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Kinetic and structural factors in graft polymerization of styrene on polyolefins

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Abstract

Radiation grafting of monomers on polymers is radical polymerization which usually takes place in viscous medium and quite often in a micro-heterogeneous semicrystalline matrix. The role of kinetic and structural factors in the graft polymerization was investigated. Grafting of styrene on polyethylene and polypropylene was initiated by radiation methods (direct irradiation of polymer and monomer, pre-irradiation of polymer in vacuum, pre-irradiation of polymer in air) and by chemical initiators (azoisobutyronitrile and benzoyl peroxide). The effect of temperature, dose rate, polymer density and specimen thickness, addition of methanol to monomer and pre-crosslinking of polymer on the grafting was investigated. It was shown that a steady-state assumption, which is conventional in homopolymerization, can be applied for radiation grafting initiated by direct irradiation of styrene and polyethylene or polypropylene. Swelling measurements have shown that monomer supply in polymer is higher than monomer consumption and the diffusion is not rate-determined step. The rate of grafting was constant and at the dose rates lower than 10^2 Gy/h the square root dependence of grafting rate on dose rate was valid as classical equation for homopolymerization request. The independence of the grafting rate on the dose rate above 10^2 Gy/h was due to participation of primary radicals in the termination reaction. The grafting rate and yield increased with the increase of the polymer density (0.92 – 0.96 g/cm³) and the film and foil thickness (0.05 – 1 mm) due to the increased viscosity of the reaction medium and consequently decreased rate of termination but lower yield of grafting and very slow reaction was observed for very rigid high density thick foils, especially at lower temperature. The effect of structural factors and crosslinking on grafting reaction has been discussed.

KEY WORDS:

crosslinking effect
gel effect
graft polymerization
grafting methods
kinetic factors
polyolefins
styrene
structural factors
specimen density and thickness
solvent effect

KLJUČNE RIJEČI:

gel-efekt
gustoća i debljina ispitka

kinetički čimbenici
polimerizacija cijepljenjem
poliolefini
postupci cijepjenja
stiren
strukturni čimbenici
utjecaj otapala
utjecaj umreživanja

Kinetički i strukturni čimbenici u reakciji cijepjenja stirena na poliolefine

Sažetak

Radijacijsko cijepljenje monomera na polimere je polimerizacija radikalima koja se normalno zbiva u viskoznome mediju, a vrlo često i u mikroheterogenome kristalastome materijalu. Istraživana je uloga kinetičkih i strukturnih čimbenika u reakciji cijepjenja. Cijepjenje stirena na polietilen i polipropilen inicirano je radijacijskim postupcima (izravno ozračivanje polimera i monomera, prethodno ozračivanje polimera u podtlaku, prethodno ozračivanje polimera u zraku) i kemijskim inicijatorima (azoizobutiro-nitriplom i benzoilperoksidom).

Istraživan je utjecaj temperature, brzine doze, gustoće polimera, debljine ispitka, dodatka metanola monomeru i prethodnog umreživanja polimera na reakciju cijepjenja. Pokazano je da se na reakciju cijepjenja iniciranu izravnim ozračivanjem stirena i polietilena ili polipropilena može primijeniti pretpostavka stacionarnog stanja koja se primjenjuje na homopolimerizaciju. Mjerenja bubrenja pokazala su da je dotok monomera u polimer brži nego njegova potrošnja u reakciji, pa difuzija ne određuje brzinu reakcije. Brzina reakcije cijepjenja bila je konstantna i za brzine doze manje od 10^2 Gy/h dobivena je ovisnost brzine cijepjenja o kvadratnom korijenu iz brzine doze kakvu zahtijeva klasična jednadžba za homopolimerizaciju. Neovisnost brzine cijepjenja o brzini doze iznad 10^2 Gy/h uzrokovana je sudjelovanjem primarnih radikala u reakciji terminacije. S porastom gustoće polimera ($0,92$ – $0,96$ g/cm³) i debljine filma ili folije ($0,05$ – 1 mm) zbog povišenja viskoznosti reakcijskog medija i posljedičnog sniženja brzine terminacije, brzina i prinos cijepjenja rastu, ali za vrlo krute deblje folije visoke gustoće opažena je vrlo mala brzina i nizak prinos cijepjenja, osobito pri niskim temperaturama. Razmatran je utjecaj strukturnih čimbenika i umreživanja na reakciju cijepjenja.

Introduction

Graft copolymers are product of the chemical combination of two macromolecules of different chemical nature. Ionizing radiation creates readily active sites in polymers and is an efficient tool to produce graft copolymers. Radiation graft polymerization is essentially radical polymerization. Radicals produced in the irradiated polymer undergo reaction with a monomer of choice to produce macromolecular chains that are covalently bound to the irradiated polymer. Among the various methods of grafting, those widely

used are:

1. Direct or simultaneous method of grafting. Polymer is irradiated in the presence of monomer or monomer-containing solution.
2. Grafting on radiation peroxidized polymer. Polymer is irradiated in the presence of air. Grafting can be performed later at the desired time. Peroxides formed during irradiation can be activated by elevated temperature to produce radicals.
3. Grafting initiated by trapped radicals. Polymer can be pre-irradiated in absence of air and then subsequently brought into contact with monomer which can diffuse into the polymer and thus reach the trapped radical sites.

Graft polymerization usually takes place in viscous medium and quite often in a micro- heterogeneous semicrystalline matrix.

To understand the mechanism of grafting at least two questions should be answered:

1. Is it possible to establish quasi homogeneous stationary state conditions where the polymerization kinetics controls the grafting reaction?
2. How does the structure of polymer influence the reaction?

To answer these questions we investigated the grafting of styrene on polyolefines as a model system, applying different grafting methods.¹⁻⁴

Direct radiation grafting of styrene on polyolefins

The graft polymerization of styrene on polyethylene by direct irradiation of polymer and monomer was investigated by several authors.⁵⁻¹⁶ The initial rate of the grafting process was found to be constant. This indicated the applicability of the stationary state kinetics. However, since the dose rate had practically no influence on the grafting rate, it was concluded that the grafting rate is controlled by the supply of monomer through diffusion.⁵ This was in contradiction with observation that in some cases the rate of grafting increases with increase of density and specimen thickness. An analogy with the emulsion polymerization has also been put forward.^{13,14}

The temptation to describe the linear conversion-time dependence by stationary kinetics has been, however, so strong that Odian¹¹ and Chandler¹² tried to evaluate informative kinetic constants from the well-known general equation for polymerization rate V

$$V = \frac{k_p V_i^{1/2} [M]}{k_t^{1/2}} \quad (1)$$

although the square root dependence on the dose rate does not hold in the investigated range. In equation 1: k_p - the rate constant of propagation, V_i - rate of initiation, k_t - rate constant of termination, $[M]$ - monomer concentration.

Chandler even tried to take into consideration quantitatively the diffusion of the monomer, similarly to the method used by Mock¹⁷ for the grafting of styrene on ethyl cellulose.

All the experiments, where the rate of grafting was found to be independent of the dose rate, were made at dose rates exceeding 10^2 Gy/h. It has been shown¹⁵ that the independence on the dose rate is analogous with the effect of termination by primary radicals, shown by Chapiro⁵ for the radiation homopolymerization, and that at intensities lower than 10^2 Gy/h the square root dependence is valid. So, in this region, the kinetics of radical polymerization can be adapted and some conclusions on the polymerization of styrene in highly viscous media can be drawn.

In our study some comparative investigations are performed on the direct radiation grafting of styrene on polyethylene and polypropylene at the dose rate below 10^2 Gy/h.

Low density polyethylene (*Cellene*; ρ (25 °C) = 0.926 g/cm³) and isotactic polypropylene (*Moplen*; ρ (20 °C) = 0.900 g/cm³) were used. Specimens of 1.2•6 cm were cut from 0.15mm thick film* and extracted in a boiling mixture of benzene-ethanol 1: 1. Styrene was three times distilled in vacuum.

