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The Effect of the Type of Polyethylene on the Grafting of Styrene onto Polyethylene. III. The Crosslinking Effect in the Grafting by Preirradiation in Vacuum

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The graft-copolymerisation of styrene onto the free radicals trapped in vacuum-irradiated polyethylene was investigated. By an increase of the rigidity of the foils, the grafting rate is also increased, because the termination of the growing chains becomes more hindered. But further increase of the rigidity causes grafting to stop at comparatively low values. Crosslinking of the foils also increases this rigidity, while raising of grafting temperature partially eliminates its effect. Based on the experimental results, some kinetic and structural factors governing the grafting reactions are discussed and some former theories are revised.

In the previous parts of this work the grafting of styrene onto polyethylene foils was investigated by different initiation methods[1,2]. 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. As greater foil density, greater foil thickness 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 extent that the grafting becomes limited by the structure of the foils. This rigidity can be brought about again by increasing density and thickness and decreasing temperature, as well as by crosslinking by high preirradiation doses. We proposed that this could have been the case in the experiments described by Ballantine and collaborators[3], where only very small grafting yield could be obtained at room temperature with 15 Mrad irradiated high-density polyethylene films, while on raising the temperature to 50° C the grafting was strongly accelerated. The authors cited have assumed, themselves, that the marked increase in grafting yield on raising the temperature is produced by the diffusion of styrene into the crystalline regions of the high-density polyethylene, where most of the free radicals had been trapped.

In this paper we describe the effect of different preirradiation doses on the grafting reaction. Some experiments with polypropylene are included for comparison.

EXPERIMENTAL

The apparatus was the same as described by Ballantine[3]. The vials were sealed in vacuum of 10^{-5} mm Hg. Twice distilled styrene and the following polymers in

the form of approximately 10 × 40 mm samples were used:
Low-density polyethylene »Fertene«, 0.15 mm thick.
Low-density polyethylene »OKITEN«, 0.15 mm thick.
High-density polyetylene »Hostalen GC«, 0.07, 0.1 and 0.3 mm.
Polypropylene 0.06 and 0.13 mm.

Irradiations were performed with ^{60}Co gamma rays at a dose rate of 340.000 rad/h, at 35° C. The foils to be exposed to the same dose and grafting time were handled together in the same vials. For further details see ref. 1.

RESULTS

The results can be seen in Figs. 1—3; the following remarks should be taken into consideration:

1. The grafting of the two types of low-density polyethylene foils gave practically the same results, with an average difference of less than 4%, and the difference was only in one case more than 15%; on the graphs only the mean values are shown.

2. The polypropylene foils of 0.06 mm gave grafting curves qualitatively similar to those of the 0.13 mm foils, while the 0.07 mm Hostalen GC foils gave qualitatively similar to the 0.1 mm foils.

DISCUSSION

The grafting onto vacuum-preirradiated polyethylene (and polypropylene) is initiated by trapped free radicals. Similar reactions can essentially be described (at least in their not too early stage) by the equations for the post-effect in radiation- or photo-initiated free radical polymerization[4,5]:

$$g = \frac{k_p}{k_t} [M]/\log k_t [R_o] t + 1 \qquad (1)$$

where g means the grafting in the post-effect (referred to sometimes, not completely correctly, as the »limiting value of grafting«), k_p the propagation rate constant, k_t the termination rate constant, [M] the monomer concentration, $[R_o]$ the concentration of free radicals at the beginning of the reaction and t the reaction time. As from equation (1)

$$E_g = E_p - E_t$$

where E stands for the activation energies, and as in highly viscous media $E_t > E_p$ (see *e. g.* 4,5), so E_g is negative. Thus, the »limiting value« should be the higher, the lower the temperature. The value of g should also be higher with higher values of the initial free radical concentration, *i. e.* with higher preirradiation dose.

Shinohara and Tomioka[6] gave another analysis for the lowering of the »limiting values« at higher temperatures. They connected the »limiting value of grafting« with the length of the kinetic chain in the stationary state. But the condition for the stationary state is that initiation and termination rates should be equal, which is definitely not the case in similar post-effect type reactions.

Let us see now, how our experiments compare with the theory.

