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### Electron Spin Resonance Study on Grafting of Tetrafluoroethylene onto Polyethylene

Yoneho Tabata<sup>a</sup>; Junichi Fujikawa<sup>a</sup>

<sup>a</sup> Department of Nuclear, Engineering University of Tokyo, Tokyo, Japan

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## Electron Spin Resonance Study on Grafting of Tetrafluoroethylene onto Polyethylene

YONEHO TABATA and JUNICHI FUJIKAWA

*Department of Nuclear Engineering  
University of Tokyo  
Tokyo, Japan*

### SUMMARY

An ESR study has been made on the course of grafting of tetrafluoroethylene onto polyethylene. Alkyl and allyl radicals trapped in the polymers were measured under various grafting conditions. It was observed that alkyl radicals decay very rapidly when monomers are in contact with the irradiated polymer, while allyl radicals decay very slowly even in the presence of monomers as in the decay of radicals in irradiated polymers without monomers. The effect of pre-irradiation temperature on grafting was also studied, and the rate of grafting was found to be much faster for lower pre-irradiation temperatures. From these experimental results it was concluded that alkyl radicals play an important role in the initiation reaction of grafting.

### INTRODUCTION

In a previous paper [1] the grafting of tetrafluoroethylene onto polyethylene was reported. It was shown that the grafting reaction proceeds very rapidly at  $-35^{\circ}\text{C}$  by a pre-irradiation method under vacuum, and high grafting yields were easily obtained.

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ESR measurements have recently been made in the course of grafting, and the mechanism of grafting has been investigated through these measurements. It was found that alkyl radicals trapped in polyethylene play a most important role in grafting and that the grafting reaction is mainly initiated by alkyl radicals, in spite of the fact that grafting of almost all other monomers is initiated by allyl radicals. These results are described in this paper.

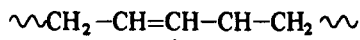
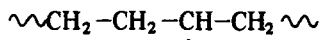
### EXPERIMENTAL

A polyethylene sample was irradiated at  $-78^{\circ}\text{C}$  under vacuum. After irradiation, tetrafluoroethylene monomers were placed with the irradiated polymers at  $-196^{\circ}\text{C}$  in the absence of oxygen and grafting was carried out at  $-35^{\circ}\text{C}$ . Takathene was used as the polymer. Experimental details were described in the previous paper [1].

For the measurement of ESR, a specially designed capillary with a breakable seal was prepared. Polymer was irradiated in the capillary tube under vacuum ( $10^{-4}$  mm Hg) at  $-78^{\circ}\text{C}$  after shielding in Position A (Fig. 1). After irradiation the capillary tube was annealed by heating to eliminate color centers produced in the tube while maintaining the polymers at  $-78^{\circ}\text{C}$  in the opposite side of the capillary. Monomers were introduced in the same way described in the previous paper [1]. ESR was measured at  $-35^{\circ}\text{C}$ . Measurement of the radical concentration was made using a standard sample of  $\text{Mn}^{2+}$ . An X-band TSE-100AX spectrometer was used for the experiment.

### RESULTS AND DISCUSSION

It is well known that three kinds of free radicals are produced in solid polyethylene by irradiation with high energy radiation [2]; that is, alkyl, allyl, and polyenyl radicals which are presented as follows:



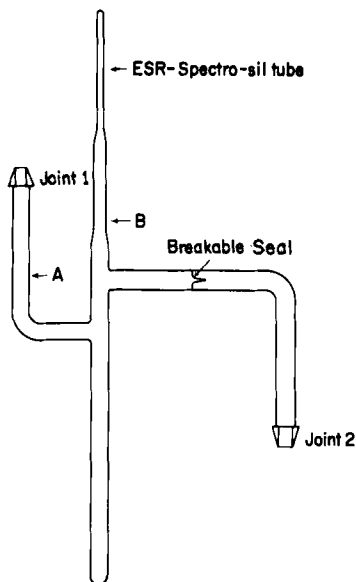


Fig. 1. Capillary tube for ESR measurement during grafting.