The grafting was performed in vials sealed individually in high vacuum. Irradiations were made in a ⁶⁰Co source with activity of about 12 TBq. Furthermore, the majority of the grafting experiments on polypropylene were performed below 70°C dilatometrically, by a 250kV X-ray apparatus.

The rate of radiation grafting was determined from the dilatometric experiments by correcting the readings for the spontaneous effects and for the simultaneous homopolymerization. In all experiments these corrections were by at least one order of magnitude less than the total effect. The grafting rate could be checked gravimetrically after the dilatometers had been opened.

The concentration of the monomer inside the film was determined by swelling measurements. The conversion-time curves of the system polyethylene-styrene are linear up to high conversions. This is illustrated in Figure 1 where the dependence of grafting yield on dose rate at 50°C is shown.

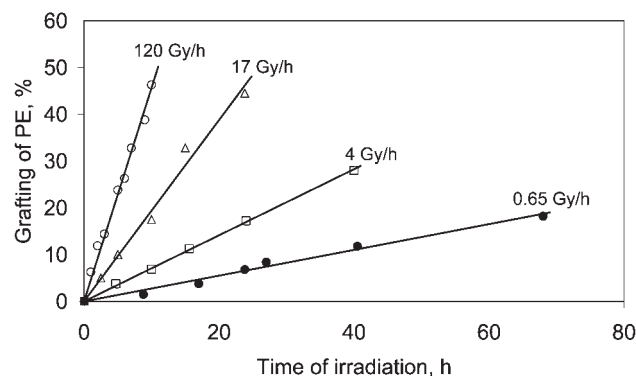


FIGURE 1 - Direct radiation grafting of styrene on polyethylene at various dose rates at 50 °C

Figure 2 shows the dependence of the grafting rate on the dose rate at different temperatures. Above 10^2 Gy/h data of references^{7,12,13} are represented for comparison. As can be seen, below 10^2 Gy/h the classical dependence of grafting rate on the square root of dose rate is followed (the slope of the curves is 0.48-0.54).

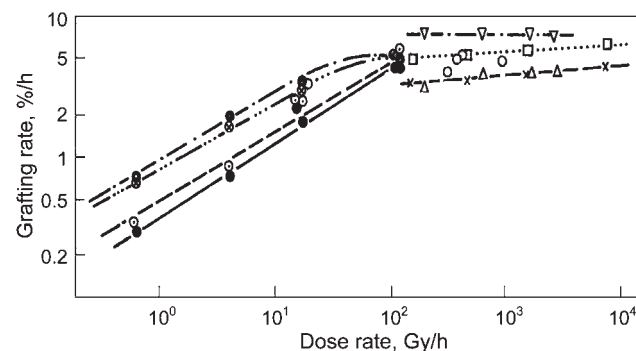


FIGURE 2 - The grafting rate of styrene on polyethylene as a function of the radiation dose rate. Our measurements: ● - 50 °C, ⊙ - 40 °C, ⊚ - 25 °C, ⊘ - 10 °C, ∇ - 25 °C; 0.25 mm foil,⁷ △ - 25 °C; 0.1 mm film,⁷ ○ - 27 °C; 1.2 mm foil,¹² □ - 18 °C; 0.076 mm film,¹³ × - 18 °C; 0.025 mm film.¹³

*Term film will be used for specimen thickness 0-0.2 mm and term foil for thickness higher than 0.2mm.

In the case of polypropylene-styrene similarly a constant grafting rate has been found up to high conversion. The dose rate dependence is illustrated in Figure 3. The square root dependence holds here as well up to about 10² Gy/h (the slope of the curve is 0.51).

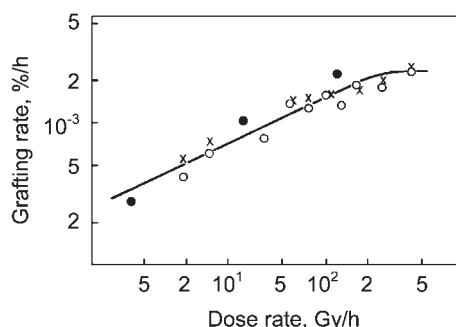


FIGURE 3 - The grafting rate of styrene on polypropylene as a function of dose rate at 40 °C, ○ - dilatometric measurements, X-rays; × - gravimetric measurements, X-rays; ● - gravimetric measurements, ⁶⁰Co

The rate of direct radiation grafting on polyethylene as well as on polypropylene is constant and depends on the 0.5th power of the dose rate. Thus we have no reason to suppose that the grafting rate is controlled by the diffusion of the monomer and we can take equation (1) as valid. This is further supported by Figure 4 showing the swelling of polyethylene in styrene. As can be seen, over 90 % of the equilibrium swelling value is achieved in a few minutes for polyethylene over 20 °C and for polypropylene over 30 °C. The swelling of the already grafted parts is presumably even more rapid.

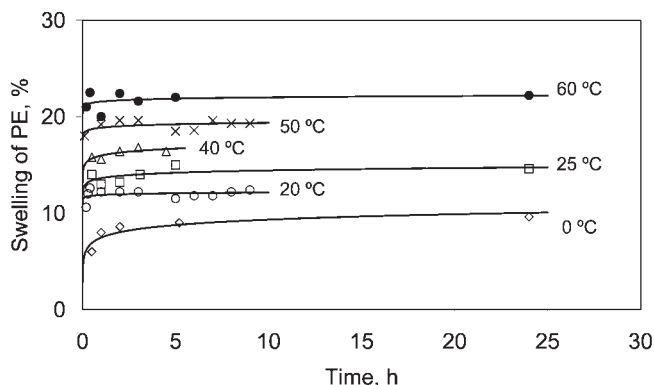


FIGURE 4 - The swelling of polyethylene in styrene as a function of swelling time at various temperatures. The swelling is expressed as g styrene/g polyethylene

Thus, the real $k_p/k_t^{1/2}$ values can be calculated from equation (1) by using the limiting values of swelling for monomer concentration and by calculating the rate of initiation from the G values.

It can be further supposed that styrene swells only the amorphous parts of the polyolefins and that grafting also is confined to this region. More generally, we may suppose that the reaction takes place in the same volume as the monomer uptake. This may be true with good approximation and makes the use of equation (1) very simple.

The rate of initiation was calculated by taking for $G_{PE} = 7$ radicals/100 eV and for $G_{PP} = 8$ radicals/100 eV. In this respect the radical production in styrene ($G_{ST} = 0.69$ radicals/100 eV) can be neglected, even if not only the radicals produced on the polyolefins initiate graft polymerization.

Supposing that all the radicals produced in the amorphous part of the polyolefins initiate grafting, the yield of initiating radicals φ in the reaction volume (consisting of the amorphous polymer swelled with the monomer) is:

$$\varphi = \frac{G \times 6.24 \times 10^{15} \times 10^3 \times \rho}{100 \times 6.2 \times 10^{23} \left(1 + \frac{D}{A}\right)} \frac{\text{mole (radicals)}}{\text{Gy dm}^3} \quad (2)$$

where ρ is the density of the reaction volume g/cm³; D is the swelling in %, A is the amorphous part in %, G is radiation chemical yield.

The $k_p/k_t^{1/2}$ values can be calculated from

$$\frac{k_p}{k_t^{1/2}} = \sqrt{\frac{dm^3}{\text{mole s}}} = \frac{V (\% / s)}{\sqrt{I \frac{\text{Gy}}{s} \times \varphi \left(\frac{\text{mole}}{\text{Gy dm}^3}\right)}} \frac{1}{[M] \%} \quad (3)$$

and are shown in Table 1, together with the values obtained by Odian¹¹ and Chandler.¹²

TABLE 1 - $k_p/k_t^{1/2}$ in the system polyethylene-styrene (dm³)^{1/2} mole^{-1/2} s^{-1/2})

Temperature, °C	Dose rate, Gy/h					Average
	6.5 · 10 ⁻²	4.0 · 10 ⁰	1.5 · 10 ¹	1.7 · 10 ¹	1.2 · 10 ²	
0	2.11	2.15		2.04		2.10
10				2.02		2.02
20			1.14			1.14
25	1.41	1.70		1.50		1.54
30			1.21			1.21
40		0.48	0.91	0.82	0.63	0.71
50			0.68	0.49	0.53	0.57
60			0.44			0.44
Odian ¹¹	Temperature		25 °C			
	Dose rate, Gy/h		7 · 10 ²			
	$k_p/k_t^{1/2}$		0.35			
Chandler ¹²	Temperature		27 °C			
	Dose rate, Gy/h		3.2 · 10 ²	3.9 · 10 ²	4.3 · 10 ²	9.7 · 10 ²
	$k_p/k_t^{1/2}$		0.53	0.58	0.60	0.37

Table 2 shows the $k_p/k_t^{1/2}$ values obtained for polypropylene.

