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Description	

# **Rheological Characterization on Thermal Degradation of Ethylene-Tetrafluoroethylene Copolymer**

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**Abstract**

Oscillatory shear modulus in the molten state is evaluated carefully considering the rheological change during the measurement at high temperature for ethylene-tetrafluoroethylene copolymer (ETFE). The results provide the information on the molecular weight distribution as well as the degradation behaviors, which is affected by the environmental condition, *i.e.*, the existence of oxygen. Even under a nitrogen atmosphere, ETFE is thermally unstable in the molten state; ETFE shows random chain scission reaction without crosslinking. The steady-state shear compliance  $J_e^0$ , which depends on the molecular weight distribution greatly, is not changed during the chain scission. It suggests that the chain scission occurs with keeping the molecular weight distribution. Considering the classical theory on the random scission reaction, the experimental result indicates that  $M_w/M_n$  of the initial ETFE sample, prior to the exposure to thermal history, is closed to 2. In contrast, under air condition, ETFE shows crosslinking reaction even in the cone-and-plate rheometer. The degree of crosslinking is quantitatively estimated by the plateau modulus  $G'_{plateau}$  in the low frequency region. The result suggests that the crosslinking occurs as a first order reaction.

**Keywords:**

Ethylene-tetrafluoroethylene copolymer; rheological properties; molecular weight distribution; degradation

## 1. Introduction

The alternative copolymer of ethylene and tetrafluoroethylene (ETFE) is one of the most important melt-processable fluoropolymers. Because of its excellent chemical and thermal stability, electrical properties and surface properties, ETFE is used in various industrial applications such as lining of a chemical plant, highly durable sheath for electrical wire, photovoltaic module, and release film for semiconductor encapsulation process [1-4].

The structure and properties in the solid state for ETFE were studied intensively by Tanigami et al. [5,6], Arai et al. [4,7,8], and Funaki et al. [9,10]. They revealed the crystalline structure and the phase transition in detail as well as the relation with its mechanical properties.

Chen et al. investigated the capillary extrusion properties as compared with those of polyethylene and perfluorinated polymers [11]. They reported that polymers having a large amount of fluorine content tend to exhibit the flow instability even at low shear stress. Furthermore, the swell ratio decreases and the flow activation energy increases with increasing the fluorine content.

The rheological measurements in the molten state are, however, not so easy for ETFE, because ETFE shows the complex melting behavior which is affected by applied thermal history [12]. The high melting point is another problem because samples show rheological change during measurements due to thermal degradation. However, the rheological properties are significantly important to understand not only processability but also molecular characterization, since the excellent anti-solvent property of ETFE makes it difficult to evaluate its solution properties. Consequently, even the exact information on the molecular weight and its distribution is barely obtained by a

conventional method like size-exclusion chromatography.

Tuminelo et al. developed the characterization technique of molecular weight distributions by rheological properties for insoluble fluoropolymers including ETFE [13-15]. They found that the ratio of weight-average molecular weight  $M_w$  to number-average molecular weight  $M_n$ , *i.e.*,  $M_w/M_n$ , of ETFE is approximately 2.8. On the contrary, Chen et al. also evaluated the polydispersity from the viscoelastic properties using a similar method and concluded that a commercially available ETFE has a significantly broad molecular distribution ( $M_w/M_n > 10$ ). They concluded that the broad molecular weight distribution is responsible for good processability at melt processing [16]. Chu et al. developed a specific method employing a laser light scattering (LLS) technique to evaluate the molecular weight and its distribution for ETFE at ca. 250 °C. They found that ETFE shows significantly narrow molecular distribution *e.g.*,  $M_w/M_n \approx 1.4$  and  $M_z/M_w = 1.4 \sim 1.8$  [17-20].

The discrepancy on the molecular weight distribution of ETFE is a serious problem for the molecular design, and thus required to be solved. In this research, oscillatory shear modulus in the molten state is evaluated carefully considering the rheological change during the measurement at high temperature. The results provide the basic molecular characterization as well as the degradation behaviors of ETFE, which is affected by the environmental condition, *i.e.*, the existence of oxygen.

## **2. Experimental**

### **2-1. Material**

The polymer used in this study was a commercially available terpolymer comprising of ethylene, tetrafluoroethylene and 3,3,4,4,5,5,6,6,6-nonafluorohexene

(CH<sub>2</sub>CHC<sub>4</sub>F<sub>9</sub>; NFH), that was synthesized by a solution polymerization method using fluorinated hydrocarbon as a solvent [21]. The molar fraction in the polymer is Ethylene/Tetrafluoroethylene/NFH=44.6/54.5/0.9 mol%, which was analyzed by the molten-state <sup>19</sup>F nuclear magnetic resonance measurement and fluorine ultimate element analysis [22].

The melt flow rate is 11.8 [g/10 min] according to ASTM D3159 (297 °C, 49 N). It is found from the differential scanning calorimetric measurement that the melting point is 258.7 °C and the crystallization temperature is 238.7 °C at a scanning rate of 10 °C/min. The sample was melt-extruded to pellet form and molded into a flat sheet with ca. 500 μm thickness by a compression-molding machine at 280 °C. The sample sheets were kept under vacuum condition at room temperature in 16 hrs prior to the rheological measurements.

## 2-2. Measurements

The frequency dependence of the oscillatory shear modulus was measured by a cone-and-plate rheometer, (Anton Parr, MCR301) at 300 °C under a nitrogen atmosphere. The diameter of the cone and plate is 25 mm and the cone angle is 2 deg. The preheating time before the measurement was 5 min. In order to clarify the thermal stability, the measurements were performed without changing the sample. The angular frequency decreases from 314 s<sup>-1</sup> to 0.132 s<sup>-1</sup>, and then increases from 0.132 s<sup>-1</sup> to 314 s<sup>-1</sup>. The same procedure was applied to the sample for 10 cycles. The duration of the measurement for one cycle is approximately 20 min.

A similar measurement was also performed under air atmosphere. The measurements were carried out from  $314 \text{ s}^{-1}$  to  $0.0188 \text{ s}^{-1}$ , and then increases from  $0.0188 \text{ s}^{-1}$  to  $314 \text{ s}^{-1}$  for 5 cycles.

### 3. Results and discussion

#### 3-1. Rheological Change under Nitrogen

The frequency dependence of oscillatory shear modulus under a nitrogen atmosphere at  $300 \text{ }^\circ\text{C}$  is shown in Fig.1. It is found that the storage modulus  $G'$  and loss modulus  $G''$  are proportional to  $\omega^2$  and  $\omega$ , respectively in the low frequency region, demonstrating that the rheological terminal zone is observed. Therefore, the rheological parameters in the terminal zone, such as zero-shear viscosity  $\eta_0$ , steady-state shear compliance  $J_e^0$ , and weight-average relaxation time  $\tau_w$ , can be obtained from the following equations.

$$\eta_0 = \lim_{\omega \rightarrow 0} \frac{G''}{\omega} \quad (1)$$

$$J_e^0 = \lim_{\omega \rightarrow 0} \frac{G'}{G''^2} \quad (2)$$

$$\tau_w = \eta_0 J_e^0 \quad (3)$$

It is well known that  $\eta_0$  of a linear polymer is determined by the weight-average molecular weight  $M_w$  as follows;

$$\eta_0 \propto M_w^{3.4} \quad (M_w > 2M_e) \quad (4)$$

where  $M_e$  is the average molecular weight between entanglement couplings.

