

Thermomechanical Behavior of Poly(vinyl Chloride) in the Process of Degradation

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Synopsis

The thermomechanical behavior of poly(vinyl chloride) (PVC) was investigated during its thermal degradation by using torsional braid analysis. In thermomechanical behavior as a function of temperature, the relative rigidity G_r decreased initially with increasing temperature, then began to increase passing through a minimum at about 200°C, and finally decreased at 340°C. Increase in G_r from 200°C was caused by formation of a conjugated polyene chain accompanied by dehydrochlorination and by crosslinking reaction, and decrease in G_r at 340°C was related to scission reactions of the crosslinking network by oxidation. In the change in logarithmic decrement Δ , three peaks were observed: at 90°C, coinciding with the glass transition of the polymer; at about 200°C, due to the melting transition of crystallites, and at about 300°C, due to a loss of mechanical energy in the rheological transition of the polymer from a liquid state to a glassy state passing through a viscoelastic region. The thermomechanical properties of PVC with different molecular weights were also measured, and the effect of molecular weight on G_r and Δ are discussed. In isothermal measurements of the relative rigidity in air, exponentially increasing curves were observed as a function of time. These curves were analyzed kinetically as a first-order reaction, and an activation energy of 22.7 kcal/mole was obtained.

INTRODUCTION

Thermal degradation of poly(vinyl chloride) (PVC) has been studied by a number of workers using various methods, such as the measurement of hydrogen chloride evolved in the early stage of degradation;¹⁻⁷ intrinsic viscosity and gel permeation chromatography (GPC);⁸⁻¹⁰ infrared, nuclear magnetic resonance, and ultraviolet/visible spectroscopy;^{4,9-13} thermogravimetry;¹⁴⁻¹⁹ and dielectric spectroscopy.²⁰

Dehydrochlorination of PVC occurs by zipper-like elimination of hydrogen chloride,²¹ a radical mechanism²² by which rupture takes place initially at a comparatively weak C-Cl bond, and ionic mechanism²³ resulting in the formation of a conjugated polyene chain. The conjugated polyene chain leads to crosslinking reactions such as copolymerization between polyene chains, chain transfer between a polyene chain and a normal polymer chain, a Diels-Alder reaction, and cross-dehydrochlorination.²²

From the viewpoint of mechanical property, an increase in modulus of elasticity or rigidity is expected when the conjugated polyene chain and the crosslinking network chain are formed in the polymer chains, because molecular motion of a segment is restricted and its mobility decreases.

In this paper, the thermomechanical behavior of PVC having various molecular weights was measured in the temperature range of 30° to 480°C using torsional braid analysis (TBA) developed by Gillham²⁴⁻²⁶ and the effects of molecular

weight and atmosphere on thermomechanical properties were investigated. Furthermore, isothermal TBA measurement was made in the temperature range of 180° and 200°C, and kinetic analysis was carried out.

EXPERIMENTAL

Materials

The PVC samples used were supplied by Nippon Zeon Co., Ltd., and Sumitomo Chemical Co., Ltd. These polymers were without any additives and were characterized by viscosity measurement.

Number-average molecular weights of these polymers were calculated by the following equation,^{16,27} and the results are given in Table I:

$$[\eta] = 20.4 \times 10^{-4} M_n^{0.56} \quad (1)$$

where $[\eta]$ is the intrinsic viscosity and M_n is the number-average molecular weight.

The polymers were purified by extraction with methanol and dried *in vacuo*.

Composite specimens of PVC and glass braid for TBA measurements were prepared by immersing glass braid in a 10% tetrahydrofuran solution of PVC. Sufficient solvent was removed by heat treatment for three days at about 70°C *in vacuo* (below 10^{-5} mm Hg).

Torsional Braid Analysis

A TBA apparatus equipped with a data analyzer to print out digitally the amplitudes and periods of oscillation was used for investigating the thermomechanical behavior of PVC. Detail of the TBA apparatus was reported previously.²⁸ The thermomechanical behavior for the composite specimens of PVC and glass braid was observed in the temperature range of 30° to 480°C. The relative rigidity G_r and logarithmic decrement Δ were calculated by the following relations:

$$G_r = (P_0/P)^2 \quad (2)$$

$$\Delta = \ln (A_1/A_3) = \ln (A_3/A_5) = \dots \quad (3)$$

or

$$\Delta = \ln (A_2/A_4) = \ln (A_4/A_6) = \dots \quad (4)$$

TABLE I
Data of Investigated Polymers

Polymer	Sample no.	M_n	Supplier
Zeon 103EP8	P-800	46,500	Nippon Zeon Co., Ltd.
Zeon 103EP	P-1050	61,300	
Zeon 101EP	P-1450	87,600	
Sumilit SX-D	P-1900	109,000	Sumitomo Chemical Co., Ltd.
Sumilit SX-DH	P-2600	166,000	

where A_1, A_2, A_3 , and so on, are the digital printed amplitudes; P_0 is the period at 30°C; and P is the period at an arbitrary temperature. The period is converted from the printed total time dividing it by a preset number of cycles.²⁸

For isothermal measurement of TBA, the relative rigidities were presented by $1/P^2$ at each time, since P_0 at time $t = 0$ was difficult to determine accurately.