TABLE 2 - $k_p/k_t^{1/2}$ in the system polypropylene-styrene ((dm³)^{1/2} mole^{-1/2} sec^{-1/2})

Dose rate, Gy/h	40 °C		50 °C		60 °C		70 °C	
	grav.	dil.	grav.	dil.	grav.	dil.	grav.	dil.
39.5	0.82	0.81						
25.9	0.88	0.78						
16.5	0.98	0.99						
12.5		0.83						
12.0 (Co)	1.40							
10.1	1.06	1.05						
7.5	1.16	1.00	0.88	0.77	0.66	0.50	0.41	
5.6	1.23	1.21						
3.5	0.90	0.90						
2.5 (Co)	1.35							
1.42	1.38	1.07						
0.92	1.28	0.94						
0.40(Co)	0.97							
Average	1.07	1.00						

Arrhenius-plots of the average $k_p/k_t^{1/2}$ values are seen in Figure 5. By supposing for $E_p = 30.33$ kJ/mole¹⁸ activation energies for chain termination in the highly viscous media can be calculated

as $E_{t,PE} = 105.01$ kJ/mole and $E_{t,PP} = 114.22$ kJ/mole. As can be seen, the rate constants calculated for both polymers lie reasonably close.

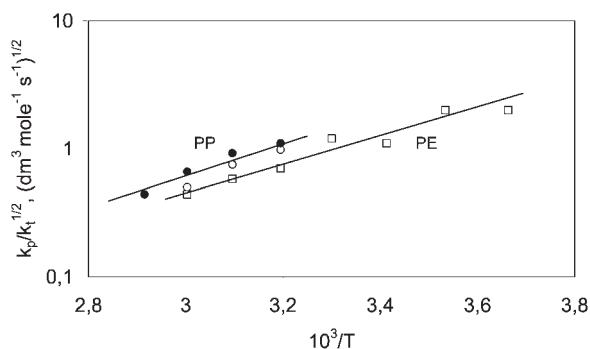


FIGURE 5 - Temperature dependence of $k_p/k_t^{1/2}$ in the graft polymerization of styrene on polyethylene (PE) and polypropylene (PP). \square - polyethylene (from the slope $E = -22.18$ kJ/mole), \circ - polypropylene, dilatometric measurements, \bullet - polypropylene, gravimetric measurements (from the slopes $E = -26.78$ kJ/mole)

It is concluded that in such *quasi-homogeneous* grafting reactions where the diffusion of the monomer is rapid, and where no significant changes take place in the crystalline structure of the polymeric matrix during the grafting, the reaction is controlled by the polymerization kinetics rather than by the structure of the base polymer.

Effect of the crystallinity and specimen thickness

Let us now consider the role of structural factors in grafting reaction. The influence of the type of polyethylene and specimen thickness on the rate and yield of grafting of styrene was studied by using four different grafting methods:

1. direct irradiation of styrene and polyethylene,
2. pre-irradiation of polyethylene in vacuum and subsequent grafting with styrene,
3. pre-irradiation of polyethylene in air and subsequent grafting,
4. grafting of styrene on polyethylene induced by chemical initiation.

Low density polyethylene (LD): Lupolen (L); ρ (25 °C) = 0.918 g/cm³; Fertene Q (F); ρ (25 °C) = 0.920 g/cm³ and high density polyethylene (HD): Hostalen GM (HGM); ρ (25 °C) = 0.95 g/cm³; Hostalen GC (HGC); ρ (25 °C) = 0.96 g/cm³ were used. Specimens 10 mm•50 mm were cut from 0.05 mm thick films to 1 mm thick foils.

Figure 6 shows the effect of type of polyethylene and film and foil thickness on the rate of grafting of styrene in temperature interval 20°C - 60°C in simultaneous irradiation.

Grafting rate was found to be higher in the high density polyethylene except at low temperature with thick foils. The effect of the specimen thickness is similar: the grafting rate increases with increase in specimen thickness.

The effect of crystallinity is closely connected with that of specimen thickness. With rising temperature, both effects decrease. Hoffman et al.⁹ assumed that larger and more cohesive crystallites are formed towards the centre of the specimen, where crystallization occurs under relatively smaller stress, than toward its surface. According to Chen et al.¹⁴ the more rapid grafting of the thicker polyethylene specimens can be ascribed to somewhat higher density of the middle layer of the specimen, resulting in a lower monomer con-

centration and a larger gel-effect or to a process similar to emulsion polymerization, assuming the number of swollen amorphous polyethylene "micelles" being greater in thicker specimen.

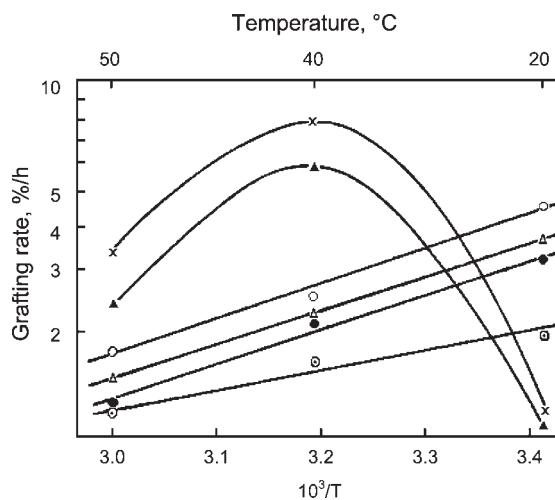


FIGURE 6 - Temperature dependence of the grafting rate of styrene on low and high density polyethylenes in simultaneous irradiation. Dose rate 30 Gy/h. HGC: \blacktriangle - 1.0 mm; \triangle - 0.05 mm, HGM: \times - 1.0 mm; LD PE: \circ - 1.0 mm; \bullet - 0.25 mm; \odot - 0.05 mm

Matsuo¹⁹ and Furuhasi²⁰ ascribed the effect of specimen thickness to a retarding effect on the grafting near the surface (10 μ m) of the film. In our opinion, this can explain the specimen- thickness effect in thin films but not in thicker foils (0.2-1.0 mm) since great differences in the grafting yield in the latter cannot be caused only by a small retarding effect.

Our measurements indicated somewhat higher density for thicker specimens than for thin ones. It seems that the higher grafting rate is due to the lower monomer concentration higher viscosity in a more rigid matrix and thus lower termination rate in the thicker specimen.

The thick HD specimens are, on the other hand, so rigid that diffusion and swelling are greatly hindered especially at low temperature. Thus the grafting cannot proceed because of a structural hindrance. This explains the observed low grafting yields at low temperature.

The grafting of styrene on polyethylene pre-irradiated in vacuum

Films of low and high density polyethylene were irradiated in vacuum at room temperature to a total dose of 10 kGy, and exposed to styrene at 20 °C, 40 °C, and 60 °C, respectively.