The concentration of each radical depends on the temperature of the system and the irradiation dose. These radicals are responsible for the initiation reaction in the grafting of several monomers onto polyethylene by the pre-irradiation technique. It is reported that allyl radicals are responsible to the initiation reaction except for the case of the grafting of ethylene [3]. It would be very interesting to know which radical, alkyl or allyl, is more important in the grafting of tetrafluoroethylene onto polyethylene.

As is well known, alkyl radicals are the most unstable in these three radicals and decay rapidly at relatively low temperatures. On the other hand, allyl radicals are very stable, even at room temperature. Therefore, the temperature dependence of grafting may yield information about the grafting mechanism. We have made some experiments along this line.

It was found that the grafting rate is profoundly influenced by the pre-irradiation temperature. One example is shown in Fig. 2. Pre-irradiation was carried out at 20, -18, -78, and  $-196^{\circ}\text{C}$ . After irradiation in a dosage of 15 MR, graft copolymerization was done at  $-78^{\circ}\text{C}$ . As is obvious from Fig. 2, the temperature effect is very pronounced and the rate of grafting is most rapid for the pre-irradiation at  $-196^{\circ}\text{C}$ , while the grafting

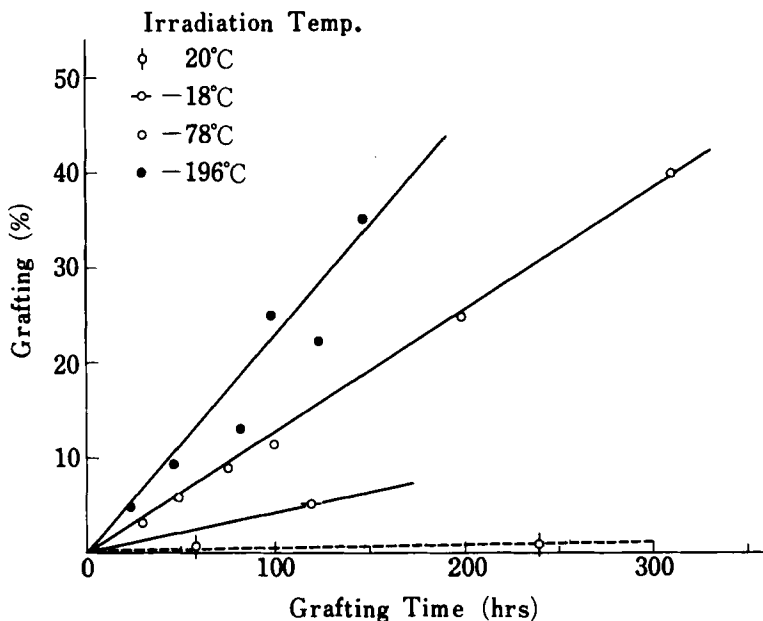
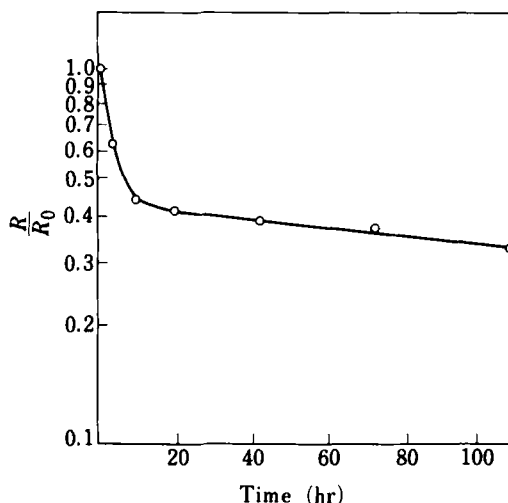


Fig. 2. Grafting % as a function of grafting time at  $-78^{\circ}\text{C}$  for various pre-irradiation temperatures. Pre-irradiation dose was  $6.0 \times 10^6 \text{ R}$ .

actually does not take place for the pre-irradiation at  $20^{\circ}\text{C}$ . These experimental results strongly indicate that unstable radicals play an important role in grafting, and this means that alkyl radicals trapped in the system may initiate grafting. It is known that although almost all alkyl radicals decay rapidly at room temperature, allyl radicals are rather stably trapped.

