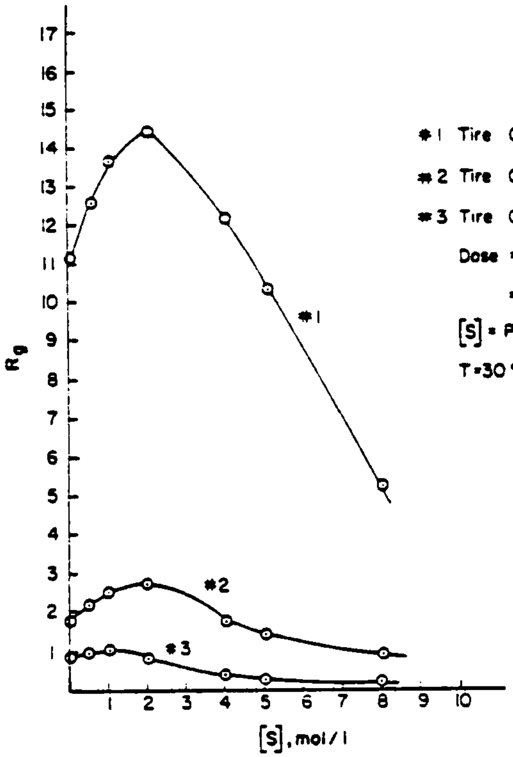

FIG. 7. Effect of pyridine concentration on the rates of grafting for three types of fiber.

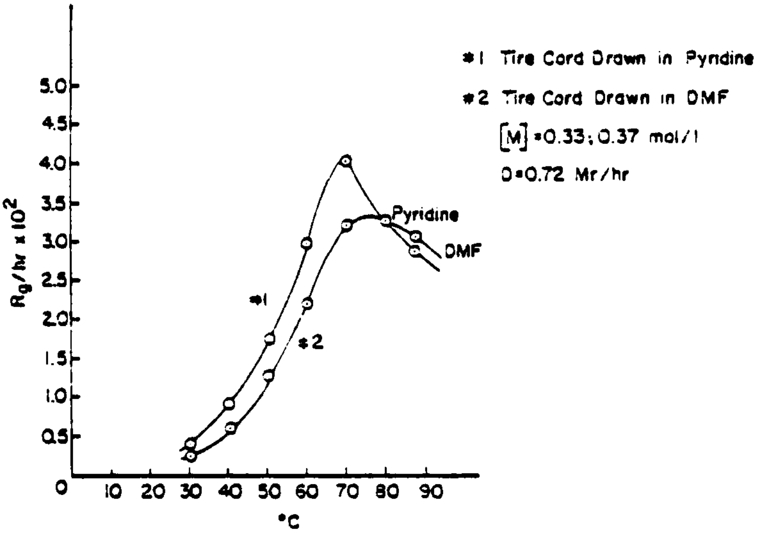

FIG. 8. Effect of temperature on the rates of grafting for drawn tire cord in pyridine and in dimethylformamide.

In general the ratio of grafting to homopolymerization will depend on the relative rates of production of P· and of S· plus M'·.

The direct production of P· is probably very small with a G(R·) values of about 0.05 [19]. M'· has a G(R·) value of 0.7 in the case of styrene. The three solvents studied have G(R·) values of 1.28 for dimethylsulfoxide [20], 2.3 - 9.2 for dimethylformamide [21], and about 0.3 for pyridine [21]. Considerable energy transfer was found to be involved with styrene and the latter two solvents [21].

Primary radicals will also be formed by chain transfer reactions; here the formation of polymer radicals should be favored. Dimethylsulfoxide has a chain transfer constant of 6.9×10^{-5}, quite similar to the value for styrene of 6.0×10^{-5}. The highly conjugated polyethylene terephthalate structure should have a much higher value.

Very little posteffect was found in this study, although the reactions are clearly diffusion controlled, so perhaps steady-state kinetics are a reasonable approximation. This would lead to a square-root dependence of the rate on the dose rate, and a rate of between 1.0 and 1.5 on the monomer concentration. Values of about 0.5 and 1.5, respectively, were found in the present study with dimethylsulfoxide.

The effect of the temperature, which shows a maximum in yield in the vicinity of the glass temperature, is in agreement with the results of

TABLE 2. Effect of Temperature and Swelling Agents on the Radiation Grafting Yield G(-M)[a]

Temp (°C)	DMSO G(-M)	DMF G(-M)	Pyridine G(-M)
30	47.7	30.89	50.21
40	87.5	74.67	102.97
50	373.4	158.34	221.43
60	642.6	413.25	514.84
70	750.0	518.40	581.54
80	699.0	492.14	509.01

[a] [M] ca. 0.35 mole/liter.

Hoigne and Schamberg [5, 6]. The results have been satisfactorily explained as due to the effect of the polymer mobility causing an increase in grafting up to a certain point when the mobility is so great that the gel effect begins to decrease, leading to a falling off in the rate. A similar effect was found by Stannett, Wellons, and Yasuda [21] when the proportion of swelling agent was increased in grafting studies of styrene to cellulose acetate. In this case the decrease in the rate with the further addition of solvent is also caused by the reduction in monomer content. It is interesting that a similar maximum is reached in the present system both with the addition of swelling agents and with increases in temperature (Table 2).

The role of the swelling agent (solvents) is obviously highly complex since they participate in the initiation and chain transfer processes as well as facilitating both the diffusion of monomer to the active sites and the termination reactions. In addition, their role is complicated by energy transfer processes. Combined ESR and kinetic studies including molecular weight determinations are needed to elucidate the significance of the various steps leading to the grafting process. Undoubtedly occluded homopolymer is also contained in the grafted fibers, and these would need to be separated for more detailed studies. Such studies are currently underway in these laboratories.

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