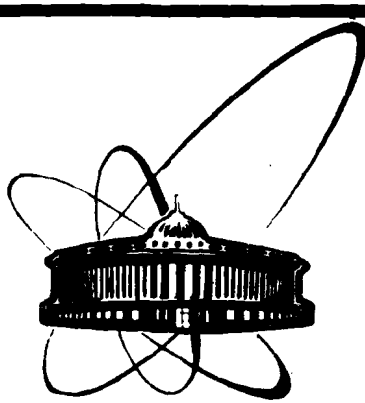

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N.I.Zhitariuk, N.I.Shtanko

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

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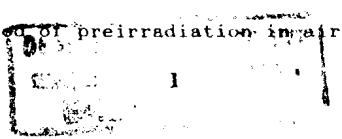
INTRODUCTION

Radiation-induced graft polymerization of styrene onto poly-(ethylene terephthalate) (PETP) has been studied in a number of papers. As a rule, for this purpose it was used direct method of grafting in which the polymer is dipped either in a pure monomer or in a monomer solution and the system is irradiated [1 - 8]. An equilibrium radical concentration in irradiated PETP is about 10^{17} radicals per gram [9]. So small concentration of paramagnetic sites must lead to insufficient activity of PETP in the grafting process. Indeed, in early works on graft polymerization PETP matrix differ from others by both the small rate of grafting and the small limit grafting yield [10].

However, subsequent works led to the results indicating a possibility of obtaining of the grafting yield reaching some tens percent. In the direct grafting method, considerable portion of radicals can be introduced into the PETP substrate from without [2]. The radicals formed in a monomer and solution surrounding polymeric matrix diffuse into the PETP volume where they initiate polymerization of monomer. Macromolecules formed this a way have not chemical bonds with the matrix but owing to molecular engagement they are retained firmly in the bulk of the polymeric matrix.

We know only two papers partly dedicated to the grafting of styrene onto PETP by using the method of preirradiation in vacuum [1,11], but we have not information on the grafting in this system with the method of preirradiation in air.



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

Application of both the grafting methods in concrete polymer/monomer system will be successful in that case if the radicals and the peroxides generated during irradiation will be stable during sample storage after irradiation. For that matter, PETP is characterized by a long lifetime of the radicals [15,16] and by a formation of the stable at the ambient temperature substances with oxygen to oxygen bond in their molecules which are the peroxides and the ozonides [17] and/or hydroperoxides [18].

In this work grafting of styrene onto the PETP nuclear membranes and films with the methods of preirradiation in a vacuum or in atmosphere contained oxygen has been studied. The relationships between the grafting yield and the dose rate, the preirradiation dose, and the storage time of the samples after a completion of irradiation have been obtained.

EXPERIMENTAL

Materials

Nuclear membranes were obtained with 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 membranes characteristics are shown in Table 1. Membranes and film were not subject to additional purification. Styrene is cleaned from inhibitor by means of rinsing in an alkali with a following double vacuum distillation.

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

Sample code	Pore density, cm^{-2}	d_b,[1] μm	d_g,[1] μm	Thickness, μm	Porosity,[2] %	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	-	-

[1] d_b, d_g are pore sizes obtained by a "bulb" and gas dynamic methods respectively; [2] porosity has been obtained by gravimetric method.

Methods

Graft polymerization was carried out by the method described earlier [20]. Nuclear membranes and film activated with γ-rays were stored at the ambient temperature (20 - 30 ^oC) 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

Typical curves of the grafted polystyrene (PS) accumulation onto PETP nuclear membranes with different pore size and onto PETP film of 10 μm thick are shown in Figure 1. The method of preirradiation in vacuum is characterized by the high initial rate of graft polymerization. On initial section of the accumulation curve the polymerization has an explosive character and its rate depends on the kinetics of the monomer sorption by the

matrix. In time the grafting rate decreases and takes the constant value. On the film L-10 the rate of grafting approximates to zero but on the membranes 1-F and 0.1-F it takes some value different from 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 with its approaching to film thickness the reaction of a radical recombination in the crystalline phase of PETP under conditions of the graft polymerization begins to compete successfully with the reaction of graft chains initiation by the radicals. It ought to point out that in the amorphous regions the radicals are accessible for monomer molecules already on the initial stage of grafting [11,15], and recombination of the radicals is more probable in the thick substrate where an access of monomer to initiating sites is more difficult.

