*89-807*

*Z 10*

N.I.Zhitariuk, N.I.Shtanko

# INFLUENCE OF TEMPERATURE
# ON RADIATION-INDUCED GRAFT POLYMERIZATION
# OF STYRENE ONTO
# POLY(ETHYLENE TEREPHTHALATE)
# NUCLEAR MEMBRANES AND FILMS

**1989**

Temperature dependence of the grafting yield is characterized by a curve with a maximum. It is usually compared the limit grafting yields $(Q_{lim})$ which are obtained at long grafting times when all the radicals and/or oxyradicals are spent in grafting process. Temperature dependence with a maximum is observed during grafting by the method of preirradiation in vacuum (MPV) (Sundardi, 1979; Haruvy and Rajbenbach, 1981; Vierkotten and Ellinghorst, 1983), by the method of preirradiation in air (MPA) (Hebeish et al., 1978) as well as by the direct method (Schamberg and Hoigne, 1970; Vlagiu and Stannett, 1972; Faterpekar and Potnis, 1979). Such relationship is fulfilled on grafting onto a number of polymeric substrates: poly(ethylene terephthalate) (PETP) (Schamberg and Hoigne, 1970; Vlagiu and Stannett, 1972; Hebeish et al., 1978; Faterpekar and Potnis, 1979; Sundardi, 1979; Zhitariuk et al., ·88), nylon (Haruvy and Rajbenbach, 1981), and polypropylene (Schamberg and Hoigne, 1970).

In MPV, extreme dependence is due to different influence on the grafting reaction, on the one hand, of the monomer diffusion rate and, on the other hand, of reactional ability and radical lifetime. Maximum on this relationship lies, in accordance to the one data, in the region of glass-transition temperature of polymer (Schamberg and Hoigne, 1970; Vlagiu and Stannett, 1972; Faterpekar and Potnis, 1979) and, according to the others, in the region of glass-transition temperature of the polymer/monomer (or monomer solution) system (Kudryavtsev et al., 1981; Zhitariuk et al., 1988).

Arrhenius plot of grafting rate is described by a linear function with a break. A place of the break point concurs as a rule with the glass-transition temperature of the polymer/monomer system. This dependence is observed during grafting carrying out by different methods: MPA (Kaji, 1985a), MPV (Chapiro et al., 1969; Hegazy et al., 1981), and direct method (Bonnefis and Puig, 1971; Kaji et al., 1973; Kaji, 1985b). Only the latter method is used for grafting of a number of monomers onto PETP.

The overall activation energy of radiation-induced grafting decreases as temperature passes over glass-transition region of polymer/monomer system from glass to high-elasticity state. This dependence takes probably place due to change of the rate limit stage of grafting as temperature raises. At temperature which is lower than glass-transition one graft polymerization is limited either by monomer diffusion or by radical migration in the bulk of irradiated polymer. In PETP, both the processes have relatively high activation energies (Illers and Breuer, 1963). At temperature which is higher than glass-transition point when monomer diffusion and radical migration in the grafting system essentially accelerate, the overall activation energy depends on kinetic parameters of graft polymerization process.

Change of temperature, when system is in high-elasticity state, affects differently the $Q_{lim}$ and the initial grafting rate $(V_i)$. In MPV and in a number of works which deal with grafting by MPA, $Q_{lim}$ decreases but $V_i$ increases with temperature. $V_i$ depends on concentration of the radicals obtained during irradiation or decomposition of peroxides and on their accessibility for monomer diffused into the volume of substrate, whereas $Q_{lim}$ is mainly de-

termined by the change of the chain termination rate with temperature. In spite of that the recombination rate of the radicals initiating grafting has a small increase with temperature in semicrystalline PETP (Campbell et al., 1970) $Q_{lim}$ decreases as a result of a grafted chains molecular weight decreasing with temperature.

