Pre-Irradiation Grafting of Styrene/Divinylbenzene onto Poly(tetrafluoroethylene-*co*-hexafluoropropylene) from Non-Solvents

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Pre-irradiation grafting of styrene/divinylbenzene (DVB) onto poly(tetrafluoroethylene-*co*-hexafluoropropylene) (FEP) films was studied with respect to the influence of solvent. Particularly favorable grafting conditions with long radical lifetimes and reasonably high polymerization rates were achieved with solvents that are precipitants for the newly formed polystyrene, *e.g.*, low-molecular-mass alcohols like ^{i}PrOH, AcOH, their mixtures with H_2O, and H_2O/surfactant systems. Using one of these solvents significantly extended the range of accessible graft levels, and a specific degree of grafting was obtained at a much lower monomer concentration and irradiation dose than with grafting in a good solvent such as toluene. As practical consequences, the monomer was used more efficiently, and the radiation damage of the perfluorinated base material was reduced with the result of improved mechanical properties of the grafted films.

Introduction. – Grafting of polymeric materials under the influence of ionizing radiation has been known since the middle of the twentieth century as a versatile method for polymer modification [1–14]. Among other methods, radiation grafting has been considered for a long time for the preparation of polymer electrolyte membranes for electrochemical applications [15]. The method is of particular interest for the functionalization of fluoropolymers, since these are difficult to modify by purely chemical methods.

The two principal methods of radiation grafting are the simultaneous-irradiation and the pre-irradiation techniques, the latter of these also being named the peroxidation method when irradiation is performed in the presence of O_2 [7–9]. The pre-irradiation grafting process is divided into two steps, as depicted in *Scheme 1*. In the first step, exposure of the polymer to ionizing radiation generates a certain amount of long-lived reactive sites located in tracks and spurs throughout the volume of the polymer [16]. In the case of irradiation of perfluorinated materials in the presence of O_2, these reactive sites include terminal double bonds as well as peroxy and alkoxy radicals [11][17][18]. In the second step, which may be performed hours, days, or even months after irradiation, the activated polymer is brought into contact with the monomer at elevated temperature, and graft chains start to grow from the reactive sites.

In most cases, grafting is conducted in the liquid phase, either in pure monomer [2] or in solution. It has repeatedly been stated that, in the latter case, a solvent should be used, which is able to significantly swell the grafted polymer [14][19–21] or the base material [22–27]. This recommendation is based on the observation that, under certain reaction conditions, swelling of the polymeric phase with a solvent will facilitate access

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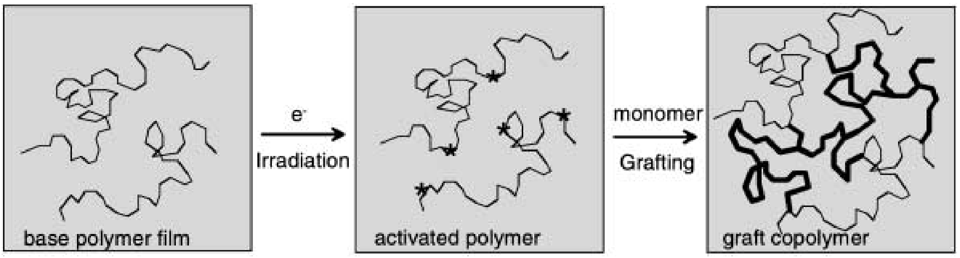
Scheme 1. *Pre-Irradiation Grafting*



of monomer to the reactive sites. This applies to simultaneous-irradiation grafting at high dose rates [20] as well as to grafting systems with base materials or graft polymers that are incompatible with the monomer but swell in monomer/solvent mixtures [21–24]. In partially just seeming agreement with these observations, benzene, toluene, and CH_2Cl_2 have been repeatedly used as solvents for radiation grafting of styrene and styrene derivatives [19][20][28–32].

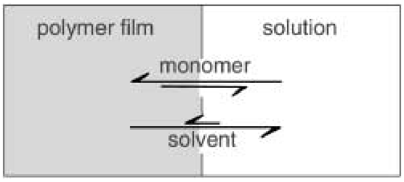
On the other hand, it was soon realized that the solvent should not dissolve the polymer, since high grafting yields strongly depend on the heterogeneity of the system that guarantees slow radical recombination [10]. Consistent with this, it was reported within the first years of radiation-grafting experiments that using thermodynamically poor solvents may have some significant advantages. In 1960, *Odian* and co-workers found that dilution of the monomer with MeOH in simultaneous-irradiation grafting of styrene to polyethylene, polypropylene, and polyvinyl chloride increases the grafting rate by more than a factor of three [33]. They demonstrated that the effect is related to a reduced termination rate and attributed this to a particularly pronounced *Trommsdorff–Norrish* effect [3][4][34][35] that is caused by an insolubilization of the grafted chains. The same observation was later explained in slightly different ways by *Matsuo et al.* [36], *Machi et al.* [37], *Wilson* [38], and *Burchill et al.* [39], focusing on the degree of swelling of the base material, entanglement effects, and solubility parameters. Even before the work of *Odian et al.* [33], *Dobó et al.* ascribed the same phenomenon to a suppression of the protective effect of styrene with respect to the radiation activation of the substrate [40].

Over the years, alcohols, and in particular MeOH and EtOH, have been frequently used as diluents for grafting monomers of low polarity onto different base materials [41–48], though some authors have reported the potential disadvantage that grafting tends to be more restricted to the polymer surface when non-solvents are used [9][49]. With a somewhat different objective (the protection of monomer-swollen polymers from O_2), inventors from *Nobel-Bozel S.A.* and *Burchill et al.* have also recommended to use H_2O as non-solvent in simultaneous-irradiation grafting [50][51].

More recently, it was realized that the addition of certain mineral acids and salts allows a further increase in grafting yields [41]. A shift in the partitioning equilibrium of the monomer between the liquid phase and the polymer was later made responsible for this 'salting-out effect' [42][43].