As can be seen in Figs. 1—3, low-density polyethylene and polypropylene foils show the expected behaviour. At each preirradiation dose, the »limiting value« falls sharply with raising temperature and when comparing different

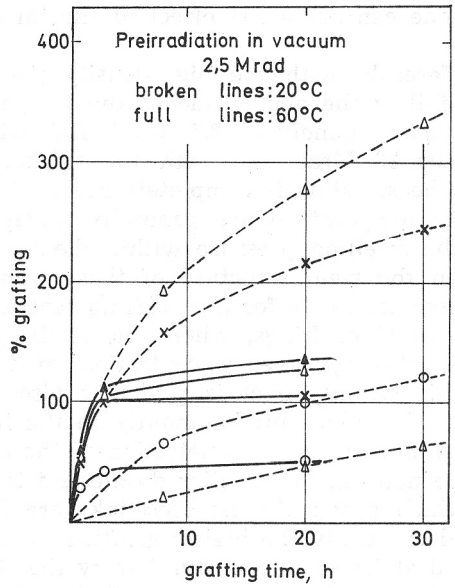

Fig. 1 The grafting of styrene onto polyethylene after 2.5 Mrad preirradiation in vacuum.

O = low-density polyethylene,	0.15 mm
△ = high-density polyethylene,	0.1 mm
▲ = high-density polyethylene,	0.3 mm
× = polypropylene,	0.13 mm

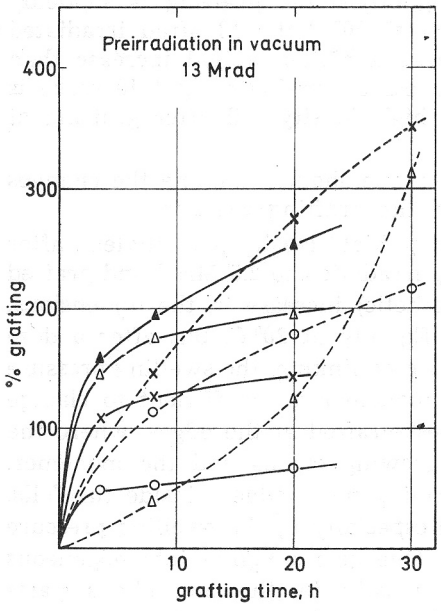

Fig. 2 The grafting of styrene onto polyethylene after 13 Mrad irradiation in vacuum. Legends see Fig. 1.

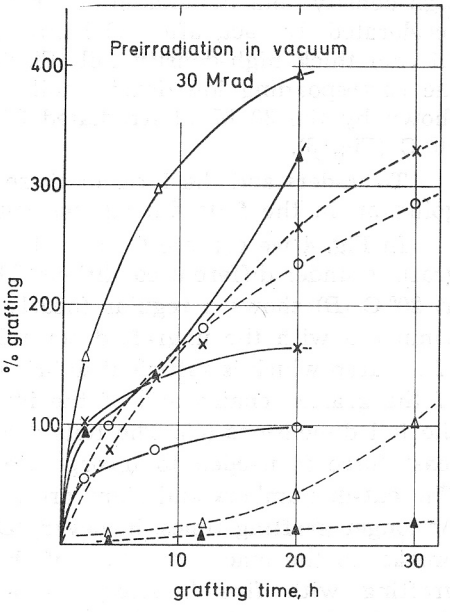

Fig. 3 The grafting of styrene onto polyethylene after 30 Mrad preirradiation in vacuum. Legends see Fig. 1.

preirradiation doses, one can see a net effect of the initial free radical concentration, too.

Things stand differently with the high-density polyethylene foils. The thinner foil seem to follow the above rule of the temperature effect at the lowest preirradiation dose, namely at 2.5 Mrad. But with this foil after a preirradiation of 13 or 30 Mrad and with the thicker foil at all of the radiation doses used, the situation is completely reversed: the grafting values obtained at the lower temperature are generally much lower. Apparently, at low temperature the swelling pressure within the grafted material is not high enough to loosen the rigid structure of these films. The crosslinking, too, makes the films less accessible for the grafting reaction. This is especially pronounced with the 20° C graftings, where the grafting rate sharply falls with increasing dose, although the concentration of the trapped radicals undoubtedly rises. This strong effect is probably also connected with the fact that crosslinking takes place predominantly in the interlamellar regions of the crystallites, thus hindering the penetration of the monomer to be grafted. It is interesting to note that no similar dose effect is shown by the polypropylene foils, in which practically no crosslinks are formed.