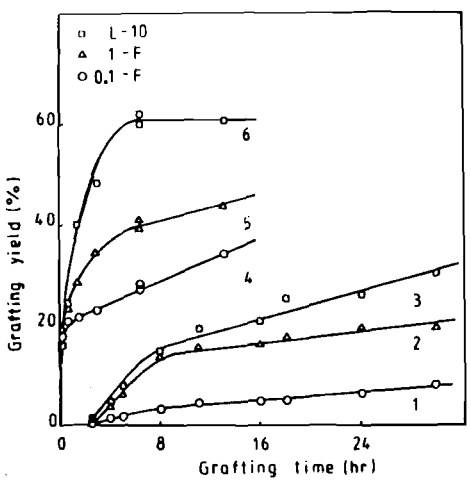


Fig. 1. Curves of PS accumulation on PETP film and nuclear membranes. 1 - 3 is a preirradiation in air, dose D = 50 kGy; 4 - - 6 is a preirradiation in vacuum, D = 50 kGy. Grafting temperature T = 70 °C, dose rate is 0.75 Gy/sec.

Grafting rate in the method of preirradiation in air is considerably lower. Except for initial range an increase of grafting yield with time is described by a linear dependence.

The dose rate does not affect the polymer activity in the grafting reaction of styrene in the method of preirradiation in vacuum (see Table 2). Grafting yield is practically constant when the dose rate is changed in 50 times. The fact has good coincidence with the literature data which have been obtained at grafting onto other polymeric matrixes [22 - 24].

The analogous picture is seen in the method of preirradiation in air when irradiation is carried out in oxygen. If PETP activation is carried out in oxygen the grafting yield has some dependence on the dose rate (Table 2). But in our opinion this dependence is defined by the reaction of oxygen radiolysis products with PETP matrix than by effect of the dose rate on radiolysis of PETP. This follows from that at low dose rate (0.015 Gy/sec) oxygen concentration in a gas phase does not affect grafting yield whereas at its rise to 0.75 Gy/sec the influence has place.

Table 2. Yields of grafted PS (in %) on nuclear membranes and film irradiated under conditions of the different dose rate and the different gas atmosphere

Sample code	Preirradiation in vacuum, t = 6.5 hr				Preirradiation in air, t = 8.2 hr, D = 50 kGy			
	D = 50 kGy		D = 25 kGy		Dose rate is 0.015 Gy/sec		Dose rate is 0.75 Gy/sec	
	Dose rate (Gy/sec):				Preirradiation in:			
	0.015	0.75	0.75	0.08	air	oxygen	air	oxygen
0.05-F	-	-	-	-	0.4	0.3	$1.2^{\pm}0.6$	2.3
0.1-F	29	$29^{\pm}2$	19	21	3.7	4.8	$4.5^{\pm}1$	8.4
1-F	39	$38^{\pm}3$	29	30	10.3	10.4	$10.8^{\pm}0.3$	14.3
L-10	58	$60^{\pm}3$	33	38	11.9	11.3	$14^{\pm}2$	18.1

Similar phenomenon was observed in [25] at radiolysis of polyethylene and was explained by influence of the ions O_2^- formed in gas phase during irradiation on polymer. It is known that concentration of ozone and of oxygen ions increases during oxygen radiolysis with a rise of its concentration and with the dose rate. Besides, an interaction of ozone with organic compounds occurs already at room temperature [26].

Preirradiation dose

In both grafting methods, a dependence of grafting yield on preirradiation dose has a form of prominent curve an incline of which decreases with dose. On these plots grafting yield at constant dose increases at grafting on the samples placed in a series: O.1-F < 1-F < L-10 (Figures 2 and 3).