Temperature control of the furnace of the TBA apparatus was carried out by using a program control unit (Chino Works Co., Ltd., Model NP 163) equipped with thyristor regulator (Chino Works Co., Ltd., Model OL-12); the temperature errors were then within $\pm 1^\circ\text{C}$. The heating rate for measuring the thermomechanical properties of PVC was $1^\circ\text{C}/\text{min}$.

For the isothermal TBA measurement, the furnace was preheated to an arbitrary temperature and the composite specimen was introduced. About 5 min or less were needed to reach the required temperature. The distance between chucks of the TBA apparatus was 80 mm.

Thermogravimetry and Differential Thermal Analysis

Thermogravimetry (TG) was carried out by using a microelectrobalance equipped with a DTA unit in a vertical tubular oven (Rigaku Denki Co., Ltd.). These thermal analyses were done in an atmosphere of air and nitrogen gas for the granular PVC samples of 8–10 mg each which were contained in platinum pans (5 mm in diameter). Heating rates were $1^\circ\text{C}/\text{min}$ and $5^\circ\text{C}/\text{min}$ for TG and DTA measurement, respectively.

RESULTS AND DISCUSSION

Figure 1 shows the curves of the thermomechanical behavior and TG for P-800 ($M_n = 46,500$) in air at $1^\circ\text{C}/\text{min}$. Decrease in G_r and a peak in Δ at about 90°C are due to the glass transition of PVC. In the vicinity of 200°C , a minimum in G_r and a peak in Δ occur. Salovey and Badger¹⁷ observed an endothermic peak caused by melting of crystallites at about 200°C in DTA measurements. Bateille and Van¹⁶ also reported a peak in the DTA curve at 280°C where all the crys-

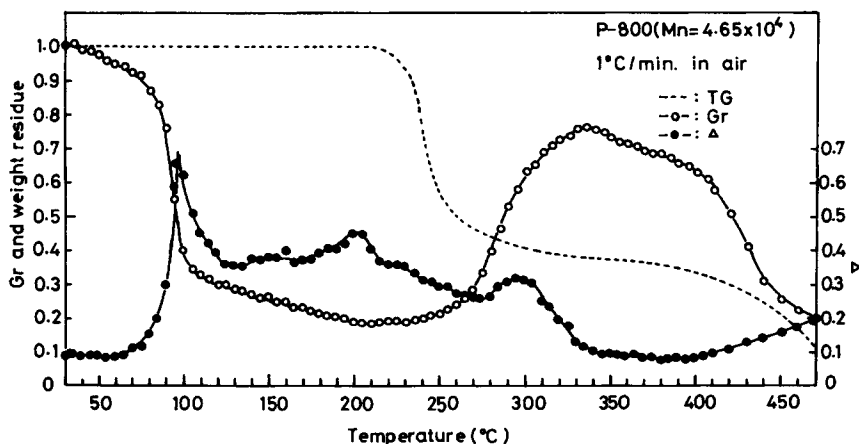
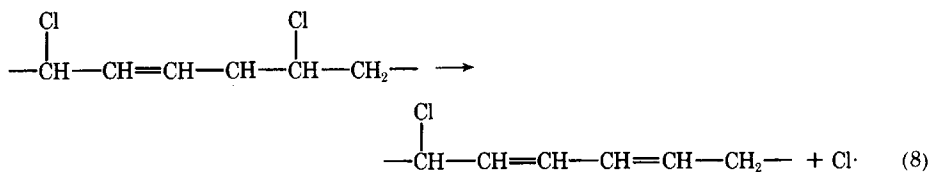
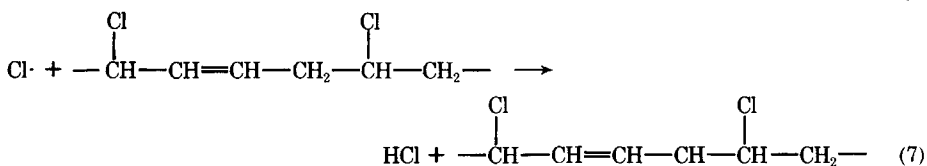
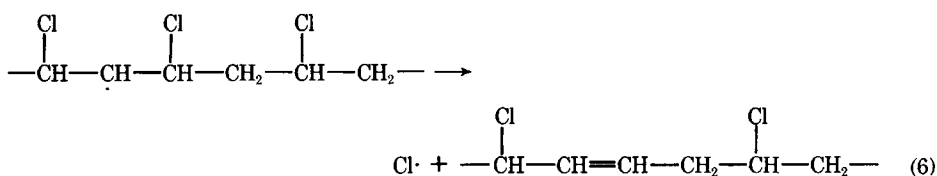
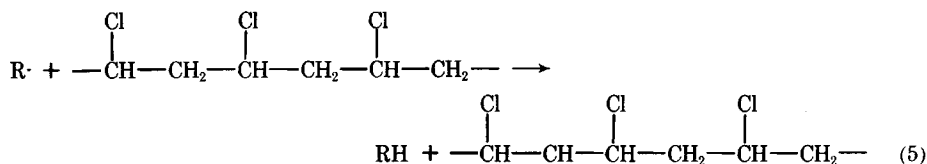


Fig. 1. Thermomechanical behavior and thermogravimetry for P-800 in air at $1^\circ\text{C}/\text{min}$.

tallinity was lost. Therefore, a peak in Δ at 200°C coincides with the melting transition of the crystallites contained in PVC.

