

Copolymerizations Initiated by Mechano-Radicals on Particle Surfaces of Poly(tetrafluoroethylene)

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Synopsis

Mechanical fracture of solid poly(tetrafluoroethylene) (PTFE) produces main-chain scissions of the polymer, and free radicals, called mechano-radicals, are trapped on fresh surfaces generated by the fracture. These radical conversions were verified by ESR observation when several monomers—methylmethacrylate, vinylacetate, and ethylene—were brought into contact with these mechano-radical, and the copolymerizations of PTFE with these monomers were demonstrated. It was found that a new surface property, wettability of water, was added to the solid PTFE by the copolymerization with vinyl acetate, although the bulk nature of PTFE was not changed.

INTRODUCTION

It has been established by various researchers¹⁻⁶ that mechanical action, such as fracture or large-scale deformation, applied to solid polymers produces main-chain scissions of polymers to produce free radicals. By ball milling of solid polymers at 77°K, mechano-radicals⁷ were formed and stabilized, and also polymer flakes were fractured into fine powder. This fact means that both fresh surfaces and mechano-radicals were simultaneously produced by the milling. Thus, it is reasonable to assume that the mechano-radicals were formed and stabilized on the fresh surface. If so, copolymerization is probably initiated by the mechano-radicals, which are the living polymers formed on the fresh surface, and block copolymers may be selectively produced when some monomers are accessible to the mechano-radicals. It is interesting to verify experimentally whether the copolymerization really proceeds. The investigation was carried out on the poly(tetrafluoroethylene) (PTFE) mechano-radical, and the copolymerizations of PTFE with methyl methacrylate, vinyl acetate and ethylene were experimentally proved. By this surface copolymerization, the surface nature of PTFE was exclusively changed in spite of the fact that the bulk physical properties of PTFE were not.

EXPERIMENTAL

Materials

Samples. The poly(tetrafluoroethylene) (PTFE) used in this experiment was a powder sample produced by Asahi Glass Co.

Monomers. Methyl methacrylate (MMA) and vinyl acetate (VAc) monomers made by Nakarai Chemical Co. were freed from inhibitors by washing with sodium hydroxide solution and water, dried over anhydrous calcium oxide, and distilled under reduced pressure in nitrogen atmosphere. The samples were

introduced into the ampoule attached to the ball mill immediately after the purification. Ethylene monomer (Toshiba Co. purity 99.5%) was freed from impurity gases (mainly oxygen) by the freeze-pump-thaw method.

Production of Mechano-Radicals. PTFE mechano-radicals were produced by ball milling⁷ combined with the special ampoule described below. PTFE powder was milled under vacuum of 10^{-4} torr at 77°K.

Special Ampoule for the Copolymerization. A special ampoule, shown in Figure 1, was designed for copolymerization initiated by the mechano-radicals. This ampoule has two arms. Arm A is for evacuation before production of the mechano-radicals. Arm B, having a breakable seal, connects the tube containing a reactant. In Figure 1 arm A has been sealed off before the milling, and the crushed polymer powder is at the bottom of the ESR sample tube, which is cooled with liquid nitrogen in a Dewar flask. The reactant in the evacuated vessel is transferred to the ESR sample tube by breaking the seal in the connecting arm B. In this way reactant vapor comes into contact with the mechano-radicals at low temperature, 77°K; temperatures of the sample after the contact can be controlled at any temperature above 77°K.

Copolymerization Procedures

Postpolymerization Method. After the PTFE mechano-radicals have been produced in the vacuum and the sample is placed at the bottom of the ESR sample tube, the sample is brought into contact with the reactant monomer by breaking the seal after crushing. The temperature of the sample in contact with the monomer is raised, if necessary, to accelerate the reaction with the monomer after contact.

