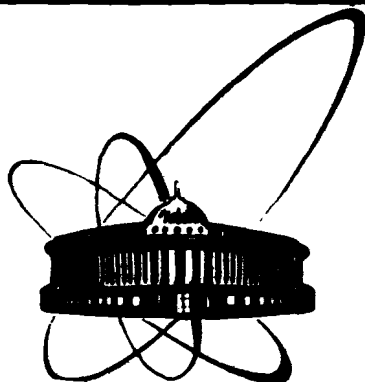89-91

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INFLUENCE OF THE MATRIX THICKNESS
ON RADIATION-INDUCED GRAFTING OF STYRENE
ONTO POLY(ETHYLENE TEREPHTHALATE) FILMS
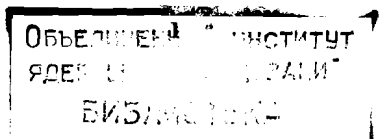# AND NUCLEAR MEMBRANES

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INTRODUCTION

Radiation-induced graft polymerization is a well-known method for modification of the chemical and physical properties of polymeric materials, and is of particular interest for achieving specifically desired membrane properties as well as excellent permeability and selectivity. The improved properties are in particular inherent in modified nuclear membranes based on poly(ethylene terephthalate) (PET).[1] The grafting rate onto the nuclear membranes with different parameters (pore diameter, pore density and porosity) is different and depends on the parameters.[2]

Several papers have reported the influence of the matrix thickness on grafting kinetics. They consider both preirradiation in air[3-6] and preirradiation in vacuum.[4,7-10] In both the methods the initial grafting rate V_i decreases and the limit grafting yield increases with thickness.[3,7] The limit grafting yield expressed as a mass of the grafted polymer per area unit of the backbone polymer is proportional to thickness.[8] These relations indicate a limitation of the grafting rate by monomer diffusion. The maximum rate obtained during grafting onto thin films is apparently brought nearer to the rate of monomer diffusion into the matrix volume. In some cases of preirradiation in vacuum the limit grafting yield is not a function of the thickness. This is the case when active centers within the polymeric matrix are sufficiently stable and do not disappear until monomer molecules approached them. The grafting onto this matrix is spread to its inner part.

Contrary to the relations, in some other papers it was found that the grafting yield increases with thickness.[6,11] These and the above - stated results are likely to be described by the common dependence obtained by Stirikovich et al.[12] The authors investigated preirradiation grafting of methylmethacrylate and styrene onto polypropylene. The thickness of polypropylene films changed within a wide range of 10 - 700 μm. The extremal dependence of the grafting yield on the thickness has been obtained. We do not know the papers which deal with the thickness effect at radiation-induced grafting onto PET.

The aim of the present study is to investigate influence of the average distance between pores, which is a general parameter for all nuclear membranes, on graft polymerization kinetics at its

initiation by the methods of preirradiation in air and in vacuum. In this case nuclear membranes are of great value because they allow the distance between pore walls (which is equivalent to the thickness) equal to several tenths of a micrometer. PET films of this thickness, with which one could easily perform experiments, cannot be produced either commercially or in the laboratory.

EXPERIMENTAL

Materials

Nuclear membranes were obtained by the known method from a PET film (lavsan, made in the USSR) 10 μm thick.[13] The pore diameter was measured by the bubble-point (d_b), gas-dynamic (d_g), and microscopic (d_m) methods. Porosity was measured by the weight method. The average distance between pore axes L was calculated on computer CDC-6500. Some parameters of the nuclear membranes used are shown in Table 1.

Commercially available double oriented PET films (lavsan, Hostaphan of Kalle, West Germany) 1.5 - 190 μm thick were used (see Table 1). Technical grade styrene made in the USSR was purified by double distillation under vacuum. Films and membranes were not subjected to additional cleaning.

Methods

In the method of preirradiation in vacuum grafting was carried out in a glass ampoule with two side arms divided by break seal. The first arm with PET films and membranes was evacuated for 2 - 3 hr and sealed under reduced pressure of about 5×10^{-3} mm Hg. Then the ampoule was exposed to γ-ray irradiation from Cs-137 at a dose rate of 0.75 Gy/sec. Styrene was then introduced in the second arm of the ampoule, evacuated by means of three freeze-thaw cycles and sealed. After destruction of the break seal styrene was brought in contact with the films and membranes. Polymerization of styrene was carried out at a given temperature (T_g).