The relative rigidity G_r begins to increase gradually after passing through a minimum and then increases rapidly at 260°C corresponding to weight loss (dotted line in Fig. 1). The increment in G_r may be related to a stiffening process of the molecular chain according to dehydrochlorination and crosslinking reactions of the PVC.

Winkler²² reported that dehydrochlorination of PVC proceeds with the following radical mechanisms resulting in the formation of a conjugated polyene chain:



It is believed that the mean length of the polyenes formed during dehydrochlorination is small, i.e., seven to eight double bonds because of readdition of hydrogen chloride to the double bonds formed²⁹ and termination of zipper reactions at a change in structure of the chain caused by oxidation, chain branching, or some other defect.²²

If the length of the polyene chain is small, a significant increase in rigidity is not expected. However, crosslinking reactions occur by copolymerization between polyene chains, by chain transfer between a polyene chain and a segment of a normal polymer chain, by a Diels-Alder reaction, and by cross-dehydrochlorination.^{6,7,10,11,22,31} Furthermore, in air, alkoxy radicals and alkylperoxy radicals are formed by oxidation, and these radicals also lead to crosslinking reactions.^{11,29} As a result of formation of polyene chains and crosslinking network chains during the thermal degradation of PVC, molecular motion is restricted and the rigidity of the polymer is markedly increased. During the reaction described above, the polymer transforms into a glassy state from a liquid

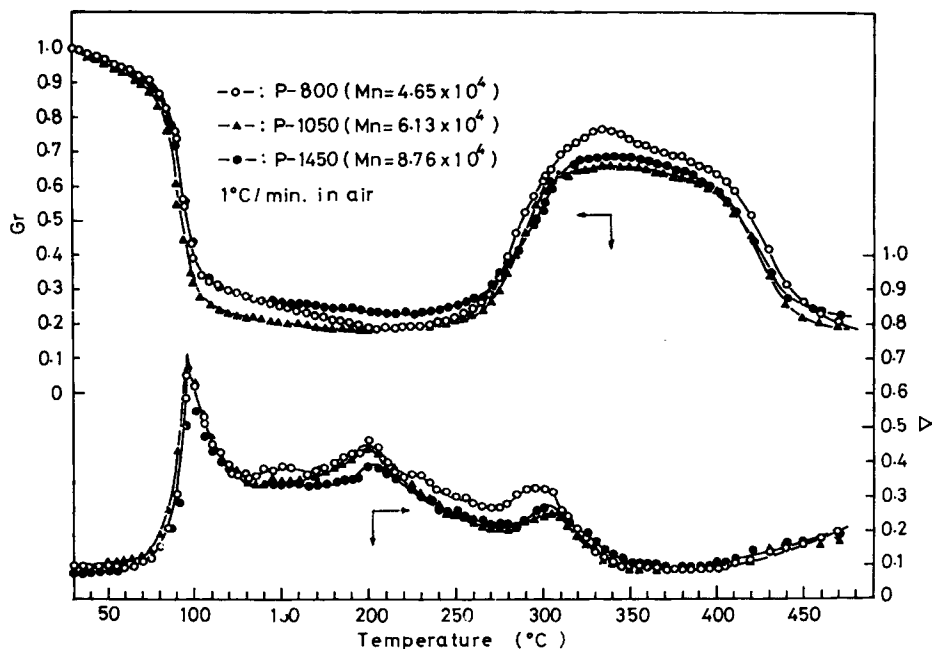


Fig. 2. Thermomechanical behavior for P-800, P-1050, and P-1450 in air at 1°C/min.

state passing through a viscoelastic region, and, accordingly, a peak in Δ at 295°C appears together with an increase in G_r .

At 330°C, G_r decreases gradually and then rapidly from 410°C. Stronberg, Straus, and Bernard¹⁸ analyzed the decomposition products by mass spectrometry and detected carbon chain breakdown products such as low molecular weight saturated and unsaturated hydrocarbons, benzene, and toluene at 400°C. Iida, Nakanishi, and Gotō³² also analyzed the decomposition products by using a gas chromatograph, detecting small amounts of benzene at 300°C and benzene, toluene, ethylbenzene, *o*-xylene, styrene, and naphthalene above 400°C. Consequently, the gradual decrease in G_r at 330°C may be due to the formation of low molecular weight materials based on the scission reaction of the network chain formed; and the rapid decrease in G_r from 410°C reflects marked scission reaction including vaporization of low molecular weight materials from the glass braid. These results are consistent with the data of TG (dotted line in Fig. 1) and DTA (Fig. 5).