The decay of trapped radicals produced by  $\gamma$ -irradiation at  $-78^{\circ}\text{C}$  was measured at  $25^{\circ}\text{C}$ . The result is shown in Fig. 3. There are two components in the trapped radicals. The decay time,  $\tau_{1/2}$ , is 2.5 hr for the short lifetime component and 510 hr for the long lifetime component, respectively. It is probable that the former corresponds to the alkyl radical and the latter to the allyl radical. From the experimental results the amounts of trapped alkyl radicals are roughly estimated to be about 60%.

Decay of trapped radicals at  $-35^{\circ}\text{C}$  after irradiation at  $-78^{\circ}\text{C}$  was measured and the results are shown in Fig. 4. The shape of the spectrum obtained at  $-78^{\circ}$  deviates from that of alkyl radicals trapped in crystalline polyethylene. The spectrum is composed of alkyl radicals in the crystalline and amorphous parts and also of allyl radicals. When the temperature is

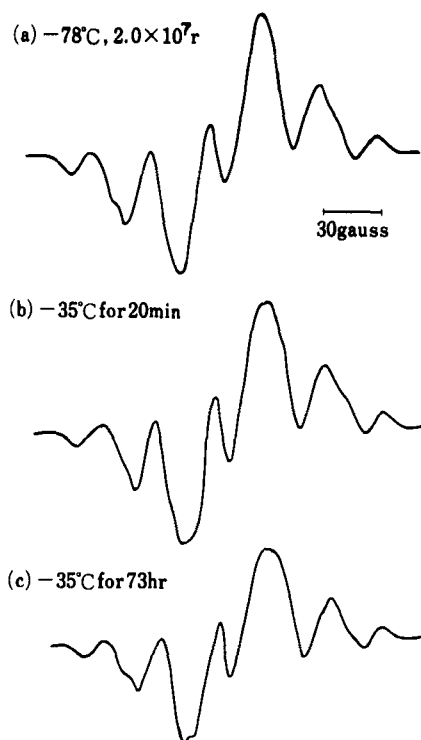


**Fig. 3.** Decay curve of trapped radicals at 25°C. Pre-irradiation was carried out at -78°C in a total dose of  $2 \times 10^7$  R.

elevated through the glass transition temperature of polyethylene at about -40°C, most alkyl radicals trapped in the amorphous part decay. Therefore, the concentration of alkyl radicals decreases in the amorphous region by elevating the temperature to -35°C and the spectrum becomes sharper.

The decay curve of the trapped radicals is shown in Fig. 5. The decay time was estimated to be about 77 hr. After irradiation at a dose of  $2.0 \times 10^7$  R at -78°C, the concentration of radicals was measured in the presence of monomers at -35°C. The results are shown in Fig. 6.

By introducing monomers to the irradiated polyethylene and by keeping the system at -35°C, the shape of the spectrum changes and the concentration decreases rapidly. Spectrum (a) contains about 30% allyl radical and 70% alkyl radical. The concentration decreases by a factor of 2/3 from the initial state (a) to the intermediate state (10 min after the introduction of monomers) (b). In the absence of monomers the rapid decrease in concentration was only 5%, as shown in the previous section. At least a part of the radicals in the decrease should participate in grafting. There are possibilities that the radicals are consumed by the formation of cross-links with a short bridge of tetrafluoroethylene polymer chain between a pair of sites, or by the formation of short branched polymers through a disproportionation reaction between polymer radicals which originate from the pair of sites, or by reaction with impurities in polymers, or by chain