In the method of preirradiation in air films and membranes were exposed to γ-ray irradiation from Cs-137 at a dose rate of 0.75 Gy/sec. Styrene and polymeric matrices were then introduced in the glass ampoule. Polymerization was carried out in the argon atmosphere at a given temperature (T_g).

The grafted films and membranes thus obtained were removed from the ampoule and thoroughly washed with boiling benzene for 24 hr. The grafted materials were then dried at 60 - 80 $^{\circ}$C to a constant

TABLE I.

Parameters of Membranes and Films

Desig-nation	Pore density N, cm^{-2}	d_b, μm	d_g, μm	d_m, μm	Thickness l, μm	Porosity %	L, μm
			Nuclear membranes				
0.05-F	2×10^9	-	0.05	0.11 ± 0.01	9.9 ± 0.3	8.0 ± 0.5	0.25
0.1-F	3.2×10^8	0.095	-	0.29 ± 0.01	10.1 ± 0.2	8.1 ± 0.7	0.67
0.2-F	$(4 \pm 2) \times 10^8$	0.22	-	0.34 ± 0.05	9.7 ± 0.4	8.4 ± 1	0.57
0.3-F	6×10^7	0.34	-	0.33 ± 0.04	9.1 ± 0.3	7.5 ± 1	1.5
0.5-F	6.7×10^7	0.45	-	0.43 ± 0.05	8.5 ± 0.3	9 ± 1	1.4
1-F	5×10^6	0.93	-	1.6 ± 0.2	8.6 ± 0.2	7.7 ± 0.2	5.1
0.05-F (2×10^8)	3.3×10^8	-	0.05	0.056 ± 0.008	10 ± 1	-	0.66
0.05-F (6×10^6)	5.7×10^6	-	0.05	0.08 ± 0.02	10 ± 1	-	4.8
1-F (6×10^6)	5.7×10^6	0.5	-	1.2 ± 0.1	9.5 ± 1	-	4.8
1.5-F (6×10^6)	5.7×10^6	1.0	-	1.6 ± 0.2	9 ± 1	-	4.8

			Films				
Designation	L-1.5	L-3	L-5	L-10	L-20	L-50	L-190
Thickness l, μm	1.6 ± 0.1	2.9 ± 0.1	5.0 ± 0.2	10.2 ± 0.2	20 ± 2	50 ± 5	190 ± 19

weight and weighed. The grafting yield was determined by percentage increase in weight.

In order to separate the graft chains from the trunk polymer for molecular weight determination of polystyrene (PS), grafted PET was immersed in a sodium hydroxide solution (10 mol/l) for 6 - 8 hr at 60 $^{\circ}$C. The trunk polymer was decomposed by alkaline. The remained PS was rinsed in hydrochloric acid, then in water to the neutral reaction and was dried to a constant weight. PS thus obtained was dissolved in benzene, the solution was filtered through nuclear membrane with pores 0.5 μm in diameter. The filtrate was poured into cold ethanol and PS was precipitated. The molecular weight of the isolated PS was measured by the Waters gel-permeation chromatograph, model 150C, with the differential refractometer as a detector.

RESULTS AND DISCUSSION

The curves of the grafted PS accumulation on the PET nuclear membranes and film are shown in Figure 1. The aim of the grafting onto the film is to obtain comparative results which would reflect a change in the kinetic parameters of the grafting process on a polymeric matrix without pores.

The method of preirradiation in vacuum is characterized by a high initial grafting rate V_i. At the initial moment of the grafting time polymerization has an explosive character and its rate is determined by the monomer sorption kinetics.