From that fact some conclusions can be done. In accord with a radical polymerization theory at increasing of the dose rate more and more higher number of the growing macroradicals is terminated on free radicals from PETP. For this reason at a sufficiently high dose rate the rate of polymerization is not a function of the dose rate [27, p.219]. Analogous picture is seen in the case of graft

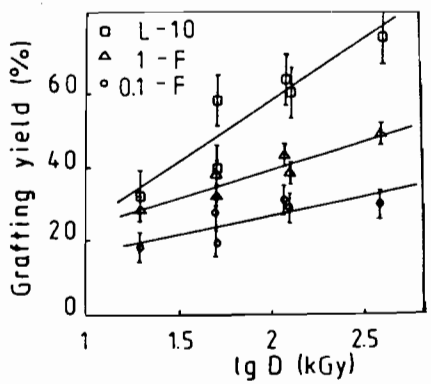


Fig. 2. Effect of preirradiation dose on PS grafting yield. Preirradiation in vacuum, T = 70 °C, grafting time t = 6.5 hr.

polymerization. As a preirradiation dose, which in the preirradiation method is in principle an analogue of the dose rate, increases, the degree and the rate of grafting has a less and less dependence on a concentration of the radicals in PETP. This brings to a decrease of an incline of a relationship between grafting yield and dose as dose increases. In the method of preirradiation in vacuum, at dose which corresponds to an achievement of the constant grafting rate the radical concentration does not still reach a limit value.

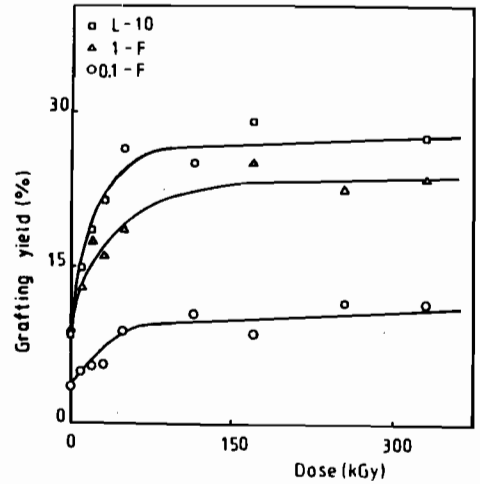


Fig. 3. Effect of preirradiation dose on PS grafting yield. Preirradiation in air, T = 70 °C, t = 24 hr.

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

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

where k_p and k_t are kinetic constants of chain propagation and termination, respectively, [M] is a monomer concentration and t is a grafting time.

In that case when a concentration of the radicals is proportional to dose, a linear relationship between Q and a logarithm of preirradiation dose will be fulfilled. This relationship is shown in Figure 2. The linearity is fulfilled up to a maximum dose 0.4 MGy which was reached in our work. On the other hand, as follows from [15,16] at PETP irradiation a linear dependence of the radical accumulation curve (the dose rate similar to that used in our work) stretches to the dose which lies in the range of 0.2 - 0.4 MGy. This coincides with the data shown in Figure 2.

Grafting of styrene onto the irradiated in air nuclear membranes, on condition that graft polymerization is carried out in an inert gas atmosphere, brings to an appearing of the induction period τ, τ decreases with preirradiation dose.

The dependence of τ on reciprocal dose is shown in Figure 4.

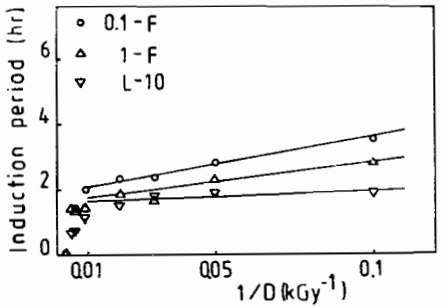


Fig. 4. Induction period as a function of reciprocal dose. Preirradiation in air, T = 70 °C.

