

Influence of temperature on radiation-induced graft polymerization of styrene onto poly(ethylene terephthalate) nuclear membranes and films

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The effect of temperature on the kinetics of radiation-induced graft polymerization of styrene onto poly(ethylene terephthalate) (PETP) nuclear membranes with varying parameters (pore diameter, pore density and average distance between the pores) and onto PETP films of different thickness has been studied. Graft polymerization was carried out by preirradiation in air and in vacuum. The overall activation energy of grafting and the activation energy of swelling of PETP in toluene have been obtained. It was found that for preirradiation in vacuum, an Arrhenius plot has two linear ranges for the initial grafting rate. The activation energy in the low temperature range correlates with the activation energy for PETP swelling. The activation energy in the high temperature range is determined by the kinetics of graft polymerization. For preirradiation in air, the Arrhenius plot of the initial grafting rate gives an activation energy which approximately corresponds to the initiation of grafting by oxy radicals. The dependence of the critical thickness of the PETP matrix on temperature has also been obtained for preirradiation in vacuum. The form of this dependence is identical to that of the rate of graft polymerization.

(Keywords: polyester; radiation grafting; grafting of styrene; nuclear membrane)

INTRODUCTION

The temperature dependence of grafting yield is characterized by a curve with a maximum. It is usually compared with limiting grafting yields (Q_{lim}) which are obtained at long grafting times when all the radicals and/or oxy radicals are spent during grafting. Temperature dependence with a maximum is observed during grafting by the methods of preirradiation in vacuum (MPV)¹⁻³ and in air (MPA)⁴ and by the direct method⁵⁻⁷. Such a relationship is fulfilled during grafting onto a number of polymeric substrates: poly(ethylene terephthalate) (PETP)^{1,4-8}, nylon² and polypropylene⁵.

For MPV, extreme dependence is due to different influences on the grafting reaction, on the one hand, of the monomer diffusion rate and, on the other hand, of reactivity and lifetime of the radicals. The maximum for this relationship lies, in accordance with one set of data, in the region of the glass transition temperature, T_g , of the polymer⁵⁻⁷ and, according to other data, in the region of the T_g of the polymer/monomer (or monomer solution) system^{8,9}.

The Arrhenius plot of the grafting rate is described by a linear function with a break. The break point usually concurs with the T_g of the polymer/monomer system. This dependence is observed during grafting using different methods: MPA¹⁰, MPV^{11,12} and the direct method¹³⁻¹⁵. Only the latter is used for grafting a number of monomers onto PETP. The overall activation energy of radiation-induced grafting decreases as the temperature passes the T_g region of the polymer/monomer system from the glass to the high-elasticity state. Such a dependence probably takes place due to the change in

the rate limiting stage of grafting as the temperature increases. At temperatures lower than T_g graft polymerization is limited either by monomer diffusion or by radical migration in the bulk of irradiated polymer. In PETP, both processes have relatively high activation energies¹⁶. At a temperature above T_g when monomer diffusion and radical migration in the grafting system essentially accelerate, the overall activation energy depends on the kinetic parameters of graft polymerization.

One of the features of graft polymerization is a sharp increase in the chain termination activation energy (E_t) in comparison with its value for liquid-phase polymerization of the same monomer. For example, for bulk polymerization of styrene¹⁷, $E_t = 6.3-8.4 \text{ kJ mol}^{-1}$. Grafting of styrene onto different polymeric substrates¹⁸ gives $E_t = 50-110 \text{ kJ mol}^{-1}$. Such an increase in E_t during grafting reflects the viscosity of the swelled polymer to be 10^7-10^{10} times higher than that of the monomer. As a result the growing grafted chain ends have very low diffusion coefficients in the bulk of the polymer and their termination is sharply restrained. Therefore the grafting system is very sensitive to the smallest change in temperature. A high E_t value leads to a negative value^{18,19} for the difference between the activation energy for chain propagation (E_p) and E_t . Sundardi¹, performing grafting of a number of monomers onto PETP, came to the conclusion that E_t depends on the nature of the substrate but not of the monomer.