The rate of the grafted polymer accumulation in the method of preirradiation in air is considerably lower. The growth of the grafting yield with the grafting time is described by linear dependence apart from the initial section of the accumulation curve. The linearity is maintained in the whole range of the investigated grafting time scale up to 40 hours (high grafting times are not shown in Figure 1).
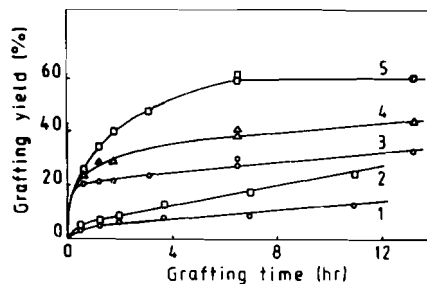

Fig. 1. The curves of grafted polystyrene accumulation onto film and nuclear membranes. 1,2 - grafting by preirradiation in air, dose D = 175 kGy; 3 - 5 - grafting by preirradiation in vacuum, D = 50 kGy. Grafting temperature T_g = 70 °C. 1,3 - 0.1-F; 4 - 1-F; 2,5 - L-10.

Fig. 2. The curves of grafted PS accumulation onto the nuclear membranes with constant pore density (N = 5.7x10^6 cm^{-2}) but different pore diameter. Grafting by preirradiation in air, T_g=70 °C.
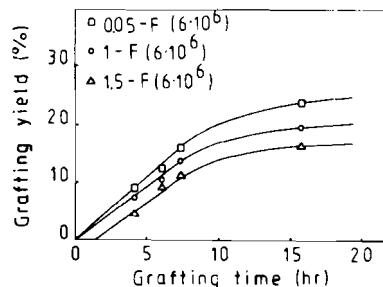
In both the grafting methods the current grafting rate of styrene increases in the following order: 0.1-F < 1-F < L-10 (except for the initial section of the accumulation curves, viz. at grafting time up to ~ 10 minutes).

The curves in Figure 1 describe the grafting of styrene onto the nuclear membranes with different pore diameter and constant porosity (about 8 %). To investigate the influence of thickness (or the average distance between pore walls) on the grafting process special membranes were prepared. The accumulation curves for PET nuclear membranes with the constant pore density (the number of pores per unit of the surface area) but with different pore diameter are shown in Figure 2. In these membranes the average distance between the axes of cylindrical pores L is constant while the average distance between pore walls H is determined by their diameter. The mutual location of the accumulation curves, as follows from Figure 2, is opposed to the case described above (Figure 1), that is the accumulation curve runs lower as the pore diameter increases. Consequently, in both cases an identical regularity is fulfilled: the rate of the graft polymerization increases with the average distance between pore walls.

The regularity is also shown in Figure 3. For nuclear membranes with the constant pore diameter but with the different pore density the grafting rate increases with the average distance between pores and decreases as the pore density increases.

For the previously investigated membranes (see Table 1) with the approximately constant porosity there is a similar relation between the grafting yield and the thickness, which in this case is determined by the average distance between the pore walls; it is shown in Figure 4.

In order to vary the thickness of the PET matrix broader, the films of different thickness were also applied for grafting along with the nuclear membranes (see Table 1). The dependence of the grafting yield on the film and membrane thickness is shown in Figure 5. Similar curves running significantly lower were obtained during grafting by preirradiation in air.

In both grafting methods the same regularity is fulfilled: at first the grafting yield increases and, after passing through the maximum, gradually decreases. Absence of the sharp decrease in the grafting yield at the matrix thickness higher than 20 μm can be explained by growth of the number of microcavities within the volume of the PET film as its thickness increases. The microcavities were often observed during electron microscopy investigations of

Fig. 3. The influence of the distance between pores (L) and the pore density (N) on the initial grafting rate of styrene. Pore diameter is 0.05 μm. Grafting by preirradiation in air. $T_g = 70\ ^{\circ}C$.
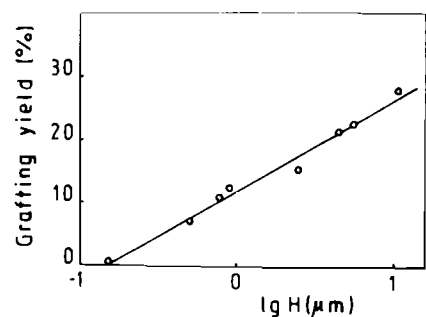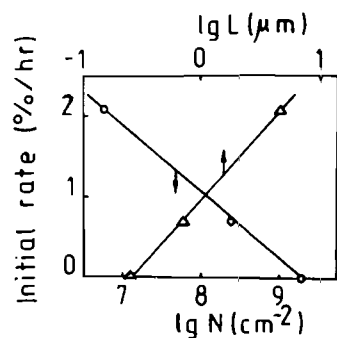

Fig. 4. The grafting yield of PS as a function of the average distance between pore walls for nuclear membranes with a different pore diameter and pore density. Grafting by preirradiation in air. $T_g = 70\ ^{\circ}C$. The grafting time is 18.2 hr.