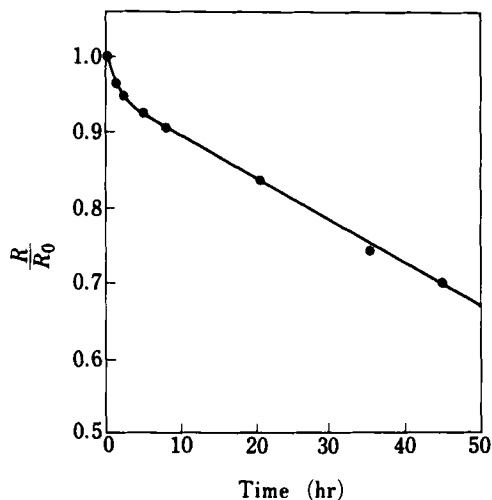


**Fig. 4.** Changes of electron spin resonance spectrum by decay of radicals. (a) After irradiation at  $-78^{\circ}\text{C}$  in a dose of  $2 \times 10^7 \text{R}$ . (b) After 20 min at  $-35^{\circ}\text{C}$ . (c) After 73 hr at  $-35^{\circ}\text{C}$ .

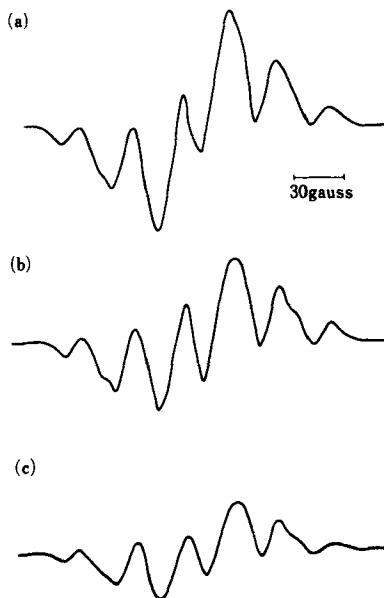
transfer to monomers. Since the C-F bond energy is large in comparison with that of C-H, chain transfer from the polymer radicals to monomers may not be promoted by these possibilities in the presence of the monomers. From these reasons, it seems that almost all radicals participate in the grafting initiation.

If the polymer radicals participate in the initiation of grafting in a manner corresponding to decay of the radicals, propagating radicals should be observed. However, only the decay of radicals was observed in the system. In the grafting of styrene onto polyethylene, the growing radicals were also not detected. This has not yet been explained clearly, but some possible explanations follow.

A part of the polymer radicals are produced by the ionic or hot atom



**Fig. 5.** Decay curve of trapped radicals at  $-35^{\circ}\text{C}$ . Pre-irradiation was carried out at  $-78^{\circ}\text{C}$  in a dose of  $2.0 \times 10^7$  R.



**Fig. 6.** Changes of electron spin resonance spectrum by grafting. (a) After irradiation in a dose of  $2 \times 10^7$  R at  $-78^{\circ}\text{C}$ . (b) 10 min after introducing monomers at  $-78^{\circ}\text{C}$ . (c) 20 hr after introducing monomers at  $-78^{\circ}\text{C}$ .



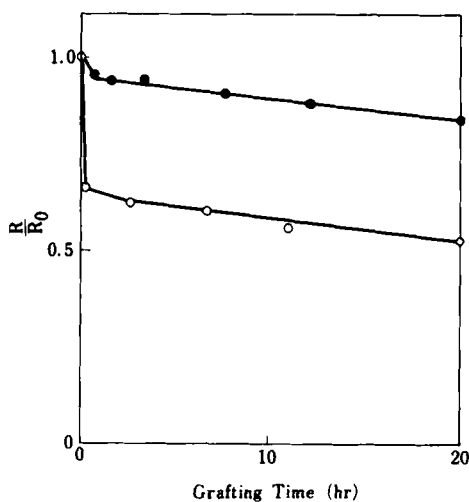


Fig. 7. Decay curves of trapped radicals in the presence and absence of monomers at  $-35^{\circ}\text{C}$ . Pre-irradiation was at  $-78^{\circ}\text{C}$  in a dose of  $2.0 \times 10^7$  R.