The aim of this study is to investigate the temperature influence on the kinetics of radiation-induced graft polymerization of styrene onto PETP nuclear membranes with different pore diameters, pore densities and

Table 1 Characteristics of membranes and films used for graft polymerization

Nuclear membranes							Films	
Sample code	Pore density (m^{-2})	d_b^a (μm)	d_g^a (μm)	Thickness (μm)	Porosity ^b (%)	Average distance between pores ^c (μm)	Sample code	Thickness (μm)
0.05-F	2×10^{13}	—	0.05	9.9 ± 0.3	8.0 ± 0.5	0.25	L-1.5	1.6 ± 0.1
0.1-F	3.2×10^{12}	0.095	—	10.1 ± 0.2	8.1 ± 0.7	0.70	L-3	2.9 ± 0.1
1-F	5×10^{10}	0.93	—	8.6 ± 0.2	7.7 ± 0.2	5.0	L-5	5.0 ± 0.2
							L-10	10.2 ± 0.2
							L-20	20.0 ± 2.0

^aPore diameters d_b and d_g were obtained by a 'bubble-point' and gas dynamic method, respectively

^bPorosity was determined by a gravimetric method

^cThe calculation of the average distance between the pores of nuclear membranes with different pore density was carried out using the model of square-nest mode for pore distribution on a membrane surface

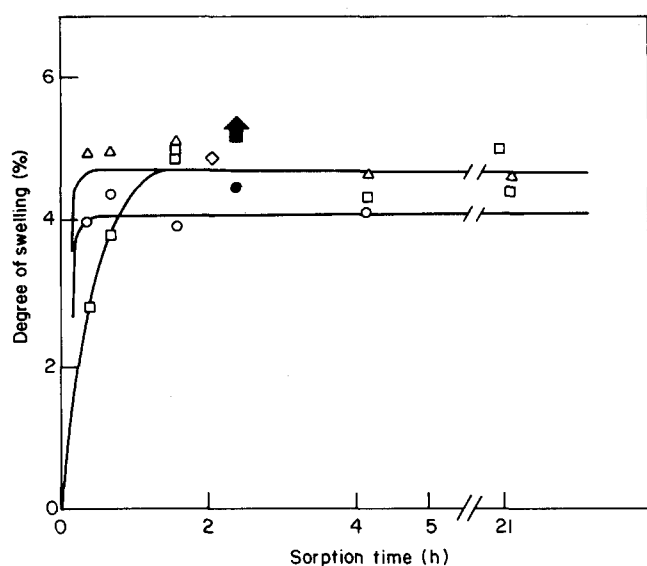


Figure 1 Swelling of nuclear membranes and films. Open symbols refer to swelling in toluene and closed symbols refer to swelling in styrene with addition of 0.15 wt% sulphur. Temperature = 70°C. ○, ●, 0.1-F; △, ▲, 1-F; □, ■, L-10; ◇, L-1.5

average distances between the pores, and onto films of different thicknesses. We have also made a tentative attempt to establish the dependence of critical thickness of polymeric substrate on grafting temperature.

EXPERIMENTAL

Biaxially oriented PETP films (1.5, 10, and 20 μm thick) manufactured in the USSR (lavsan film prepared in accordance with State Standard 24234-80) were used (Table 1). The draw ratio was ~ 3 . The films were filled with 0.2 wt% kaolin. Hostaphan films from Kalle, West Germany (3 and 5 μm thick) were also used (Table 1). Films and membranes were not subjected to additional cleaning. Technical grade styrene (USSR) was purified by double distillation under vacuum and was stored at -12°C for not longer than 1 month. Toluene of 'chemical pure' grade was used without purification.

Irradiation of the PETP film with accelerated heavy ions $^{132}\text{Xe}^{8+}$ was carried out in a cyclotron U-300. To sensitize the heavy ion tracks the PETP film was

irradiated with ultraviolet light in air. The etching of tracks was carried out on an etching plant in sodium hydroxide solution. The film (320 mm wide) was passed successively through baths for etching, preliminary washing, neutralization of alkali residues, final washing and drying with hot air. The characteristics of the membranes prepared are shown in Table 1.

Irradiation of the films and nuclear membranes was carried out in vacuum or in air by γ -rays (^{137}Cs) at a dose rate of 0.75 Gy s^{-1} . The temperature in the irradiation chamber was $30\text{--}35^\circ\text{C}$. Graft polymerization was carried out as described earlier²⁰. The grafting yield is defined as the percentage weight gain of the sample.

The swelling of the polymer was investigated using a gravimetric method. After swelling the sample in liquid in suitable conditions the polymer was removed from the swelling agent, excess liquid was carefully removed by filter paper and the sample was quickly weighed. After removal of liquid by heating in air at $\sim 60^\circ\text{C}$ the sample was weighed. The degree of swelling was calculated as the percentage increase in weight.