One of the features of graft polymerization is a sharp increasing of chain termination activation energy $(E_t)$ in comparison with its value at liquid-phase monomer polymerization. For example, for polymerization of styrene in the bulk $E_t$ is from 6.3 to 8.4 kJ/mole (Odian, 1970). Grafting of styrene onto different polymeric substrates gives $E_t$ from 50 to 110 kJ/mole (Dobo and Somogyi, 1962). Such increasing of $E_t$ during grafting process reflects the viscosity of the swelled polymer to be $10^7 - 10^{10}$ times higher in comparison with that of monomer. As a result the growing grafted chain ends have too low diffusion coefficients in the bulk of polymer and process of their termination is sharply restrained. Therefore the grafting system is very sensitive to the smallest temperature change. High $E_t$ value brings to negative value of the difference between activation energy of chain propagation $(E_p)$ and $E_t$ (Chandler et al., 1962; Dobo and Somogyi, 1962; Bartl and Wuckel, 1976). Sundardi, 1979, carrying out the grafting of a number of monomers onto PETP, come to the conclusion that $E_t$ depends on the nature of the substrate but not of the monomer.

It is further interesting to note some features of monomer diffusion in PETP. This polymer has a low degree of swelling in the majority of monomers. Therefore it is used the monomer mixture with organic solvents (Avny et al., 1978; Memetea and Stannett, 1979; Kaji, 1985b). As follows from Memetea and Stannett,

1979, $Q_{lim}$ increases about one order of value at styrene grafting onto preirradiated PETP in that case if instead of pure styrene is used its solution in methylene chloride.

The aim of our work is to investigate temperature influence on kinetics of radiation-induced graft polymerization of styrene onto PETP nuclear membranes with the different pore diameter and the different average distance between the pores as well as onto films of different thickness.

### EXPERIMENTAL

#### Materials

It is used biaxially oriented PETP films of 1.5, 10, and 20 $\mu$m thick (Table 1) manufactured in the USSR (lavsan film prepared in accordance with State Standard 24234-80). Draw ratio is 3. The films were filled with 0.2 wt. % of kaolin. Hostaphan films of Kalle, West Germany, of 3 and 5 $\mu$m thick were also used (see Table 1). Films and membranes were not subjected to additional cleaning. Technical grade styrene made in the USSR was purified by double distillation under vacuum and was stored at -12 $^{o}$C not longer than one month. Toluene of "chemical pure" grade was used without puri-fication.

#### Methods

Irradiation of the PETP film with accelerated heavy ions $^{132}Xe^{8+}$ was carried out in cyclotron U-300 at JINR. For sensibilization of heavy ions tracks the PETP film is irradiated by UV light. Etching of tracks was carried out on etching plant in sodium hydroxide solution. The film of 320 mm width passed

successively through the bathes: etching, preliminary washing, neutralization of alkali residua, final washing, drying with hot air. The characteristics of membranes prepared are shown in Table 1.

Table 1. Characteristics of membranes and films used for
graft polymerization

| | | | | Nuclear membranes | | |
|---|---|---|---|---|---|---|
| Sample code | Pore density, $cm^{-2}$ | $d_b$,[1] $\mu$m | $d_g$,[1] $\mu$m | Thickness l, $\mu$m | Porosity,[2] % | Average distance between pores,[3] $\mu$m |
| 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 | – | $10.1^{+}_{-}0.2$ | $8.1^{+}_{-}0.7$ | 0.7 |
| 1-F | $5*10^6$ | 0.93 | – | $8.6^{+}_{-}0.2$ | $7.7^{+}_{-}0.2$ | 5 |

| | | Films | | | |
|---|---|---|---|---|---|
| Sample code | L-1.5 | L-3 | L-5 | L-10 | L-20 |
| Thickness, $\mu$m | $1.6^{+}_{-}0.1$ | $2.9^{+}_{-}0.1$ | $5.0^{+}_{-}0.2$ | $10.2^{+}_{-}0.2$ | $20^{+}_{-}2$ |

[1] $d_b$, $d_g$ are pore diameters obtained by "bubble-point" and gas dynamic methods, respectively.

