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Grafting of Tetrafluoroethylene onto Polyethylene by Pre-irradiation Technique

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SUMMARY

Grafting of tetrafluoroethylene onto polyethylene was carried out by a pre-irradiation technique. It was found that grafting proceeds very rapidly at -35°C in the liquid phase of tetrafluoroethylene. Takathene, which was prepared by a radiation process at Takasaki Radiation Chemistry Research Establishment, was found to be most suitable for grafting compared to other polyethylenes. The specific surface is extremely high in the Takathene, and this may be the most important reason for the high grafting speed. On the other hand, IR measurements of the grafted copolymers showed a characteristic absorption band at 1110 cm^{-1} which may be attributed to the structure of the grafting (branching) position. It was also found that grafted polytetrafluoroethylene can be crystallized during grafting. This is the first case of grafted polymers being in a crystalline state.

INTRODUCTION

Grafting of various monomers onto polytetrafluoroethylene has been reported. However, there has been little work on the grafting of tetrafluoroethylene onto polyethylene.

We have recently succeeded in obtaining the graft copolymer of tetrafluoroethylene-polyethylene by the pre-irradiation method.

There is a report on grafting of fluorine-containing monomers onto nylon 6, polyethylene-terephthalate, polypropylene, and viscose rayon by Kurilenko et al. [1]. In their study the grafting was carried out by a simultaneous irradiation method and tetrafluoroethylene was found to be difficult to graft onto polyethylene.

The grafting of tetrafluoroethylene onto polyethylene was recently tried in the vapor phase of the monomer by the pre-irradiation technique [2], and only about 3% grafting was possible. A saturation of 3% for the grafting was observed.

EXPERIMENTAL

Glass ampoules with a breakable joint were prepared for the experiment, as shown in Fig. 1. After introducing a 100-mg powderlike polyethylene

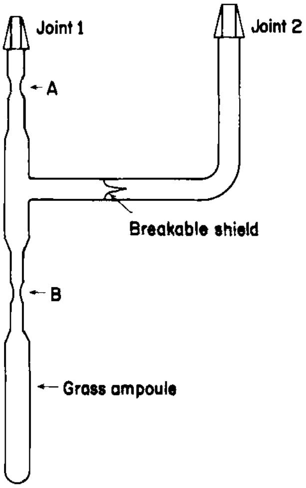

Fig. 1. Schema of ampoule for grafting.

sample, the ampoule was evacuated to 10^{-4} mm Hg and then sealed. The polymer was irradiated at various temperatures by γ-rays from a ^{60}Co source at a dose rate of 3.0×10^5 R/hr. After irradiation, the irradiated polymer was kept at -78°C. The breakable seal was broken and the gases evolved under irradiation were purged. Then the irradiated sample was cooled to liquid nitrogen temperature and monomers were introduced through the broken joint.

After freezing the monomers at -196°C, the monomers were melted again at -78°C. By repeated solidification at -196°C and melting at -78°C, gases generated in the system were completely purged. After this treatment the ampoule was sealed.

The ampoule containing the mixture of monomers and the irradiated polyethylene was kept at -35°C in a mixture of solid and liquid 1,2-dichloroethylene and grafting was done. After grafting, unreacted monomers were purged by opening the ampoule, and the product was dried.

Grafting yield was calculated by

$$\text{grafting yield (\%)} = \frac{W_t - W_i}{W_i} \times 100$$

where W_t is the total weight of product and W_i is the initial weight of non-grafted polymer.

Polyethylene (Takathene) was polymerized in the vapor phase by γ-rays at Takasaki Research Establishment (JAERI). Marlex 15 and Sholex 6602 were employed as polymers. Samples of the former were used without purification, whereas samples of the latter were purified by dissolving them in hot xylene. The polymer was crystallized at 70°C for 24 hr. Tetrafluoroethylene of 99% purity was provided by Asahi Glass Co.

ESR measurement of irradiated polyethylene was made during grafting by a TSE-100AX ESR spectrometer to get information about the mechanism of grafting.

An attempt was made to extract homo polyethylene from the crude graft copolymer by hot xylene at 110°C.

IR spectra and X-ray diffraction measurements were also made to determine the structure of the grafted copolymer.

RESULTS AND DISCUSSION

The relations between grafting and reaction time at -35 and -78°C for various pre-irradiation doses are shown in Fig. 2. The pre-irradiation was carried out at -78°C in a dose rate of 3.0×10^5 R/hr.

As is obvious from the figure, although the grafting does not take place at all at -78°C in 20 hr, the grafting proceeds rapidly at -35°C.