RESULTS AND DISCUSSION

Swelling of nuclear membranes and films

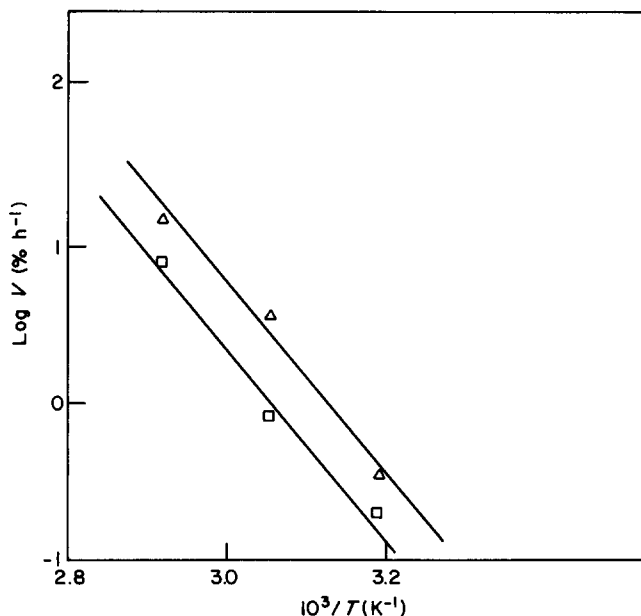
To determine monomer concentration in the bulk of PETP substrate the swelling of membranes and films in toluene is studied. Toluene is used as a saturated analogue of styrene with the nearest overall solubility parameter. Preliminary experiments on the swelling of membranes in toluene and styrene with addition of 0.15 wt% sulphur acting as polymerization inhibitor showed approximate agreement for the degree of swelling in both liquids. Swelling curves are shown in Figure 1.

Depending on the average distance between the pores (or film thickness) the initial swelling rate increases in the order L-10, 1-F, 0.1-F. All points in Figure 1 are obtained on the basis of membrane and film weight obtained after removal of sorbed toluene (m'_0). This weight is less than the weight of the original membrane (m_0). Such a weight loss can occur as a result of oligomer extraction from PETP²¹. The relative weight decrease of nuclear membranes and film after extraction with water and benzene in Soxhlet apparatus is shown in Table 2.

In the case of membrane swelling, the relative weight

Table 2 Weight change of PETP nuclear membranes and film after Soxhlet extraction

Sample code	$(1 - m'_0/m_0) \times 100$ (%) ^a	$(1 - m'_0/m_0) \times 100$ (%) ^b
0.05-F	1.1	2.3 ± 0.3
0.1-F	0.9	1.7 ± 0.2
1-F	0.2	1.2 ± 0.2
L-10	0	0

^aExtraction with water over 9 h^bExtraction with benzene over 36 h**Figure 2** Temperature dependence of the swelling rate of PETP samples in toluene. Δ , 1-F; \square , L-10

loss is higher as the average distance between pores is smaller. Remarkably there is no weight loss of films L-10 and L-1.5 after swelling in toluene and solvent removal. The thickness of film L-1.5 is smaller than the average distance between pores of membrane 1-F. In spite of this, extraction of oligomers did not occur whereas it does in the case of the membrane. This indicates a change in PETP structure during membrane preparation from the film, or more accurately, the presence in the bulk of the membrane side by side with cylindrical channels (pores) of micropores formed as a result of the difference between the etching rates of crystalline and amorphous regions of PETP²².

As follows from Figure 1, an equilibrium degree of swelling for membrane 0.1-F is lower than that of 1-F, L-1.5, and L-10 in spite of the weight loss in the course of extraction. If solvent-induced crystallization takes place, it would occur in all samples irrespective of their thickness or average distance between pores. Therefore a more reliable explanation is offered, namely, an increase in the evaporation rate of the swelling agent as the average distance between pores (or, in other words, the effective thickness of sample) decreases.