[2] Porosity was determined by gravimetric method.

[3] Calculation of average distance between the pores of nuclear membranes with different pore density was carried out proceeding from the model of square-nest pore distribution mode on membrane surface.

Irradiation of the films and nuclear membranes was carried out in vacuum and in air with $\gamma$-rays (Cs-137) at the dose rate of 0.75 Gy/sec. Temperature in the irradiation chamber was 30 - 35 $^{o}C$. Graft polymerization was carried out as described in (Zhitariuk et al., 1989b). The grafting yield is defined as percentage weight gain of the sample.

Swelling of polymer was investigated with gravimetric method. After sample swelling in liquid at suitable conditions the polymer was taken out from swelling agent, plenty of liquid is carefully removed with filter paper and polymeric sample is quickly weighed. After liquid removal by means of heating at ~ 60 $^{o}C$ the sample is weighed. Degree of swelling was calculated as percentage increasing in weight.

### RESULTS AND DISCUSSION

### Swelling of nuclear membranes and films

To determine the monomer concentration in the bulk of PETP substrate it is elucidated swelling of membranes and films in toluene which is used as a saturated analog of styrene with the nearest solubility parameter. Preliminary experiments on swelling of membrane in toluene and in styrene with addition of 0.15 wt. % of sulfur as inhibitor of polymerization showed approximate coincidence of the degree of swelling in both the 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 of L-10, 1-F, 0.1-F. All points in Figure 1 are built on the basis of membrane
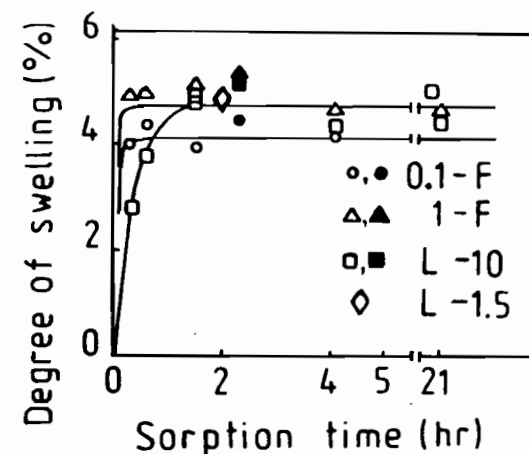


Fig. 1. Swelling of nuclear membranes and films: open symbols are swelling in toluene, closed ones are swelling in styrene with addition of 0.15 wt. % of sulfure. Temperature is 70 $^{o}C$.

and film weight obtained after removal of sorbed toluene ($m_o'$). This weight is less than the weight of initial membrane ($m_o$). Weight decreasing can occur as a result of oligomers extraction from PETP (Hudgins et al., 1978). The relative weight decreasing of nuclear membranes and film after extraction with water and benzene in Soxlet apparatus is shown in Table 2.

In case of swelling of membrane sample the relative weight loss is higher as the average distance between the pores is smaller. It is remarkable that weight loss of the films L-10 and L-1.5 does not occur after swelling in toluene and solvent removal. Thickness of the film L-1.5 is smaller than the average distance between the pores of the membrane 1-F. In spite of this, as mentioned above, ext-

6

7

Table 2. Weight change of PETP nuclear membranes and film after

Soxlet extraction

| Sample code | $(1-m_o'/m_o) * 100, \%$ [1] | $(1-m_o'/m_o) * 100, \%$ [2] |
|---|---|---|
| 0.05-F | 1.1 | $2.3 \pm 0.3$ |
| 0.1-F | 0.9 | $1.7 \pm 0.2$ |
| 1-F | 0.2 | $1.2 \pm 0.2$ |
| L-10 | 0 | 0 |

[1] extraction with water during 9 hr,

[2] extraction with benzene during 36 hr.

raction of oligomers from this film did not occur whereas in case of membranes that takes place. This indicates the change of PETP structure during membrane preparation from the film, and more concretely - presence in the bulk of membrane side by side with cylindrical channels (pores) of the micropore structure which is formed as a result of the difference between the etching rates of crystalline and amorphous regions of PETP (Komaki and Seguchi, 1982).