Simultaneous Polymerization Method. Before milling, the reactant monomer has been introduced into the evacuated ball-mill branch through arm B and frozen together with the polymer powder. The polymer powder has been covered with the frozen layer of the reactant monomer by this procedure. The

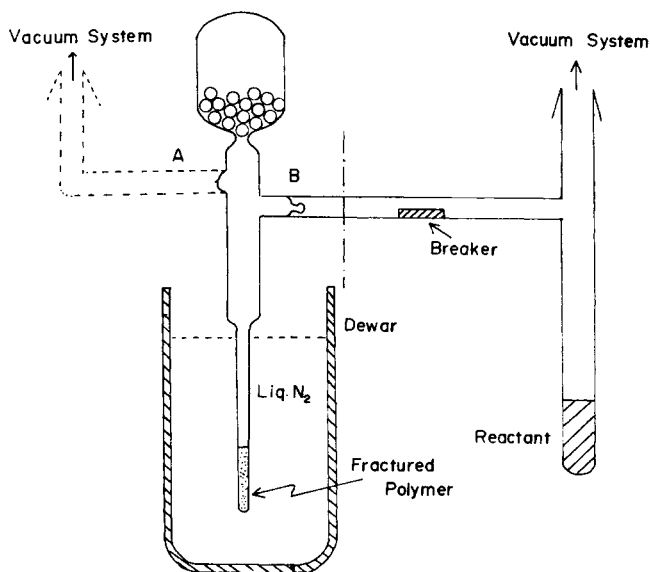


Fig. 1. Ampoule specially designed for copolymerization initiated by mechano-radicals.

milling of the monomer-covered PTFE is carried out at 77°K. By this method both the polymer and the monomer solid are simultaneously fractured.

ESR and IR Spectra

A PE-3X ESR spectrometer made by JEOL Co. with 100 kHz modulation was used for ESR observation. An IR spectrum was obtained by a Hitachi EPI-G 2 grating infrared spectrometer.

RESULTS AND DISCUSSION

Copolymerization of Methyl Methacrylate Initiated by PTFE Mechano-Radical

ESR spectra of the sample in contact with MMA monomer by the postpolymerization method were observed at 77°K after each heat treatment. The observed spectrum, shown in Figure 2(a), before the heat treatment is same as that of the PTFE mechano-radicals.⁷ The sample was heat treated at 273°K for 1 and 5 min (ESR spectra Figs. 2(b) and 2(c), respectively). The line shape of spectrum (c) is nearly same as the well-known spectrum⁸ of the PMMA

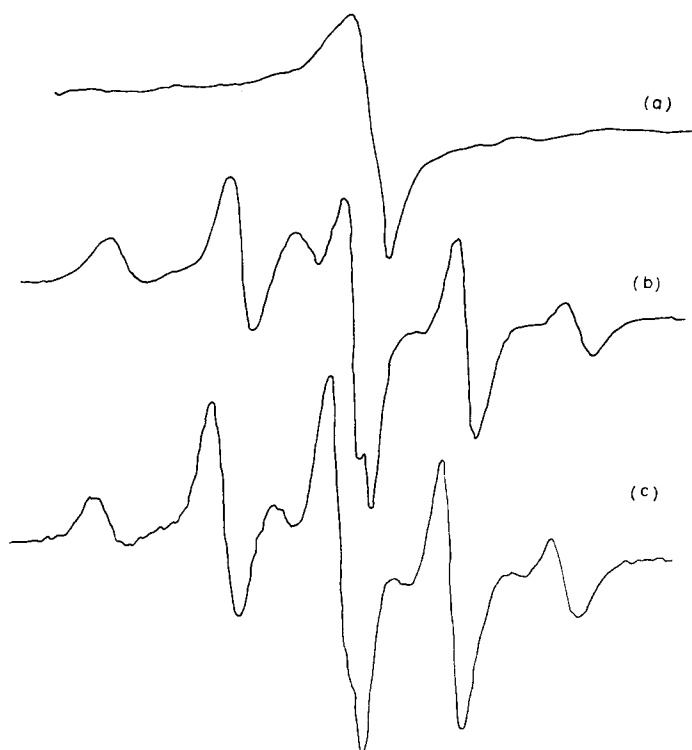
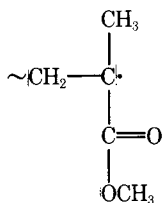


Fig. 2. ESR spectra observed at 77°K by postpolymerization with MMA: (a) spectrum from PTFE mechano-radical obtained after contact of MMA at 77°K; no heat treatment; (b) observed at 77°K after heat treatment at 273°K for 1 min; (c) observed at 77°K after heat treatment at 273°K for 5 min.

propagating radical



Since a change in the spectrum from the PTFE mechano-radicals into the PMMA propagating radicals is caused by the heat treatment, the PMMA propagating radical is presumably formed from the PTFE mechano-radical by the warming.