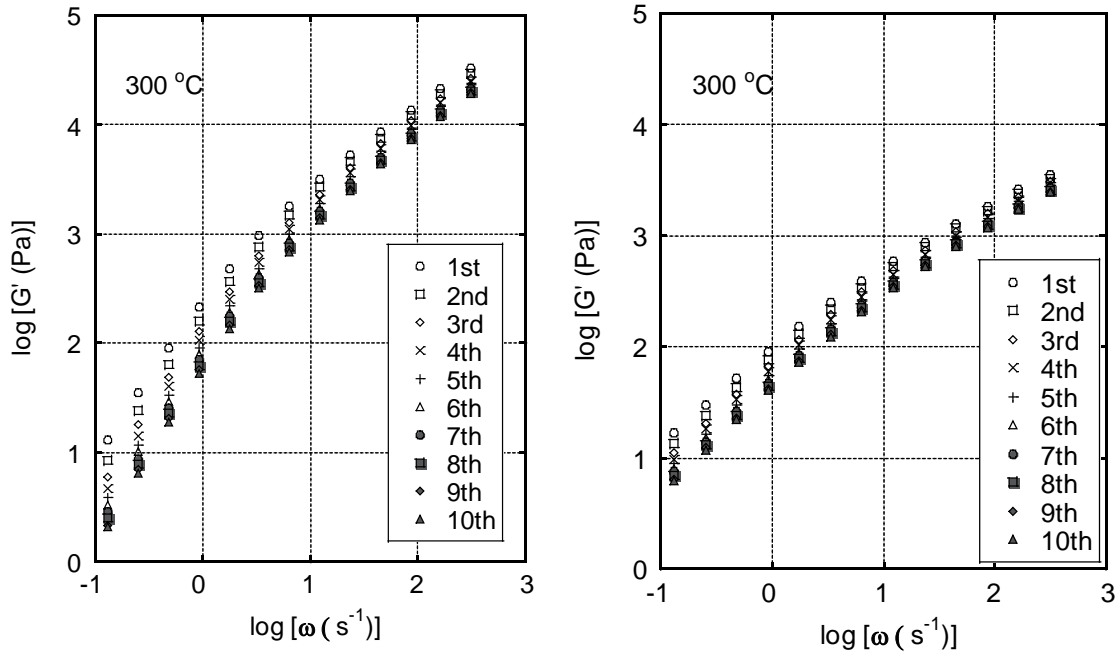


Fig.1 Frequency dependence of (a) shear storage modulus  $G'$  and (b) loss modulus  $G''$  for ETFE at 300 °C under a nitrogen atmosphere. The measurements were performed from  $314 \text{ s}^{-1}$  to  $0.132 \text{ s}^{-1}$ , and then increases from  $0.132 \text{ s}^{-1}$  to  $314 \text{ s}^{-1}$ , which was applied to the same sample for 10 cycles.

As seen in Fig. 1(b),  $\eta_0$  and thus  $M_w$  decrease with the residence time  $t$  in the rheometer by chain scission reaction, although the rheological change is not so obvious compared with polyethylene [23-25] owing to the high intrinsic bond dissociation energy of ETFE [26]. Here, the normalized  $M_w$ , *i.e.*,  $M_w(t)/M_w(0)$ , calculated from eq. 5 assuming  $M_w \gg M_e$  without generation of long-chain branches, is plotted as a function of the residence time  $t$  in the rheometer.



$$\frac{M_w(t)}{M_w(0)} = \left[ \frac{\eta_0(t)}{\eta_0(0)} \right]^{1/3.4} \quad (5)$$

As shown in Fig. 2, the normalized  $M_w$  of ETFE in an inert gas decreases monotonically, demonstrating that chain scission occurs.

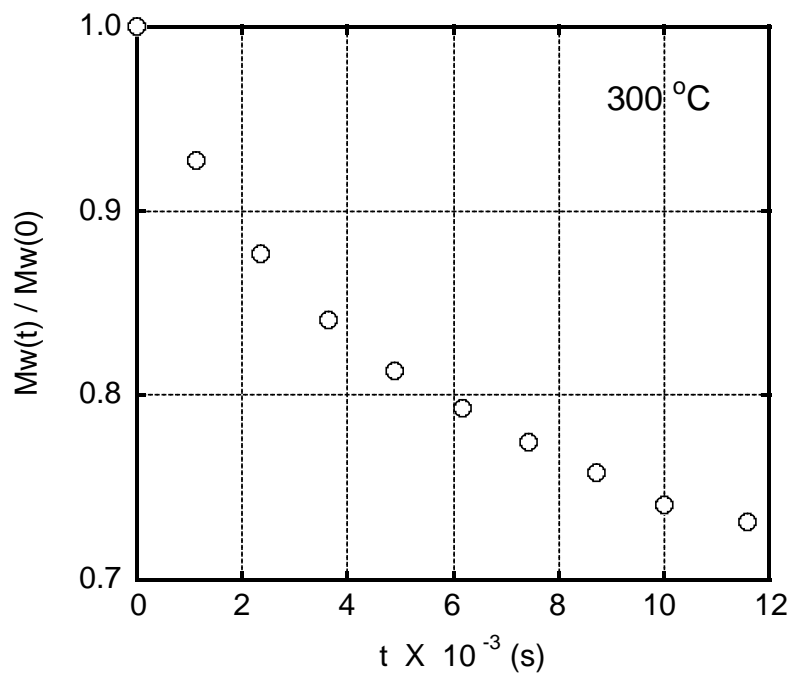


Fig.2 Residence time dependence of the normalized weight-average molecular weight  $M_w(t)/M_w(0)$ , calculated from the results in Figure 1.

Moreover,  $J_e^0$  is also evaluated as a function of the residence time. It is well known that  $J_e^0$  of a linear polymer is strongly sensitive to the polydispersity as shown in the following relation [27];

$$J_e^0 \propto \left( \frac{M_z}{M_w} \right)^{3.4-3.7} \quad (6)$$

The time variation of  $J_e^0$  is shown in Fig. 3. Apparently, the sample shows almost a constant value irrespective of the residence time in the rheometer. The result demonstrates that the molecular weight distribution does not change during the rheological measurement, although the chain scission reaction occurs. Moreover, this result indicates that long-chain branches are not generated at this experiment, because  $J_e^0$  is greatly enhanced by long-chain branches [27].

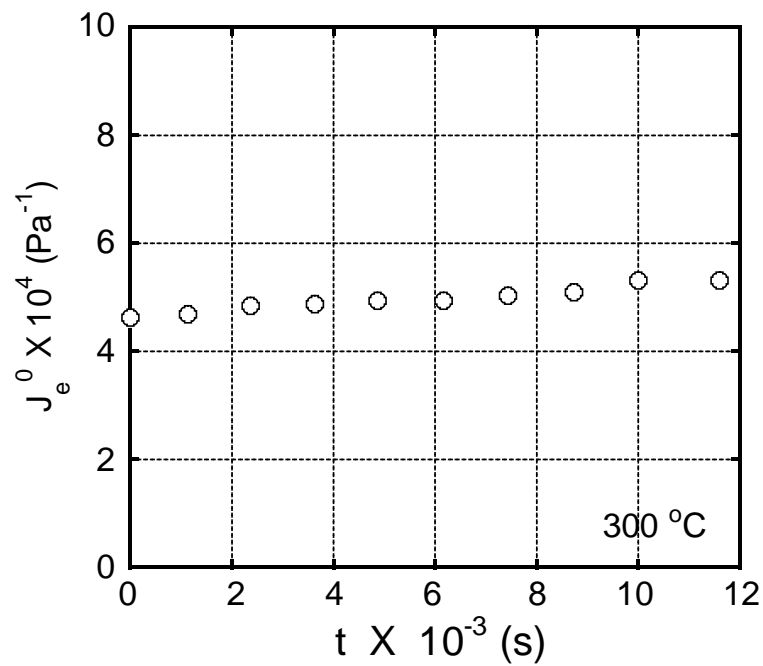


Fig.3 Residence time dependence of the steady-state shear compliance  $J_e^0$ , calculated from the results in Figure 1.

