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INFLUENCE OF SOME FACTORS ON RADIATION GRAFTING OF STYRENE ON POLY(ETHYLENE TEREPHTHALATE) NUCLEAR MEMBRANES

N. I. ZHITARIUK and N. I. SHTANKO

Laboratory of Nuclear Reactions, Joint Institute for Nuclear Research, Dubna, P.O. Box 79, 101000 Moscow, U.S.S.R.

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Abstract—Radiation-induced graft polymerization of styrene from the liquid phase on to poly(ethylene terephthalate) nuclear membranes and films has been investigated. Grafting was carried out by the methods of pre-irradiation in air and in vacuum. It is shown that dose rate does not affect the rate of graft polymerization. Linear dependence of the limiting grafting yield on dose has been obtained for pre-irradiation in vacuum. The influence of sample storage time after completion of the irradiation on graft polymerization kinetics has been studied: for pre-irradiation in vacuum, grafting yield passes through a maximum; for pre-irradiation in air, grafting yield decreases continuously and the rate of its decrease is greater for samples kept in air than in vacuum.

INTRODUCTION

Radiation-induced graft polymerization of styrene onto poly(ethylene terephthalate) (PETP) has been studied in several papers. In most cases, the direct method of grafting was used; the polymer was dipped either in pure monomer or in a monomer solution and the system was irradiated [1–8]. The equilibrium radical concentration in irradiated PETP is *ca* 10^{17} radicals per gram [9]. Such a small concentration of paramagnetic sites must lead to insufficient activity of PETP in the grafting process. Indeed, in early work on graft polymerization, PETP matrix was different from others in both the small rate of grafting and the small limiting grafting yield [10]. Subsequent work led to results indicating the possibility of grafting yields reaching 20–30%. In the direct grafting method, a considerable proportion of the radicals can be introduced into the PETP substrate from the outside [2]. The radicals formed in a monomer and the solution surrounding a polymeric matrix diffuse into the PETP where they initiate polymerization. Macromolecules thus formed have no chemical bonds with the matrix but, because of molecular entanglement, they are retained firmly in the bulk of the polymeric matrix.

We know of two papers partly concerned with the grafting of styrene onto PETP by using the method of pre-irradiation in vacuum [1, 11] but we have no information on grafting in this system using pre-irradiation in air.

In the method of pre-irradiation in air, the concentration of the peroxides in PETP is proportional to dose up to 50–100 kGy [12, 13]. Further increase in dose leads either to saturation connected with dissociation of peroxides and/or hydroperoxides, as a result of their radiolysis, or to a relationship between grafting rate and dose showing a maximum [14].

Application of both grafting methods in a particular polymer/monomer system will be successful if the radicals and the peroxides generated during irradiation are stable during storage after irradiation. In that connection, PETP is characterized by a long life-time of the radicals [15, 16] and by the formation of substances with oxygen-to-oxygen bond in their molecules (peroxides and ozonides [17] and/or hydroperoxides [18]), which are stable at ambient temperature.

In this work, grafting of styrene onto the PETP nuclear membranes and films by the methods of pre-irradiation in vacuum or in an atmosphere containing oxygen has been studied. The relationships between grafting yield and dose rate, pre-irradiation dose and storage time for the samples after completion of irradiation have been obtained.

EXPERIMENTAL PROCEDURES

Materials

Nuclear membranes were obtained by a known method on the basis of PETP film (Lavsan made in the U.S.S.R. in accordance with State Standard 24234-80) of 10 μm thick (designated as L-10 in Table 1) [19]. Nuclear membrane characteristics are shown in Table 1. Membranes and film were not subject to additional purification. Styrene was cleaned from inhibitor by washing with alkali and then double vacuum distillation.

Methods

Graft polymerization was carried out as described earlier [20]. Nuclear membranes and film activated with γ-rays were stored at ambient temperature (20–30°C) in vacuum (10^{-2} torr) or in air, in the dark. The grafting yield (Q) is defined as percentage weight gain of the sample.