On the other hand, the ESR spectrum observed at 77°K after the simultaneous polymerization at 77°K is shown in Figure 3. The spectrum is identical to that of the PMMA propagating radical and has no component from the PTFE mechano-radical, as indicated by the absence of the wing peaks characterizing the PTFE spectrum at 77°K.⁷ It is known that mechano-radicals are not produced by mechanical destruction of solids consisting of low molecular weight compounds.⁶ Accordingly, PMMA propagating radicals produced by the simultaneous polymerization are not initiated by a direct mechanical action but by the PTFE mechano-radicals. It was found that the mechano-radicals are formed and trapped on fresh surfaces produced by the milling.⁹ In the simultaneous polymerization, the PTFE powder is covered with the frozen MMA, and therefore the PTFE mechano-radical may easily attack a MMA monomer nearby. Polymerization may then propagate by successive additions of MMA monomers. In the postpolymerization, it is less probable that a MMA monomer comes into the neighborhood of a PTFE mechano-radical and also that the monomers are successively supplied to a trapping site of the mechano-radical at 77°K. Consequently, diffusion of MMA monomers is needed for contact with the PTFE mechano-radical in order to lead to polymerization. Accordingly, no polymerization of MMA was initiated by the mechano-radical until the sample was warmed to temperatures above the melting point of MMA.

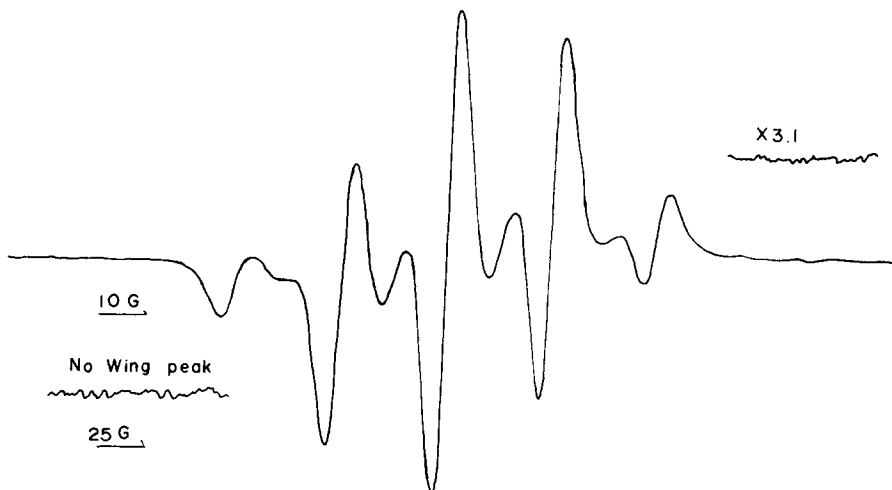


Fig. 3. ESR spectrum observed at 77°K after simultaneous polymerization.

Experimental Evidence of Copolymerization

After complete conversion of the PTFE mechano-radical to the PMMA radical had been checked by ESR, the radicals in the sample were thoroughly annihilated by heat treatment. The sample was then washed with a large amount of hot benzene in order to remove excess MMA monomers and PMMA homopolymers. The washed sample was dried under vacuum at room temperature. An IR spectrum from the dried sample free from either excess monomers or homopolymers was obtained by the KBr pellet method at room temperature. The IR spectrum of the sample is shown by the dotted line in Figure 4(c). In the same figure spectra of both PTFE and PMMA are shown for comparison. Apparently, the characteristic peaks of C=O (1735 cm^{-1}) and of CH₃ (2960 cm^{-1}) of PMMA appear in the spectrum from the washed sample, while the intense and broad band ($1100\text{--}1400\text{ cm}^{-1}$) in the spectrum is assigned to the CF. The former two peaks are not observed in the spectrum of PTFE, and no band near 1300 cm^{-1} is detected from PMMA homopolymer. Therefore, such a comparison of the IR spectra of these three samples provides experimental evidence for the copolymerization of MMA to PTFE. The copolymerization is also experimentally supported by the ESR spectra from the washed sample.¹⁰ Thus, one is led to conclude that the copolymerization of MMA to matrix PTFE is initiated by the PTFE mechano-radicals on the fresh surface.