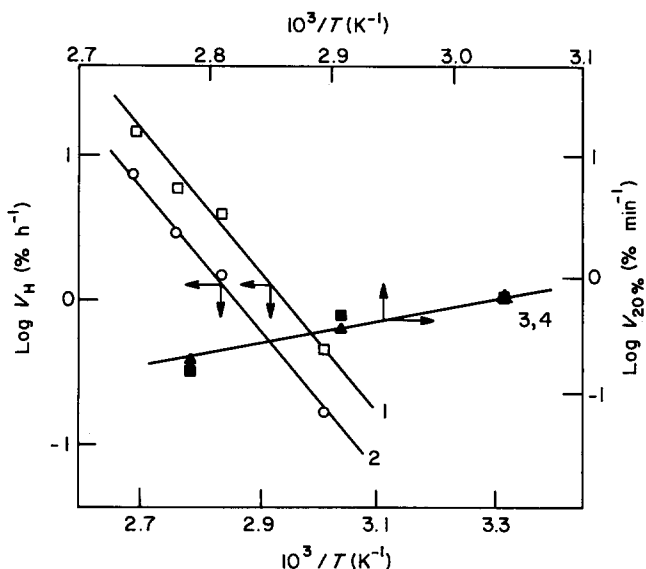
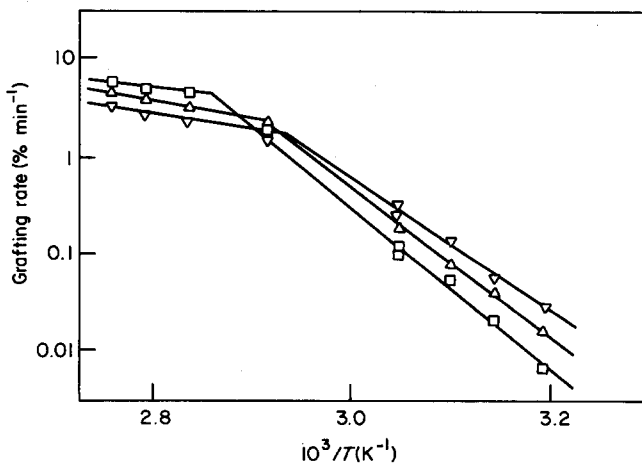
Grafting temperature

Graft polymerization begins by monomer sorption on irradiated PETP substrate. The Arrhenius plot of swelling rate in toluene is shown in Figure 2. The activation energy of swelling, E_s , is equal to 120 ± 20

kJ mol^{-1} . On the basis of times at which the membrane or film sample sorbed half the equilibrium quantity of monomer the diffusion coefficient, D , of monomer in the bulk of PETP can be calculated⁸. From the data, D changes with temperature with an activation energy of 110 kJ mol^{-1} which is close to E_s .

The temperature dependence of the grafting rate is shown in Figure 3 (curves 1 and 2). In MPA, the overall activation energy, E_0 , in the temperature range from 60 to 100°C is equal to $91 \pm 8 \text{ kJ mol}^{-1}$. This value indicates that by increasing temperature the initiation of graft polymerization probably occurs by the radical products formed during the dissociation of peroxides. Consequently, the contribution of the trapped radicals to initiation decreases^{23,24}.

The Arrhenius plot of the initial grafting rate in MPV consists of two ranges (Figure 4). In the low temperature range E_0 is $150 \pm 20 \text{ kJ mol}^{-1}$ (this is the average value for all samples shown in Figure 4). This value approximately agrees with the activation energy of

**Figure 3** Dependence of styrene grafting rate in MPA (1 and 2 are the initial rates) and in MPV (3 and 4 are the rates at grafting yield 20%) on reciprocal temperature. Preirradiation dose is 180 kGy for MPA and 50 kGy for MPV. \circ , 0.1-F; Δ , 1-F; \square , \blacksquare , L-10**Figure 4** Arrhenius plot of the initial grafting rate. Grafting by MPV, preirradiation dose is 50 kGy. ∇ , 0.05-F; Δ , 1-F; \square , L-10

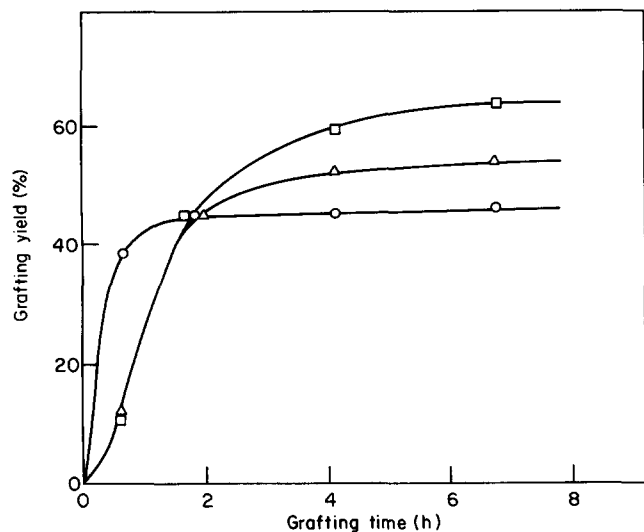


Figure 5 Curves of polystyrene accumulation onto PETP film and nuclear membranes. Grafting by MPV, preirradiation dose is 50 kGy, grafting temperature is 55°C. □, L-10; △, 1-F; ○, 0.1-F

substrate swelling in toluene. In the plot, a bending region displaces to higher temperature as the thickness of the sample increases. Therefore, for thicker PETP substrate the transition from the diffusion region of graft polymerization to the kinetic region occurs at higher temperature.