The thermomechanical properties in the temperature range of 30° to 480°C for PVC with number-average molecular weights of 46,500 (P-800), 61,300 (P-1050), and 87,600 (P-1450) are shown in Figure 2. Those of PVC with number-average molecular weights of 109,000 (P-1900) and 166,000 (P-2600) are shown in Figure 3. All G_r curves resemble each other; G_r decreases initially with increasing temperature, subsequently increases owing to the dehydrochlorination and crosslinking reactions, and finally decreases with temperature. Because of different dehydrochlorination rates for each PVC, minimum points in the G_r -versus-temperature curves for PVC with the higher molecular weights shift to the higher temperature side. These minimum points for P-800, P-1050, P-1450, P-1900, and P-2600 are at 215°, 225°, 235°, 240°, and 245°C, respectively.

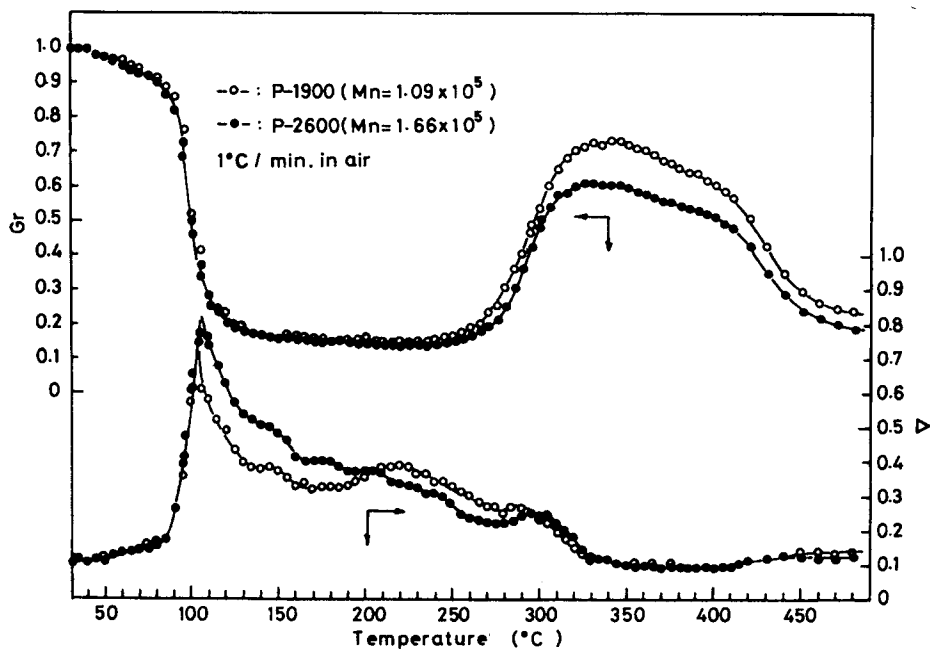


Fig. 3. Thermomechanical behavior for P-1900 and P-2600 in air at 1°C/min.

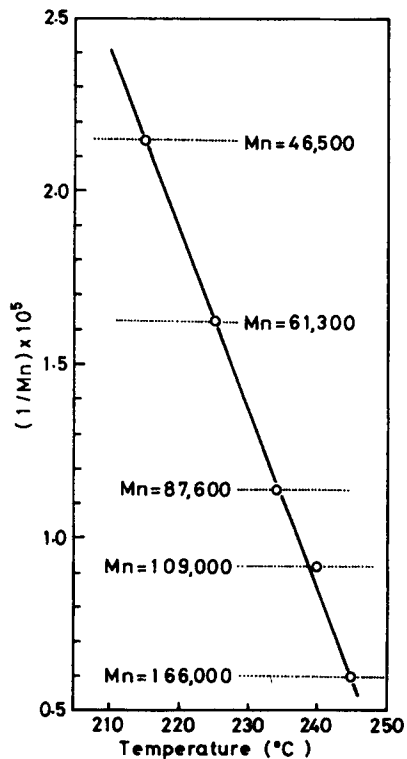


Fig. 4. Plot of temperature at minimum in G_r , in Figs. 2 and 3 against reciprocal of number-average molecular weights.