In summary, the effect of precipitants in radiation grafting may be represented as depicted in *Scheme 2:* incompatibility of the solvent with the polymer phase reduces the mobility of the growing polymer chains and extends the radical lifetime; preferential accumulation of the monomer in the polymer phase increases the local monomer concentration and, therefore, the polymerization rate.

Scheme 2. *Influence of a Poor Solvent on the Partitioning of Monomer and Solvent between Solution and Swollen Polymer*



Several more-specific influences of solvents and additives on radical polymerization are well known from solution polymerization [35][52]. These include preferential adsorption [45][53], complex formation with the growing radical and with the monomer, as well as template effects and chain-transfer activity. It has to be expected that these effects are also active in the case of graft copolymerization. An increased amount of radical formation due to radiolysis of certain solvents (alcohols and halogenated hydrocarbons in particular) has been considered as another solvent effect that may result in higher grafting yields [22][23][41][44][50]. It is understood that this effect is limited to simultaneous-irradiation grafting, and it has to be assumed that a significant part of the so formed 'grafted' polymer is not covalently linked to the base material but only physically interlocked with it [3][54].

Here, we present experimental results concerning the solvent influence on pre-irradiation grafting of styrene/divinylbenzene (DVB) onto poly(tetrafluoroethylene-*co*-hexafluoropropylene) (FEP). It was the objective of these investigations to make high graft levels more easily available to be able to reduce monomer concentration, reaction time, and radiation dose. The latter is of particular interest since it is well known that perfluorinated materials degrade at high radiation doses [6][11][13][18]. This is obviously unfavorable for the mechanical properties of the product.

Results and Discussion. – *Solvents, Chain-Transfer Agents, Inhibitors, and Retarders.* As a first screening step for potentially advantageous diluents, grafting kinetics were determined for 1 : 1 (*v*/*v*) mixtures of monomer with cyclohexane, toluene, THF, AcOH, ^{i}PrOH, and MeOH covering a large range of solubility parameters of the solvent. The results in *Fig. 1,a* show almost identical grafting behavior for all these solvents within the first hour. After this time, the curves for toluene and cyclohexane level off very fast, and no further grafting occurs. With the other solvents, the degree of grafting increases over a much longer period of time and reaches up to four times higher values for reactions in ^{i}PrOH than for those in toluene under identical reaction conditions.

Additional experiments were performed with small amounts of a chain-transfer agent (CBr_4), an inhibitor (TEMPO = 2,2,6,6-tetramethylpiperidin-1-yloxy), and a retarder (nitrobenzene) added to the monomer/^{i}PrOH solution, *i.e.*, with additives that are known to influence the lifetime of the macroradicals. Both CBr_4 and TEMPO cause a dramatic shortening of the time over which grafting increases, whereas addition of

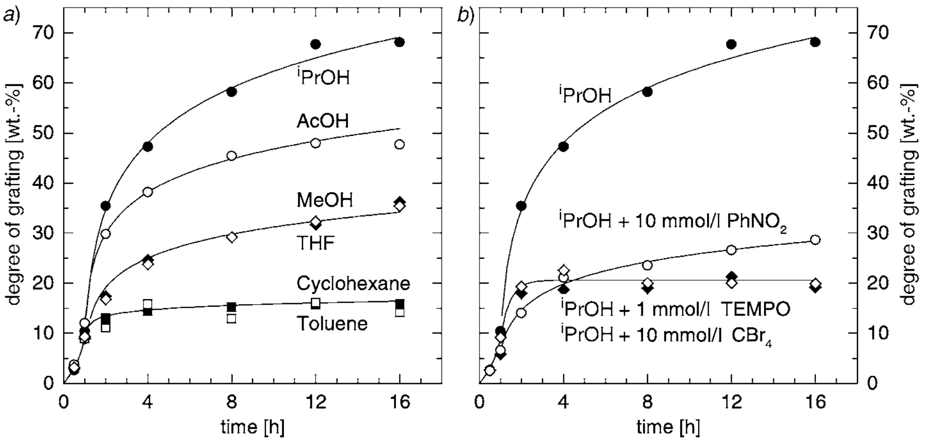


Fig. 1. *Influence of* a) *solvent and* b) *additives on the grafting kinetics.* FEP 25 μm, 10 kGy, 50% monomer concentration, 10% DVB, 60°.

nitrobenzene results in an even more extended but slower increase of the degree of grafting, as shown in *Fig. 1,b*. These results confirm that the curvature of the kinetics plots is a measure of the lifetime of the radicals in the polymer film[2]).

Due to its higher relevance for practical applications, all of these experiments were performed with a 9:1 (*v*/*v*) mixture of styrene and DVB as monomer. To make sure that the differences in grafting behavior are not simply due to different cross-linking efficiencies, grafting kinetics were also determined for pure styrene. As shown in *Fig. 2*, very similar dependence of the graft level on the type of solvent is observed in the absence and in the presence of DVB, even though each solvent system responds somewhat differently to the presence of DVB. In particular, in the absence of DVB, the graft levels obtained in MeOH are closer to those obtained in AcOH and ^{i}PrOH, whereas the graft levels obtained in THF almost drop to the values achieved with cyclohexane and toluene. Limiting the degree of swelling by cross-linking obviously has a particularly large and positive effect on grafting in THF but a rather small influence on grafting in MeOH.

Despite the peculiar behavior of THF and MeOH solutions, it is clear from the experiments that the solvent influence on the grafting reaction correlates with the solvent quality, and that one aspect of this influence is a significant change in radical lifetime (or termination rate). Therefore, it seems obvious to attribute the observed solvent influence – consistent with the literature – to a *Trommsdorff*-type effect. Nevertheless – and despite the quite significant differences in grafting behavior – almost identical degrees of equilibrium swelling of the polystyrene domains of irradiation-grafted films were determined for 1:1 (*v*/*v*) mixtures of the different solvents and ethylbenzene (*Table 1*). The differences in grafting have, therefore, to be

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[2]) In addition, the very different grafting kinetics in the absence and in the presence of CBr$_4$ indicate that the alcohol itself does not cause a significant amount of chain transfer. This is consistent with the assumption that the alcohol is excluded from the sites of polymerization.