It follows from Figure 1 that in spite of accounting of the weight loss in the course of extraction, an equilibrium degree of swelling for membrane 0.1-F is lower than that for 1-F, L-1.5, and L-10. If the solvent induced crystallization of polymer would take place, it would occur in all the samples irrespective of their thickness or average distance between the pores. Therefore it is conceived more reliable other explanation, namely, an increasing of the swelling agent evaporation rate as the average distance between

the pores (or, in other words, the effective thickness of sample) decreases.

### Grafting temperature

Graft polymerization is begun by the monomer sorption with irradiated PETP substrate. Arrhenius plot of the swelling rate in toluene is shown in Figure 2. The activation energy of swelling $E_s$ is equal to $120 \pm 20$ kJ/mole.

Temperature dependence of the grafting rate is shown in Figure 3 (curves 1 and 2). In MPA, the overall activation energy $E_o$ within the temperature range from 60 to 100 $^o$C is equal to $91 \pm 8$ kJ/mole. This value indicates that with raising of temperature the initiation of graft polymerization more and more realizes probably by the radical products which are formed during dissociation of peroxides and so the contribution of the trapped radicals to initiation decreases (Robalewski and Stolarczyk, 1970; Zhitariuk et al., 1989a).
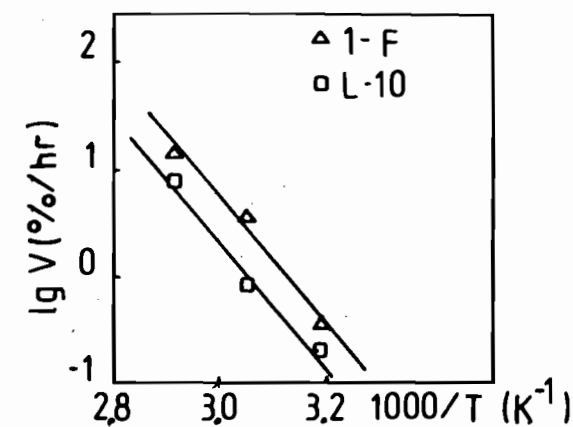


Fig. 2. Temperature dependence of the swelling rate of PETP samples in toluene.

Arrhenius plot of the initial grafting rate in MPV consist of two ranges (see Figure 4). In low temperature range $E_o$ is $150\pm20$ kJ /mole (this is the average value for all samples shown in Figure 4). This value approximately agrees with the activation energy of substrate swelling in toluene. A bending point displaces to higher temperature as thickness of sample increases. Therefore for thicker PETP substrate the transition from diffusion region of graft polymerization to kinetic one takes place at higher temperature.
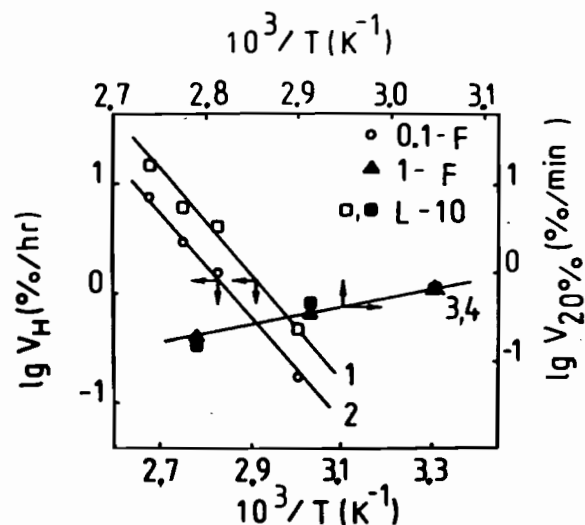


Fig. 3. Dependence of styrene grafting rate in MPA (1 and 2 are the initial rates) and in MPV (3 and 4 are the rates at grafting yield 20 %) on reciprocal temperature. Preirradiation dose is 180 kGy in MPA and 50 kGy in MPV.