It has been well known that random chain scission results in  $M_w/M_n = 2$ , irrespective of the molecular weight distribution of a virgin sample [28]. Based on the classical theory on the random scission reaction [28], the present result indicates that  $M_w/M_n$  of the virgin sample prior to the rheological measurement is closed to 2. Although there have been a controversy on the molecular weight distribution of ETFE as mentioned in the introduction, this study reveals that a commercial ETFE has relatively narrow distribution of molecular weight.

### 3-2. Rheological Change under Air Condition

Fig. 4 shows the frequency dependence of oscillatory shear moduli for the sample in the air condition. As seen in the figure, the effect of thermal history on the rheological properties is significantly different from that under a nitrogen atmosphere even at the same temperature. Both moduli show plateau values in the low frequency region, which increase with the residence time. In contrast, the moduli in the high frequency region do not change, suggesting that the chain scission does not occur so much.

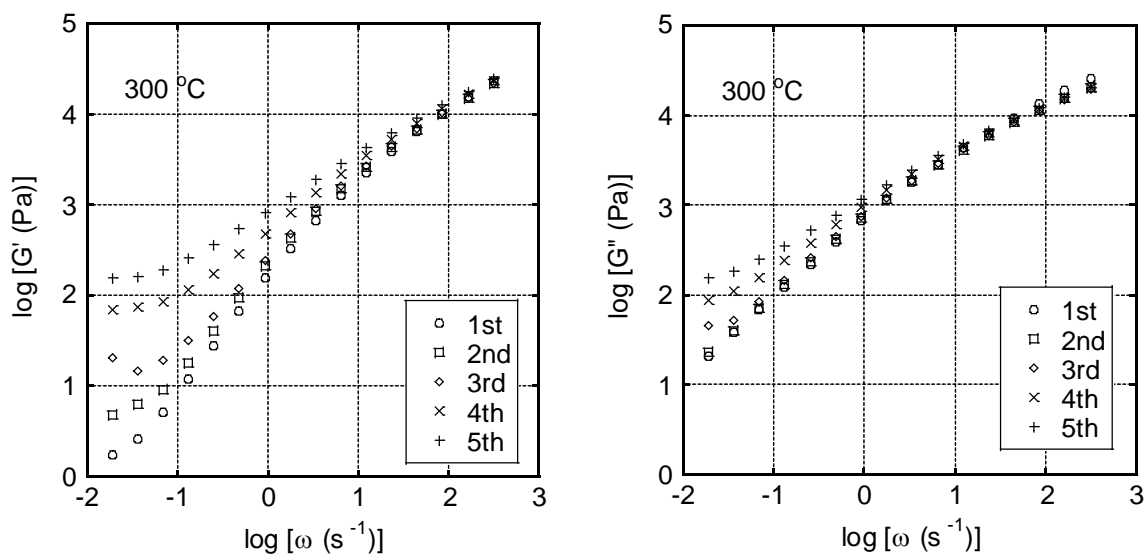


Fig.4 Frequency dependence of (a) shear storage modulus  $G'$  and (b) loss modulus  $G''$  for ETFE at 300 °C in air condition. The measurements were performed from 314 s<sup>-1</sup> to 0.132 s<sup>-1</sup>, and then increases from 0.132 s<sup>-1</sup> to 314 s<sup>-1</sup>, which was applied to the same sample for 5 cycles.

The plateau values of  $G'$ , *i.e.*,  $G'_{plateau}$ , are plotted against the residence time in Fig. 5. The plateau modulus is found to increase with the residence time greatly. The result demonstrates that the network structure appears in the sample during the measurements, suggesting that the reaction with oxygen gas provides the branching and/or crosslinking points.

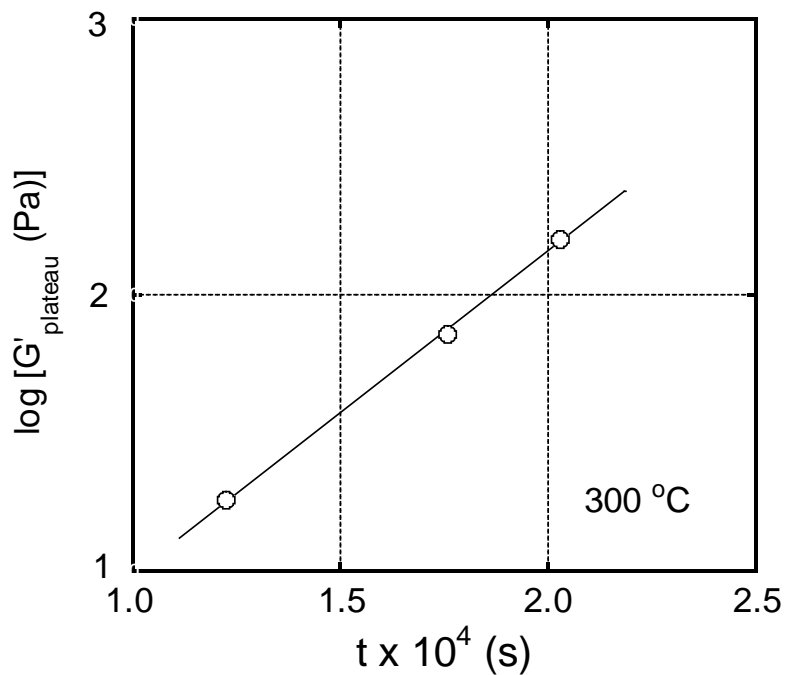


Fig.5 Residence time dependence of the plateau modulus in the low frequency region  $G'_{plateau}$  evaluated from Figure 4.

For a crosslinked polymer,  $G'_{plateau}$  is proportional to the density of crosslinking points  $\nu_e$ , which is expressed by the following classical rubber theory [29],

$$G'_{plateau} = \nu_e k_B T \quad (7)$$

where  $\nu_e$  is the crosslink density (mol/m<sup>3</sup>) and  $k_B$  is the Boltzmann constant.

As seen in Fig. 5, the plateau modulus, and thus the crosslinking points, increases exponentially with the residence time as follows;

$$\nu_e \propto \exp[k_1 t] \quad (8)$$

It indicates that the crosslinking occurs as a first-order reaction with a reaction rate of  $k_1$ . At the present condition, the reaction rate is calculated to be  $2.68 \times 10^{-4} \text{ s}^{-1}$ .

Considering the previous researches, the following degradation mechanism, illustrated in Fig.6, is predicted at the experimental temperature.