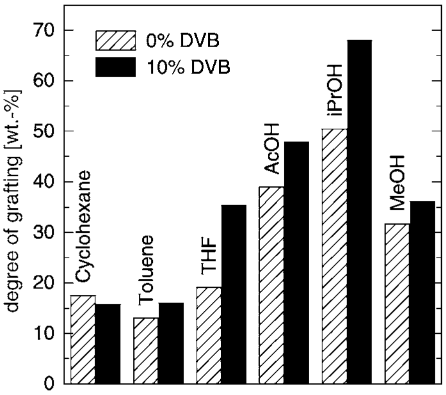

Fig. 2. *Degrees of grafting in the absence and in the presence of DVB.* FEP 25 μm, 10 kGy, 50% monomer concentration, 16 h reaction time, 60°.

explained within the limits of very small variations in the degree of swelling of less than 4% with respect to the polystyrene mass. However, not only the *amount* but also the *type* of liquid taken up by the grafted film will have some influence, *e.g.*, on local viscosity, radical mobility, and reaction rate. In addition, the individual exchange rates that determine how far the system deviates from equilibrium during grafting might be of some relevance as well and are possibly affected by the type of solvent used.

Table 1. *Swelling of Grafted Polymer Films in Pure Solvents and in 1:1* (*v*/*v*) *Mixtures of Solvent and Ethylbenzene.* Degrees of swelling are given as mass(solvent)/mass(polystyrene).

Solvent	Degree of swelling of non-cross-linked films		Degree of swelling of cross-linked films (10% DVB)	
	pure solvent	solvent/ ethylbenzene 1:1	pure solvent	solvent/ ethylbenzene 1:1
Cyclohexane	0.28 ± 0.01	0.33 ± 0.02	0.25 ± 0.02	0.26 ± 0.02
Toluene	0.33 ± 0.04	0.34 ± 0.03	0.26 ± 0.04	0.25 ± 0.04
THF	0.38 ± 0.02	0.35 ± 0.05	0.28 ± 0.04	0.26 ± 0.04
AcOH	0.17 ± 0.01	0.34 ± 0.03	0.15 ± 0.02	0.25 ± 0.03
^{i}PrOH	0.11 ± 0.01	0.31 ± 0.03	0.13 ± 0.02	0.25 ± 0.02
MeOH	0.06 ± 0.01	0.33 ± 0.01	0.06 ± 0.01	0.24 ± 0.02

A mathematical description of the kinetic curves in *Fig. 1* was attempted for a more-quantitative interpretation of the grafting behavior. In a simplified model that neglects any local differences in monomer concentration or reactivity as well as volume changes during grafting, the rate r_t for the loss of polymer-bound radicals $P\cdot$ by recombination may be written as *Eqn. 1*, and the rate of polymerization r_p, that may be defined as the change in the degree of grafting X_G, is given by *Eqn. 2*. In *Eqn. 2*, the last approximation assumes that the local monomer concentration [M] near the reactive sites does not change over time since conversions are always low. Integration of *Eqn. 1* yields the time-dependence correlation of *Eqn. 3* for the local radical concentration $[P\cdot]$ within the polymer film; where $[P\cdot]_0$, k_t, and t are the initial radical concentration, the recombination rate constant, and the reaction time, respectively. Integration of *Eqn. 2* with the inclusion of *Eqn. 3* yields the time-dependence correlation of *Eqn. 4* for the degree of grafting X_G, with k_p and $[M]_0$ being the polymerization rate constant and the initial local monomer concentration, respectively (*cf.* also [55][56] for *Eqn. 4*).

$$r_t = \frac{d[P\cdot]}{dt} = -k_t[P\cdot]^2 \tag{1}$$

$$r_p = \frac{dX_G}{dt} = k_p[P\cdot][M] \approx k_p[P\cdot][M]_0 \tag{2}$$

$$[P\cdot] = \frac{[P\cdot]_0}{1 + k_t[P\cdot]_0 t} \tag{3}$$

$$X_G = \frac{k_p[M]_0}{k_t} \ln\left(1 + k_t[P\cdot]_0 t\right) \tag{4}$$

It is evident from *Fig. 1* that grafting does not start instantaneously. Instead, a delay time is observed that may be attributed to slow warming of the solution (*ca.* 5 min) and (first of all) slow diffusion of the first monomer molecules to reactive sites at the interior of the FEP film (also known as front mechanism [3][20][36][55–57]). As the simplest model to account for this, one may assume a linear increase of the number of reacted initiator sites within the time interval $0 \leq t_i \leq t_0$. The concave part of the kinetics curves may then be described by *Eqn. 5*, in which the parameter $r_{p0} = k_p\ [M]_0\ [P\cdot]_0$ gives the apparent initial polymerization rate, $\gamma = k_t\ [P\cdot]_0$ is a measure for the radical lifetime, and t_0 is the delay time until all initiator sites on the base polymer have reacted. For experiments with a constant initial radical concentration, the prelogarithmic factor $r_{p0}/\gamma = k_p/k_t\ [M]_0$ may be considered an indication of the grafting efficiency, *i.e.*, the amount of polymer that can be formed per initiator site.

$$\begin{aligned} X_G &= \frac{k_p[M]_0}{k_t t_0} \int_0^{t_0} \ln\left(1 + k_t[P\cdot]_0(t - t_i)\right) dt_i \\ &= \frac{k_p[M]_0}{k_t} \left\{ \ln\left(1 + k_t[P\cdot]_0(t - t_0)\right) - 1 - \frac{t + 1/\left(k_t[P\cdot]_0\right)}{t_0} \ln\left(1 - \frac{t_0}{t + 1/\left(k_t[P\cdot]_0\right)}\right) \right\} \\ &\approx \frac{k_p[M]_0}{k_t} \ln\left(1 + k_t[P\cdot]_0(t - t_0)\right) = \frac{r_{p0}}{\gamma} \ln(1 + \gamma(t - t_0)) \end{aligned} \tag{5}$$