Time conversion curves of polystyrene grafting (Figure 5) indicate in particular a diffusion control of grafting reaction at
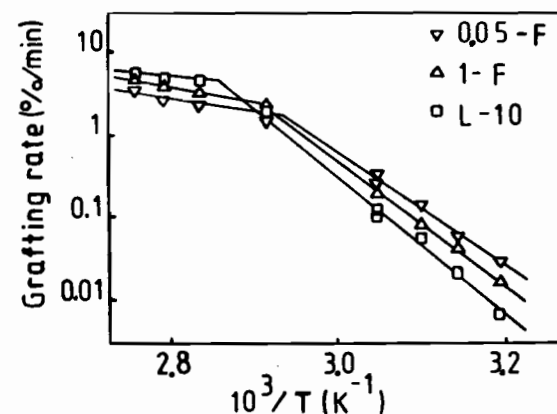


Fig. 4. Arrhenius plot of the initial grafting rate. Grafting by MPV, preirradiation dose is 50 kGy.
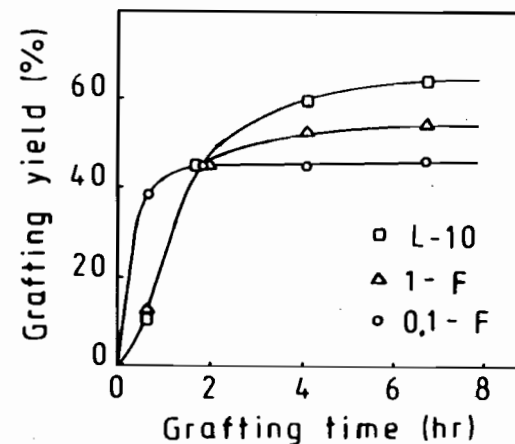


Fig. 5. Curves of polystyrene accumulation onto PETP film and nuclear membranes. Grafting by MPV, preirradiation dose is 50 kGy, grafting temperature is 55 $^{o}$C.

55 °C (grafting by MPV). In the initial period of time grafting onto membrane O.1-F proceeds more quickly than that onto other substrates, since the average distance between the pores in membrane O.1-F is lower than that in 1-F and than the thickness of the film L-10 (see Table 1). As the content of grafted polystyrene in the bulk of substrate increases and the grafting front moves towards the middle part of substrate (which in the case of membrane is equal to a half of average distance between the pores), polymerization continues to proceed on the samples with higher effective thickness (1-F and L-10) while it stops completely on the membrane O.1-F due to exhaustion all the active sites in the bulk of this substrate. In contrast to writing above, at higher temperature ( > 70 °C ), as follows from Figure 4, the initial grafting rate increases with the effective PETP thickness (up to the thickness of 10 $\mu$m).

The overall activation energy of grafting averaged for all samples shown in high temperature range of Figure 4 is equal to $25^{+}_{-}6$ kJ/mole.This value is close to the activation energy of the chain propagation step ($E_p$) 23 kJ/mole (the average for $E_p$ from Bagdasar'yan, 1966;and Soh and Sundberg, 1982). In such a manner, in the initial moment of graft polymerization (up to about 300 sec), when the chain termination does not yet take place so long as the average life time of the polystyril radicals in the grafting process is equal to several thousands of seconds Yasukawa et al., 1972; Bhattacharyya and Maldas, 1983), the overall activation energy consists of the activation energy of chain propagation only. As duration of grafting increases an entanglement of grafted chain takes place, the viscosity of the reaction medium increases and as a consequence of this the activation energy of chain termination raises as compared with that of styrene polymerization in the bulk. As a result $E_o$ acquires the negative value ($-40^{+}_{-}4$ kJ/mole as can be seen from Figure 3, curves 3 and 4).

