Parameter Study for the Pre-Irradiation Grafting of Styrene/Divinylbenzene onto Poly(tetrafluoroethylene-*co*-hexafluoropropylene) from Isopropanol Solution

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Pre-irradiation grafting of styrene/divinylbenzene (DVB) onto poly(tetrafluoroethylene-*co*-hexafluoropropylene) (FEP) films from isopropanol (^{i}PrOH) solution was investigated with respect to the effect of irradiation dose, film thickness, cross-linker concentration, and reaction temperature. A mathematical model was applied to the kinetic curves to extract information on the polymerization rate, the radical-recombination rate, and the grafting through time. It turned out that the two closely correlated reaction rates for polymerization and radical recombination can be varied over a wide range by changing the irradiation dose, the cross-linker concentration, and the reaction temperature. On the other hand, the time until the grafting front has progressed to the center of the film is mainly affected by the film thickness and the reaction temperature. The formation of homopolymer in the grafting solution increases steeply with temperature and cross-linker concentration.

Introduction. – In a previous publication [1], we have shown that precipitants (*e.g.* alcohols) are preferred diluents in pre-irradiation grafting of styrene/divinylbenzene (DVB) onto poly(tetrafluoroethylene-*co*-hexafluoropropylene) (FEP). Due to their incompatibility with the polymer phase, these solvents allow to adjust the monomer concentration within the film without penetrating themselves into the polymer. This leads to a pronounced increase in radical lifetime and a more-favorable ratio of propagation to termination rate as compared to grafting in a good solvent, and a significantly higher amount of polymer may be formed per initiator site [1–6]. As we have shown as well, the extent of this improvement depends on the exact type of solvent, the monomer concentration, and the reaction time.

Several additional parameters have to be expected to influence the grafting behavior and have to be taken into account for an optimal choice of the grafting conditions [7–11]. These parameters include in particular the irradiation dose, the film thickness, the cross-linker concentration, and the reaction temperature. The evaluation of the effect of these variables on grafting of styrene/DVB onto FEP films in the presence of a non-solvent is the subject of the present publication. For simplicity, a 1:1 (*v*/*v*) mixture of monomer and ^{i}PrOH was chosen for these studies, and the reference point was set at 3 kGy irradiation dose, 25 μm film thickness, 10 vol.-% DVB concentration in the monomer mixture, and 60° reaction temperature.

For a more-quantitative description of the different effects on grafting, we fitted the grafting kinetics with the previously derived *Eqn. 1* [1][12][13], with X_G being the

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degree of grafting and t the reaction time. The parameter $r_{p0} = k_p[M]_0[P\cdot]_0$ in this equation gives the apparent initial polymerization rate, $\gamma = k_t[P\cdot]_0$ gives the characteristic radical recombination rate (*i.e.*, the initial recombination rate divided by the initial radical concentration), and t_0 is a delay time that is caused by the slow progression of the grafting front to the center of the polymer film. k_p, k_t, $[M]_0$, and $[P\cdot]_0$ are the polymerization rate constant, the rate constant for bimolecular termination, the monomer concentration, and the initial radical concentration, respectively. For experiments with a constant initial radical concentration, the ratio $r_{p0}/\gamma = k_p/k_t\ [M]_0$ (or the difference $\ln r_{p0} - \ln \gamma$) may be considered an indication of the grafting efficiency, *i.e.*, the amount of polymer that can be formed per initiator site.

$$X_G = \frac{r_{p0}}{\gamma} \ln(1 + \gamma(t - t_0)) \tag{1}$$

Results and Discussion. – *Pre-Irradiation Dose.* As expected, the pre-irradiation dose is one of the important parameters that determines the degree of grafting. This is evident from *Fig. 1.* In the first instance, this confirms that radiation-induced reactive sites on the base polymer are indeed responsible for initiating the graft polymerization.