If radicals are lost by a first-order process (*e.g.*, in the presence of a constant concentration of a radical scavenger or a chain-transfer agent), one obtains by an analogous mathematical derivation *Eqn. 6*, with r_{p0} being again the initial polymerization rate, $\gamma = k_t$ being the characteristic decay rate of the radicals, and t_0 being the delay time that is caused by the slow progression of the grafting front.

$$X_G = \frac{k_p}{k_t}[\mathrm{M}]_0[\mathrm{P}\cdot]_0\left(1 - \frac{1}{k_t t_0}\left(1 - \mathrm{e}^{-k_t t_0}\right)\mathrm{e}^{-k_t(t-t_0)}\right) \approx \frac{r_{p0}}{\gamma}\left(1 - \mathrm{e}^{-\gamma(t-t_0)}\right) \tag{6}$$

The results from fitting the data in *Fig. 1* with *Eqns. 5* or *6* are summarized in *Table 2*. Despite the semiquantitative character of the fits, it is evident that the initial polymerization rate r_{p0} drops dramatically when switching from toluene and cyclohexane to THF and the three non-solvents, whereas γ decreases to an even slightly higher extent. As a result, the ratio r_{p0}/γ is higher for the poor solvents than for the good ones. A particularly favorable situation with respect to high degrees of grafting (*i.e.*, high kinetic chain lengths) is given for grafting in ^{i}PrOH. Grafting in this solvent constitutes a good compromise between extended radical lifetimes and low polymerization rates on the one hand and good monomer supply and high radical-recombination rate on the other. The initial polymerization rate r_{p0} in this particular system has a value of more than 100%/h. The value of γ amounts to about 10 h^{-1}. According to *Eqn. 3*, this means that 50% of the initial radicals are still alive 6 min after initiation, and 1% of the radicals have not yet recombined 10 h after initiation. These times are amazingly long for radical lifetimes in radical polymerization; nevertheless, within few minutes after initiation, the majority of the radicals have disappeared, and only few chains continue to grow. Considering that initiation is spread over a rather long period of time t_0, the number of active chain ends at any time is only a tiny fraction of the total amount of reactive sites $[\mathrm{P}\cdot]_0$. This may explain why polystyrene radicals in radiation grafting have not been detected by ESR spectroscopy [47].

Table 2. *Results from Fitting the Data Points in* Fig. 1 *with* Eqns. 5 *or* 6

Solvent	*Eqn.*	t_0 [h]	$\ln(r_{p0}/[\mathrm{h}^{-1}])$	$\ln(\gamma/[\mathrm{h}^{-1}])$
Cyclohexane	*5*	1.0	12.2	12.2
Toluene	*5*	1.0	11.5	11.5
THF	*5*	0.6	3.7	1.7
AcOH	*5*	0.9	5.7	3.5
^{i}PrOH	*5*	0.9	5.0	2.4
MeOH	*5*	0.7	4.0	2.0
^{i}PrOH + $\mathrm{PhNO_2}$	*5*	0.8	3.7	0.8
^{i}PrOH + $\mathrm{CBr_4}$	*6*	0.8	4.1	2.3
^{i}PrOH + TEMPO	*6*	0.7	3.8	0.8

The third fitting parameter, the induction period t_0, amounts to a roughly constant value of 1 h for all solvents. This indicates that the type of solvent has only a minor influence on the advancement of the grafting front inside the polymer film.

In summary, one can state that poor (polar) solvents are generally good solvents for pre-irradiation grafting of nonpolar monomers onto fluorinated base materials. As long as the monomer itself is already a good solvent for the grafted polymer, there is no need to dilute it with a solvent inside the swollen polymer. However, to adjust the swelling of the polymer with monomer, dilution of the liquid phase with a non-solvent may be favorable. Under this assumption, mixtures of solvents with H_2O should have even better properties as diluents than the pure alcohols.

Water as Cosolvent. The influence of H_2O on pre-irradiation grafting is best seen when looking at the monomer- and H_2O-concentration dependence of the degree of grafting as depicted in *Fig. 3*.

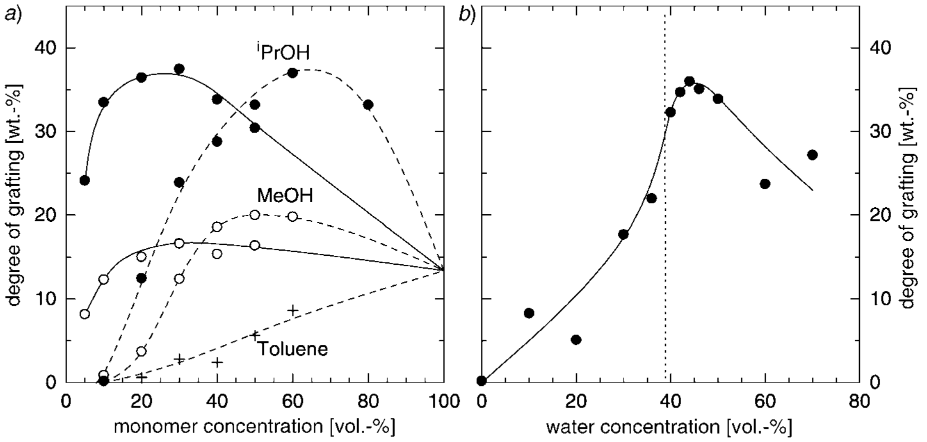

Fig. 3. *Influence of* a) *monomer concentration and* b) *H_2O concentration in ^{i}PrOH at 10% monomer concentration on the degree of grafting.* Dashed lines (---) in *a*) refer to reactions in pure solvent, continuous lines (—) to reactions in H_2O-saturated solution, the dotted (···) vertical line in *b*) indicates the H_2O saturation limit. FEP 25 µm, 3 kGy, 10% DVB, 20 h reaction time, 60°.