These results, and especially the higher grafting of the thin high density foils at lower dose and at lower temperature, show that the low-temperature grafting in Ballantine's experiment[3] was not limited by the absence of a sufficient quantity of free radicals in the amorphous phase, but by the rigid, crosslinked foil structure. Nevertheless, the fate of the crystalline parts and of the free radicals therein is not yet completely clear and should be investigated by further experiments.

An interesting situation arises after prolonged grafting times with some high-density foils irradiated to crosslinking doses: the grafting is suddenly accelerated. In fact, after 30 hours grafting at 20° C the 13 Mrad irradiated 0.1 mm thick high-density foil (Fig. 2) shows a higher weight increase than the corresponding low-density foil. A not less surprising weight increase is shown by the 30 Mrad irradiated 0.3 mm high-density foil after grafting at 60° C (Fig. 3).

To understand the form of these curves, one should examine the changes going on in the foils during the course of the grafting reaction.

In Fig. 4 we can see 0.1 mm thick foils of high density polyethylene after grafting under different conditions. The foil irradiated to 2.5 Mrad and grafted at 20° C (*B*) shows a regular (nearly homothetic) increase in the dimensions, compared with the ungrafted control (*A*). Equally at 20° C, but after a dose of 13 Mrad which is sufficient to bring about crosslinking, the swelling pressure of the grafted chains and of the imbibed monomer is insufficient to change the foil dimensions (*C*). The foils 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 are also forming new »edges« inside the foils. At longer grafting times, however, (*D*, and especially *E*) the swelling pressure breaks up the macro-structure of the foil. One gets a highly inhomogeneous grafting with fine bubbles, presumably mostly in the amorphous parts throughout the whole foil, an increase of the dimensions and at the same time an accelerated reaction. At 60° C, on the other hand, even after cros-

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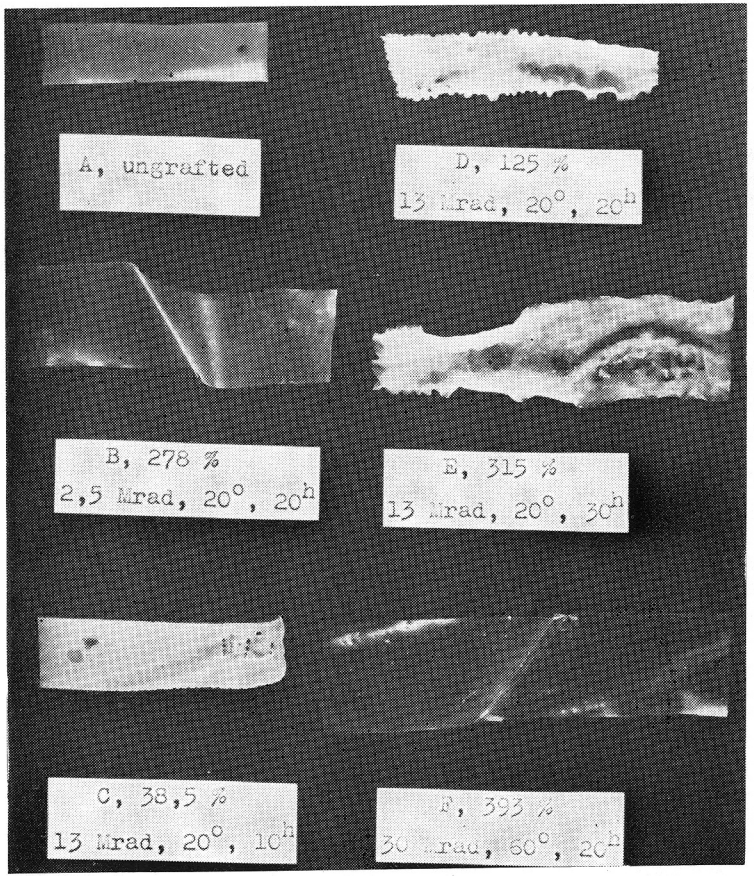

Fig. 4 High-density polyethylene foils (0.1 mm thick) grafted by styrene (foils *A* to *F*). The grafting percentage and the conditions of grafting are marked under the foils.