Time-conversion curves of styrene grafting (Figure 5) indicate diffusion control of the grafting reaction at 55°C (grafting by MPV). In the initial time period grafting onto membrane 0.1-F proceeds more quickly than onto other substrates since the average distance between pores for membrane 0.1-F is smaller than for 1-F and the thickness of film L-10 (Table 1). As the content of grafted polystyrene in the bulk of substrate increases and the grafting front moves towards the middle of the substrate, which in the case of membrane is equal to half the average distance between pores, polymerization continues on samples with higher effective thickness (1-F and L-10) while it stops completely on membrane 0.1-F due to exhausting all the active sites in the bulk of the substrate. In contrast to the above, at higher temperature (>70°C), as follows from Figure 4, the initial grafting rate increases with effective PETP thickness (up to a thickness of 10 μm).

The overall activation energy of grafting averaged for all samples shown in the high temperature range of Figure 4 is $25 \pm 6 \text{ kJ mol}^{-1}$. This value is close to the activation energy of the chain propagation step (E_p) of 23 kJ mol^{-1} (the average for E_p from refs 25 and 26). In the initial period of graft polymerization (up to ~300 s), prior to chain termination since the average lifetime of the polystyryl radicals in the grafting process is equal to several thousand seconds^{27,28}, the overall activation energy consists of the activation energy of chain propagation only. As grafting time increases the grafted chains begin to terminate but because of chain entanglement and high viscosity of the reaction medium, the activation energy of chain termination is high compared with its value during styrene polymerization in the bulk. As a result, E_0 becomes a negative value (-40 kJ mol^{-1}) as can be seen from Figure 3 (curves 3 and 4).

Critical thickness as a function of temperature

A critical thickness of film substrate is defined as that thickness above which the grafting rate per unit surface area becomes constant (or decreases) as film thickness continues to increase. The critical thickness can be expressed by²⁹:

$$l_c = \left(\frac{8Dc_0}{V} \right)^{1/2} \quad (1)$$

where c_0 is the saturation concentration of monomer in the substrate and V is the grafting rate. As follows from equation (1), l_c is a function of temperature since of the three variables D and V are temperature dependent (as follows from our work c_0 does not depend on temperature).

The temperature dependence of critical thickness shown in Figure 6 resembles an Arrhenius plot obtained for graft polymerization (Figure 4). In the low temperature range, when the reaction is controlled by monomer diffusion in the bulk of PETP, the activation energy of critical thickness change $E_1 = 147 \pm 4 \text{ kJ mol}^{-1}$ which coincides with the activation energy of grafting (150 kJ mol^{-1}). In the high temperature range $E_1 = 25 \text{ kJ mol}^{-1}$.

CONCLUSIONS

The overall activation energy, E_0 , of radiation-induced graft polymerization of styrene onto PETP nuclear membranes and films performed by MPV and MPA and the activation energy of PETP swelling in toluene has been studied. For MPV, the initial rate of grafting in the Arrhenius plot consists of two linear ranges with a bending point which passes to higher temperature when the sample is thicker. The low temperature range has an E_0 which corresponds to monomer diffusion in the bulk of substrate whereas in the high temperature range E_0 is determined by the kinetic parameter of grafting. The critical thickness of PETP substrate is a function of temperature. In the Arrhenius plot, this latter dependence has the same form as that of the initial grafting rate.

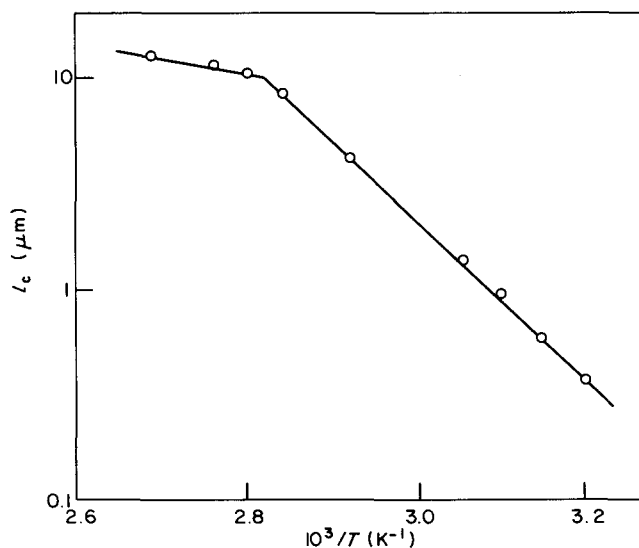


Figure 6 Critical thickness, l_c , of PETP substrate as a function of reciprocal temperature. Grafting by MPV, preirradiation dose is 50 kGy

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