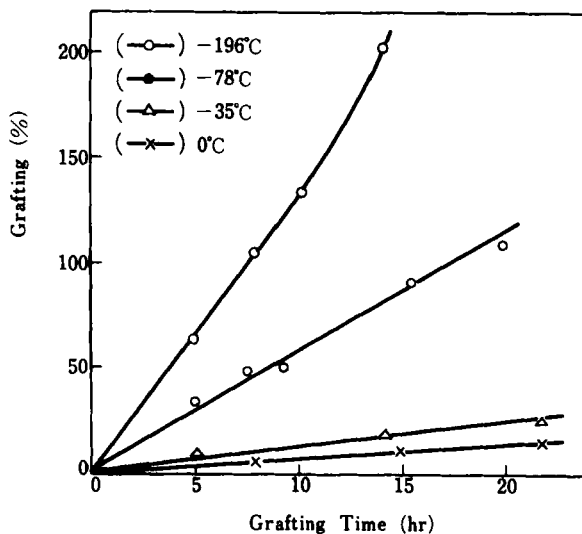
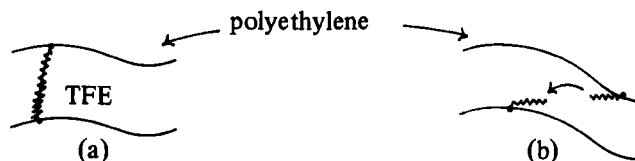


Fig. 8. Dependence of rate of grafting on pre-irradiation temperature at  $-35^{\circ}\text{C}$ . Total pre-irradiation dose was  $6.0 \times 10^6$  R. The pre-irradiation temperatures are given in the figure.

process, and a pair of radicals should be formed a relatively short distance apart. If monomers are introduced into the system, there is the possibility of forming cross-links by the insertion of a short polymer chain of tetrafluoroethylene (a) or of forming short grafted chains by disproportionation (b). Similar phenomena may also occur between radicals produced by the usual process and densely distributed spatially.



Appreciable amounts of polymer radicals will therefore be consumed by the formation of cross-links and short branched chains. Only a few radicals grow to form very long grafted chains. It may be difficult to detect the propagating radicals under such condition.

In the previous paper [1] IR spectra of grafted polymers were presented, and appreciably large amounts of branching were shown. This is an exceptional case in that the branching points can be detected directly.

On the other hand, in the extraction experiment of the grafted copolymer, almost all parts containing branching were extracted by hot xylene. This strongly suggests that the branched polymer chains are very short. Furthermore, in the propagation stage an extremely small amount of oxygen has large influence. This suggests that the number of growing polymer radicals is very low. These reasons may explain why the propagating radical cannot be detected.

Decay of the trapped radicals in the absence and the presence of monomers is presented in Fig. 7. Alkyl radicals are consumed in few minutes after the introduction of monomers, and then the residual radicals decay as in irradiated polyethylene without monomers.

The effect of pre-irradiation temperature on the grafting is shown by the example in Fig. 8.

In this case, the grafting was done at  $-35^{\circ}\text{C}$  and the temperature effect is very significant. The rate of grafting is faster by a factor of 2 in the polymer irradiated at  $-196^{\circ}\text{C}$  than in that at  $-78^{\circ}\text{C}$ . This may be due to the different amounts of alkyl radicals trapped at  $-196^{\circ}$  and  $-78^{\circ}\text{C}$ . For the  $-35$  and  $0^{\circ}\text{C}$  irradiation, there is no proportionality between rate and amount of trapped radicals. This may be due to the retardation of diffusion of monomers in the system because above the transition temperature

(-40°C) the cross-linking takes place easily, and then the diffusion of monomers may be disturbed.

### ACKNOWLEDGMENT

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