The observed dependence of grafting rate on time (Figure 7) is characteristic for this type of initiation.²¹ After a short equilibration period the rate of grafting decreases with time according to the equation

$$V = k_p \frac{R_0 M}{k_t R_0 t + 1} \quad (4)$$

where k_p and k_t mean the rate constants of propagation and termination, and R_0 and M the initial concentration of free radicals and the concentration of monomer, respectively. Equation 4 requires also, that the rate should increase with the initial concentration of the free radicals. The apparent activation energy of termination is higher than that of the propagation. It follows further from Equation 4 that the amount of polymer formed after a sufficiently long reaction time should be less at higher temperature. With the exception of the low temperature thick specimen experiments, a

much higher grafting yield was observed in HD (Figure 7, Table 3). With rise of temperature, the initial grafting rate increased whereas the total grafting decreased.

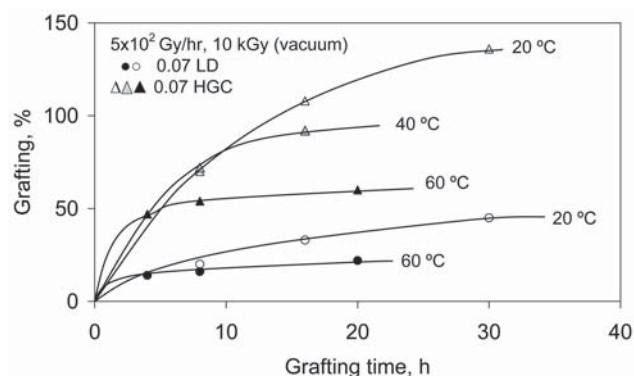


FIGURE 7 - Grafting of styrene on low (LD) and high density (HD) polyethylenes pre-irradiated in vacuum at room temperature. Total dose: 10 kGy. Reaction temperatures: 20°C, 40°C and 60°C. Thickness of film in all cases: 0.07mm.

TABLE 3 - Effect of specimen thickness on the grafting yield in grafting of styrene on polyethylene pre-irradiated in vacuum

Density, g/cm ³	Thickness of specimen, mm	Graft at 20 °C, %	Graft at 60 °C*, %
0.92	0.05	24.1	5.9
	0.30	42.0	10.4
	1.00	48.2	23.0
0.96	0.05	150.0	53.4
	0.30	90.0	69.9
	0.50	46.4	76.2
	1.00	19.7	64.5

* Reaction time: 24h at 20°C; 5h at 60°C

The effect of the specimen thickness was the same as that in direct grafting of styrene on polyethylene (Table 3). The grafting rate was higher in thicker specimens of LD over the entire temperature range whereas in HD the same was observed at 60°C.

Free radicals in pre-irradiated polyethylene which induce graft polymerization, can remain trapped if the mobility of polymeric segments is small; this is more likely in the crystalline regions.²² According to Ballantine et al.,²³ the trapped free radicals responsible for the grafting reaction are located within crystalline regions, and cannot be reached at 20°C by the monomer. This was supported by the observation that at 22°C LD films (0.1mm) gave much higher grafting yield than the high density ones. However, increasing temperature to 50°C permits diffusion of styrene into the crystalline regions of the high density polyethylene, resulting in a considerable increase of the grafting yield in this type of polyethylene, while only a small increase in LD was observed.

Our results show that even at 20°C the grafting yield in HD is much higher. The main difference between our experiments and Ballantine's²³ is the total dose (10 and 150kGy respectively). Polyethylene irradiated to a total dose of 150 kGy is crosslinked to some extent and, therefore, the swelling by monomer and the grafting rate at 20°C can be limited even in thin films, especially in the high density polyethylene which has a more rigid structure. At the low doses used in our experiments, crosslinking is negligible and swelling is not strongly hindered so that monomer can reach trapped radicals at 20°C in thin films of both types of polyethylene. At this temperature, the initial penetration of the monomer into the crystalline regions of polyethylene is, no doubt, very low. Accordingly, grafting starts in the amorphous regions and on the surface of crystalline regions. Extension of grafting into the crystal layer aggregates could

be brought about by higher temperature and/or the mechanical action of the growing and swelling chains. In this way, new trapped radicals can be reached by the monomer which diffuses through the amorphous channels. Considering the type of the polyethylene, one can expect smaller volume of the amorphous regions and smaller chain mobility in the more rigid highly crystalline polyethylene. This results in greater efficiency for trapping free radicals and also in a highly hindered termination reaction and thus in high pressure of the growing chains on the crystallites, which permits some grafting in the intercrystalline regions. In thick HD specimens, on the other hand, grafting is strongly limited through the rigid structure; an effect somewhat analogous to that observed by Ballantine with thin, but radiation crosslinked HD films. Our results seem to agree with the findings that radiation crosslinking is effective if it occurs between the lamellae,²⁴ and, that grafting in the intercrystalline regions is inter-lamellar also,²⁰ destroying the spherulites but not affecting much the lamellae themselves. Thus, it seems reasonable that inter-lamellar crosslinking retards the grafting reaction, especially at low temperature.

The fact that the positive effect of the greater specimen thickness, often observed in direct radiation grafting, also occurs in the trapped free radical method indicates that this effect cannot be explained by the inclusion of higher amounts of homopolymer into the thicker specimens.¹³ The amount of homopolymer is in any case very small in the vacuum pre-irradiation method and is insufficient to produce the observed effect of specimen thickness.

Grafting of styrene on polyethylene pre-irradiated in air

LD and HD specimens of different thicknesses were irradiated in air at 10Gy/h. After 1 day storage at room temperature, the specimens were exposed to styrene at 40 °C and at 60 °C.

The behaviours of the two types of polyethylene can be seen from Figure 8. For LD, linear time-dependence of the grafting yield was obtained. For HD, however, a limiting grafting yield was obtained. There is no marked dependence of the grafting rate upon the specimen thickness in LD, but an indication that thinner specimens are grafted more rapidly. For HD, thick specimens are grafted more rapidly than thin ones.

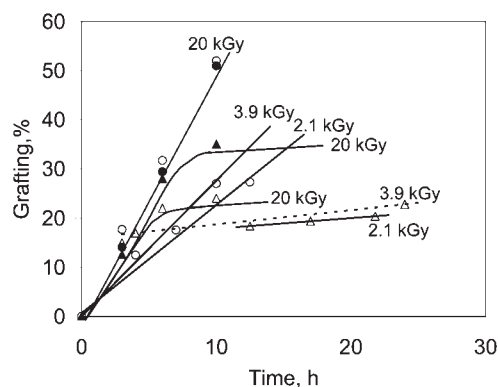


FIGURE 8 - Grafting of styrene on low (○ and ●) and high density (△ and ▲) polyethylenes pre-irradiated in air at room temperature, to different total doses. Reaction temperature: 60 °C. Thickness: empty symbols-0.05 mm; full symbols-1 mm.

Rise in temperature increases the initial rate and the grafting yield for LD, but in HD it increases the initial rate and decreases the limiting yield.

Chapiro⁵ reported that peroxides (hydroperoxides) are formed by pre-irradiation of polyethylene in air and that they can be subsequently decomposed at elevated temperature in the presence of monomer, inducing the graft polymerization. Using high dose rates Shinohara et al.²⁵ have observed a remarkable number of trapped

radicals in polyethylene pre-irradiated in air. These radicals are effective in initiation graft polymerization.

It has been suggested that the disagreement between the results obtained by Chapiro⁵ and Shinohara²⁵ is due to difference in the dose rates. Our results, obtained at a low dose rate, show that the mechanism of the grafting reaction depends also on the polymer structure.

The data for low density polyethylene agree with the published data which show that peroxides induce graft polymerization. Our data for high density polyethylene, however, demonstrate the role of trapped radicals even at low dose rates. The form of the kinetic curves is the same as for pre-irradiation in vacuum. The higher grafting yield in thick HD specimens can be understood by considering the role of trapped radicals. The temperature dependence of the initial rate and of the limiting value of the grafting yield are, in HD, similar as obtained by pre-irradiation in vacuum. In the case of pre-irradiation in air, the diffusion of oxygen should be considered. In thicker specimens of HD peroxidation is slower, the lifetime of radicals is longer and, therefore, the concentration of trapped radicals remaining after irradiation and the grafting yield are higher than in thin specimens. A slightly higher grafting yield could be expected in thin specimens if peroxides initiate the grafting reaction, because in thin specimens peroxidation is more efficient. This has been observed for LD²⁵. There is practically no dose-dependence in HD, while for LD a square-root dependence holds approximately.