With changing monomer concentration (*Fig. 3,a*), an almost linear change of the degree of grafting is observed when toluene is used as solvent. This is easily understood from the fact that dilution of the monomer with toluene in the liquid phase results in an equivalent reduction in monomer concentration in the swollen polymer; the grafting rate will decrease accordingly, whereas the termination rate will remain unchanged. When low-molecular-mass alcohols are used as diluent, the different partitioning of monomer and solvent between solution and polymer results in a concentration-dependent deviation of the local monomer concentration and monomer/solvent ratio inside the film from the values in solution. As a consequence, the grafting yield is not a linear function of the total monomer concentration anymore but passes through a maximum. This maximum is weak for MeOH but quite pronounced for ^{i}PrOH and any other C_2 to C_4 alcohols. When H_2O is added up to the saturation limit (as given by the phase diagrams in *Fig. 4*), the maximum degree of grafting for 20 h reaction time remains essentially unchanged but shifts to significantly lower monomer concentration. For the present monomer/polymer system, the highest graft levels at low monomer concentration are obtained with ^{i}PrOH/H_2O as diluent.

The increase in the degree of grafting upon addition of H_2O at low monomer concentration sensitively depends on the exact H_2O concentration, as shown in *Fig. 3,b*. At 10% monomer concentration, the highest degrees of grafting are obtained when the grafting solution contains a slight excess of H_2O. In this case, the grafting solution separates macroscopically in a H_2O-rich lower phase containing the irradiated polymer film and a smaller upper, monomer-rich phase. This ensures that, even upon consumption of part of the monomer by polymerization, the grafting solution is still

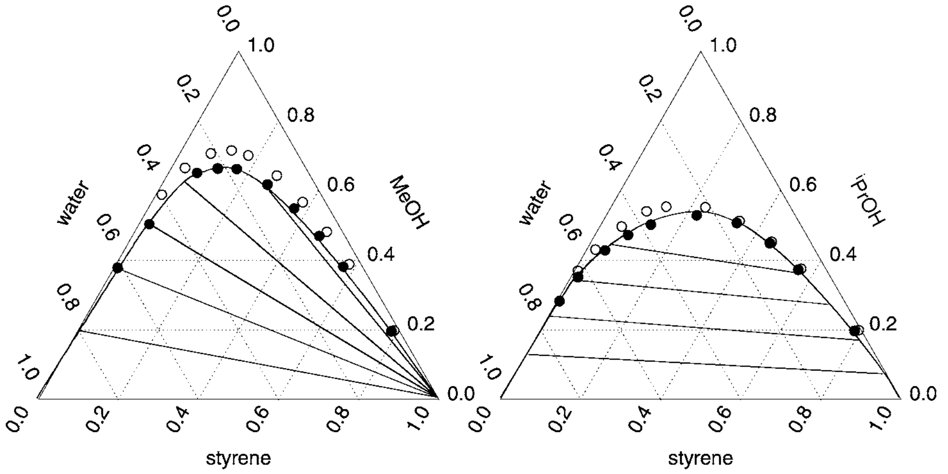

Fig. 4. *Phase diagrams for styrene/MeOH/H_2O and styrene/ⁱPrOH/H_2O at room temperature* (○) *and 60°* (●)

saturated with monomer and guarantees the highest possible monomer concentration in the swollen film.

A three-dimensional representation of the influences of monomer, ⁱPrOH, and H_2O concentration based on the same values as in *Fig. 3* is shown in *Fig. 5*. It is seen that, with decreasing monomer concentration, the (almost constant) maximum degree of grafting shifts from the ⁱPrOH-rich side of the phase diagram into the two-phase region on the H_2O-rich side of the phase triangle.

Looking at the concentration-dependent grafting kinetics may help us understand the influences of monomer concentration and H_2O saturation on the grafting behavior in more detail. From *Fig. 6*, it is seen that high initial grafting rates and short radical lifetimes result from high monomer concentrations in ⁱPrOH. The exact opposite is true

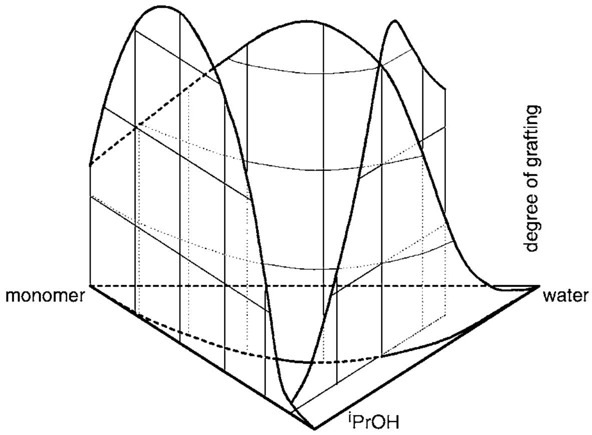

Fig. 5. *Three-dimensional representation of the influences of monomer, ⁱPrOH, and H_2O concentration on the degree of grafting.* FEP 25 µm, 3 kGy, 10% DVB, 20 h reaction time, 60°.