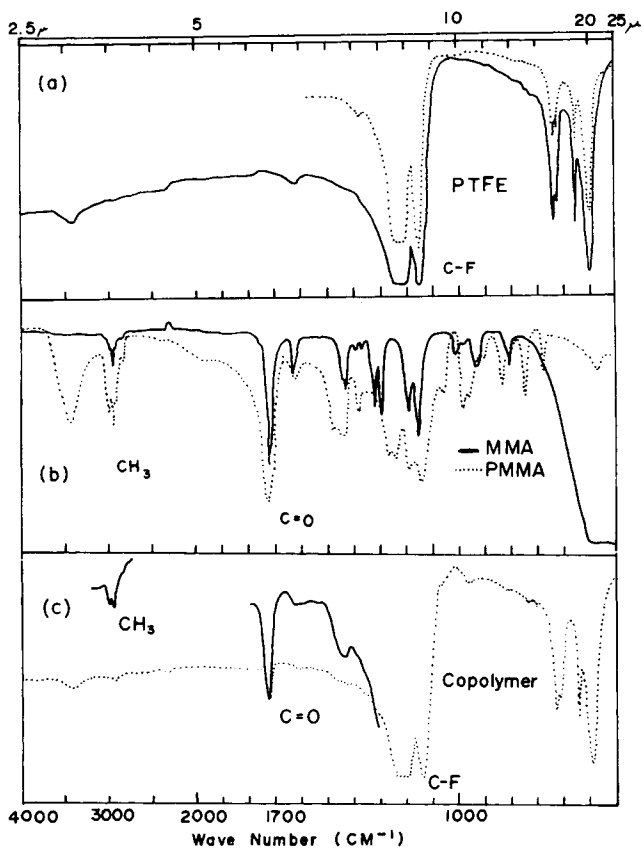


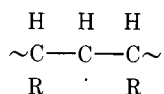
Fig. 4. IR spectra: (a) PTFE; (b) MMA and PMMA; (c) spectrum from washed sample.

Effect of Oxygen to Copolymerization

The sample in which a fraction of the PTFE mechano-radicals had been converted to the PMMA radicals by the short heat treatment was brought into contact with air at 77°K. The spectrum observed at 77°K after air contact is shown in Figure 5. The spectrum apparently is a superposition of the asymmetric component in the center, which is attributed to a peroxy radical, and the other component, marked by arrows, which corresponds to the characteristic spectrum of the PMMA propagating radical. This result demonstrates that oxygen reacts exclusively with the PTFE mechano-radicals even at 77°K to form peroxy radicals. After the formation of the PTFE peroxy radicals, no conversion to the PMMA propagating radicals was observed by the heat treatment in the presence of air at 273°K. This fact indicates that the copolymerization of MMA is inhibited by oxygen.

Copolymerization of Vinyl Acetate (VAc)

An ESR spectrum obtained at 77°K by simultaneous polymerization at 77°K is shown in Figure 6. The spectrum in no way resembles that of the PTFE mechano-radical, but is a quartet. Since the reported spectrum of the poly(vinyl acetate) chain radical



where R is —OCOCH₃, is not a quartet,^{11,12} the radical species produced from the VAc is not the chain radical. It is reasonable to assume that the quartet is ascribed to the PVAc propagating radical