RESULTS AND DISCUSSION

Dose rate

Figure 1 gives typical curves showing accumulation of grafted polystyrene (PS) on PETP nuclear membranes with different pore sizes and on PETP film

Table 1. Some characteristics of membranes and film used for graft polymerization

Sample code	Pore density (cm^{-2})	d_b* (μm)	d_g* (μm)	Thickness (μm)	Porosity† (%)	L (μm)
0.05–F	2×10^9	—	0.05	9.9 ± 0.3	8.0 ± 0.5	0.25
0.1–F	3.2×10^8	0.095	—	10.1 ± 0.2	8.1 ± 0.7	0.67
1–F	5×10^6	0.93	—	8.6 ± 0.2	7.7 ± 0.2	5.1
L–10	—	—	—	10	—	—

*d_b, d_g are pore sizes obtained by a "bulb" and gas dynamic methods, respectively.
†Porosity obtained by a gravimetric method.

of 10 μm thick. The method of pre-irradiation in vacuum is characterized by high initial rate of graft polymerization. In the initial part of the accumulation curve, the polymerization has an explosive character and its rate depends on the kinetics of monomer sorption by the matrix. The grafting rate later decreases and becomes constant. On the film L–10, the rate of grafting is *ca* zero but, on the membranes 1–F and 0.1–F, it is not zero. This form of the accumulation curves is apparently explained by the fact that, with an increase of the average distance between the pore axes L (see Table 1) and when it approaches the film thickness, radical recombination in the crystalline phase of PETP under the conditions of the graft polymerization begins to compete successfully with the initiation of graft chains by the radicals. It should be pointed out that, in the amorphous regions, the radicals are accessible to monomer molecules even in the initial stage of grafting [11, 15], and recombination of the radicals is more probable in the thick substrate where access of monomer to initiating sites is more difficult.

Grafting rate in the method of pre-irradiation in air is considerably lower. Except for the initial range, grafting yield increases linearly with time.

The dose rate does not affect the polymer activity in the grafting of styrene in the method of pre-irradiation in vacuum (see Table 2). Grafting yield is practically constant when the dose rate is changed 50-fold. This finding agrees with literature data obtained for grafting on other polymeric matrixes [22–24].

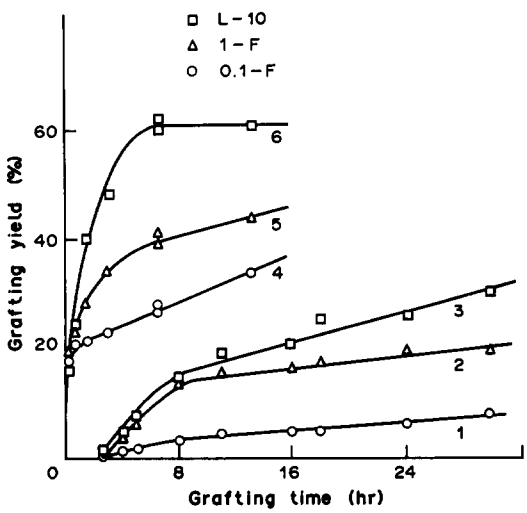

Fig. 1. Curves of PS accumulation on PETP film and nuclear membranes. 1—3, Pre-irradiation in air, dose D = 50 kGy; 4—6, pre-irradiation in vacuum, D = 50 kGy. Grafting temperature = 70°, dose rate = 0.75 Gy/sec.

An analogous picture is seen for pre-irradiation in air when irradiation is carried out in oxygen. If PETP activation is carried out in oxygen, the grafting yield depends somewhat on dose rate (Table 2). In our opinion, this dependence is caused by the reaction of radiolysis products with PETP matrix rather than by an effect of the dose rate on the radiolysis of PETP. This view follows from the finding that, at low dose rate (0.015 Gy/sec), the oxygen concentration in the gas phase does not affect grafting yield whereas there is an influence for 0.75 Gy/sec. A similar effect was observed during radiolysis of polyethylene and was explained by influence on the polymer of the ions O_2^- formed in the gas phase during irradiation [25]. It is known that the concentrations of ozone and oxygen ions increase during radiolysis of oxygen with rise of its concentration and with the dose rate. Further, interaction of ozone with organic compounds occurs even at room temperature [26].

Preirradiation dose

In both grafting methods, the dependence of grafting yield on pre-irradiation dose has a characteristic form, the slope of which decreases with dose. On these plots, grafting yield at constant dose increases for samples in the series: 0.1–F < 1–F < L–10 (Figs 2 and 3).