Fig. 5. The grafting yield of PS as a function of the distance between pore walls and of the film thickness. Dark symbols - grafting onto nuclear membranes, light symbols - grafting onto films. Grafting by preirradiation in vacuum. The grafting time: 4 hr (1) and 13.25 hr (2). $T_g = 70\ ^{\circ}C$.
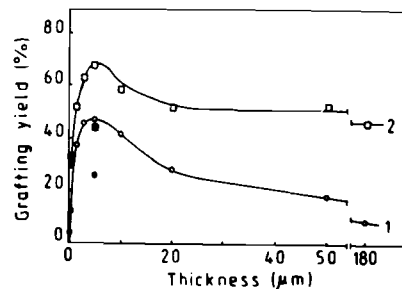
the splits of nuclear membranes made of films more than 20 μm thick. Thus, the effective thickness of these films for monomer diffusion into their volume becomes lower than the nominal one.

Since there were no thin PET films (with the nominal thick-

ness lower than 1.5 μm), the initial section of each curve in Figure 5 is presented by styrene grafting onto nuclear membranes with different average distance between pores and different pore diameter at the constant porosity (about 8 %).

In some cases grafting was carried out both onto the film and the membrane (on condition that the film thickness is approximately equal to the average distance between the pore walls of the nuclear membrane - see dark and light symbols at thickness of 5 μm in Figure 5). As follows from the Figure, grafting onto the membrane has a lower rate than grafting onto the film.

It also follows from Table 2 that the difference in the initial grafting rate onto the film and the membrane at the film thickness (1) equal to the average distance between the pore walls (H) is of universal character and occurs at different thicknesses and at different temperatures of graft polymerization.

TABLE 2·

Initial Rate of Styrene Grafting (%/sec) onto Nuclear Membranes and Films on Condition that H^{*} = 1 (Grafting by Preirradiation in Vacuum)

T_g, $^{\circ}C$	45	50	55	70	80	90
0.3-F ($H=1.2\ \mu$m)	7.4×10^{-4}	1.9×10^{-3}	2.8×10^{-3}	3.6×10^{-2}	4.5×10^{-2}	8.7×10^{-2}
L-1.5	121×10^{-4}	21×10^{-3}	37×10^{-3}	4.4×10^{-2}	5.4×10^{-2}	5.8×10^{-2}
1-F ($H=4\ \mu$m)	3.1×10^{-4}	4.5×10^{-4}	0.3×10^{-3}	4.7×10^{-2}	5.3×10^{-2}	9.8×10^{-2}
L-5	8.3×10^{-4}	–	4.3×10^{-3}	5.0×10^{-2}	5.5×10^{-2}	11.3×10^{-2}
L-3	14.2×10^{-4}	2.4×10^{-3}	5.3×10^{-3}	5.9×10^{-2}	5.6×10^{-2}	10.7×10^{-2}

* $H = L - d_m$

Difference in the graft polymerization rates onto the film and the membrane on condition that H = 1 can be probably explained by higher defectiveness of the membrane material. The defectiveness develops during the etching of the film, irradiated by heavy ions and by UV-light, with the alkaline solution and is a consequence of the difference between the etching rates of the amorphous and crystalline regions of PET.[14] The growing number of the defects can

lead to an increase in the radical concentration as a result of the migration process towards the formed phase boundaries.[15] An increase in the local concentration of active centers and in the mobility of macromolecular segments at these places favours the proceeding of bimolecular reactions between radicals (see radical concentration N_R in Table 3).[16] Besides, the increased mobility of the growing macroradicals at the defect boundaries leads to a larger chain termination rate constant already during the process of graft polymerization (see the values of the weight average molecular weight $\bar{M}_w$ in Table 3).[17]

TABLE 3.

Parameters of Polystyrene Grafted Chains*

Sample	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	G(b), molecules/100 eV	$N_R \times 10^{-20}$ radicals/kg
0.1-F	2.41×10^5	9.03×10^5	3.75	0.014	3
0.5-F	1.84×10^5	1.02×10^6	5.54	0.03	6.6
1-F	1.82×10^5	1.37×10^6	7.52	0.05	11
L-10	2.27×10^5	1.18×10^6	5.19	0.05	11

* Grafting by preirradiation in air.