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. As follows from (Wilson, 1974), the critical thickness can be expressed by equation:

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

where D is monomer diffusion coefficient in substrate volume, $c_o$ is stationary monomer concentration in substrate volume, and V is grafting rate. As follows from equation (1) $l_c$ is a function of temperature since from three variable quantities the two (D and V) are the function of temperature (as follows from our work $c_o$ does not depend on temperature).

Temperature dependence of critical thickness showing in Figure 6 resembles Arrhenius plot obtained in graft polymerization process (Figure 4). In the low temperature range when the reaction is controlled by monomer diffusion in the bulk of PETP $E_l = 147^{+}_{-}4$ kJ/mole that coincides with grafting activation energy (150 kJ/mole). In the high temperature range $E_l = 25$ kJ/mole.

The overall activation energy of radiation-induced graft polymerization of styrene onto PETP nuclear membranes and films carrying out by the methods of preirradiation in air and in vacuum as well as the activation energy of PETP swelling in toluene has been studied. In MPV, the initial rate of grafting in Arrenius plot consists of two linear ranges with a bending point which lies at

the higher temperature the thicker sample is. Low temperature range has $E_o$ which corresponds to monomer diffusion in the bulk of substrate. $E_o$ in high temperature range is determined by kinetic parameter of grafting. The critical thickness of PETP substrate is a function of temperature. In Arrhenius plot, this dependence has a form as that of temperature dependence of the initial grafting rate.
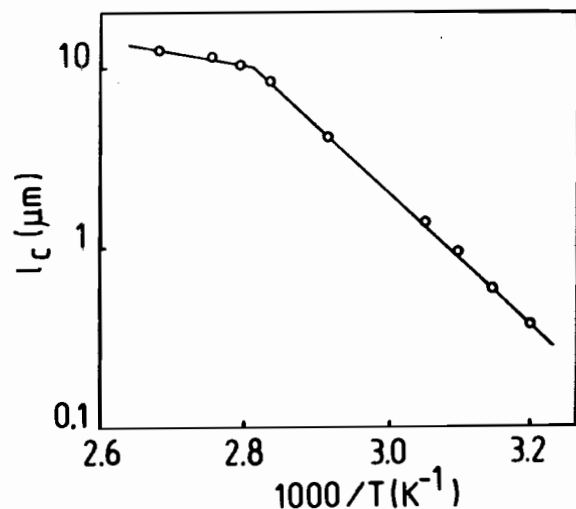


Fig. 6. Critical thickness of PETP substrate as a function of reciprocal temperature. Grafting by MPV, preirradiation dose is 50 kGy.

## ACKNOWLEDGEMENTS

### References

Avny Y., Rebenfeld L., and Weigmann H.-D. (1978) The In Situ Polymerization of Vinyl Monomers in Polyester Yarns. J. Appl. Polym. Sci. **22**, 125-147.

Bagdasar'yan H.S. (1966) Teoriya radikalnoj polimerizatsii (in Russian), Nauka, Moscow.

Bartl A. and Wuckel L. (1976) On the Grafting of Polyethylene Initiated by Pre-Irradiation in Air. In Proc. 4-th Tihany symp. on radiation chemistry, pp. 561-568. Akademiai Kiado, Budapest.

Bhattacharyya S.N. and Maldas D. (1983) Radiation-Induced Graft Copolymerization of Mixture of Styrene and Acrylamide onto Cellulose Acetate. II. Studies on Bromine Labeling. J. Polym. Sci.: Polym. Chem. Ed. **21**, 3281-3290.

Bonnefis J.C. and Puig J.R. (1971) Greffage Radiochimique de l'Acide Acrylique sur les Fibres de Polyester. J. Appl. Polym. Sci. **15**, 553-570.

Campbell D., Monteith L.K. and Turner D.T. (1970) Post-Irradiation Free-Radical Reaction in Poly(ethylene Terephthalate). J. Polym. Sci.: Part A-1 **8**, 2703-2711.

Chandler H.W., Henley E.J., and Trachtenberg E.N. (1962) The Mechanism of Radiation-Induced Graft Copolymerization. Intern. J. Appl. Radiat. Isotopes **13**, 239-246.