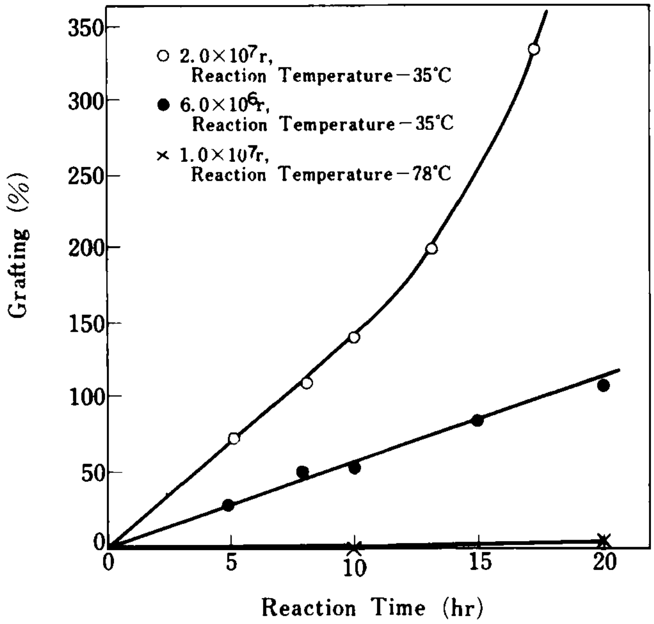

Fig. 2. Relations between grafting and reaction time in hours at -35 and -78°C. The pre-irradiation temperature was -78°C and the dose rate was 3×10^5 R/hr.

Higher pre-irradiation doses yield more grafting at the same grafting temperature. For the grafting onto polyethylene, pre-irradiated at a dose of 2.0×10^7 R at -35°C, an auto-acceleration effect was observed.

Comparison of Takathene with Sholex 6002 in the grafting was made under the same grafting conditions. These results are shown in Fig. 3. It is clear from the figure that there is an extremely large difference between the two. The specific surface of Takathene is about 10^2 m^2/g, which is extremely large in comparison with Sholex (1~10 cm^2/g). This may be an important reason for the difference in the rates of the two kinds of polyethylene. The decay curves of trapped radicals during temperature elevation from the liquid nitrogen temperature are also different and the decay start earlier (at a lower temperature) in Takathene than in Sholex. The initiation reaction for tetrafluoroethylene polymerization may be much simpler in Takathene than in Sholex, since the diffusion of monomers in the polymer is much easier in Takathene.

Acceleration phenomena above 100% grafting were observed for the

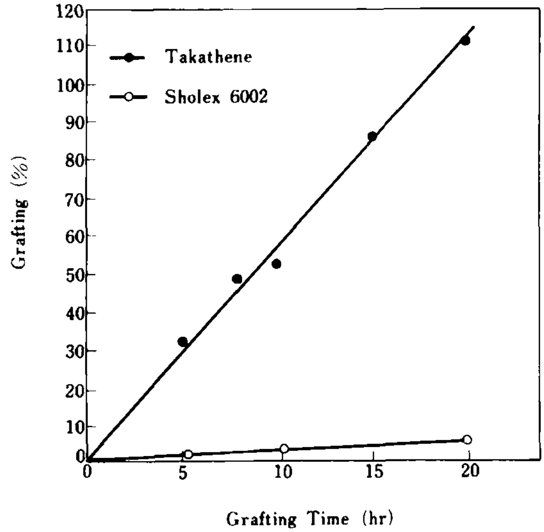

Fig. 3. Relations between grafting % and reaction time in hours at -35°C for Takathene and Sholex 6002. Pre-irradiation was carried out at -78°C at a dose rate of 3.0 X 10^5 R/hr.

systems which were evacuated to an order of 10^{-5} mm Hg before grafting. There was no acceleration phenomenon if the vacuum was insufficient (below 10^{-5} mm Hg). This indicates that an extremely small amount of oxygen is very influential for the acceleration phenomena. In the later stage of grafting above 100%, only a small number of growing radicals survive and grow rapidly. Trace amounts of oxygen may have a large influence on the growing process under such condition.

The rate of grafting in Takathene was 5.67%/hr at -35°C for a pre-irradiation dose of 6.0 X 10^6R at -78°C, while the rate was 0.26%/hr in Sholex 6002 under the same condition.

The specific surface of Takathene is 100 times larger than that of Sholex, and the diameter of Takathene is 10 times smaller than that of Sholex. The diffusion of monomers in the polymer matrix is therefore quite different. This is the most important factor affecting the grafting, and the important reason for the difference described above. The degree of crystallinity, the crystalline state, and the distribution of crystallites are also important in explaining the difference.