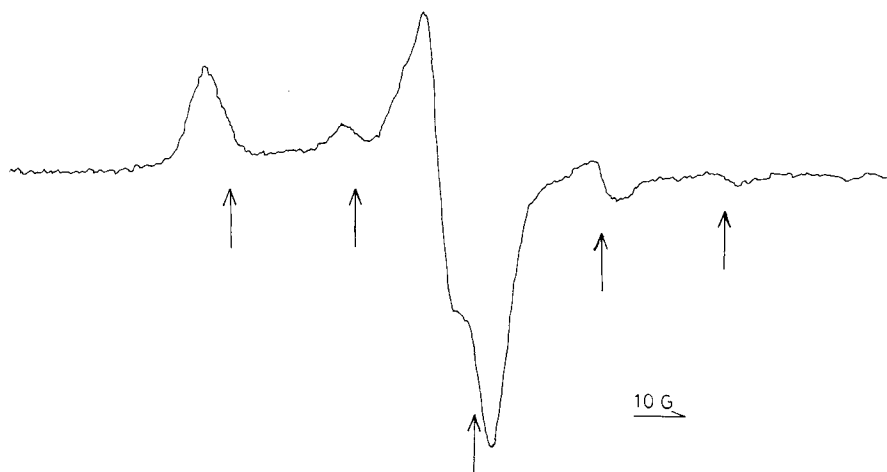


Fig. 5. ESR spectrum observed at 77°K after air contact. Arrows indicate peaks corresponding to the major peaks of the PMMA spectrum.

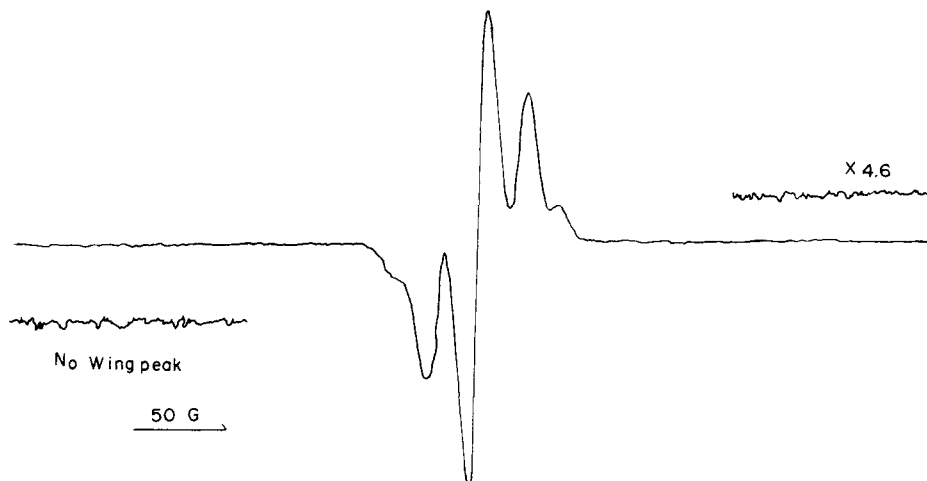


Fig. 6. ESR spectrum observed at 77°K after simultaneous polymerization with vinyl acetate at 77°K.

Because no component other than PTFE and VAc exist in the system, the quartet, whose relative intensity is 1:3:3:1, is theoretically expected from the propagating radical of PVAc based on the equal coupling of the unpaired electron with the three protons. Equal coupling is derived in the case of rapid rotation, for the average value of the β -proton coupling is nearly equal to that of the coupling of the two α -protons.¹³ Such rapid rotation is only probable for the propagating radical because of the open end, while it is less probable for the chain radicals trapped in the solid matrix of PVAc.

IR Spectra

Both the excess VAc monomers and the PVAc homopolymer were removed from the sample by the procedure described above, and the IR spectrum was observed from the sample. As shown in Figure 7, the small peak at 1735 nm^{-1} assigned to the C=O group appears in the spectrum, while the major peak of the spectrum is the C—F band. Thus, PVAc is copolymerized with the PTFE of the matrix. It is worth mentioning that the wettability of the PVAc-copolymerized PTFE is much increased. Since PTFE is actually not wettable with water, this wettability of the sample indicates that the surface nature of the sample is determined by PVAc in spite of the fact that the bulk properties of the sample are those of PTFE.