Random scission provides the radical species at first by breakage of main chains. The reaction must occur at CH<sub>2</sub>-CH<sub>2</sub> bond because of its low level of bond association energy [30]. The obtained terminal radical (I) leads to the generation of the intramolecular radical (II) by hydrogen abstraction from main chains. It was also reported that ETFE shows the HF elimination when it degrades at high temperature (> 250 °C) [31]. The C=C bond (III), which can react with the intramolecular radical (II), is generated by the HF elimination. Thus, crosslinked structure is formed due to the reactions between (II) and (III) and/or (II), although the reactions barely occur without

oxygen as demonstrated in this study. In presence of oxygen, the reaction between oxygen and (II) generates the hydroperoxide (V) and then the hydroxyl radical (VII) [32,33]. The hydroxyl radical (VII) greatly accelerates the generation of intramolecular radical (II) because of its marked reactivity. As a result, the intermolecular crosslinking reaction occurs dominantly under the oxygen. In addition, the reaction between (VI) and (III) can also generate the intermolecular crosslinking by C-O-C bond.

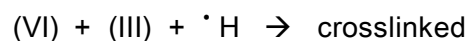
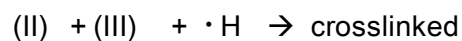
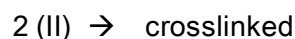
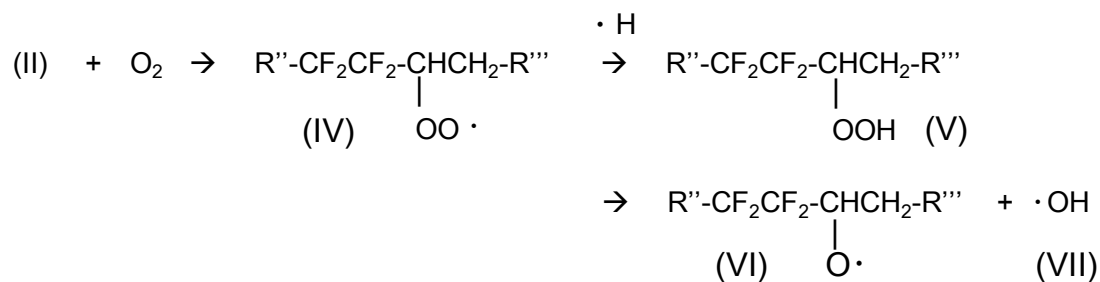
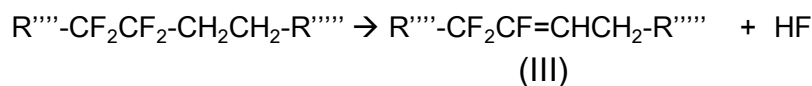
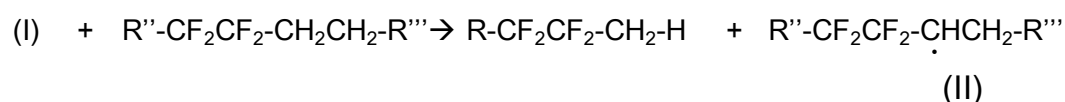
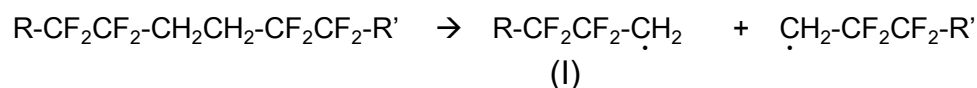


Fig.6 Degradation mechanism during the thermal treatment of ETFE at 300 °C

#### 4. Conclusion

The rheological properties in the molten state and their residence time dependence in the rheometer were evaluated employing a commercially available ETFE. It was found that rheological properties change with the time even under a nitrogen atmosphere, in which ETFE shows random chain scission reaction without crosslinking and/or branching reaction. Furthermore, the steady-state shear compliance  $J_e^0$  was unchanged during the measurements, suggesting that the molecular weight distribution is unchanged during the chain scission reaction. This result indicates that  $M_w/M_n$  of the initial ETFE sample, prior to the exposure to thermal history, is closed to 2.

Under air condition, on the contrary, ETFE shows crosslinking reaction even in the cone-and-plate rheometer. The degree of crosslinking was quantitatively estimated by the plateau modulus  $G'_{plateau}$  in the low frequency region. It was found that the crosslinking reaction, and thus the number of crosslink density, increase with the residence time exponentially, indicating the first-order reaction. The reaction rate at this experiment following was calculated to be  $2.68 \times 10^{-4} \text{ s}^{-1}$ .