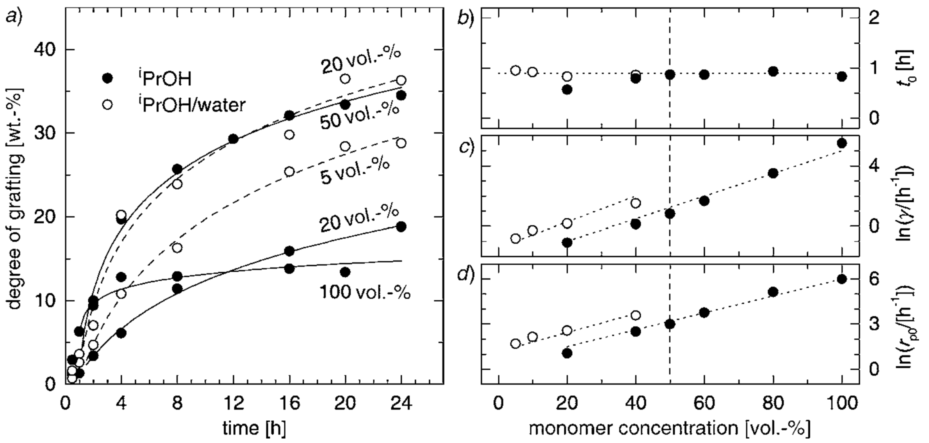

Fig. 6. a) *Grafting kinetics as a function of monomer concentration in* ^{i}*PrOH and* ^{i}*PrOH/*H_2O *and* b–d) *results from fitting the data with* Eqn. 5. FEP 25 µm, 3 kGy, 10% DVB, 60°.

for low monomer concentrations, and, at 20% monomer concentration in ^{i}PrOH and less, grafting rates are already so low that it becomes difficult to obtain reproducible yields. Somewhere in between the two extremes, a good compromise between high initial reaction rates and long radical lifetimes results in a maximum degree of grafting for a specific reaction time. Like for the grafting in different solvents, the quite significant changes in reaction rate correspond to only slight variations in equilibrium swelling of the grafted films in the corresponding monomer/solvent mixtures. Saturation of the grafting solution with H_2O implicates that the initial polymerization rate and radical recombination rate are both markedly increased for a given monomer concentration, which is obviously due to an increased swelling of the polymer with monomer. As a consequence, optimal grafting conditions are achieved at significantly lower monomer concentration, and a H_2O-saturated solution with 20% monomer concentration behaves almost identically to a binary monomer/^{i}PrOH solution with 50% monomer concentration.

Grafting with Water/Surfactant as Solvent. The ternary mixtures with H_2O may be looked at in a more-general way as a mixture of monomer with an immiscible liquid (H_2O) that is made compatible by a third component (alcohol). It is, therefore, tempting to substitute the alcohol with a surfactant, and, indeed, radiation-grafting procedures with emulsions as monomer reservoirs have been described for grafting onto natural rubber latex [58–60], rayon [61], leather [62], and polymer films [63].

Fig. 7 shows the concentration and time dependences of the degree of grafting when emulsions are used for grafting in the present styrene/FEP system. Similar grafting results are obtained with only 5 vol.-% monomer concentration as with 20 vol.-% monomer concentration in H_2O-saturated ^{i}PrOH. Besides favorable environmental and safety aspects and a simplified purification of the grafted films, the possibility to work at very low monomer concentration is a particularly interesting aspect of this type of grafting system. A disadvantage of this system is that the monomer supply from the

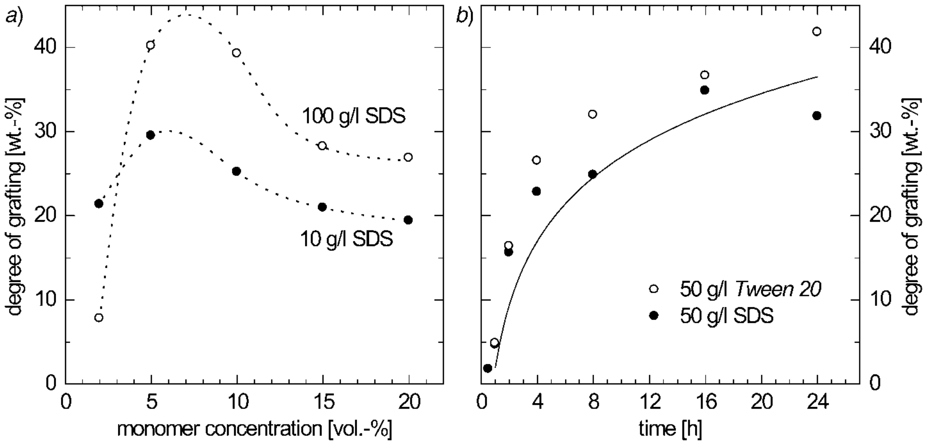

Fig. 7. *Grafting in emulsion systems:* a) *influence of monomer and SDS* (sodium dodecyl sulfate) *concentration on the degree of grafting after 20 h reaction time and* b) *grafting kinetics for SDS and* Tween 20 *at 5% monomer concentration.* FEP 25 μm, 3 kGy, 10% DVB, 60°. The continuous line (—) is a reproduction of the grafting kinetics for 20% monomer concentration in ^{i}PrOH/H_2O from *Fig. 6,a* for comparison.

solution tends to be less homogeneous over the whole film area. Sufficient convection in the solution during grafting is, therefore, important.

Mechanical Properties of Grafted Films. The effect of the variation in radiation dose and type of grafting solution on the mechanical properties of pre-irradiation-grafted 25-μm FEP films was evaluated by measuring the elongation at break as a function of the degree of grafting. As is evident from *Fig. 8,b*, the type of solvent used has no measurable influence on the elongation at break by itself. Data points from samples that were prepared in toluene (squares), ^{i}PrOH (circles), ^{i}PrOH/H_2O (diamonds), and H_2O/SDS (triangles) lie largely on one curve. Similarly, no significant influence of a variation of the monomer concentration between 5 and 60 vol.-% was observed. Contrary to this, a change in irradiation dose from 1 or 3 kGy (crossed and filled symbols) to 30 kGy (open symbols) results in a systematic deterioration of the mechanical properties. For 3-kGy-irradiated films, the elongation at break decreases to 50% of its value for the non-grafted film at a degree of grafting of 16 wt.-% (35 vol.-%), whereas for 30-kGy-irradiated films, this point is already reached at a degree of grafting of 12 wt.-% (25 vol.-%). Specific mechanical properties are obtained at a degree of grafting that is up to 10% absolute higher for 3-kGy-irradiated films than for 30 kGy irradiated films. Since the loss in elongation at break with higher irradiation dose is already observed for the non-grafted irradiated films, it is unlikely that these differences are due to a different microstructure of the films depending on the irradiation dose. On the contrary, the decrease in mechanical properties has to be attributed to increased radiation damage to the trunk polymer.