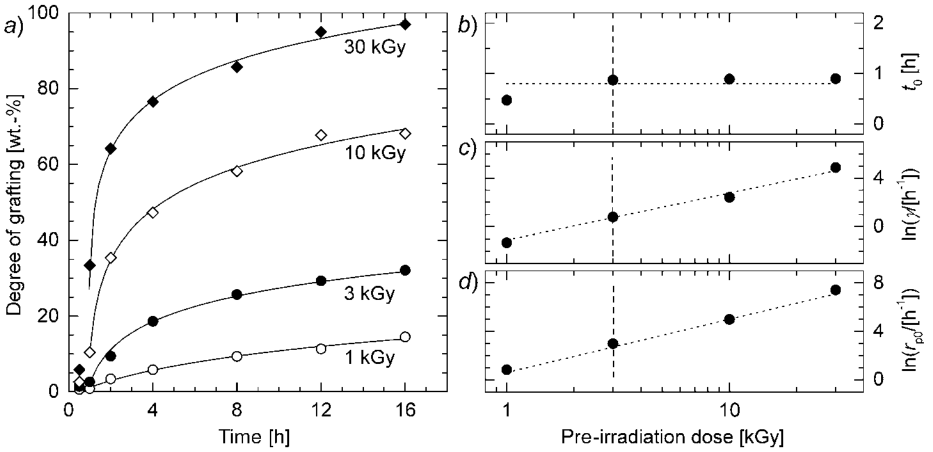

Fig. 1. a) *Grafting kinetics as a function of pre-irradiation dose and* b–d) *results from fitting these data with* Eqn. 1. FEP 25 µm, 50% monomer concentration in ^{i}PrOH, 10% DVB, 60°.

Fitting of the kinetic data in *Fig. 1* with *Eqn. 1* indicates that both the initial reaction rate r_{p0} and the characteristic radical recombination rate γ change by almost three orders of magnitude when changing the dose from 1 to 30 kGy. Double-logarithmic plots for r_{p0} and γ as a function of dose show a close to quadratic dose dependence for the two parameters. Contrary to this, a linear increase of the number of initiator sites $[P\cdot]_0$ with irradiation dose is expected at these rather low doses. This difference seems to indicate that not only the number of initiator sites but also the rate constants k_p and k_t are functions of the irradiation dose. Irrespectively of this, an essentially constant value of 12 is obtained for the ratio r_{p0}/γ, the pre-logarithmic factor in *Eqn. 1.* As a consequence of this mutual compensation of the dose dependence of r_{p0} and γ in the pre-logarithmic factor, at sufficiently long reaction times and high irradiation doses (*i.e.*, $\gamma(t-t_0) \gg 1$) the degree of grafting changes linearly with the logarithm of the irradiation dose. This has already been experimentally shown for other grafting systems [12][13]. It signifies that the dose dependence of X_G changes with 1/dose, *i.e.*, X_G becomes less and less dose sensitive with increasing irradiation dose, and it becomes more and more difficult to achieve higher degrees of grafting through a further increase in irradiation dose. Therefore, besides the previously discussed disadvantage of a deterioration of the mechanical properties [1], high irradiation doses are a rather inefficient way to increase the degree of grafting. On the other hand, at high irradiation doses, only slight improvements in radical efficiency can compensate for a significant reduction in irradiation dose.

The third parameter, the delay time t_0, is almost unaffected by irradiation dose. Since the preceding rate of the grafting front should depend on the local monomer concentration, this indicates that the availability of monomer in the grafted zone (and in particular at the grafting front) does not change with increasing number of reactive sites [13]. Therefore, monomer diffusion through the polystyrene phase does not seem to be a limiting factor for the grafting reaction. Otherwise, the monomer concentration at the grafting front should decrease with increasing monomer conversion rate.

Film Thickness. The parameter that varies the most with film thickness is t_0. *Fig. 2* shows that the delay time increases from less than 10 min (*i.e.*, almost instantaneous grafting through) for FEP 12.5 μm to roughly 6 h for FEP 75 μm. On the other hand, r_{p0} and γ vary by less than a factor of three over the same range of film thickness and can be considered nearly constant within the accuracy of the fitting. The strong variation of t_0 with film thickness establishes that the progression of the grafting front, *i.e.*, the monomer diffusion through the perfluorinated substrate to the next reactive sites, is the determining factor for the delay time.