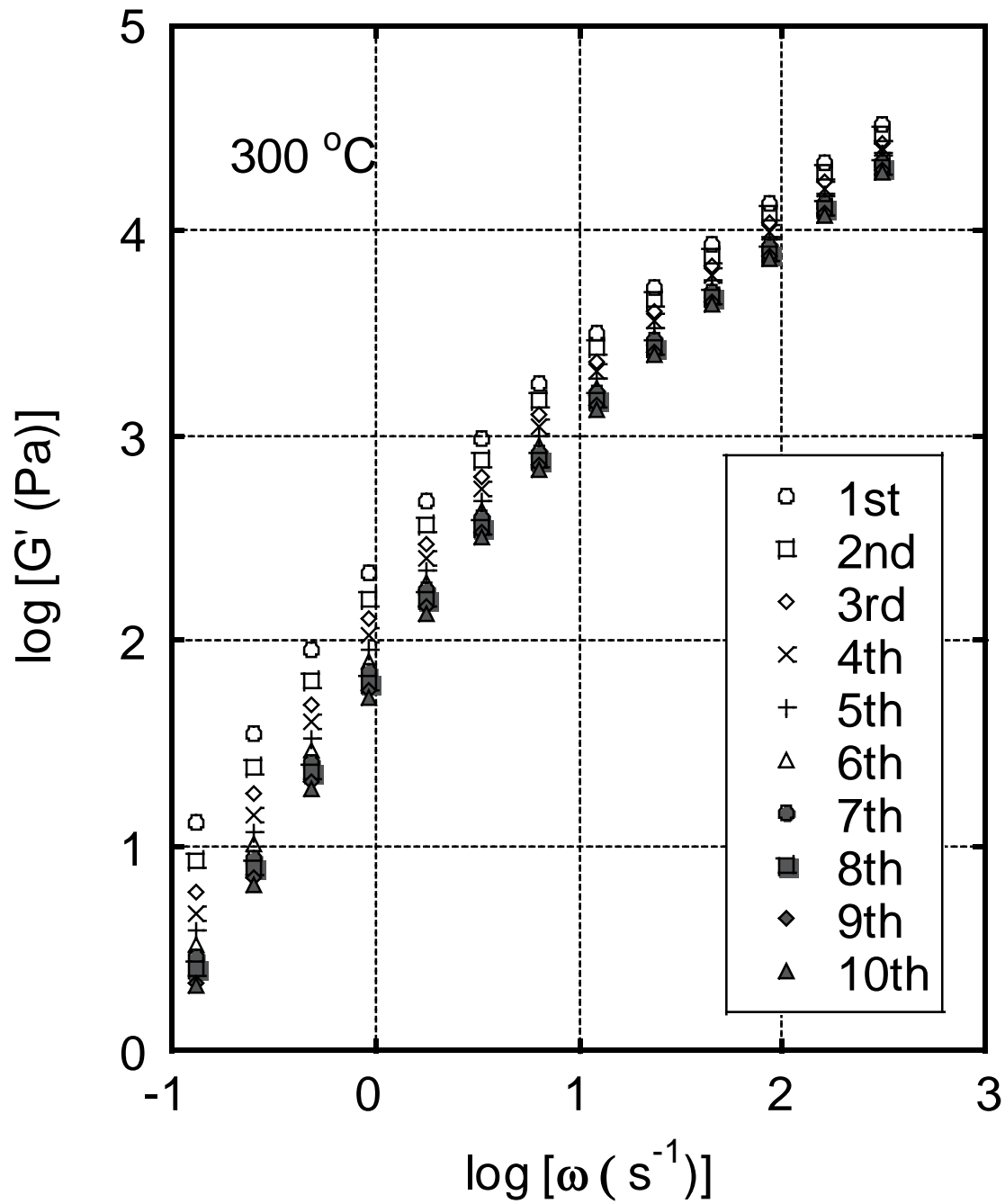
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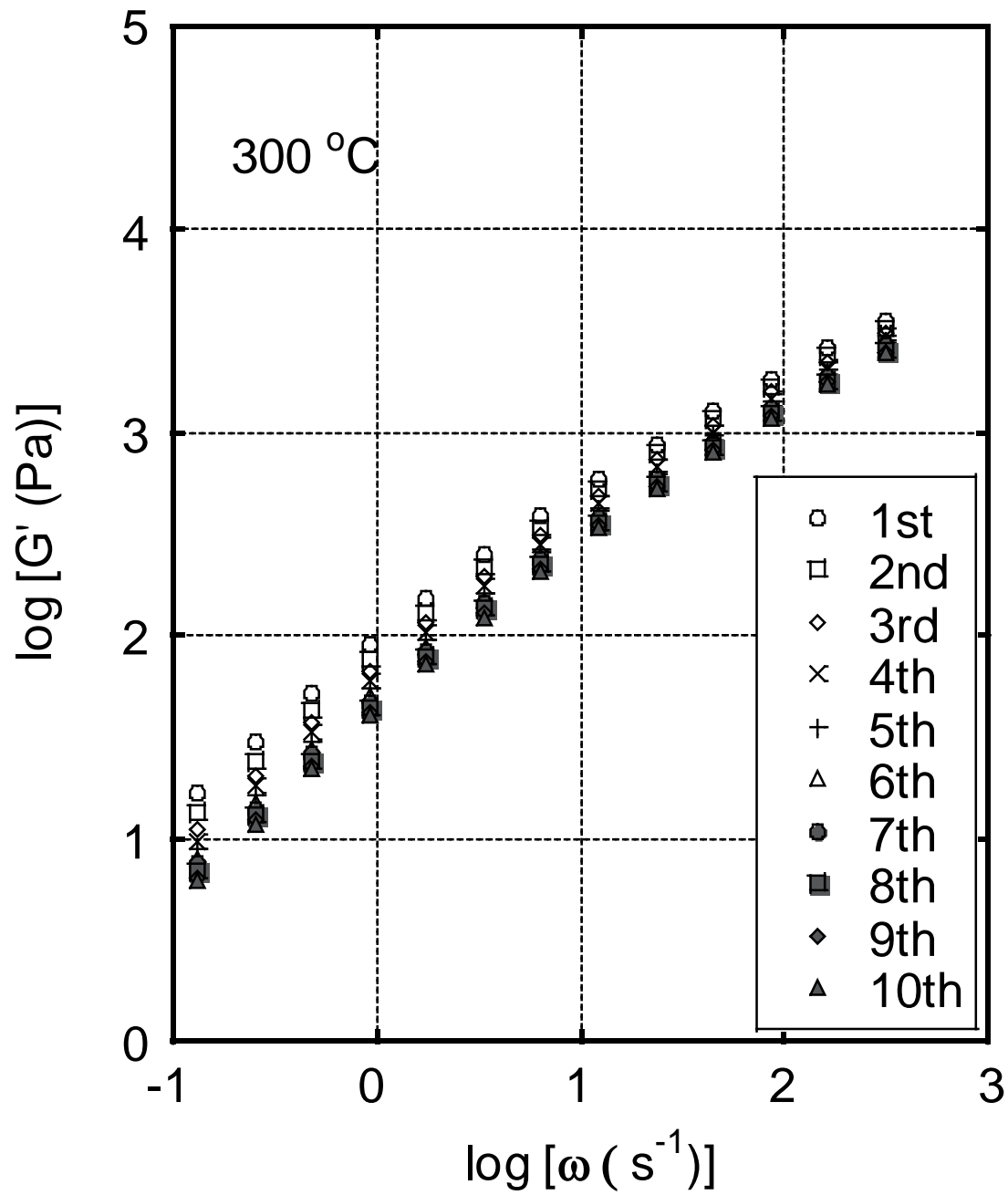
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