It can be concluded that graft copolymerization is induced mostly by peroxides in LD and by trapped radicals in HD. We detected trapped peroxy radicals in HD by ESR spectroscopy several weeks after irradiation of PE in air.

Grafting of styrene on polyethylene induced by chemical initiators

LD and HD foils were used. For LD, higher grafting yields were obtained than for HD when graft copolymerization was initiated by azoisobutyronitrile (0.03%) at 40°C and 60°C, or by benzoyl peroxide (0.1%) (Table 4). The effect of the foil thickness in LD was the same as that in the radiation induced grafting: thicker foils are grafted more rapidly (Table 4). Very rigid thick HD specimens are not grafted by chemical initiators.

TABLE 4 - Effect of foil thickness on the yield in grafting of styrene on low density polyethylene initiated by azoisobutyronitrile (AIBN) and benzoyl peroxide (Bz₂O₂) at 40°C. Foils of different thickness grafted in the same vial.

Initiator, %	Foil thickness, mm	Graft, %	Reaction time, h
AIBN 0.03	0.5	23.6	48
	1.0	32.1	
AIBN 0.03	0.3	40.4	74
	0.5	51.5	
	1.0	69.8	
Bz ₂ O ₂ 0.1	0.5	10.4	36
	1.0	14.5	
Bz ₂ O ₂ 0.1	0.2	28.8	72
	0.5	40.5	
	1.0	58.0	

When graft copolymerization is induced by radiation methods, active sites are formed on a polymeric chain and monomer molecules diffuse to them through the polymer. When graft copolymerization is induced by chemical methods, the initiator and the monomer diffuse together into the polymer. After thermal decomposition of the initiators, chain transfer to the polymer occurs.²⁶

There may be at least three reasons for the fact that grafting yields are in all cases higher for low density polyethylene:

1. The diffusion of monomer and initiator can be faster for LD; however, the preliminary results showed that the grafting rate in thin foils of low and high density polyethylenes, under the same experimental conditions, is not controlled by monomer diffusion. So this is probably not a decisive factor.
2. The possibility for the chain transfer reaction can be different for the types of polyethylene. It seems reasonable to assume that chain transfer to branched low density polyethylene, containing tertiary C-atoms, is much more effective than that to linear polyethylene. It has been shown that chain transfer from AIBN and BZ₂O₂ to LD is very effective.²⁶
3. In chemical initiation in contrast to radiation initiation, radicals can be produced only in the amorphous parts of the polymer and the fraction of amorphous regions is much higher in low density samples. At the same time, there is more swelling in the less rigid LD films. In chemical grafting, the greater swelling means higher rate of initiation also, and this can lead to further increase of the grafting rate.

In chemical grafting also a specimen thickness effect is observed, thicker specimens being grafted somewhat more rapidly (Table 4). Since here no radicals are formed in the crystalline regions, the specimen thickness effect cannot be influenced by such factors as: (a) migration of radicals from the interior to the surface of crystals and (b) extension of the grafting reaction into the crystalline regions. Accordingly, the thickness effect must be caused mainly by a decrease in the termination rate constant with an increase of the specimen thickness. This agrees with our assumption that in thicker more rigid specimen, due to lower monomer concentration and lower mobility of polymer segments and growing chains, the termination rate constant decreases and the grafting rate increases. The specimen thickness effect is thus caused by structural features of the polyethylene.

The specimen thickness effect and the effect of the density of polyethylene are comparable over a wide range and are closely connected. We can conclude generally that the main factors causing different grafting efficiency in HD and LD are also of structural nature; the rigidity of the polymer matrix, and the volume of the amorphous regions in which reaction occurs. These factors exert their influence mainly through changing the termination rate constant and in some cases through changing the concentration of initiating radicals.

Effect of solvent and pre-crosslinking on radiation grafting of polyethylene

Direct proof that the gel effect plays essential role in grafting reaction was obtained by addition of methanol to the reaction mixture. By dilution of styrene with methanol the concentration of styrene inside PE decreases, the viscosity increases and due to the gel-effect the grafting rate and yield increase until optimal concentration of monomer is reached. Further dilution leads to slowing down the grafting reaction (Figure 9).

The methanol does not dissolve PE and has no direct effect on viscosity of the amorphous region of the PE where grafting takes place. Its sole function is to reduce the concentration of the styrene in the PE.²⁷ When less styrene is present to swell the growing polystyrene radicals they are less mobile and the rate of their mutual termination is lower. The decreased radical termination rate overcompensates for the decrease in the rates of initiation and propagation which also accompany the monomer dilution. Hence the decrease in monomer concentration results in longer polystyrene chains and higher overall reaction rate and yield.

The evidence on incorporation of polystyrene in polyethylene by grafting was obtained by electron microscopy.²⁸ Electron micrographs in Figure 10 show the morphology of the original PE film (a) and of the graft with a high PS content (b). As seen in Figure 10a the PE film consists of row-nucleated columns, the so-called

cylindrites, with partially twisted crystalline lamellae.²⁹ The row axes are oriented along the extrusion direction, hereafter referred to as *M*. The largest portion of the lamellae lies perpendicular to *M*. They are seen edge on in the micrograph and appear as horizontal white lines (crystal core) with dark edges (stained interlamellar layers). WAXS and SAXS patterns of the film (insert in Figure 10a) are in accordance with the described row structure.²⁸⁻³⁰

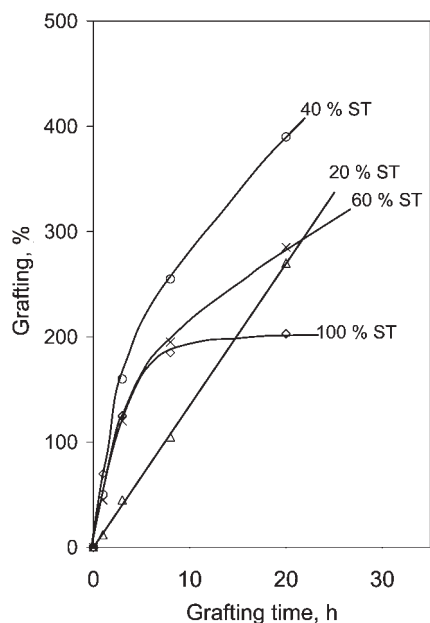


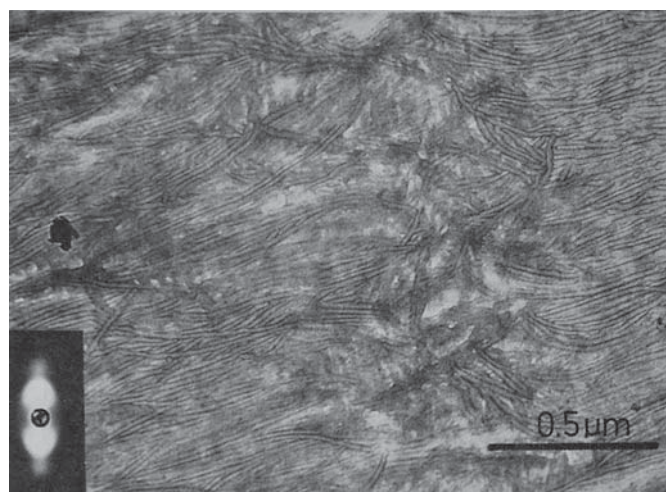
FIGURE 9 - Dependence of grafting yield of polyethylene on styrene (ST) monomer concentration in styrene-methanol mixture at 45°C. Pre-irradiation in vacuum, $D = 25\text{kGy}$.

When the film is grafted to a PS/PE ratio of less than about 0.6 PS incorporates into intercrystalline layers of PE.³¹ As seen in Figure 10b, in more highly grafted material (PS/PE = 1.9) separate grey PS zones are formed by breaking up of the compact lamellar piles.³² This pattern of PS incorporation manifests itself in a characteristic anisotropy of film growth as a function of increasing PS content (Figure 11).