From that fact, some conclusions can be drawn. In accord with a radical polymerization theory, on increasing the dose rate more and more of the growing macroradicals are terminated on free radicals from PETP. For this reason at sufficiently high dose rate, the rate of polymerization is not a function of the dose rate [27, p. 219]. A similar picture is seen for graft polymerization. As a pre-irradiation dose (which in the pre-irradiation method is in principle an analogue of the dose rate) increases, the degree and the rate of grafting depend less and less on the concentration of the radicals in PETP. This causes a decrease of the slope of the relationship between grafting yield and dose as dose increases. In the method of pre-irradiation in vacuum, at a dose which corresponds to achievement of constant grafting rate, the radical concentration has not reached a limiting value.

In the method of pre-irradiation in vacuum, at long grafting time as follows from equation (1), the grafting yield is proportional to the logarithm of the initial radical concentration $[R^{\cdot}]_0$ [28]:

$$Q = k_p k_t^{-1}[M]\ln(k_t[R^{\cdot}]_0 t), \qquad (1)$$

where k_p and k_t are rate constants for propagation and termination, respectively, [M] is monomer concentration and t is grafting time.

In the case when the concentration of the radicals is proportional to dose, there is a linear relationship

Table 2. Yields of grafted PS (in %) on nuclear membranes and film irradiated for various dose rates and gas atmospheres

	Pre-irradiation in vacuum, $t = 6.5$ hr				Pre-irradiation in air $t = 8.2$ hr, $D = 50$ kGy			
	$D = 50$ kGy		$D = 25$ kGy		Dose rate, 0.015 Gy/sec		Dose rate, 0.75 Gy/sec	
	Dose rate (Gy/sec)				Pre-irradiation in			
Sample code	0.015	0.75	0.75	0.08	Air	Oxygen	Air	Oxygen
0.05–F	—	—	—	—	0.4	0.3	1.2 ± 0.6	2.3
0.1–F	29	29 ± 2	19	21	3.7	4.8	4.5 ± 1	8.4
1–F	39	38 ± 3	29	30	10.3	10.4	10.8 ± 0.3	14.3
L–10	58	60 ± 3	33	38	11.9	11.3	14 ± 2	18.1

between Q and the logarithm of pre-irradiation dose (see Fig. 2). The linearity is satisfied up to the maximum dose 0.4 MGy which was reached in our work. On the other hand, as follows from published work [15, 16] on PETP irradiation, a linear dependence of the radical accumulation curve (the dose rate was similar to that used in our work) continues up to a dose in the range of 0.2–0.4 MGy. This coincides with the data shown in Fig. 2.

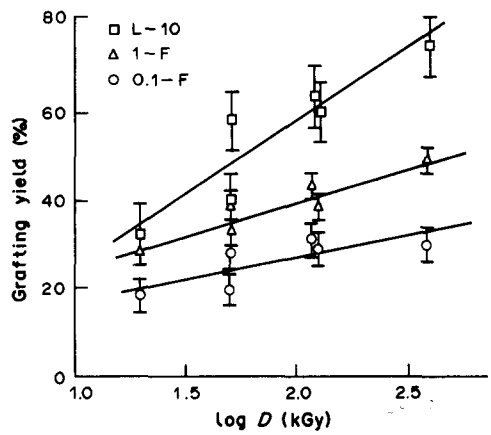

Fig. 2. Effect of pre-irradiation dose on PS grafting yield. Pre-irradiation in vacuum, $T = 70°$, grafting time = 6.5 hr.

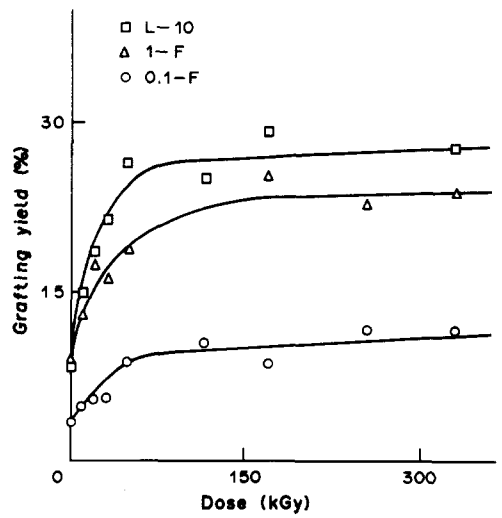

Fig. 3. Effect of pre-irradiation dose on PS grafting yield. Pre-irradiation in air, $T = 70°$, $t = 24$ hr.