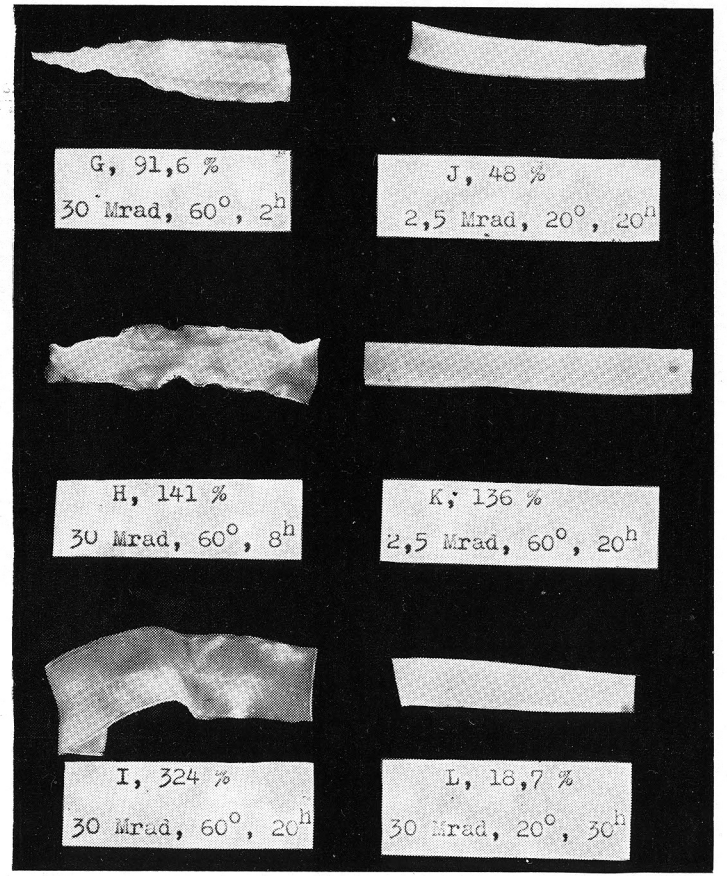

Fig. 5 High-density polyethylene foils (0.3 mm thick) grafted by styrene (foils *G* to *L*). The grafting percentage and the conditions of grafting are marked under the foils.

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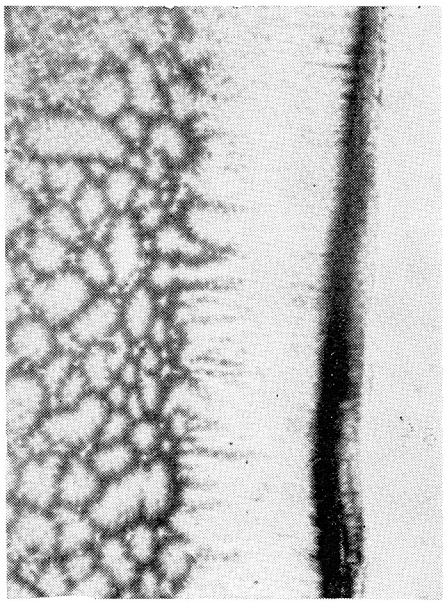

Fig. 6 Microphotograph of a part of foil *J* in Fig. 5 (replica technique).

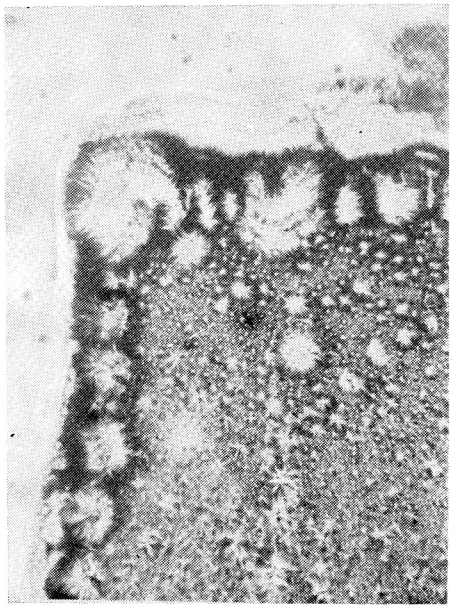

Fig. 7 Micrograph of a part of foil *L* of Fig. 5 (replica technique).