At low dose (up to about 0.1 MGy) we obtain a linear relationship between τ and 1/D. Indeed, in accordance with the data of [29]:

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

In such a manner, if a concentration of the radicals (or of oxyradicals as it has place in our case) is proportional to dose,

then a linearity between τ and 1/D must be fulfilled. This is shown in Figure 4. It is interesting to note that a deviation from the linearity takes place in the same dose range as the curves of a dependence of grafting yield on dose reache a limit value.

Storage after irradiation

A relationship between the grafting yield in the method of preirradiation in a vacuum and storage time of the samples is shown in Figure 5. All the curves have a maximum. This form of the dependence can indicate some processes which occur with the radicals in the PETP matrix in time of its storage in vacuum. The data shown in Table 3 also indicate these processes. In the Table a kinetics of an activity decrease for the membranes and films irradiated in vacuum is compared with the kinetics for the samples irradiated in air. The curves shown in Figure 6 also indicate these processes.

A capture of the radicals in the irradiated polymer and their time stability is a function of the matrix structure and in particular of its crystallinity. In regular lamelar structure of the crystallite the radicals can live over a long period of time.

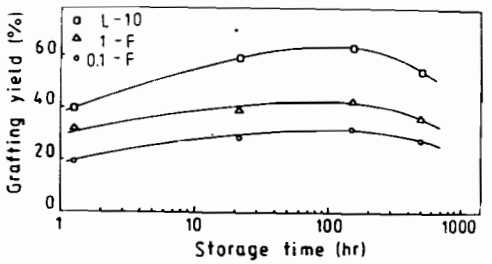


Fig. 5. Yield of grafted PS vs. samples storage time. Storage conditions: room temperature, in vacuum, in the dark; grafting conditions: T = 70 °C, t = 6.5 hr; irradiation conditions: D = 50 kGy, in vacuum.

Table 3. Yields of grafted PS (in %) onto irradiated PETP nuclear membranes and film after storage in air

(D = 50 kGy, T = 70 °C, t = 6.5 hr)

Sample code	Irradiation in vacuum with a following grafting	After storage in air during 1 hr		After storage in air during 150 hr	
		irradiation in vacuum	irradiation in air	irradiation in vacuum	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

For this, they were protected not only from an oxidation but also from a monomer access. In this way, the radicals cannot initiate polymerization. But results obtained at radiolysis of polyethylene [30] and in the process of grafting on a number of irradiated polymeric matrices indicate a possibility of a radical migration from the bulk of crystallites to their surface with a subsequent initiating of grafting [31 - 33].

Graft polymerization proceeds both in the amorphous regions and on the surface of crystallites. At a storage of the irradiated PETP a migration of the active centers from the bulk of the crystallites to their surface has place. This migration can apparently be conditioned by a different radical concentration in crystalline and amorphous phases [16].

Since a 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 brings to a grafting yield increase with time of storage (Figure 5). Later on with a damping of the migration process and because of the loss of part of all generated radicals grafting yield begins to decrease slowly.

An access of oxygen to the PETP samples irradiated in vacuum leads to oxidation of the radicals which are placed in the amorphous phase. Thus, in [15,34] it is used a short contact of the PETP irradiated in a vacuum with an air to obtain good precision and to remove the background in the ESR spectra. The authors are believed that oxygen destroys the macroradicals which are localized in the amorphous regions retaining ones which localized in the crystallites. Then, if grafting would be initiated by only the products of peroxides dissociation a rise of contact time of irradiated PETP with oxygen would increase grafting yield. But as follows from Table 3 and Figure 6 an opposite phenomenon has place that is the grafting yield decreases with a time of sample storage in air. Even after 1 hr storage in air the samples irradiated in a vacuum show higher activity in the initiation of grafting than PETP irradiated in air. Since a decrease of average distance between the pores leads to an acceleration of radical oxidation so a 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 in [21] about the participation in grafting carried out by the method of preirradiation in air of the radicals migrated from a crystalline phase of PETP.

More detailed idea about an effect of oxygen on behaviour of irradiated sample with storage time can be obtained from Figure 6.