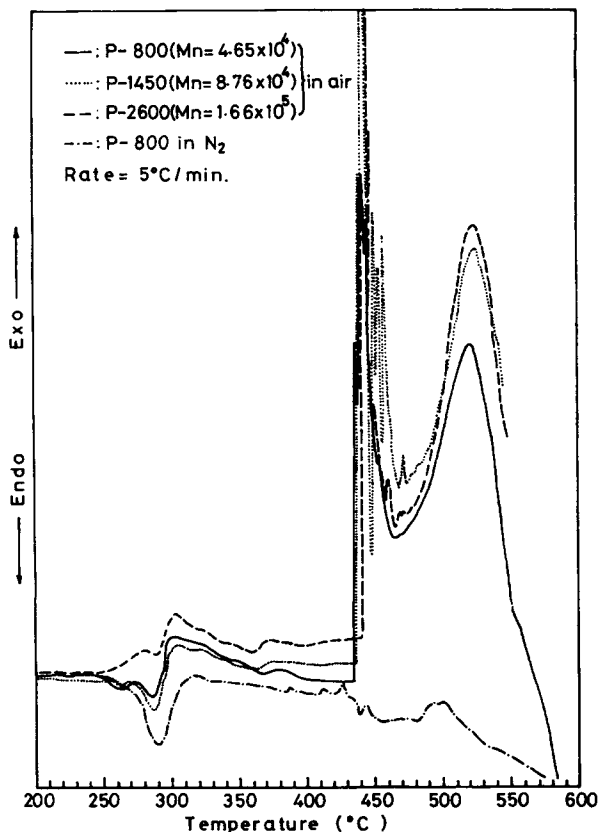


Fig. 5. DTA curves for P-800, P-1450, and P-2600.

Talamani and Pezzini³³ and Bataille and Van¹⁶ reported that the plot of the rate of dehydrochlorination against the reciprocal of molecular weights gave a linear relation.

Thus, plotting the temperature at minimum points in G_r -versus-temperature curves against the reciprocal of number-average molecular weights gives a straight line as shown in Figure 4. It is found that the temperature where G_r begins to increase, i.e., the temperature of a minimum in G_r , is controlled by the dehydrochlorination rate, and PVC with the higher molecular weights has a slower rate of dehydrochlorination. This result is consistent with that of isothermal measurements (Fig. 11) described later.

The temperature of formation of low molecular weight products due to the scission of the network chain molecules, namely, the temperature of the decrease in G_r , is 345°C for P-800, but for other polymers this temperature is in the range of 350° to 355°C, and there is no remarkable difference corresponding to the molecular weights. The temperature of rapid decrease in G_r is also independent of molecular weight, being from about 400° to 410°C.

As to change in Δ arising from the melting transition, a peak appears at about 200°C for P-800, P-1050, and P-1450, but for P-1900 it appears at about 220°C shifting to the higher-temperature side. For P-2600, no peak appears in this

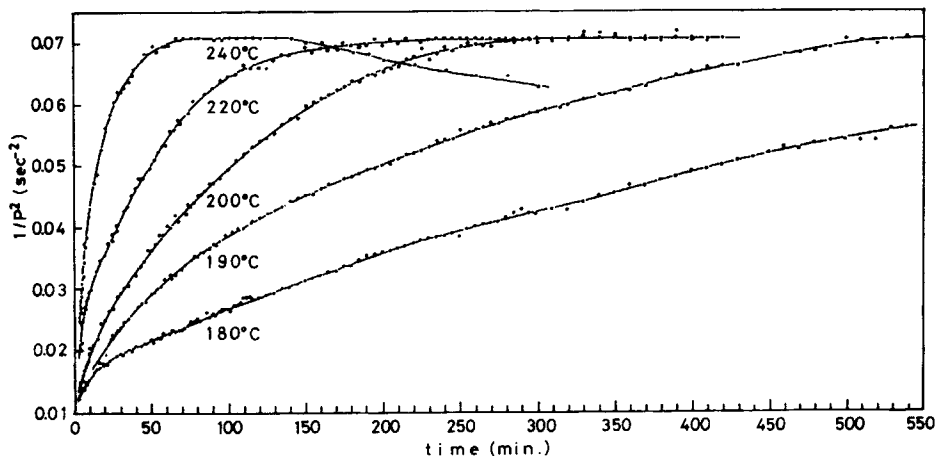


Fig. 6. Isothermal curve of relative rigidity for P-800 in air at temperatures between 180° and 240°C.

temperature region. The peak appearing in the temperature range of 270° to 320°C is independent of molecular weight.

Figure 5 shows DTA curves of P-800, P-1450, and P-2600 in air and of P-800 in nitrogen at a heating rate of 5°C/min. An endothermic peak of P-800 and P-1450 at about 260°C is attributable to the melting transition of crystallites of PVC.¹⁷ This peak does not appear in P-2600, since it may be difficult to crystallize because of its higher molecular weight ($M_n = 166,000$). Consequently, a peak in Δ for P-2600 is not observed at about 200°C. An endothermic peak in the vicinity of 290°C is assigned to dehydrochlorination.¹⁷ Marked peaks