Chapiro A., Bex G., Jendrychowska-Bonamour A.M., and O'Neill T. (1969) Preparation of Permselective Membranes by Radiation Grafting of Hydrophilic Monomers into Polytetrafluoroethylene Films. Adv. Chem. Ser. **91**, 560-573.

Dobo J. and Somogyi A. (1962) Grafting of Styrene onto Pre-Irradia-

ted Teflon. In Proc. 1-st Tihany Symp. on Radiation Chemistry, pp. 195-203. Akademiai Kiado, Budapest.

Faterpekar S.P. and Potnis S.P. (1979) Modification of polyester fibre by radiation grafting. In Proc. Symp. on Industrial Polymers and Radiation, pp. 254-274. Sardar Patel University Vallabh Vidyanagar, Gujarat, India.

Haruvy Y. and Rajbenbach A.L. (1981) Nylon 6 Water-Permeable Membranes Prepared by Electron Beam Radiation-Induced Graft Copolymerization. J. Appl. Polym. Sci. **26**, 3065-3071.

Hebeish A., Shalaby S.E., and Bayazeed A.M. (1978) Graft Copolymerization of 2-Methyl-5-Vinyl Pyridine to Poly(ethylene Terephthalate) Fibres using a Post-Radiation Technique. J. Appl. Polym. Sci. **22**, 3335-3342.

Hegazy E.-S.A., Ishigaki I., and Okamoto J. (1981) Radiation Grafting of Acrylic Acid onto Fluorine-Containing Polymers. I. Kinetic Study of Preirradiation Grafting onto Poly(tetrafluoroethylene). J. Appl. Polym. Sci. **26**, 3117-3124.

Hudgins W.R., Theurer K., and Mariani T. (1978) Separation of poly(ethylene terephthalate) oligomers by high-performance liquid chromatography and thin-layer chromatography. J. Appl. Polym. Sci.: Appl. Polym. Symp. **34**, 145-155.

Illers K.H. and Breuer H. (1963) Molecular motions in polyethylene terephthalate. J. Colloid Sci. **18**, 1-31.

Kaji K., Okada T., and Sakurada I. (1973) Radiation-Induced Graft Copolymerization to Polyester XIII. Grafting of Methacrylic Acid onto Drawn Poly(ethylene Terephthalate) Fibers with Immersion Method. Japan Atomic Energy Research Institute, Annual Report No 5, JAERI-5028, pp. 52-60.

Kaji K. (1985a) Graft Polymerization of Acrylic Acid onto Polyethylene Film by Preirradiation Method. Japan Atomic Energy Research Institute, Annual Report No 17, JAERI-M 84-239, pp. 47-55.

Kaji K. (1985b) Radiation-Induced Grafting of Acrylic Acid onto Polyester Fiber. Ind. Eng. Chem. Prod. Res. Dev. **24**, 95-102.

Komaki Y. and Seguchi T. (1982) Scanning electron microscopy of clear pore filters in poly(ethylene terephthalate) and ethylenetetrafluoroethylene copolymer. Polymer **23**, 1143-1146.

Kudriavtsev Val. N., Kabanov V.Ya., Chalih A.E., and Spitsin V.I. (1981) Vliyanie relaksatsionnih perehodov na radiatsionnuyu kationnuyu privivochnuyu polimerizatsiyu. Dokl. AN SSSR (in Russian) **261**, pp. 418-421.

Memetea T. and Stannett V.T. (1979) Radiation grafting to poly(ethylene terephthalate) fibres. Polymer **20**, 465-468.

Odian G. (1970) Principles of Polymerization, McGraw-Hill book company, New York.

Robalewski A.M. and Stolarczyk L.W. (1970) Gamma-Rays Induced Graft Copolymerization of Poly(ethylene Terephthalate) with Acrylic and Methacrylic Acids. Part I - The Effect of Radiation and Grafting Conditions. Mechanism of the Reaction. Nukleonika **15**, 55-68.