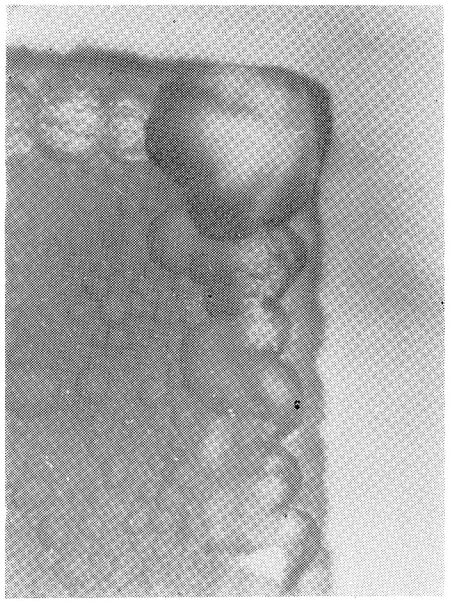

Fig. 8 Direct microphotograph of a part of foil *L* of Fig. 5.

slinking doses of 13 or 30 Mrad, the foils are grafted quite homogeneously (*F*), like at low doses at all temperatures.

The peculiar indentment of foils *C*, *D* and *E* is a consequence of the inhomogeneous grafting of the foil edges. It is presumably connected with the very long lifetime of the grafted polystyrene chains at the low temperature used. Similar dented edges have been observed by one of us[7] in the system teflon-methyl methacrylate (methyl methacrylate having an even lower termination rate constant at high polymer concentrations than styrene) as well as in teflon-styrene-methanol, and in polyvinyl alcohol-styrene-methanol-water, where the growing polystyrene side chains are precipitated.

With the thicker foil, the effect of foil structure and crosslinking is even more marked. On the foils *G*, *H* and *I* of Fig. 5 (30 Mrad, 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 of the foil are yet ungrafted and undeformable. (The examination of the crystal structure of similar foils will be the object of a later work.) At low dose and low temperature (less free radicals, but still high foil rigidity) surface- and edge-grafting is produced while conserving the original foil dimensions (foil *J*). At low dose and hight 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*).

Fig. 6 is a microphotograph of the surface of foil *J*. One can see how the grafting occurs in an almost homogeneous way at the edges of the foil, while the inner surface can be grafted only in bulge-like bubbles. Figs. 7 and 8 show microphotographs of the same part of foil *L*. Here the bulges appear only at the edges, while the surface is covered by separate, extruding micro--bubbles. (Figs. 6 and 7 were made by Mrs. D. Kallo, Plastics Research Institute, Budapest, and Fig. 8 by Mrs. M. Azori, Central Chemical Institute of the Hungarian Academy of Sciences, Budapest. The authors acknowledge thankfully their cooperation.)

CONCLUSIONS

1. 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 preirradiating in vacuum, high--density foils are grafted much better at 50° than at 20° C[3]. Thus, the inferences concerning the accessibility of the radicals in the crystallites at comparatively low temperature, *e. g.* at 50° C, should be investigated anew.

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

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

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IZVOD

Utjecaj tipa polietilena na cijepljenje stirena na polietilen. III. Efekt umrežavanja pri cijepljenju na polietilen prethodno zračen u vakuumu

J. Dobó, F. Ranogajec i I. Dvornik

Ispitivana je graft-kopolimerizacija (cijepljenje) stirena inicirana slobodnim radikalima uhvaćenima u polietilenu koji je prethodno zračen u vakuumu. Povećanje krutosti polietilenske folije izaziva porast brzine cijepljenja što se tumači usporavanjem terminacije rastućih lanaca polistirena. Znatniji dalji porast krutosti dovodi nasuprot tome do zaustavljanja cijepljenja pri relativno niskim vrijednostima prinosa. Krutost folija povećava se i umrežavanjem, dok porast temperature cijepljenja djelomično eliminira ovaj efekt. Polazeći od eksperimentalnih rezultata, diskutiraju se kinetički i strukturni faktori koji određuju reakcije graft-kopolimerizacije u ovom sistemu, te se revidiraju neke ranije teorije.

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