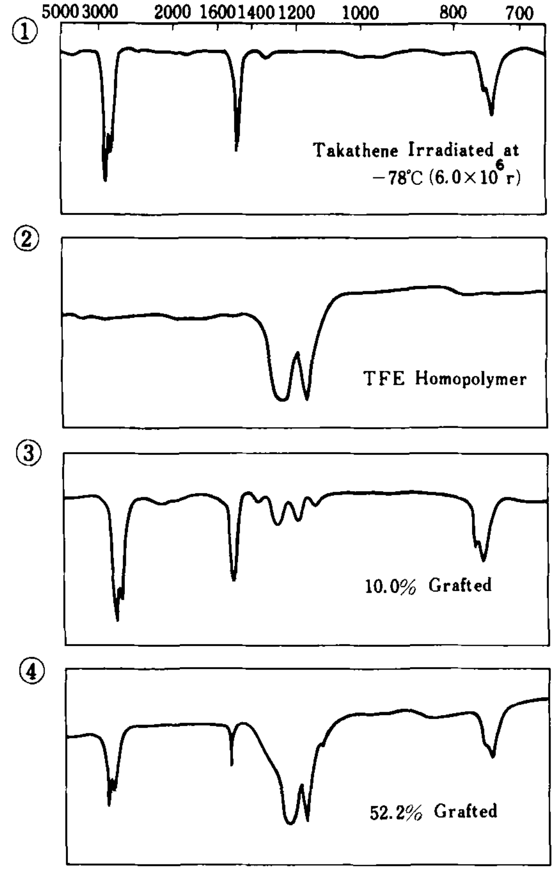

Fig. 4. IR spectra of grafted copolymers, (3 and 4) polyethylene (1), and polytetrafluoroethylene (2).

Infrared Spectra of the Grafted Copolymer

The IR spectra of irradiated polyethylene, polytetrafluoroethylene polymerized at -78°C by the radiation process, and grafted copolymers are shown in Fig. 4. It is very interesting that a new absorption peak which has never been observed in either of the homopolymers, polyethylene and polytetrafluoroethylene, appears for the grafted copolymers. The absorption band appears at about 1110 cm^{-1} near the C–F stretching bands at 1230 and 1163 cm^{-1}. The absorption band is particularly distinguished for the grafted copolymers in low yields.

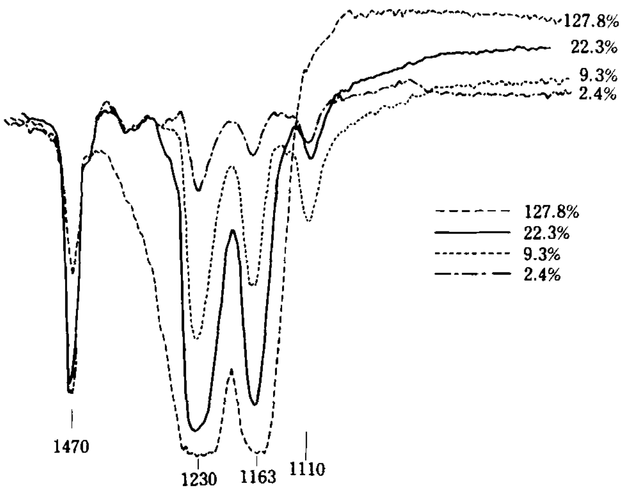

Fig. 5. IR spectra of graft copolymers with different grafting contents.

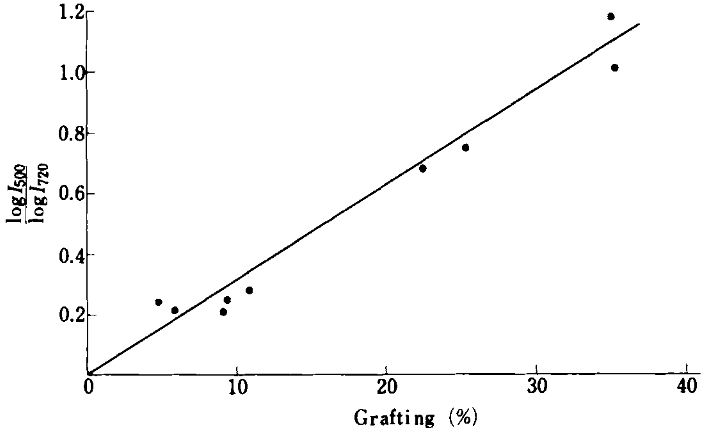

Fig. 6. Relative intensity of the absorption band at 500 cm^{-1} to the band at 720 cm^{-1} as a function of grafting %.