The characteristic parameter of the grafting process α is given by the equation:[18]

$$\alpha = \left[\left(-\frac{k_p^2}{k_t} \ G(R) \right)^{1/2} \frac{P^{1/2}}{D_m} \right]^{1/2} \frac{1}{2}, \qquad (1)$$

where G(R) is the radical yield in PET,[19] D_m is the coefficient of monomer diffusion in a PET matrix ($D_m = 10^{-14}$ m^2/sec[20,21]), k_p and k_t are the rate constants of propagation and termination respectively (calculated from kinetics of the grafting process[22]), P is the dose rate, l is the film thickness or the average distance between pore walls (for nuclear membranes l = H).

The values of α are shown in Table 4. They indicate that the grafting process onto the nuclear membranes shown in Table 4 is either not controlled by monomer diffusion (onto 0.1-F) or the control only begins to appear (onto 1-F and L-10). This conclusion is also confirmed by the values of the critical thicknesses

l_{cv} and l_{cs}. It is necessary to point out that the critical thickness l_c, calculated from the equation:[23]

$$l_c = \left[\frac{8 \ D_m \ c_o}{V} \right]^{1/2}, \qquad (2)$$

(where c_o is the equilibrium monomer concentration within the volume of the polymeric matrix, V is the rate of monomer absorption during grafting), is in good agreement with the maximum of the curves shown in Figure 5 (see Table 4).

TABLE 4.

Some Parameters Indicated Influence of Thickness on Radiation-Induced Grafting of Styrene onto PET Membranes and Films at 70 °C

Sample	α	l_c, μm from eq.(2)	l_c, μm from Fig. 5	l_{cv}*, μm	l_{cs}*, μm
0.1-F	0.02	4	5	3	80
1-F	0.2	4	5	2	70
L-10	0.4	5	5	2	70

* l_{cv} is the critical thickness below which the grafting rate is essentially completely independent of thickness, that is $\alpha <$ < 0.1; l_{cs} is the critical thickness above which the grafting reaction is essentially completely surface grafting, that is $\alpha > 3$.[18]

The initial increase in the grafting yield with thickness is a consequence of the gel-effect.[6,11,12] As the film thickness (or the average distance between pore walls in the membrane) increases, the monomer concentration within its middle part decreases. This leads to an increase in viscosity and to a decrease in the chain termination rate. In this case the viscosity growth effect prevails over the possible decrease in the chain growth rate as a result of the monomer concentration decrease.

When the monomer is absorbed by unirradiated PET, its swelling is determined by the thermodynamic equality of the energy which is released as a result of the interaction between the polymer and the monomer, and of the energy which is spent for a polymer volume growth. For this reason stresses appear within the polymer matrix. If the stresses lead to reorganization of the polymer structure,

it can absorb an additional quantity of the monomer. For quick swelling of the polymer matrix in the whole volume it is necessary that the stress value is sufficient for tension of not only the swelled layer but also of the adjacent sublayer.

During sorption of the monomer by the irradiated PET film or membrane, a tendency to inhomogeneous swelling is higher because of monomer polymerization on active centers. It is clear then why at the constant grafting time the yield of the graft polymer begins to decrease at some thickness.

CONCLUSIONS

The grafting of styrene onto PET nuclear membranes with different characteristics and onto PET films with different thicknesses has been studied by using the preirradiation technique in air and in vacuum. The experimental results discussed above allow the following conclusions:

(1) The grafting rate of styrene onto nuclear membranes with different parameters (at the constant pore diameter, or porosity, or pore density) increases with the average distance between pores.

(2) While the investigated range of PET matrix thicknesses increases owing to grafting onto films, the curve of the grafting yield change passes through the maximum.

(3) If the film thickness is equal to the average distance between pore walls of the membrane, the grafting rate onto the film is higher than that onto the nuclear membrane.

(4) The values of the characteristic parameter α and of the critical thickness at styrene grafting onto nuclear membranes and films at 70 $^{\circ}$C have been determined. The calculated value of the critical thickness is in good agreement with the experimental one and is equal to 5 μm.

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