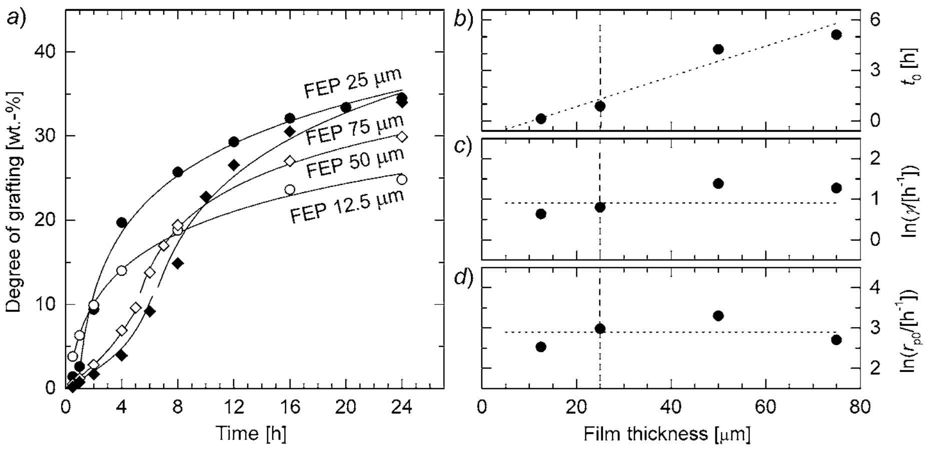

Fig. 2. a) *Grafting kinetics as a function of film thickness and* b–d) *results from fitting these data with* Eqn. 1. 3 kGy, 50% monomer concentration in ^{i}PrOH, 10% DVB, 60°.

From a more-practical point of view, the thickness dependence of t_0 means that grafting becomes significantly more time-consuming for thicker substrates. In addition, due to the increasing delay between initiation of the polymerization at the film surface and in the middle, there will be an increasing tendency toward gradients in the degree of grafting with increasing film thickness; homogeneous degrees of grafting throughout the whole film can be expected only for reaction times that significantly exceed t_0.

Cross-Linker Concentration. More pronouncedly than other grafting parameters, the cross-linker concentration influences numerous film properties. Of course, a variation in cross-linker concentration will be considered first of all in this respect. Some effects of the cross-linker concentration on film properties are immediately visible to the naked eye: with decreasing DVB concentration in the solution, a change in opacity of the grafted film is observed from highly transparent at 10% and 20% DVB concentration to almost white when grafted with pure styrene as the monomer. This indicates that the degree of cross-linking influences the characteristic dimensions of phase separation between polystyrene and FEP. In addition to this, the wettability of grafted films with the grafting solution is significantly higher at very low degrees of cross-linking than for high degrees of cross-linking. This may be explained by a higher flexibility of non-cross-linked polystyrene chains at the surface. It is evident that film properties such as the degree of swelling in organic solvents and the mechanical and chemical stability are affected by the degree of cross-linking as well.

Independently of this, the cross-linker concentration influences the grafting behavior. This has already been observed for other styrene-based simultaneous and pre-irradiation grafting systems [14–16]; both positive and negative effects on the grafting yield have been reported. For the present system, the kinetics curves in *Fig. 3* show that the degree of grafting for a given monomer concentration and reaction time passes through a (weak) maximum with respect to cross-linker concentration. Small amounts of polyfunctional monomers may, thus, be used to increase the degree of grafting. Presumably, in this particular case, the effect is due to the fact that DVB provides a higher concentration and more reactive double bonds to the system. At a DVB concentration above 5%, the initial polymerization rate r_{p0} and the characteristic