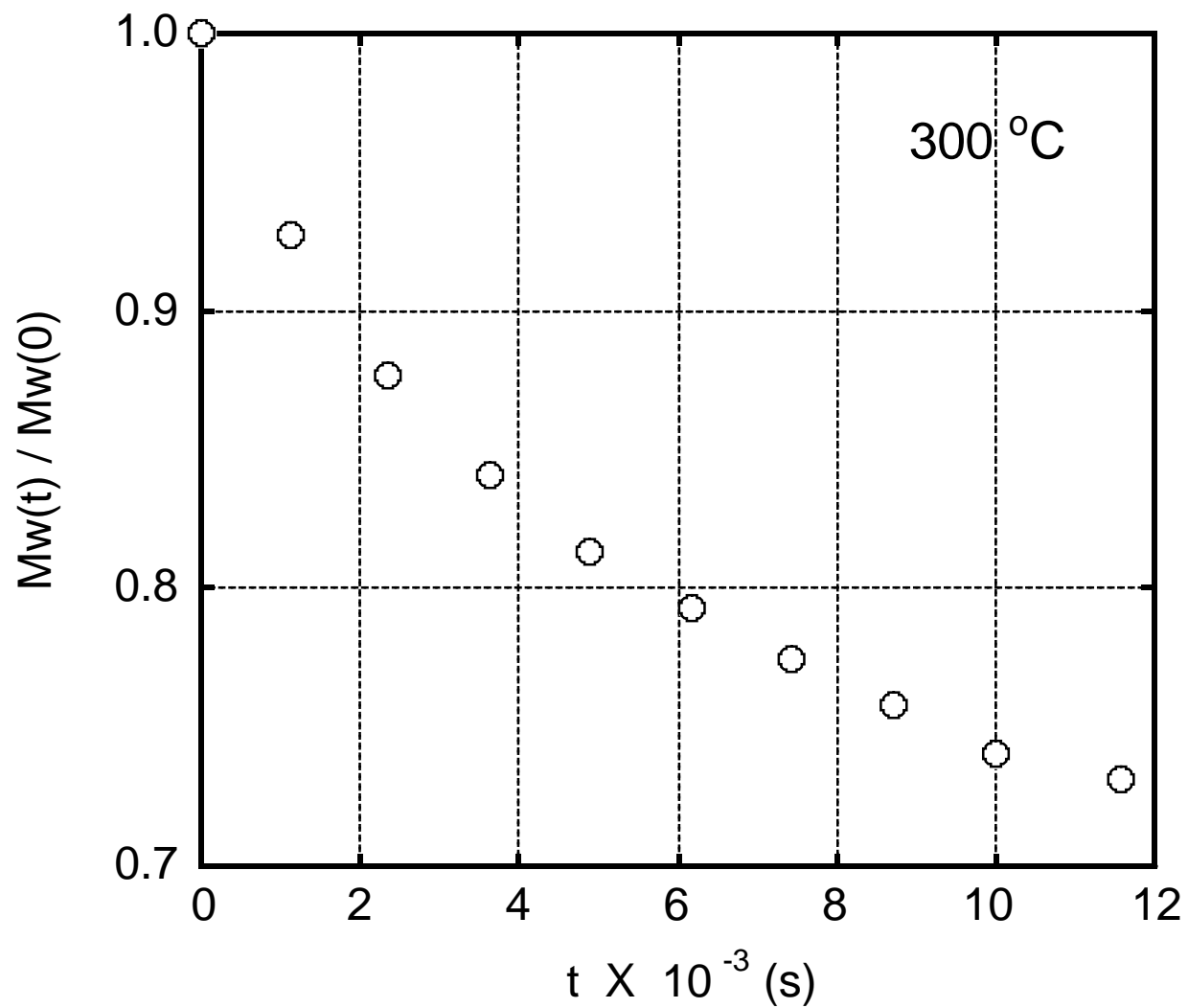
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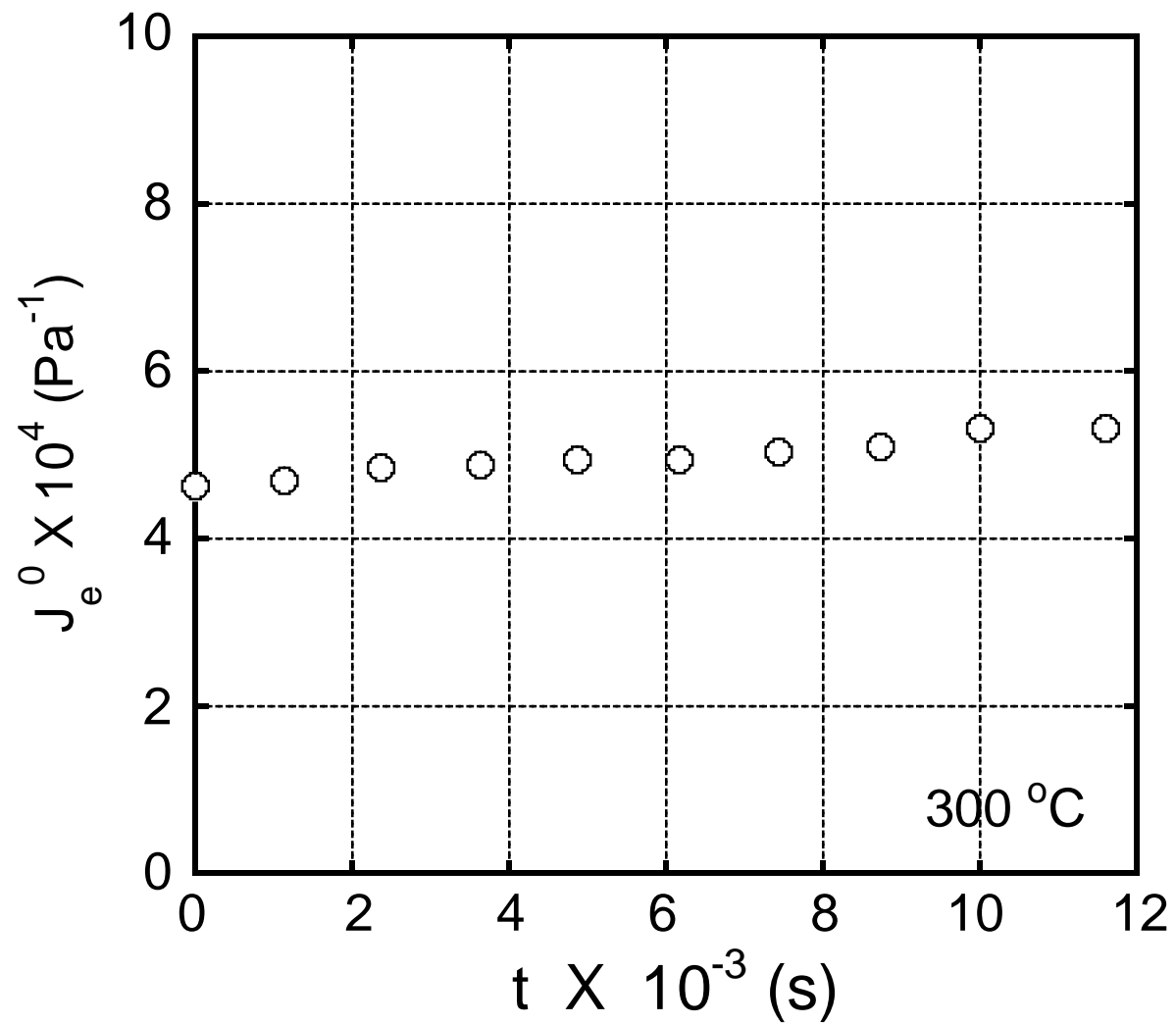
Kotera and Yamaguchi, Fig.1(a)