The IR spectra of the grafted copolymer in various yields are shown in Fig. 5. The relative intensity of the 1110 cm^{-1} band decreases with increasing grafting yield. This indicates that the band at 1115 cm^{-1} may be due to ν(C—F) stretching which may originate from that of polytetrafluoroethylene, and the C—F bondings may be located around the branching point.

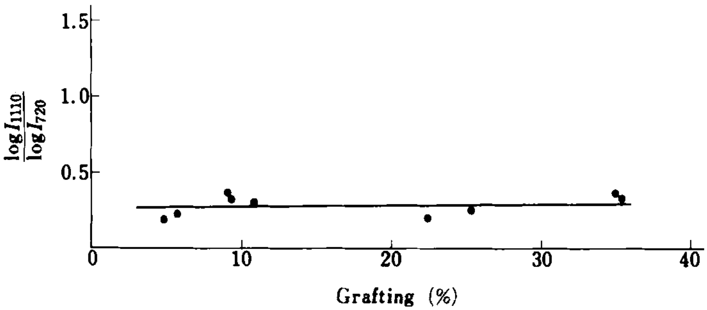

Fig. 7. Relative intensity of the absorption band at 1110 cm^{-1} to the band at 720 cm^{-1} as a function of grafting per cent.

Other characteristic bands have been also observed in the higher wavelength region, i.e., 670, 460, and 418 cm^{-1}. All these absorption bands have never been observed in either homopolymer, so they may also be due to the structure closely connected with the branching position.

The relative intensities of the absorption band at 500 cm^{-1} compared to that at 720 cm^{-1} were plotted as a function of grafting % and shown in Fig. 6. The ratio roughly corresponds to the amount of grafted polytetrafluoroethylene. This means the ratio is proportional to the grafting %.

On the other hand, the relative intensity of the absorption band at 1110 cm^{-1} compared to that at 720 cm^{-1}, shown in Fig. 7, is a function of grafting %. In this case, the relative intensity does not depend on the grafting yield. This clearly indicates that absorption at 1110 cm^{-1} is due to the structure introduced by the grafting.

Because the grafting reaction takes place at -35°C immediately after the introduction of monomers to the irradiated polyethylene, the increase in grafting yield is due to the addition of monomers to propagating radicals. The initiation reaction may therefore be independent of the grafting yield. This fact is clearly demonstrated in Fig. 7. This is the first case in which the structure introduced by grafting has been clearly detected. A high value of the extinction coefficient of ν(C–F) seems to make it easy to detect the branching positions.

The absorption intensity at 730 cm^{-1}, which is due to C–H_2 rocking in the crystalline state, decreases with increasing grafting. This suggests that the crystalline structure of polyethylene can be gradually destroyed by the growth of grafted polymer radicals.

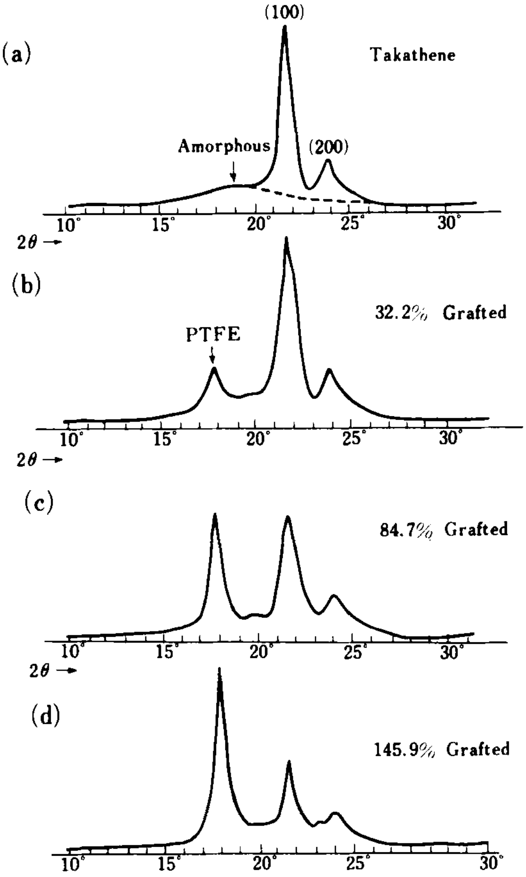

Fig. 8. X-Ray diffraction patterns of polyethylene (a), polytetrafluoroethylene (b), and grafted copolymers (b, c, and d).

X-Ray Diffraction of Grafted Polyethylene

X-Ray diffraction of polyethylene, polytetrafluoroethylene, and graft copolymers was measured and the diffraction curves were compared. The results are shown in Fig. 8.