In contrast to our observation, *Walsby et al.* reported poorer mechanical properties for polymer films grafted in PrOH as compared to films grafted in toluene [49]. These observations most likely can be explained by the fact that thicker films (80-μm) were used and that the irradiation dose was not adapted to the higher grafting rates. As a

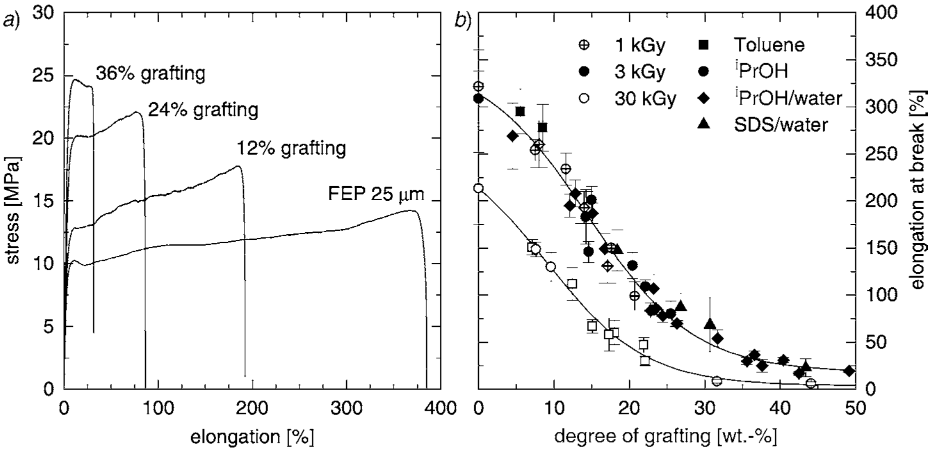

Fig. 8. a) *Stress-strain curves for pristine FEP and grafted films with different degrees of grafting and* b) *elongation at break of grafted films as a function of degree of grafting, pre-irradiation dose* (indicated by the filling of the symbols), *and type of solvent used* (indicated by the form of the symbol). FEP 25 µm, 10% DVB.

result, depending on the solvent, very different grafting profiles throughout the film thickness were obtained for the same degree of grafting.

Homopolymer Formation. The formation of homopolymer [7] [8] is well known for simultaneous-irradiation grafting; due to the irradiation of the whole grafting system, it is unavoidable that monomer and solvent are activated as well. Homopolymer formation is also observed when the peroxidation method is applied; in this case, the initiation is attributed to hydroxy radicals that originate from the disintegration of hydroperoxides. Homopolymer formation is generally undesirable since it results in loss of monomer and contamination of the product. Therefore, methods have been proposed to suppress this side reaction with inhibitors such as metal ions, metallic copper, methylene blue, or O_2 [11] [17] [61] [64].

Particularly favorable conditions for homopolymer formation are also given with the solvent systems investigated here, since alcohols have been described as preferred solvents for proliferous radical polymerization of styrene and DVB [65]. Therefore, we have looked more closely at the amount of homopolymer formed as a function of the monomer concentration, the reaction time, and the type of solvent used. The results, depicted in *Fig. 9*, show that the amount of homopolymer increases with reaction time, whereas it passes through a maximum with respect to monomer concentration. Interestingly, whether ⁱPrOH or ⁱPrOH/H_2O is used as solvent has no influence on the degree of homopolymer formation. Working with H_2O-based solutions at low monomer concentration, therefore, helps to keep homopolymer formation low without suffering any loss in grafting yield.

Control experiments show that the presence of the irradiated film is not required for homopolymer formation. This indicates that in the present system, homopolymer formation is dominated by spontaneous, thermally initiated polymerization. It is not primarily caused by radicals exiting the polymer film (*e.g.*, after chain transfer to monomer or solvent).

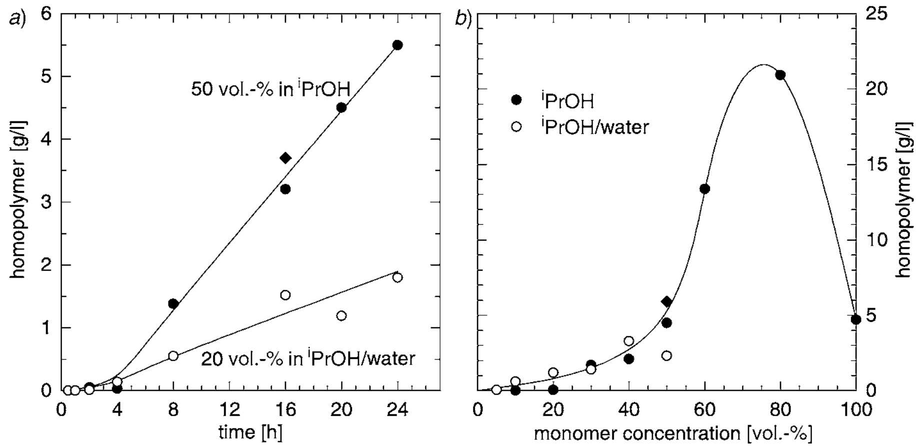

Fig. 9. *Homopolymer formation* a) *as a function of reaction time and* b) *as a function of monomer concentration after a constant reaction time of 20 h.* 10% DVB, 60°; diamonds indicate experiments in the absence of irradiated FEP.

It is worth mentioning here that no homopolymer could be precipitated when grafting reactions were performed in AcOH. Therefore, from the point of view of homopolymer formation, this solvent (or eventually a mixture of AcOH with other solvents) seems to be particularly favorable. The observation can be explained by the known phenomenon that acids accelerate the transformation of initiator molecules for the spontaneous thermal polymerization of styrene into stable compounds [66].