Grafting of styrene onto the nuclear membranes irradiated in air, provided that graft polymerization is carried out in an atmosphere of inert gas, brings an induction period τ which decreases with pre-irradiation dose. The dependence of τ on reciprocal dose is shown in Fig. 4. At low doses (up to *ca* 0.1 MGy), we obtain a linear relationship between τ and $1/D$ in accordance with published data [29]:

$$\tau = 1/k_t[\mathrm{R}^{\cdot}]_0. \qquad (2)$$

In such a manner, if the concentration of radicals (or of oxyradicals in our case) is proportional to dose, then there must be linearity between τ and $1/D$, as shown in Fig. 4. It is interesting to note that deviation from linearity occurs in the same dose range as the curve of dependence of grafting yield on dose reaches a limiting value.

Storage after irradiation

Figure 5 shows the relationship between the grafting yield and storage time of the samples in the method of pre-irradiation in vacuum. All the curves have a maximum. This form of the dependence may indicate that some processes occur with the radicals in the PETP matrix during storage in vacuum. The data in Table 3 also indicate these processes. In the table, the kinetics of activity decrease in air for the membranes and films irradiated in vacuum are compared with those for the samples irradiated in air. The curves shown in Fig. 6 also indicate these processes.

Capture of the radicals in the irradiated polymer and their time stability depend on the matrix structure and in particular on its crystallinity. In regular lamellar structures of the crystallite, the radicals can

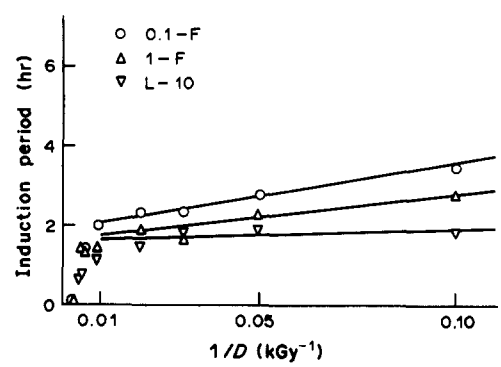

Fig. 4. Induction period as a function of reciprocal dose. Pre-irradiation in air, $T = 70°$.

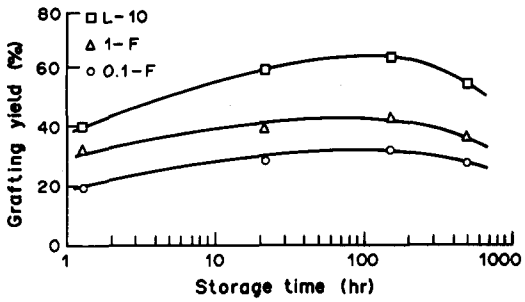

Fig. 5. Yield of grafted PS vs sample storage time. Storage conditions: room temperature, in vacuum in the dark; grafting conditions: $T = 70°$, $t = 6.5$ hr; irradiation conditions: $D = 50$ kGy, in vacuum.

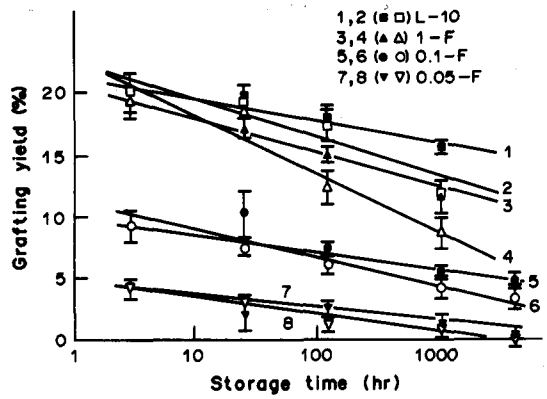

Fig. 6. Yield of grafted PS vs sample storage time. Storage conditions: room temperature in the dark; grafting conditions: $T = 70°$, $t = 8.2$ hr; irradiation conditions: $D = 175$ kGy, in air. Open symbols refer to storage in air; closed symbols refer to storage in vacuum.

live over a long period. They were protected not only from oxidation but also from monomer access. In this way, the radicals cannot initiate polymerization. Results obtained for radiolysis of polyethylene [30] and for grafting on a number of irradiated polymeric matrices indicate the possibility of a radical migration from the bulk of crystallites to their surface with subsequent initiating of grafting [31–33].