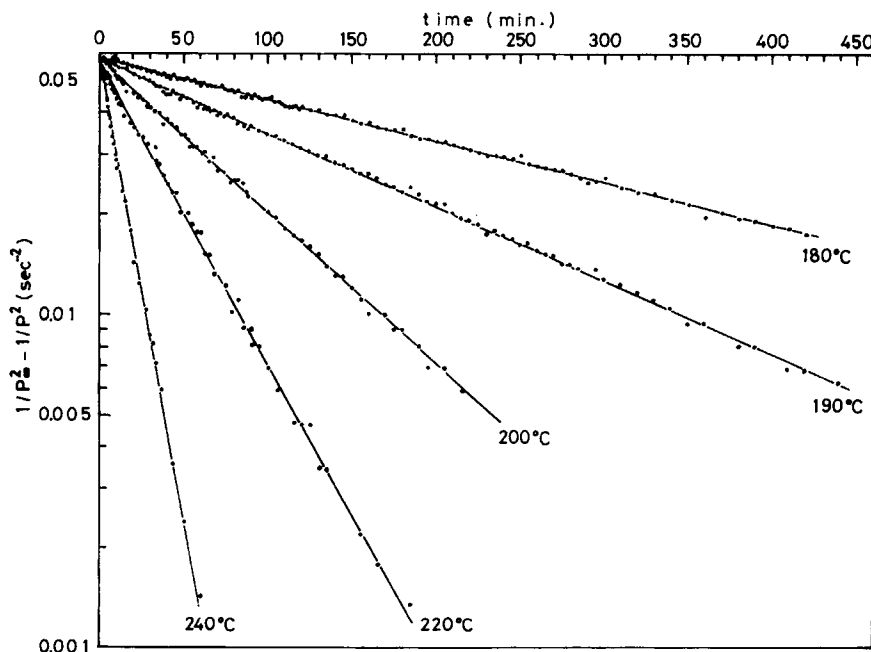


Fig. 7. Plot of $\ln(1/P^2_\infty - 1/P^2)$ vs t for P-800.

TABLE II
Rate Constants for P-800 at Different Temperatures

Temperature, °C	k , min ⁻¹
180	2.84×10^{-3}
190	5.06×10^{-3}
200	1.01×10^{-2}
220	2.06×10^{-2}
240	6.09×10^{-2}

in air at temperatures between 440° and 600°C are due to the formation of low molecular weight products by oxidation, and these peaks are not observed in nitrogen.

Figure 6 shows isothermal measurements of relative rigidities for P-800 in air at 180°, 190°, 200°, 220°, and 240°C. The relative rigidity increases exponentially with elapsed time owing to formation of polyene chains, chain branching, crosslinking between double bonds, and cross-dehydrochlorination, and then reaches equilibrium asymptotically. At 180°C, equilibrium is not reached in the range of time observed. At 240°C, after equilibrium is reached, the relative rigidity decreases with time after 140 min according to the scission of the network chains as shown in the case of the temperature dependence of G_r (Figs. 1, 2, and 3).

For these isothermal curves as a function of time, a first-order reaction is assumed just as in the case of thermosetting plastics,³⁴ and they are analyzed kinetically. When rigidity at time $t = 0$, G_0 , increases to G_t at time t and reaches equilibrium rigidity G_∞ , then the equation for a first-order reaction is

$$d(G_\infty - G_t)/dt = k(G_\infty - G_t) \quad (9)$$

Integrating eq. (9) gives eq. (10):

$$\ln (G_\infty - G_t)/(G_\infty - G_0) = -kt \quad (10)$$

where k is the rate constant. As $G_0 \propto 1/P_0^2$, $G_t \propto 1/P^2$, and $G_\infty \propto 1/P_\infty^2$, eq. (10) is converted into eq. (11):

$$\ln (1/P_\infty^2 - 1/P^2) = -kt + \ln (1/P_\infty^2 - 1/P_0^2) \quad (11)$$

where P_0 , P , and P_∞ are the period at $t = 0$, $t = t$, and $t = \infty$, respectively. Thus, plotting of $\ln (1/P_\infty^2 - 1/P^2)$ against t gives a linear relation, and the rate constant k is obtained from the slope of the straight line. In Figure 7, a plot of $\ln (1/P_\infty^2 - 1/P^2)$ against t from the data of Figure 6 is represented. For 180°C, calculation is done by using the equilibrium value of $P_\infty = 0.0703$ for measurements at other temperatures, since equilibrium is not reached in the range of time observed. As shown in Figure 7, linear relations are obtained at each temperature, and from the slope of the straight lines, the rate constants are obtained as collected in Table II.

As shown in Figure 8, the plot of the rate constant k versus the reciprocal of the absolute temperature, $1/T$, is linear; and from the slope of the straight line, an activation energy of 22.7 kcal/mole is calculated according to the Arrhenius relation. The activation energies for the thermal degradation of PVC have been observed by a number of workers and they agree with our result: Abbās and

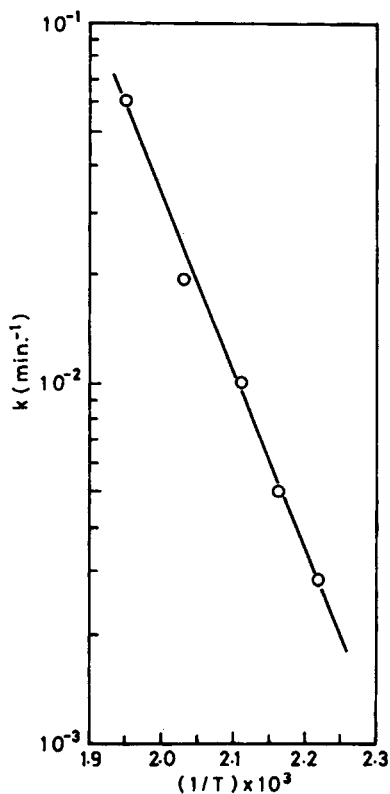


Fig. 8. Arrhenius plot.