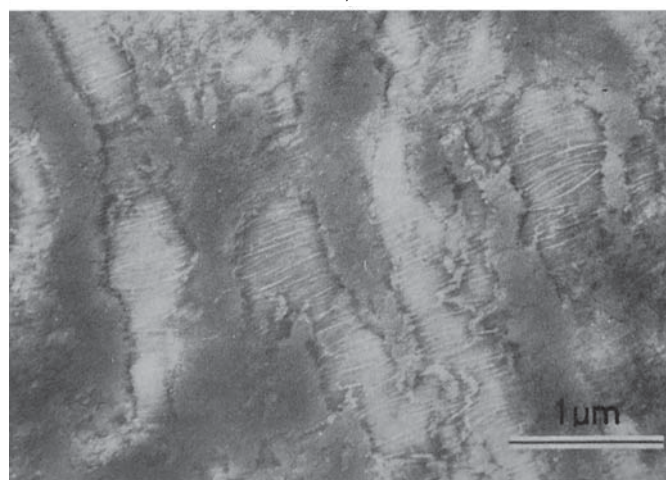
At earlier stages of grafting the film expands primarily along *M* as PS pushes the lamellae apart. Later on the growth along *M* reaches saturation and transverse growth takes over, which is consistent with the formation of lateral PS zones seen in Figure 10b. Only at much larger PS contents, not considered here, does the film growth tend to finally become isotropic.³³ It must be mentioned that in simultaneous irradiation a large proportion of PS within these films is occluded high molecular weight homopolymer.^{33,34} However our work³¹ showed that essentially the same features as described above are also seen in material produced by post-irradiation grafting which therefore contains practically no styrene homopolymer. The structure of the present *simultaneous* graft was fairly uniform throughout the film and no macroscopic heterogeneities such as *bubbles* appeared.

It is known that crosslinking of PE influences its swelling properties. Accordingly, it could be expected that pre-crosslinking of PE influences the rate and yield of grafting as well. We demonstrated this by pre-crosslinking PE and by its subsequent grafting with styrene after the trapped radicals had been annealed out.³⁵ Grafting was induced by simultaneous irradiation (Figure 12).

For pre-crosslinked PE the grafting rate is higher than for the uncrosslinked polymer. We interpret the increase of grafting yield with crosslink density by hindered mobility of polymer chains and in terms of the gel-effect, since the monomer concentration within the film is reduced, viscosity increased and the rate of termination of growing grafted chains decreases.



a)



b)

FIGURE 10 - Electron micrographs of thin stained section of the original PE film (a) and of the grafted film to PS/PE = 1.9 (b). Extrusion direction *M* is approximately vertical. Inset in (a) is a SAXS pattern showing 1st and 2nd order meridional reflections.

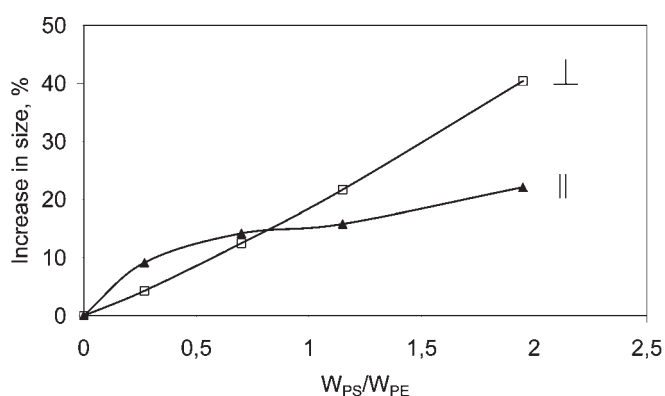


FIGURE 11 - Increase in film dimensions parallel (||) and perpendicular (⊥) to *M* as a function of PS/PE weight ratio

With the aim to influence the efficiencies of crosslinking two solvents different in chemical structure and radiation sensitivity were used for swelling of PE during radiation crosslinking: benzene with aromatic structure and high radiation resistivity and hexane similar in chemical structure and radiation sensitivity to PE. If the PE was swollen with benzene and then crosslinked the subsequent increase in the grafting yield was lower than in the case when dry polyethylene was crosslinked. This result suggested that crosslinking

could be less efficient in the presence of benzene. When hexane was used as the swelling agent similar results were obtained as with benzene.

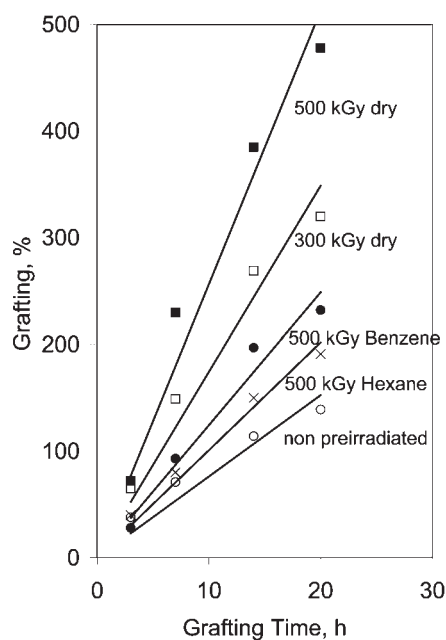


FIGURE 12 - Dependence of grafting yield on crosslinking density of PE. Grafting by simultaneous irradiation at 45°C. Dose rate = 0.5kGy/h

In order to obtain more direct information about the influence of swelling agent on PE crosslinking we investigated the crosslinked polyethylene for its elastic modulus in the molten state.

Stress-strain curves of polyethylene samples irradiated in different environments were recorded in the molten state at 165°C. According to the elementary theory of rubber elasticity the relation between stress and extension ratio is given by

$$\sigma = \frac{\rho RT}{M_c} \left(\lambda^2 - \frac{1}{\lambda} \right) \quad (5)$$

where ρ , R and T are polymer density, gas constant and absolute temperature, respectively. M_c is molecular weight of the average chain segment between cross-links, λ is the ratio of the extended length to the original length. Hence, a plot of

$$\sigma \text{ vs } \left(\lambda^2 - \frac{1}{\lambda} \right) \quad (6)$$

should give a straight line with a slope proportional to the crosslink density. In Figures 13 such plots are shown for the 300 and 500kGy crosslinked specimens. The departure from linearity is partly due to the oversimplifications in the theory, and partly to time-dependent viscosity effects which were not fully eliminated although a very low strain rate was applied (1mm/min). In spite of these drawbacks it can be concluded beyond doubt that irradiation of swollen polyethylene produces fewer effective crosslinks than does irradiation of the dry polymer. Furthermore, fewer crosslinks are created with hexane compared to benzene as swelling agent.

The present solvent has a chemical and physical effect on the crosslinking reaction of PE. In simultaneous irradiation the radiolytic decomposition of PE and solvent mainly occurs by the breakage of a carbon-hydrogen bond giving the parent radical and a hydrogen atom. Although the mechanism may be similar very different yields of radical are found for PE and benzene being more than one order of magnitude higher for PE. On the other hand the radical yields for hexane and PE are very close. If only the chemistry of the crosslinking reaction were responsible for the observed differences in

effective crosslinking in solvents then the effect of hexane should be much more pronounced. Therefore, the physical effect of solvents on effective crosslinking should be taken into account.

Sorption of solvents occurs in the amorphous phase of PE. It is known that crosslinking occurs mainly in the amorphous regions of the polymer and predominantly on the surface of the crystallites present. Interlamellar crosslinks contribute to network formation. For high density PE equilibrium swelling in benzene is about 7%. As stated above, benzene is radiation resistant solvent and its physical interaction with PE may have much more important influence on the effective radiation crosslinking than the participation of active species produced in its radiolysis. Benzene and hexane due to their swelling effect increase the distance between the polymer chains causing decreased crosslink efficiency. Furthermore, the lamellar separation increases with swelling²⁸ probably resulting in decrease of effective interlamellar interchain crosslinks and increase of intra-lamellar intrachain non effective crosslinks. In the case of hexane both stronger chemical and physical negative effect on effective crosslinking may be expected, as our results indicate.