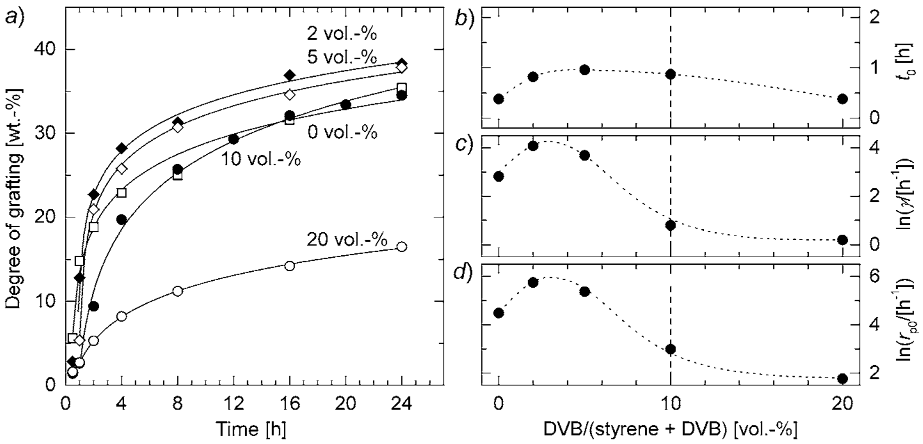

Fig. 3. a) *Grafting kinetics as a function of cross-linker concentration and* b–d) *results from fitting these data with* Eqn. 1. FEP 25 μm, 3 kGy, 50% monomer concentration in ^{i}PrOH, 60°.

radical recombination rate γ drop dramatically. Apparently, only at this point does cross-linking reduce the degree of swelling of the polymer phase to a critical extent, with the consequences of slowing down the polymerization reaction and increasing the radical lifetime. As a result, with increasing degree of cross-linking, the range of degrees of grafting that is accessible within a finite reaction time becomes more and more restricted. Nevertheless, since the DVB-concentration dependence is almost identical for r_{p0} and γ, the radical efficiency as given by the ratio r_{p0}/γ remains essentially constant over the whole range of cross-linker concentration.

As seen from *Fig. 4*, the cross-linker concentration also affects the amount of homopolymer that is formed by spontaneous thermal initiation. The amount of polymer that can be precipitated from solution after a given reaction time increases approximately linearly with cross-linker concentration. Several factors may account for this increase: a reduced recombination rate of the macroradicals in cross-linked particles, the higher reactivity of DVB, and radical scavenging by pending double bonds.

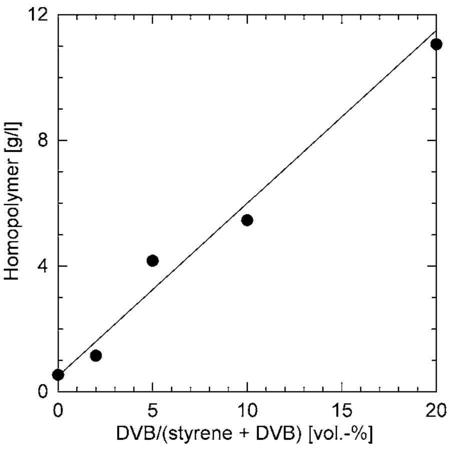

Fig. 4. *Homopolymer formation as a function of cross-linker concentration.* 3 kGy, 50% monomer concentration in ^{i}PrOH, 20 h reaction time, 60°.

Temperature. A major consequence of varying the reaction temperature concerns the rate of progress of the grafting front [17]. As is evident from the kinetics curves in *Fig. 5*, this effect is particularly pronounced in the case of thicker films: for 75-µm films, the induction period t_0 decreases from more than 10 h at 50° to *ca.* 2 h at 70° and less than 1 h at 85°. Therefore, grafting at rather high temperatures is a convenient way to significantly reduce reaction times when working with thicker films.