Conclusions. – Non-solvents are attractive diluents for pre-irradiation grafting of styrene/DVB onto fluorinated base materials. With this type of solvent, the grafting efficiency may be significantly increased by adjusting the degree of swelling of the polymer phase. In very general, high grafting efficiencies are advantageous to cope with (or to compensate for) low grafting yields due to other unfavorable reaction conditions. More specifically, they permit a certain degree of grafting with a markedly reduced irradiation dose compared to grafting in a good solvent. As a consequence, due to reduced base-polymer degradation, the mechanical properties of the grafted films are markedly improved. The most-favorable solvents include alcohol/H_2O and H_2O/surfactant systems since these allow working at particularly low monomer concentrations, with positive implications for costs and homopolymer formation.

Experimental Part

Chemicals. Divinylbenzene (DVB; 56.3% *meta*-isomer, 24.4% *para*-isomer, and 20% ethylvinylbenzene; stabilized with 0.1% 4-(*tert*-butyl)catechol), styrene (99%; stabilized with 0.005% 4-(*tert*-butyl)catechol), ethylbenzene (98%), cyclohexane (99.5%), ^{i}PrOH (99%), THF (99.5%), *Tween*® *20* (polyoxyethylene sorbitan monolaurate), CBr_4 (98%), nitrobenzene (99.5%), and 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO; 98%) were all purchased from *Fluka*, sodium dodecyl sulfate (SDS, 90%) was purchased from *Riedel-de-Haën*, AcOH (99.8%), MeOH (99.8%), and toluene (99.5%) were obtained from *Merck*. All chemicals were used without further purification.

Teflon® FEP 100A films of 25-µm thickness were purchased from *DuPont*. The films were cut into pieces of 100 mm length (parallel to the extrusion direction) and 70 mm width, corresponding to a weight of *ca.* 0.4 g. The pieces were washed with EtOH, dried under vacuum, weighed and sealed into PE plastic bags for protection from contamination. A sheet-metal beaker was used for weighing to avoid errors from electrostatic charging of the films.

Electron-Beam Irradiation (*Studer AG*, Däniken, Switzerland). Samples were spread on cardboard on a conveyor and passed under the electron beam two times with an interruption of a few seconds. The conveyor speed was kept constant at 17.4 m/min, and an acceleration voltage of 1.05 MV was used. The current was set to 1, 3, 10, and 30 mA to obtain irradiation doses of 1, 3, 10, and 30 kGy, respectively. Irradiation doses were verified with radiachromic film dosimeters from *Far West Technology, Inc.* (Goleta, California), containing the dye tris{4-[bis(2-hydroxyethyl]amino)phenyl} acetonitrile dispersed in 50-µm thick polyamide films. The irradiated films were stored at −80° starting 1 h after irradiation.

Grafting. Irradiated films were rolled up and inserted into 50 ml of the appropriate grafting soln. in a cold trap-type reaction tube with threaded joint and *Teflon* stopcocks. In doing so, the extrusion direction of the original film was always kept parallel to the axis of the reaction tube. After bolting together the threaded joint, N_2 was passed through the soln. for 30 min at a flow rate of 10 Nl/h for deoxygenation. The stopcocks were closed, and the reaction tube was put in a temp.-controlled water bath at 60° for the appropriate time.

The concentrations of monomer, solvent, and H_2O in the grafting soln. are always given as fraction of the total volume, the DVB concentration is given as fraction of the total volume of monomer. Due to some evaporation of the solvent during N_2 purge, the concentrations for monomer, solvent, and H_2O have only an accuracy of *ca.* ±2% (absolute). For alcohol/H_2O-based solns., the transition from a phase-separated system to a homogeneous soln. upon heating was used as a rough checkup for H_2O-saturation of the soln. H_2O/surfactant-based systems were stirred at *ca.* 500 rpm during grafting.

The grafted films were removed from the grafting soln., wiped off with 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. 7.*

$$\text{degree of grafting} = \frac{\text{final weight} - \text{initial weight}}{\text{initial weight}} \times 100 = \frac{\text{mass (polystyrene)}}{\text{mass (FEP)}} \times 100 \qquad (7)$$

For separating the homopolymer, the grafting soln. was poured into a 10-fold excess of MeOH, the homopolymer was filtered off, dried, and weighed.

Control experiments with 50% styrene/DVB 9:1 in ^{i}PrOH were performed to quantify the variations in grafting level as a function of delay time between irradiation and grafting and as a function of the original position of the 70 mm × 100 mm samples on the 1.3-m-large film roll. The standard deviations of the degree of grafting over time and as a function of the position on the film roll were both ±10%. Harmlessness of the presence of 4-(*tert*-butyl)catechol during grafting was verified by adding additional inhibitor; almost identical results were obtained with up to ten times higher inhibitor concentration.

Roughly 10% of the experiments were not successful the first time, as noticed by graft levels that were obviously too low. Leaks in the reaction vessels that allowed O_2 to enter are considered to be the most likely reason for these failures.

Phase Diagrams. Mixtures of styrene and alcohol of defined composition and temp. were titrated with H_2O until turbidity set in. The position of the conodes was roughly estimated from the volume ratio of the phases formed from mixtures laying in the phase-separated region.

Swelling. Cross-linked and non-cross-linked grafted films were contacted with the soln. for at least 1 h at 60°. The films were wiped with a soft tissue and weighed within less than 30 s after removal from the soln. Ethylbenzene was used as nonpolymerizing substitute for styrene in the solns. The determined weight increases are averages of at least four measurements with different films. Check experiments confirmed that no further weight increase takes place when swelling is extended to 24 h.

Mechanical Properties. Stress-strain measurements were performed with the materials testing machine *4464* from *Instron* (High Wycombe, United Kingdom) at r.t. Dumbbell-shaped samples with a total length of 50 mm and a gauge of 15 mm length (parallel to the extrusion direction of the original FEP film) and 4 mm width were elongated at a rate of 15 mm/min or 100%/min.

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