It could be concluded that the change of crosslinking density of polyethylene influences the grafting rate and yield with styrene in similar way as the change of polymer density, thickness of polymer film or dilution of monomer with methanol. The increase of grafting yield with increase of crosslinking density was interpreted in terms of gel-effect. Higher crosslink density and more effective grafting were obtained by irradiation of dry polyethylene than by irradiation of swollen polymer. The reason could be the decrease of the interchain contacts due to the swelling effect of solvents. In hexane the participation of radicals created in radiolysis in termination of polymeric radicals could additionally reduce the effective crosslinking.

The crosslinking effect in the grafting by pre-irradiation in vacuum

In the previous parts of this work the grafting of styrene on polyethylene was investigated by different initiation methods. The main governing factor of the graft copolymerization reaction was found to be the gel-effect, i.e. the greatly hindered termination reaction in viscous gels. Since greater polyethylene density, greater specimen thickness, pre-crosslinking of polyethylene and lower temperature increase the viscosity of the swollen system, these factors have generally a favourable effect on the grafting reaction, too. In a very rigid polymeric matrix, however, the swelling can be hindered to such an extent that the grafting becomes limited by the structure of the specimens. This rigidity can be brought about again by increasing density and thickness and decreasing the temperature, as well as by crosslinking by high pre-irradiation doses. We proposed that this could have been the case in the experiments described by Ballantine and collaborators,⁶ where only very small grafting yield could be obtained at room temperature with 150kGy irradiated high-density polyethylene films, while on raising the temperature to 50°C the grafting was strongly accelerated. To get more evidence we investigated the effect of different pre-irradiation doses on the grafting reaction by pre-irradiation in vacuum.^{36,37} Some experiments with polypropylene are included for comparison.

Figures 14a,b,c show the grafting yields in dependence on grafting times.

Let us now see, how our experiments fit the theory (Equation 4).

Low density polyethylene and polypropylene show the expected behaviour. At each pre-irradiation dose the limiting value of grafting yield falls sharply with rising temperature and when comparing different pre-irradiation doses one can see a net effect of the initial free radical concentration, too.

High density films 0.1mm thick followed this kinetic pattern at a grafting temperature of 60°C for all doses and at 20°C for the lowest dose of 25 kGy and 0.3mm thick high density foils only at

60°C for 25kGy dose. With thicker HD specimen at all doses at lower temperatures grafting yields are generally much lower. Apparently, at low temperature the swelling pressure within the grafted polymer is not high enough to loosen the rigid structure of these foils. Grafting rate sharply falls with the increasing dose, although the concentration of the trapped radicals undoubtedly rises.

It should be noted that the increase in radical concentration resulted in an increase in crosslinking density. Obviously, the crosslinking makes the films and foils less accessible for the grafting reaction. Interlamellar crosslinking may hinder the penetration of the monomer to be grafted. It is interesting to note that no similar effect was observed by the polypropylene specimens in which practically no crosslinks are formed. On the other hand, in low density polyethylene and in thin films of high density polyethylene at higher temperature crosslinking can enhance grafting rate and yield due to

gel-effect, as was shown by direct simultaneous grafting of styrene on radiation pre-crosslinked polyethylene (Fig. 12).

An interesting behaviour arises after prolonged grafting times with some high density specimens pre-irradiated to crosslinking doses. The grafting is suddenly accelerated after 30-hour reaction at 20°C in the case of 130kGy pre-irradiated 0.1mm high density film (Figure 14b), and by 300kGy pre-irradiated 0.3mm high density foil after grafting at 60°C (Figure 14c).

To understand the form of the kinetic curves, one should examine the changes going on in the specimens during the course of the grafting reaction. Films 0.1mm of HD PE after grafting under different conditions can be seen in Figure 15a.

The film irradiated to 25kGy and grafted at 20°C (B) shows a regular (nearly homothetic) increase in the dimensions, compared with the

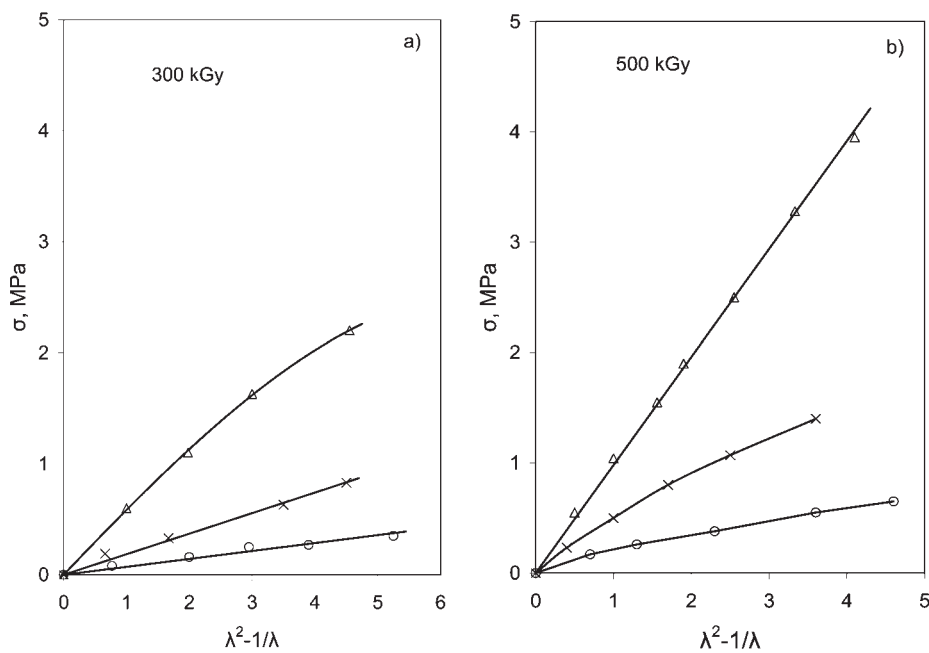


FIGURE 13 – Stress extension ratio relation of PE films irradiated (crosslinked) with total dose of 300kGy (a) and 500kGy (b) in different environments. Dose rate: 3.4kGy/h. Δ - PE dry film irradiated in vacuum; \times - PE film swollen in benzene irradiated in absence of air; \circ - PE film swollen in hexane irradiated in absence of air