The initial polymerization rate r_{p0} and the characteristic radical recombination rate γ as obtained from fitting the data in *Fig. 5* are plotted in an *Arrhenius* representation in *Fig. 6*. Both parameters increase with temperature, whereas the increase is steeper (*i.e.*, the activation energy is higher) for the recombination than for the propagation reaction. As a consequence, the ratio of polymerization and termination rate becomes less favorable with increasing temperature. The changing slope of the curves indicates that both reactions are governed by temperature-dependent cooperative processes that

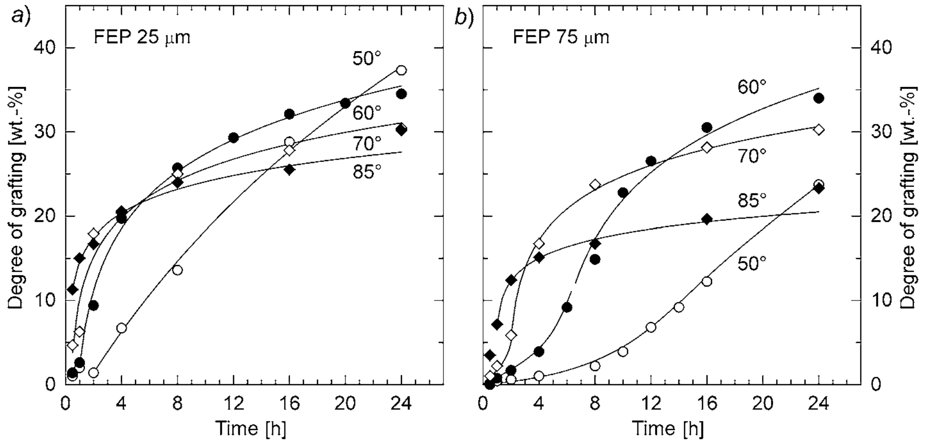

Fig. 5. *Grafting kinetics as a function of temperature for* a) *FEP-25* μ*m films and* b) *FEP 75* μ*m films.* 3 kGy, 50% monomer concentration in ^{i}PrOH, 10% DVB.

result in temperature-dependent activation energies. The temperature dependence of r_{p0} and γ may, therefore, be described by the *Vogel-Fulcher-Tamman* (*VFT*) *Eqn. 2* [18], where x_T is the value of either r_{p0} or γ at the temperature *T*. The three fitting parameters are the pre-factor *A*, the activation temperature *B*, and the *Vogel* temperature T_0. A *VFT* behavior of the initial polymerization rate is nicely seen in earlier publications as well (*e.g.*, in [7] [9]), although the data were interpreted in terms of classical *Arrhenius* activation energies.

$$\log x_T = A - \frac{B}{T - T_0} \tag{2}$$

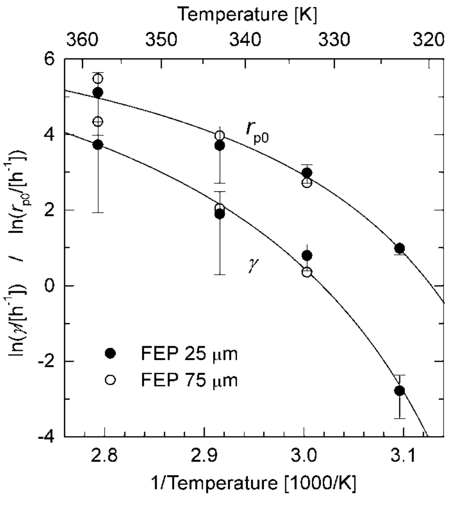

Fig. 6. *Initial polymerization rate* r_{p0} *and characteristic radical recombination rate* γ *as a function of the inverse temperature for FEP-25-*μ*m films* (solid symbols) *and FEP-75-*μ*m films* (open symbols). Results from fitting the data in *Fig. 5* with *Eqn. 1.* The temperature dependence of the reaction rates follows by *VFT* behavior.

A clear disadvantage of high reaction temperatures is a steep increase in homopolymer formation, as shown in *Fig. 7.* Contrary to the pre-irradiation grafting reaction, homopolymer formation is also affected by the rate of (thermal) initiation. The temperature-dependence of this step obviously overwhelms the variation of the recombination rate with temperature.