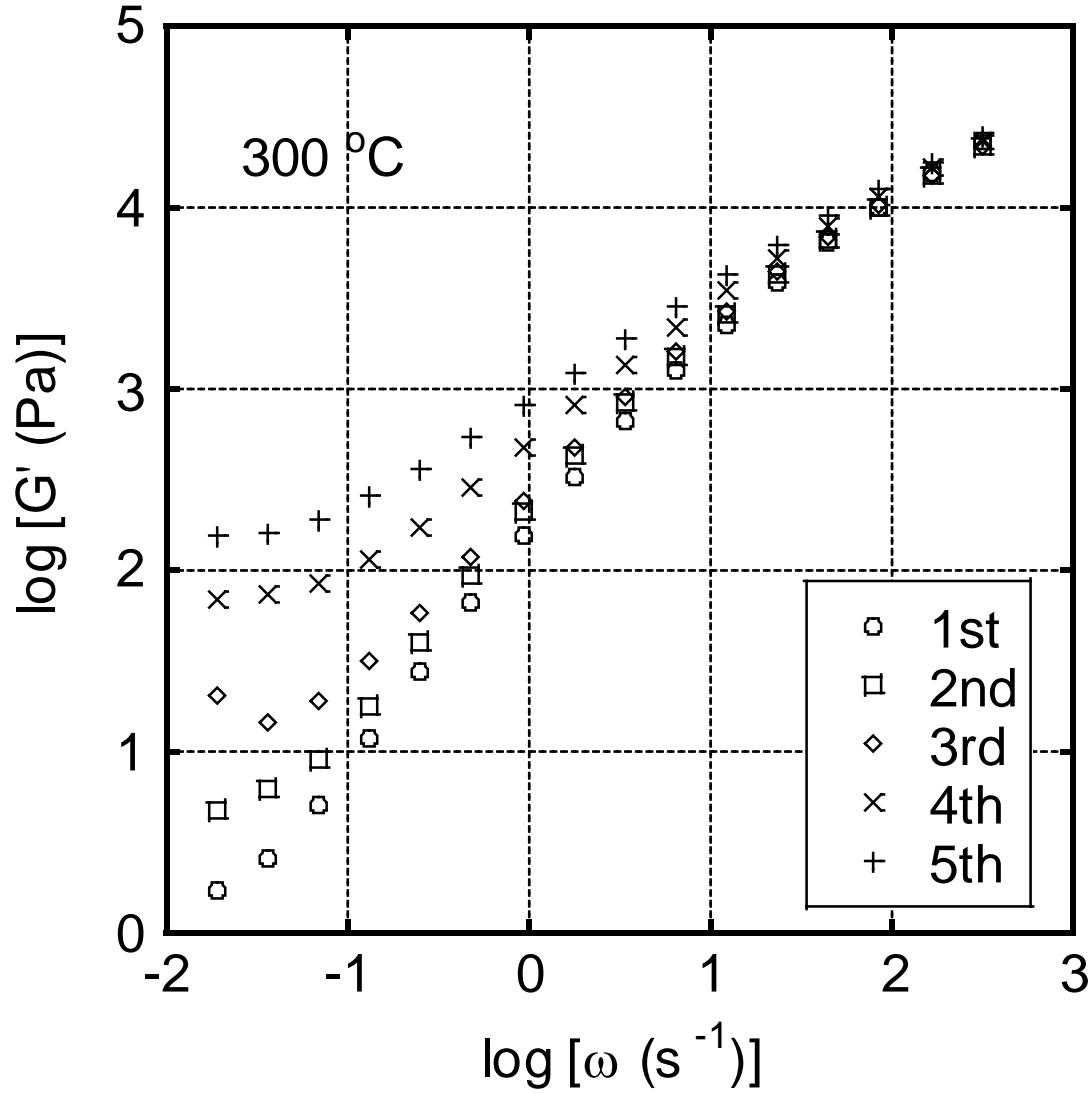
Kotera and Yamaguchi, Fig.1(b)