For any matrix storage in a vacuum decreases the grafting yield to a less degree than its storage under conditions of free oxygen access. This fact indicates that the radicals migrated during storage from crystalline regions to amorphous ones in first case become the initiators of graft polymerization and in the second one they convert into the peroxides. The latter process decreases the rate of grafting carrying out at 70 °C.

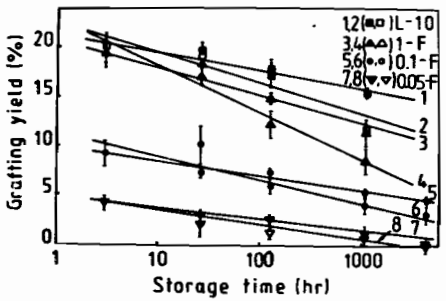


Fig. 6. Yield of grafted PS vs. samples storage time. Storage conditions: room temperature, in the dark; grafting conditions: T = = 70 °C, t = 8.2 hr; irradiation conditions: D = 175 kGy, in air. Open symbols are storage in air, closed ones are storage in vacuum.

CONCLUSIONS

In the grafting of styrene by the methods of preirradiation in air and in vacuum onto PETP nuclear membranes and film the dose rate of γ-irradiation within the region of 0.015 - 0.75 Gy/sec does not affect the grafting rate. In the method of preirradiation in vacuum, the grafting yield is proportional to logarithm of dose. Grafting yield passes through the maximum (at constant grafting time) as a storage time of the irradiated samples

increases. In the method of preirradiation in air, storage of irradiated samples in air has greater influence on a decrease of grafting yield than their storage in vacuum. Obtained results confirm the idea on participation in the initiation of grafting in both the grafting methods of the radicals migrated from crystalline phase of PETP.

The authors wish to thank G. N. Flerov, Academician of the Academy of Sciences of the USSR, V. D. Shestakov, Assistant director of the Laboratory of Nuclear Reactions, and V.I.Kuznetsov, Chief of department, for their careful guidance, continuous interest, and encouragement throughout this work.

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18.	Applied researches
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Житарюк Н.И., Штанько Н.И.

E18-89-724

Влияние некоторых факторов на радиационную прививку стирола на полиэтилентерефталатных ядерных мембранах

Исследована радиационная прививочная полимеризация стирола из жидкой фазы методами предварительного облучения на воздухе и в вакууме на полиэтилентерефталатные ядерные мембраны и пленку. Показано, что мощность дозы предварительного облучения не оказывает влияния на скорость прививочной полимеризации. Получена линейная зависимость между предельной степенью прививки и дозой при проведении процесса методом предварительного облучения в вакууме. Изучено влияние времени хранения образцов после завершения облучения на кинетику прививочной полимеризации: при применении метода предварительного облучения в вакууме степень прививки проходит через максимум; при применении метода предварительного облучения на воздухе степень прививки непрерывно снижается, причем скорость ее снижения выше в случае выдержки образцов на воздухе по сравнению с хранением их в вакууме.

Работа выполнена в Лаборатории ядерных реакций ОИЯИ.

Препринт Объединенного института ядерных исследований. Дубна 1989

Zhitariuk N.I., Shtanko N.I.

E18-89-724

Influence of Some Factors on Radiation Grafting of Styrene onto Poly(ethylene Terephthalate) Nuclear Membranes

Radiation-induced graft polymerization of styrene from liquid phase onto poly(ethylene terephthalate) nuclear membranes and films has been investigated. Grafting was carried out by the methods of preirradiation in air and in vacuum. It is shown that dose rate does not affect the rate of graft polymerization. Linear dependence of the limit grafting yield on dose has been obtained at carrying out the process by the method of preirradiation in vacuum. Influence of sample storage time after completion of the irradiation on graft polymerization kinetics has been studied: in the method of preirradiation in vacuum, grafting yield passes through the maximum; in the method of preirradiation in air, grafting yield decreases continuously and rate of its decreasing is higher for samples kept in air than in vacuum.

The investigation has been performed at the Laboratory of Nuclear Reactions, JINR.

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