Copolymerization of Ethylene

No conversion was observed after the contact of the PTFE mechano-radicals with ethylene by the postpolymerization at 77°K, which is lower than the melting point of ethylene. By heat treatment at 113°K for 51 min, a change of the PTFE spectrum to a quintet was observed, as shown in Figure 8. On the other hand, a clear quintet, shown in Figure 9, was observed at 77°K upon simultaneous polymerization. This quintet, having binominal relative intensity, is identical to that shown in Figure 7(c). Since the quintet is not from the PTFE mechano-radicals and no mechano-radical is produced by the fracture of the organic

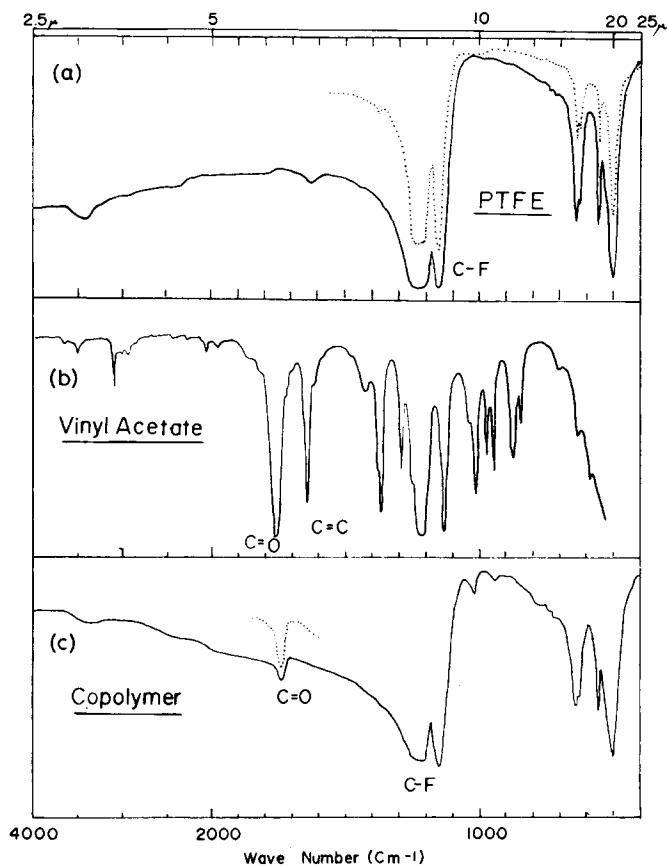
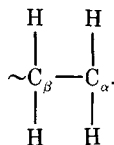


Fig. 7. IR spectra: (a) PTFE; (b) vinyl acetate; (c) spectrum from washed sample.

solids of low molecular weight compounds,⁶ the quintet is considered to originate from the propagating radical



of ethylene polymerization initiated by the PTFE mechano-radicals. By assuming rapid rotation about the $\text{C}_{\alpha}\text{-C}_{\beta}$ axis, the two β -protons become equivalent to give a coupling constant of $23G$, which is nearly same as that of the two α -protons.¹³ Consequently, the quintet with the binominal relative intensity is derived from this assumption, and this theoretical spectrum agrees very well with the observed quintet, as shown in Figure 10. It is striking that ethylene is polymerized at such a low temperature as 77°K in the case of simultaneous polymerization.