As is known, two sharp diffraction peaks $2\theta = 21.7°$ (110), $2\theta = 23.8°$ (200), and a halo $2\theta = 19°$ appear in polyethylene. There is no large difference between the polyethylene and the grafted copolymer for 10% grafting. Above about 30% grafting however, a new diffraction peak at

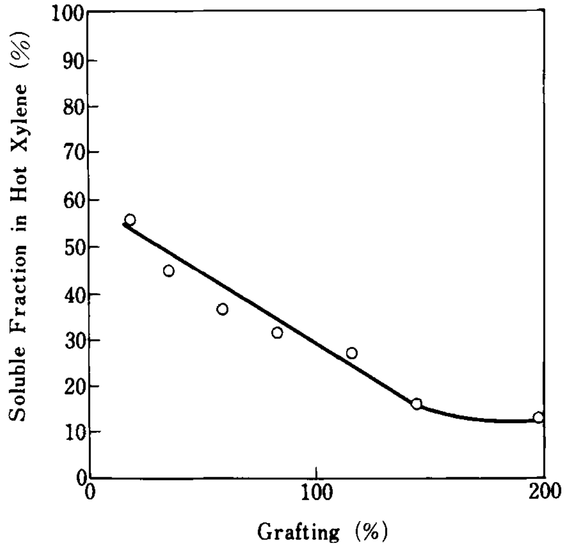

Fig. 9. Relation between solubility of copolymers in hot xylene and the grafting %.

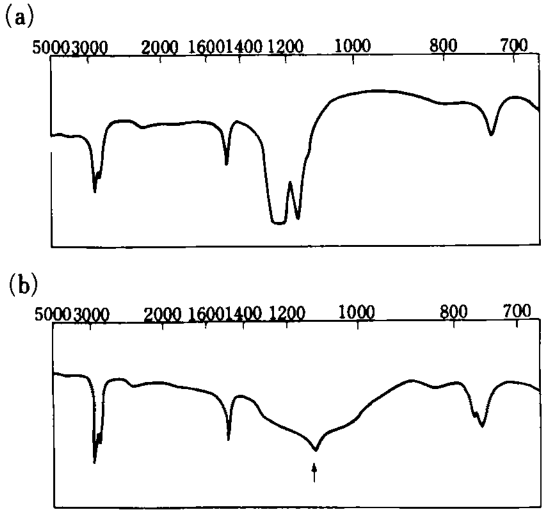

Fig. 10. IR spectra of soluble (a) and insoluble (b) parts in hot xylene.

$2\theta = 18°$, due to the crystals of polytetrafluoroethylene, was observed. There is no peak at 16° which would be due to the amorphous region of polytetrafluoroethylene. The intensity of the diffraction peak at 18° increases with grafting yield. These results coincide with those of IR measurements. This is the first case in which grafted copolymers can be crystallized in the course of grafting.

Solubility of Grafted Copolymers

The polyethylene used in this experiment was soluble in xylene at 110°C. An attempt was made to extract polyethylene from the crude grafted copolymers with the result shown in Fig. 9. Up to 150% grafting, the soluble part in xylene decreases linearly with increasing grafting.

IR measurements were made on both the extracted and residue parts. The results are shown in Fig. 10. For the insoluble part, the amount of polytetrafluoroethylene was much higher than for the soluble part, and furthermore the absorption band at 730 cm^{-1} disappeared completeely. This suggests that the chain length of tetrafluoroethylene in the insoluble part is too short for polyethylene to be crystallized under such conditions. This was also confirmed by X-ray diffraction of the insoluble part, as shown in Fig. 11.

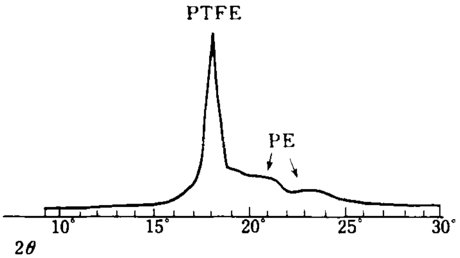

Fig. 11. X-Ray diffraction pattern of the insoluble part of grafted copolymer in hot xylene.

On the other hand a very strong broad absorption band at 1110 cm^{-1} in the soluble part was observed along with the usual polyethylene bands. The absorption band may be due to the structure in the branching position; however, the chain length of the grafted polytetrafluoroethylene may be short since the grafted copolymers can be dissolved in hot xylene.

Most of trapped radicals may therefore be consumed by the formation of short branched polymers and only residual radicals can grow to long polymer chains. This is also strongly suggested by the ESR measurement made during grafting. The details are described in another paper [3].

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