Graft polymerization proceeds both in the amorphous regions and on the surface of crystallites. During storage of the irradiated PETP, there is migration of the active centres from the bulk of the crystallites to their surface. This migration can apparently be caused by different radical concentrations in the crystalline and amorphous phases [16].

Since radical stability in PETP at room temperature is high [17], one can suppose that paramagnetic sites migrated from the crystallites take part in initiation of the graft reaction. The fact causes increase of grafting yield with time of storage (Fig. 5). Later, with a reduction of the migration process and because of the loss of part of all the generated radicals, grafting yield begins to decrease slowly.

Access of oxygen to the PETP samples irradiated in vacuum leads to oxidation of the radicals situated in the amorphous phase. Thus, in previous work [15, 34] a brief contact of the PETP irradiated in vacuum with air is used to obtain good precision and to remove the background in the ESR spectra. The authors considered that oxygen destroys the macroradicals which are situated in the amorphous regions but leaves unaffected those present in the crystallites. Then, if grafting is initiated only by the products of peroxide dissociation, increase of contact time of irradiated PETP with oxygen would increase grafting yield. It follows from Table 3 and Fig. 6 that an opposite phenomenon occurs i.e. the grafting yield decreases with time of sample storage in air. Even after 1 hr storage in air, the samples irradiated in vacuum show higher activity for initiation of grafting than PETP irradiated in air. Since decrease of average distance between the pores leads to acceleration of radical oxidation, so the relationship between the grafting yields on L–10 and 0.1–F is increased with storage time in air (the lower line in Table 3). These observations confirm an assumption made earlier [21] about the participation in grafting, carried out by the method of pre-irradiation in air, of the radicals which migrated from a crystalline phase of PETP.

More detailed understanding of the effect of oxygen on the behaviour of irradiated samples with storage time can be obtained from Fig. 6. For any matrix, storage in vacuum decreases the grafting yield to a smaller extent than storage under conditions of free oxygen access. This fact indicates that the radicals migrated during storage from crystalline to amorphous regions in the first case become the initiators of graft polymerization and in the second case they are converted to peroxides. The latter process decreases the rate of grafting performed at 70°.

CONCLUSIONS

In the grafting of styrene by the methods of pre-irradiation in air and in vacuum onto PETP nuclear membranes and film, the dose rate of γ-irradiation within the range 0.015–0.75 Gy/sec does not affect the

Table 3. Yields of grafted PS (in %) on irradiated PETP nuclear membranes and film after storage in air ($D = 50$ kGy, $T = 70°$, $t = 6.5$ hr)

Sample code	Irradiation in vacuum with a subsequent grafting	After storage in air for 1 hr: Irradiation in vacuum	After storage in air for 1 hr: Irradiation in air	After storage in air for 150 hr: Irradiation in vacuum	After storage in air for 150 hr: Irradiation in air
0.1–F	20 ± 2	4.7 ± 0.4	2.7 ± 0.3	2.6 ± 0.3	1.3 ± 0.2
1–F	32 ± 2	14 ± 1	12 ± 1	9 ± 1	8 ± 1
L–10	40 ± 3	18 ± 2	12 ± 1	9 ± 1	10 ± 1
$\frac{(Q)_{L-10}}{(Q)_{0.1-F}}$	2.0 ± 0.3	3.8 ± 0.5	4.6 ± 0.6	3.5 ± 0.6	8 ± 1.5

grafting rate. In the method of pre-irradiation in vacuum, the grafting yield is proportional to the logarithm of dose. Grafting yield passes through a maximum (at fixed grafting time) as the storage time of the irradiated samples increases. In the method of pre-irradiation in air, storage of irradiated samples in air has a greater effect on the decrease of grafting yield than storage in vacuum. The results confirm the idea of participation in the initiation of grafting, in both grafting methods, of radicals migrated from the crystalline phase of PETP.

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