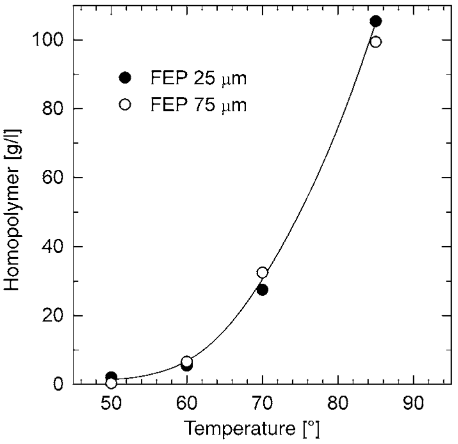

Fig. 7. *Homopolymer formation as a function of temperature in the presence of FEP-25-μm and FEP-75-μm films.* 3 kGy, 50% monomer concentration in ⁱPrOH, 10% DVB, 20 h reaction time.

Conclusions. – The following effects of irradiation dose, film thickness, cross-linker concentration, and reaction temperature are observed for grafting of styrene/DVB mixtures onto FEP films from ⁱPrOH solution: *a*) For sufficiently high irradiation doses and long reaction times, the degree of grafting increases with the logarithm of the irradiation dose. As a consequence, the dose sensitivity of the grafting reaction decreases with increasing dose. *b*) Increasing the film thickness extends the time that is required for grafting through the polymer film and, therefore, prolongs the reaction time. The reaction rates for polymerization and termination are unaffected by film thickness. *c*) Cross-linking of the polystyrene phase by copolymerization of DVB slightly increases the degree of grafting at low cross-linker concentration, whereas cross-linker concentrations of more than 5% slow the polymerization and the termination reactions significantly. As a consequence, the degree of grafting that can be achieved within a reasonable time becomes more and more restricted with increasing cross-linker concentration. *d*) An increased reaction temperature significantly accelerates the advancement of the grafting front. In particular, in the case of thicker films, a specific degree of grafting may thus be achieved within a much shorter reaction time. On the other hand, high reaction temperatures are rather unfavorable with respect to the ratio of polymerization to termination rate and with respect to homopolymer formation.

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Experimenatl Part

Chemicals. Divinylbenzene (DVB; 56.3% *meta*-isomer, 24.4% *para*-isomer, and 20% ethyl (vinyl)benzene, stabilized with 0.1% 4-(*tert*-butyl)catechol), styrene (99%; stabilized with 0.005% 4-(*tert*-butyl)catechol), and ^{i}PrOH (99%) were all purchased from *Fluka* and used without further purification. *Teflon® FEP 50A*, *100A*, *200A*, and *300A* films of 12.5, 25, 50, and 75 µm thickness, respectively, were purchased from *DuPont*. The films were cut into pieces of 100 mm length (parallel to the extrusion direction) and varying width between 25 and 70 mm. The pieces were washed with EtOH, dried, and sealed into PE plastic bags under air.

Electron-Beam Irradiation and Grafting. These were performed as described previously [1]. Film samples were spread on cardboard, irradiated at an acceleration voltage of 1.05 MV and currents of 1, 3, 10, and 30 mA, corresponding to doses of 1, 3, 10, and 30 kGy, and stored at $-80°$ starting 1 h after irradiation. Irradiated films were rolled up and inserted into 50 ml of the appropriate grafting soln. in cold trap-type reaction tubes with *Teflon* stopcocks. The concentration of monomer in the grafting soln. is given as fraction of the total volume, and DVB concentrations are given as fraction of the total volume of monomer. The soln. was purged with N_2 for 30 min at a flow rate of 10 Nl/h, and the reaction tube was put in a temp.-controlled water bath for an appropriate time. The grafted films were removed from the grafting soln., wiped off with tissue paper, and immersed in toluene overnight for extracting residual monomer and homopolymer. The films were wiped off again, dried under vacuum at 80° for several hours, and weighed. The degree of grafting in wt.-% was calculated according to *Eqn. 3:*

$$\text{Degree of grafting} = \frac{\text{final weight} - \text{initial weight}}{\text{initial weight}} \times 100 = \frac{\text{mass (polystyrene)}}{\text{mass (FEP)}} \times 100 \qquad (3)$$

For separating the homopolymer, the grafting soln. was poured into a tenfold excess of MeOH, the homopolymer was filtered off, dried, and weighed.

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