Sörvik⁹ reported that no significant difference was found between the activation energies in oxygen and nitrogen and obtained values of 26–28 kcal/mole. Hedvig²⁰ found a value of 32 kcal/mole by using dielectric spectroscopy. Stronberg, Straus, and Achhammer¹⁸ and Salovey and Bair¹⁹ analyzed kinetically the weight loss-versus-time data as a $\frac{3}{2}$ -order reaction and obtained values of 26–32 kcal/mole in vacuo and 27 kcal/mole in nitrogen, respectively. Imoto and Otsu³¹ analyzed the relation between the insoluble part in tetrahydrofuran and degradation time as a first-order reaction to obtain a value of 25 kcal/mole. And Furusho, Komatsu, and Nakagawa³⁵ investigated the isothermal TBA curve as a zero-order reaction and obtained an activation energy of 24 kcal/mole.

In Figure 9, the relative rigidities measured isothermally at 200°C in air are plotted for PVC with different number-average molecular weights. Exponential

TABLE III
Rate Constants for PVC with Different Number-Average Molecular Weights at 200°C

Sample no.	M_n	k , min. ⁻¹
P-800	46,500	1.01×10^{-2}
P-1050	61,300	8.05×10^{-3}
P-1450	87,600	6.64×10^{-3}
P-1900	109,000	6.23×10^{-3}
P-2600	166,000	4.73×10^{-3}

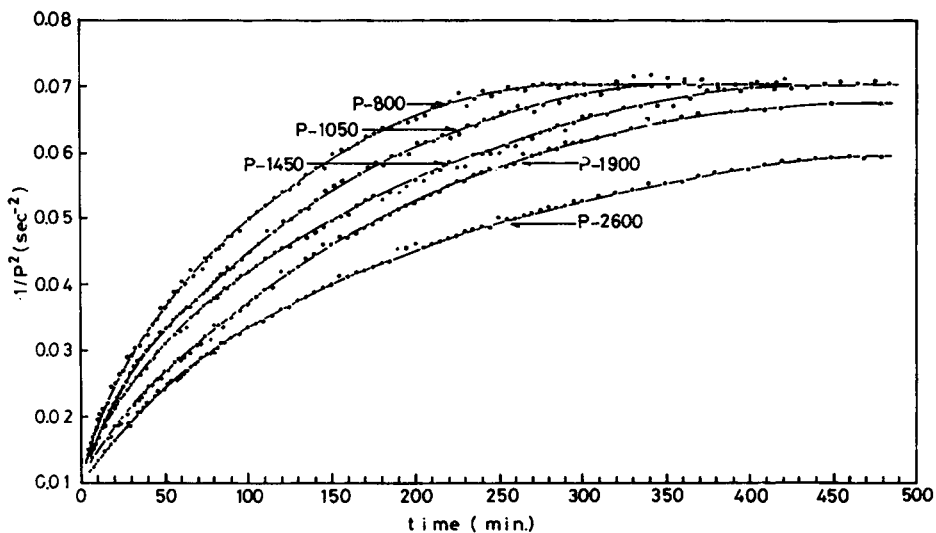


Fig. 9. Isothermal curve of relative rigidity for P-800, P-1050, P-1450, P-1900, and P-2600 in air at 200°C.

increase in relative rigidity as a function of time reaches equilibrium asymptotically for P-800, P-1050, and P-1450, but not for P-1900 and P-2600 in the range of observation time scale. When $\ln(1/P_{\infty}^2 - 1/P^2)$ is plotted against t for the data of Figure 9 according with eq. (2), then linear relations are obtained as shown

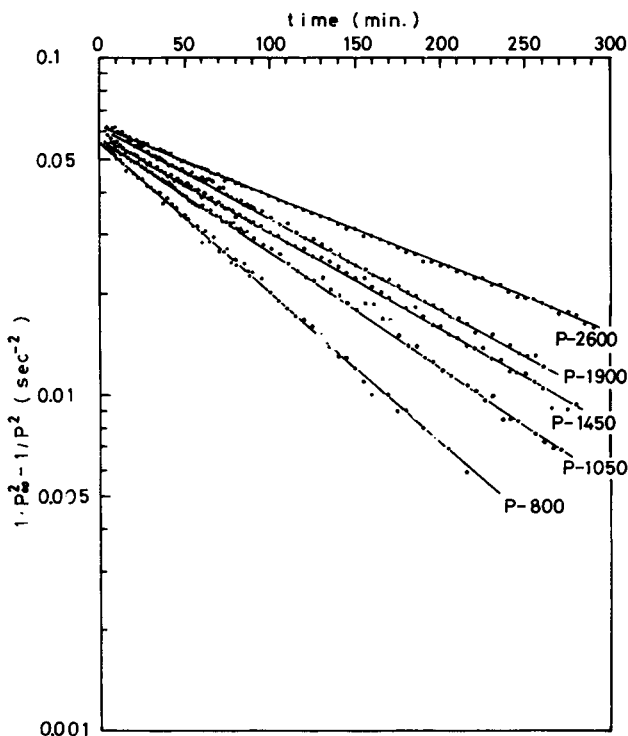


Fig. 10. Plot of $\ln(1/P_{\infty}^2 - 1/P^2)$ vs t for P-800, P-1050, P-1450, P-1900, and P-2600 at 200°C.