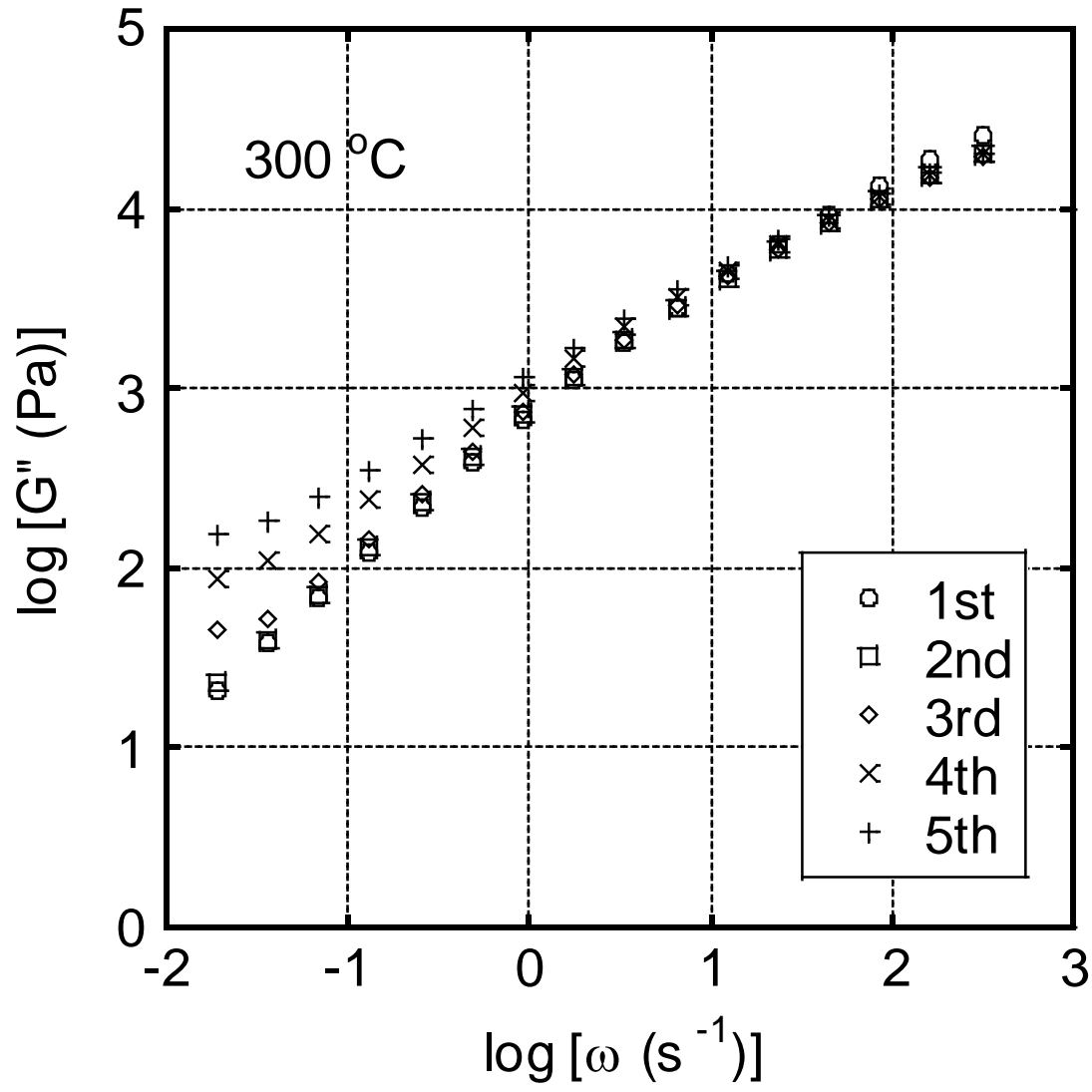
Kotera and Yamaguchi, Fig.2



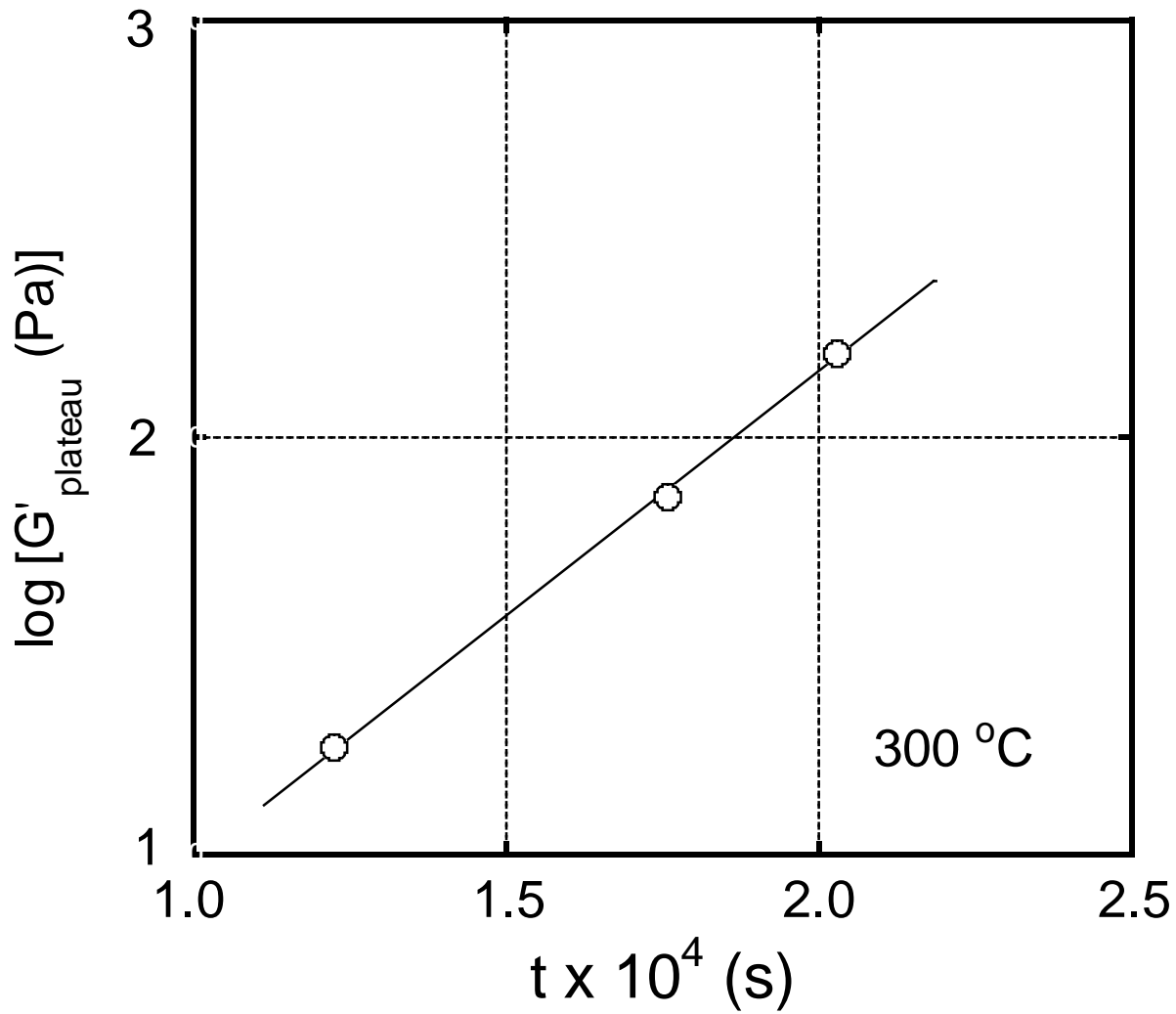
Kotera and Yamaguchi, Fig.3



Kotera and Yamaguchi, Fig.4(a)



Kotera and Yamaguchi, Fig.4(b)

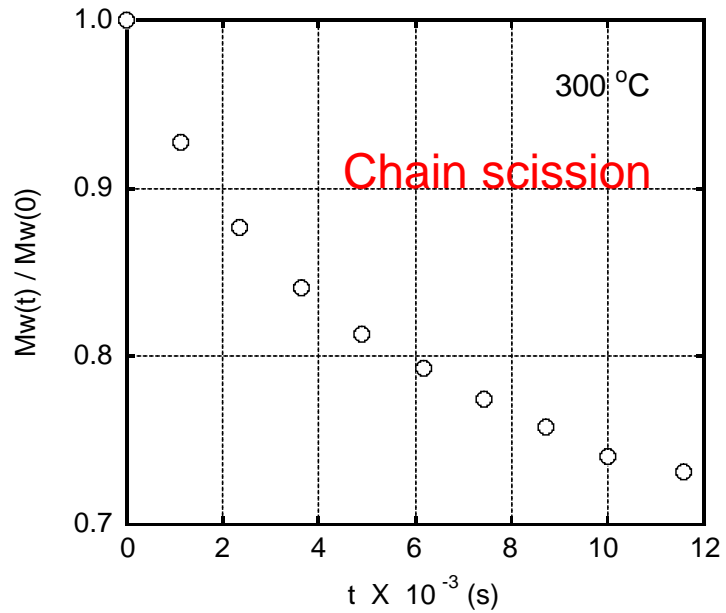


Kotera and Yamaguchi, Fig.5

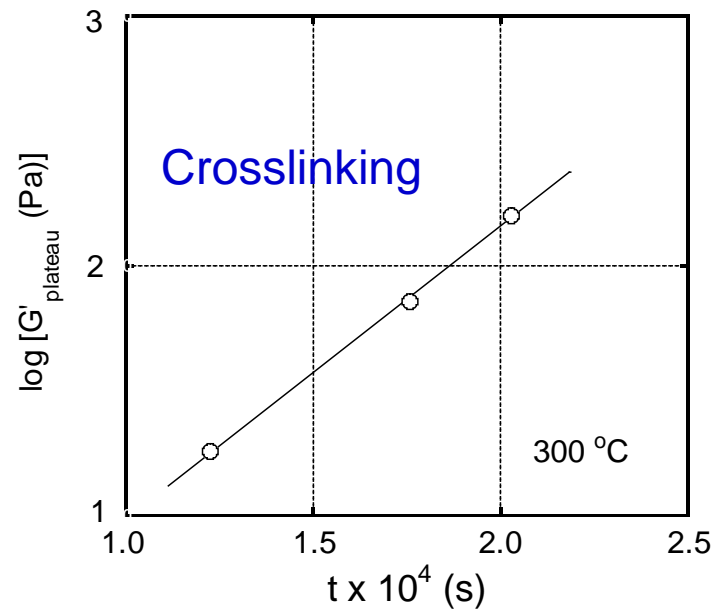


# Thermal degradation of ETFE

Under nitrogen

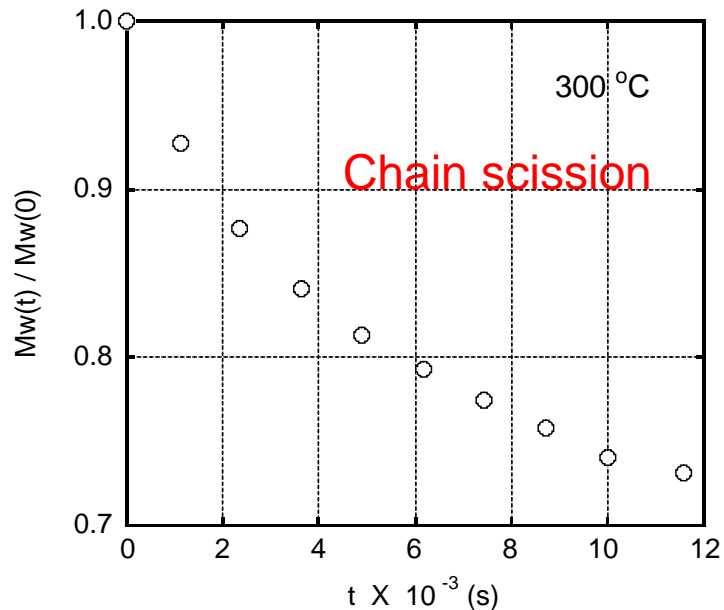


Under air



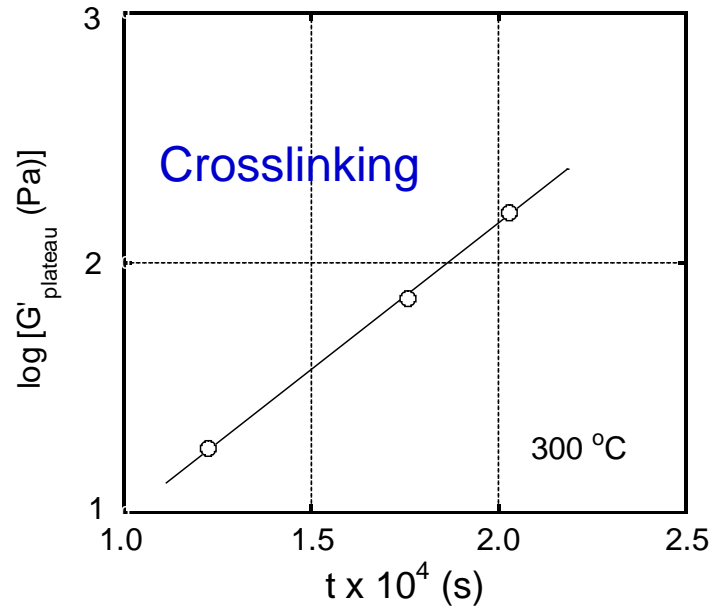
## Thermal degradation of ETFE

Under nitrogen



Under a nitrogen, random chain scission takes place. The molecular weight and its distribution were monitored by rheological change.

Under air



Under air condition, crosslinking reaction occurs as a first-order reaction, which was quantitatively evaluated by the plateau modulus in the low frequency region. rheological change.