Schamberg E. and Hoigne J. (1970) Radical and Radiation-Induced Grafting of Some Synthetic High Polymers within the Temperature Range of their Glass Transition. J. Polym. Sci.: Part A-1 **8**, 693-698.

Soh S.K. and Sundberg D.C. (1982) Diffusion-controlled Vinyl Polymerization. IV. Comparison of Theory and Experiment. J. Polym. Sci.: Polym. Chem. Ed. **20**, 1345-1371.

Sundardi F. (1979) Radiation graft copolymerization kinetics of poly(ethylene terephthalate) fibres. Polymer **20**, 1522-1526.

Vierkotten D. and Ellinghorst G. (1983) Radiation Initiated Grafting on Fluoro Polymers. II. Grafting of N-Vinylpyrrolidone on Copolymers of Vinyl Fluoride and Vinylidene Fluoride by Accelerated Electrons. Angew. Makromol. Chem., **113**, 153-168.

Vlagiu I. and Staunett V. (1972) Initial Studies on the Radiation Induced Grafting of Styrene to Polyethylene Terephthalate Fibers. Rev. Roumaine Chim.**17**, 379-383.

Wilson J.E. (1974) Radiation chemistry of monomers, polymers, and plastics, Marcel Dekker, Inc., New York.

Yasukawa T., Takahashi T., Murakami K., Araki K., Sasuga T., and Ohmichi H. (1972) Kinetics of Radiation-Induced Grafting Reactions. I. Polyethylene-Styrene Systems. J. Polym. Sci.: Part A-1 **10**, 259-273.

Zhitariuk N.I., Zagorets P.A. and Kuznetsov V.I. (1988) Temperature Effects in the Process of Radiation Graft Postpolymerization of Styrene onto Porous PET Film (in Russian). Joint Institute for Nuclear Research, Dubna, Preprint 18-88-549, pp. 1-3.

Zhitariuk N.I., Zagorets P.A. and Kuznetsov V.I. (1989a) Kinetics of Radiation-Induced Graft Polymerization of Styrene onto Poly (ethylene Terephthalate) Nuclear Membranes (in Russian). Joint Institute for Nuclear Research, Dubna, Preprint 18-89-48, pp.1-8.

Zhitariuk N.I., Zagorets P.A. and Kuznetsov V.I. (1989b) Influence of the Matrix Thickness on Radiation-Induced Grafting of Styrene onto Poly(ethylene Terephthalate) Films and Nuclear Membranes. Joint Institute for Nuclear Research, Dubna, Preprint E18-89-91, pp. 1-10.

18

Житарюк Н.И., Штанько Н.И.                                    E18-89-807
Влияние температуры на радиационную прививочную
полимеризацию стирола на ПЭТФ ядерных мембранах и пленке

Исследовано влияние температуры на кинетику радиационной прививочной полимеризации стирола на полиэтипентерефталатные ядерные мембраны с различными диаметрами пор и средними межпоровыми расстояниями, а также на пленки различной толщины методами МПЭ и ПОВ. Получены значения эффективной энергии активации процесса радиационной прививочной полимеризации стирола на ПЭТФ ядерных мембранах, а также значение энергии активации процесса набухания ПЭТФ в топуоле. Установлено, что начальная скорость прививочной полимеризации в координатах Аррениуса состоит из двух линейных участков. Энергия активации низкотемпературного участка совпадает с энергией активации процесса набухания подложки. Энергия активации на высокотемпературном участке определяется кинетическими параметрами реакции прививки. Определена зависимость критической толщины ПЭТФ подложки в процессе прививки от температуры. Установпено, что температурная зависимость критической толщины ПЭТФ подложки симбатна температурной зависимости скорости прививочной полимеризации.

Работа выполнена в Лаборатории ядерных реакций ОИЯИ.

Zhitariuk N.I., Shtanko N.I.                                    E18-89-807
Influence of Temperature on Radiation-Induced Graft
Polymerization of Styrene onto Poly(ethylene Terephthalate)
Nuclear Membranes and Films

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

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