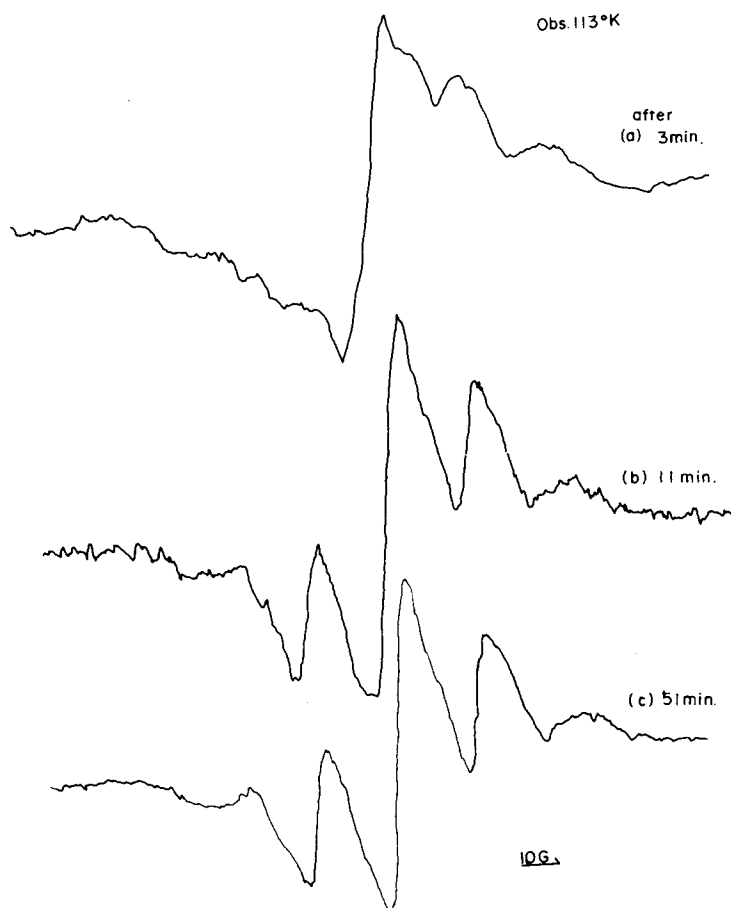


Fig. 8. ESR spectra observed at 113°K after postpolymerization of ethylene at 77°K: (a) spectrum after heat treatment at 113°K for 3 min; (b) spectrum after the 11 min of treatment; (c) spectrum after 51 min of treatment.

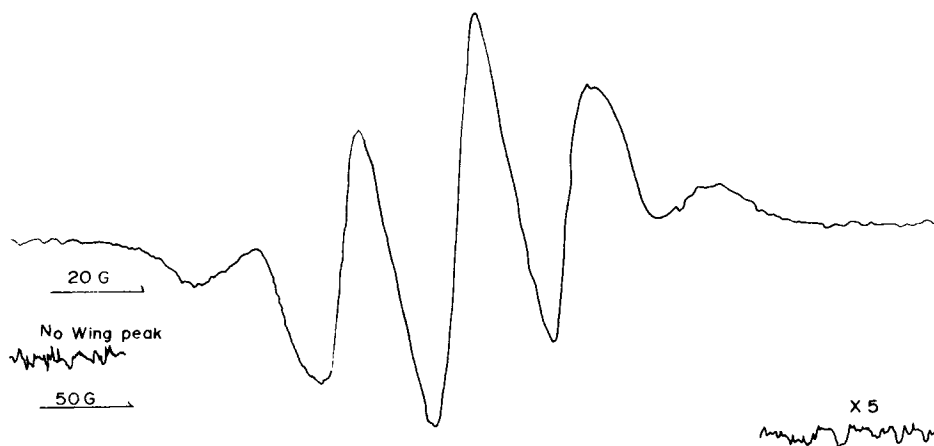


Fig. 9. Spectrum observed at 77°K after simultaneous polymerization of ethylene at 77°K.

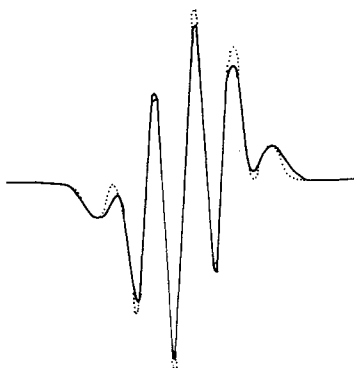


Fig. 10. Comparison between simulated spectrum (dotted line) and observed one (solid line) of the ethylene radical.

CONCLUSIONS

It was concluded from both the ESR and the IR measurements that the surface copolymerizations of PTFE with various kinds of monomers, such as methyl methacrylate, vinyl acetate, and ethylene, were initiated by the PTFE mechano-radicals at 77°K by simultaneous polymerization and at a temperature above the melting point of each substance by postpolymerization. It is reasonable to assume that this copolymerization occurred on the fresh surfaces on which the PTFE mechano-radicals had been formed by the mechanical destruction and been trapped there. A remarkable change in the surface nature, such as increase in water wettability, was found for the PTFE copolymerized with VAc.

The authors would like to express their thanks to the Asahi Garasu Kogyo Gijutsu Shoreikai, which supplied financial assistance for this research.

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Received June 15, 1977

Revised July 7, 1977