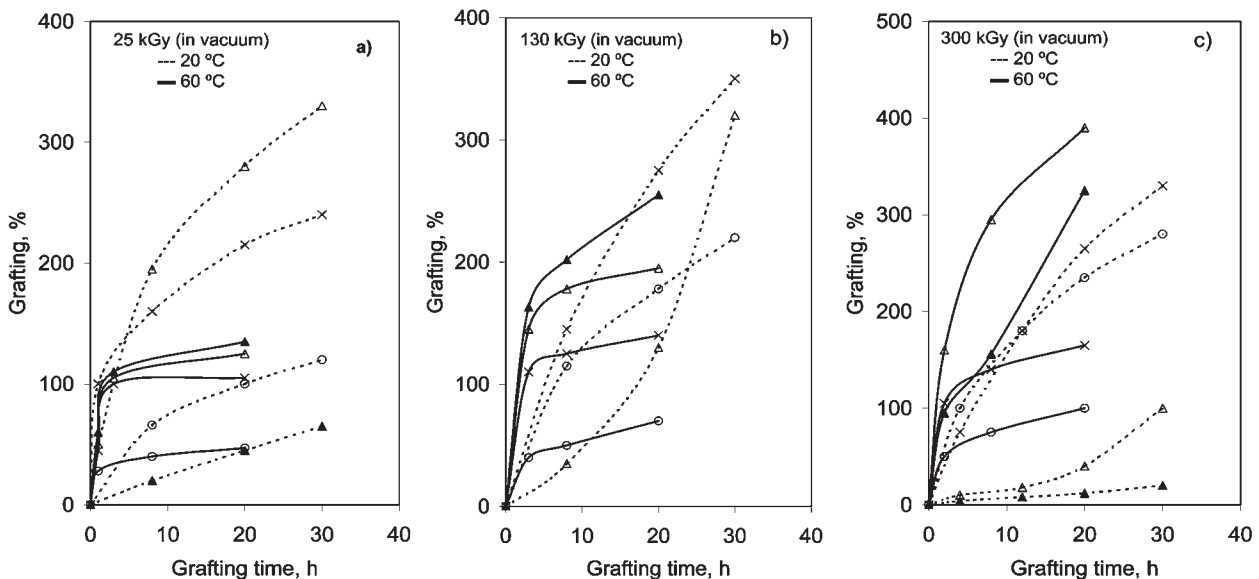


Fig. 14. The grafting of styrene on PE after 25kGy (a), 130kGy (b) and 300kGy (c) pre-irradiation in vacuum. Grafting temperature was 20°C and 60°C. \circ - low-density polyethylene-0.15mm; Δ - high-density polyethylene-0.1mm \blacktriangle - high-density polyethylene-0.3mm; \times - polypropylene-0.13mm

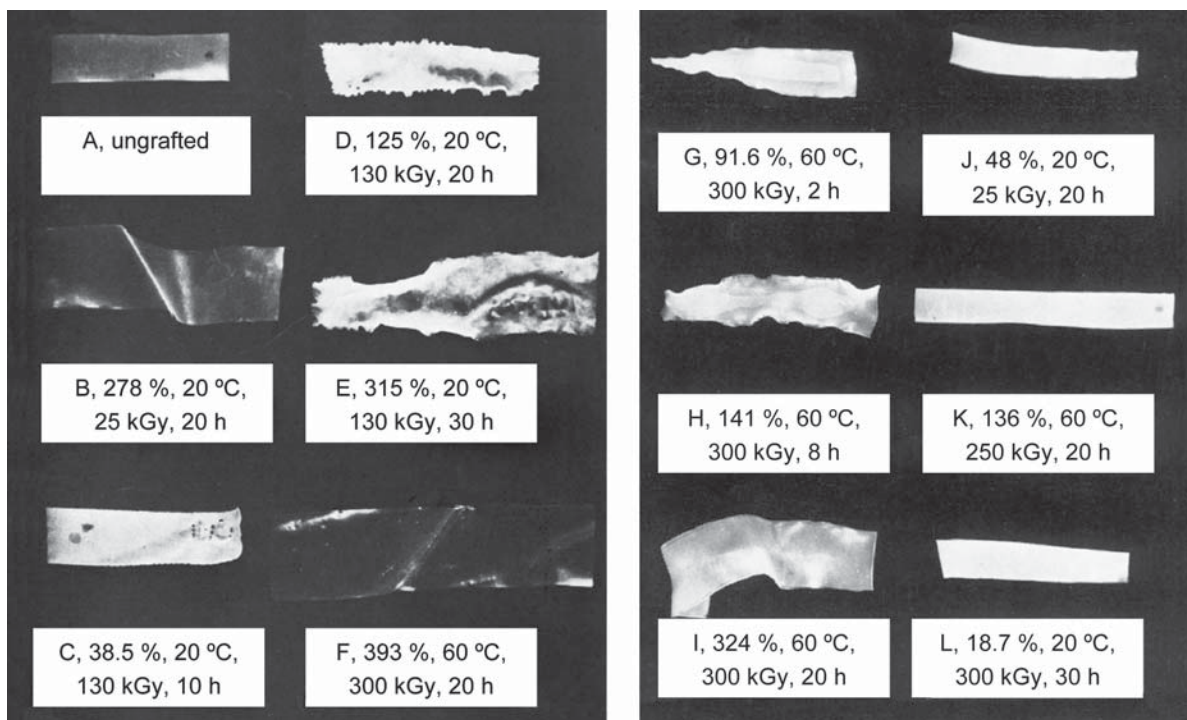


FIGURE 15: High-density polyethylene specimen grafted by styrene a) films A to F are 0.1mm thick b) foils G to L are 0.3mm thick. The grafting percentage and the conditions of grafting are marked under the specimen.

ungrafted control (A). Equally at 20°C, but after a dose of 130kGy which is sufficient to bring about crosslinking, the swelling pressure of the grafted chains and of the imbibed monomer is insufficient to change the film dimensions (C). The films can be best grafted at the edges, where the least force is needed to incorporate the growing chains and the monomer. The cut-in numbers and signs also form new "edges" inside the specimens. At longer grafting times, however, (D, and especially E) the swelling pressure breaks up the macro-structure of the film. One gets a highly inhomogeneous grafting with fine bubbles; presumably mostly in the amorphous parts throughout the whole specimen, and increase of the dimensions and at the same time an accelerated reaction. At 60°C, on the other hand, even after crosslinking doses of 130kGy or 300kGy, the films are grafted quite homogeneously (F), like at low doses at all temperatures.

The peculiar intendment of films C, D and E is a consequence of the inhomogeneous grafting of the films edges. It is presumably connected with the very long lifetime of the grafted polystyrene chains at the low temperature used.

With the thicker foil, the effect of foil structure and crosslinking is even more marked. On the foils, G, H and I of Figure 15b (300kGy, 60°C) one can see how the grafting proceeds to the inner parts of the foil, allowing a strong increase in the foil dimensions when the ungrafted central parts of the foil disappeared. The wave-like shape of the foil-edges is a result of their growing when the middle parts are yet ungrafted and undeformable. At low dose and low temperature (less free radicals, but still high specimen rigidity) surface- and edge-grafting is produced while conserving the original foil dimensions (foil J). At low dose and high temperature a remarkably homogeneous graft results (foil K). Finally, at high dose and low temperature the dimensions of the foil do not change, but we can observe a roughening of the surface, caused by thousands of surface- and edge-bubbles (L).

It could be concluded that the crosslinking of high-density polyethylene makes its structure less accessible for grafting. The raising of the temperature loosens this structure. This, and not the free radicals trapped in the crystalline parts, is the main cause of the

early observation that when pre-irradiating in vacuum, high-density specimens are grafted much better at 50°C than at 20°C.

The grafting can cause a wide variety of physical changes in the grafted specimens. Only the combination of kinetic measurements and physical examination of the grafted specimens can give a true picture of the grafting process. This is especially true if the specimens are not grafted in a quasi homogeneous manner in their whole mass.

The form and dimensions of the polymer to be grafted, influencing its rigidity, may play a decisive role in the grafting reaction.

Conclusion

Kinetics of styrene homopolymerisation could be applied to direct grafting of styrene on PE and PP. Monomer supply was higher than monomer consumption and propagation rate was not diffusion controlled. Square root dependence of grafting rate on dose rate has been verified at dose rates lower than 10^2 Gy/h.

Polymer structure strongly influenced the grafting rate. Grafting rate increased with the increase of PE density and specimen thickness and decreased with the increase of temperature which indicated the effect of monomer concentration on viscosity of reaction medium and on termination rate. Termination reaction of growing polystyrene radicals is diffusion controlled and the increase of viscosity leads to gel effect. Direct proof that the gel effect plays essential role in grafting was obtained by addition of methanol in reaction mixture. By dilution of styrene with methanol the concentration of styrene inside PE decreases, the viscosity increases and due to the gel effect the grafting rate and yield increase until an optimal concentration of monomer is reached. The decreased radical termination rate overcompensates for decrease in the rates of initiation and propagation which also accompany the monomer dilution. Hence the decrease in monomer concentration results in longer polystyrene chains and higher overall reaction rate. Crosslinking of PE decreases the degree of swelling and may increase the yield of grafting.

In thicker high density specimens crosslinked with higher doses the grafting at lower temperature is restricted because the

swelling pressure of the grafted chains and of the imbibed monomer is insufficient to loose the rigid polymer structure and diversified changes in form and appearance of the grafted specimens may occur.

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