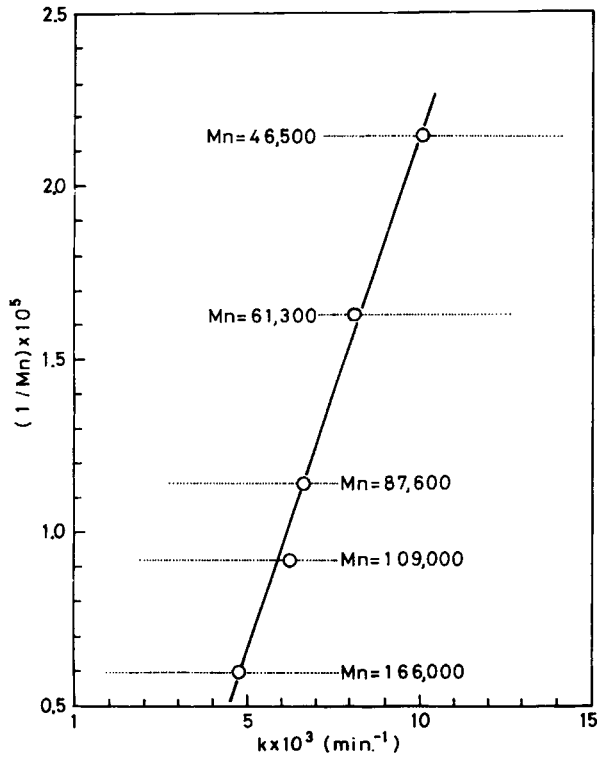


Fig. 11. Plot of rate constant vs reciprocal of number-average molecular weight.

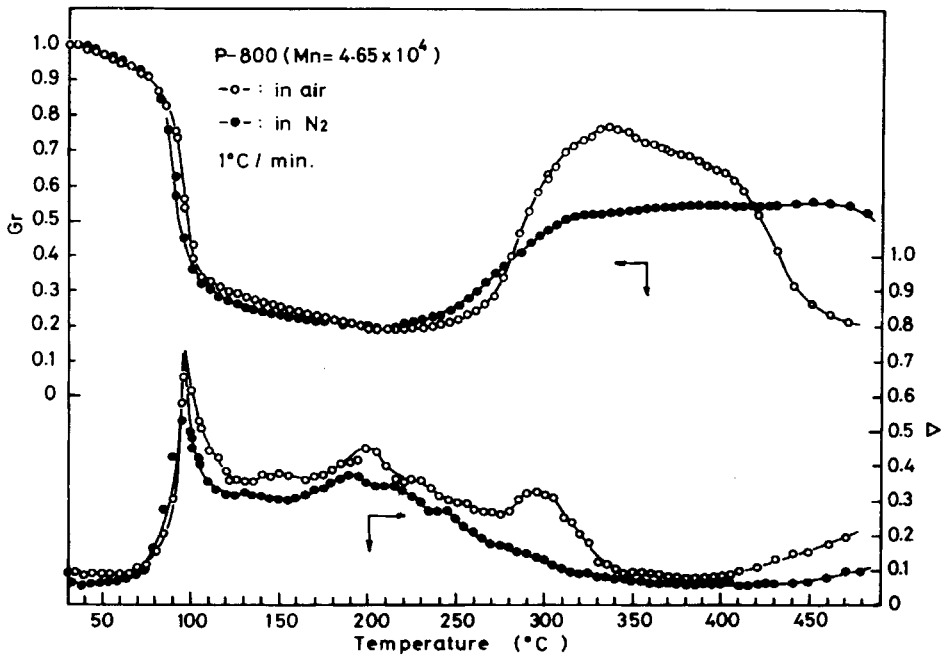
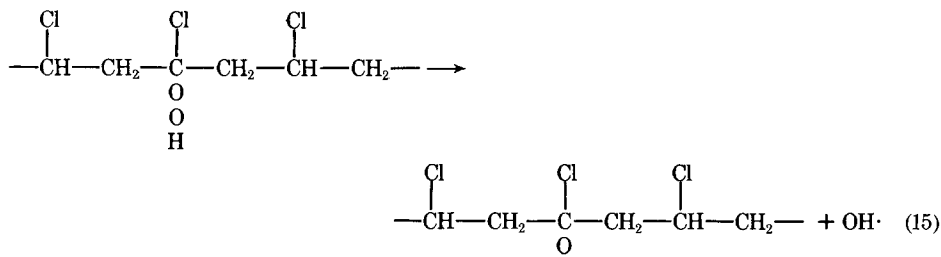
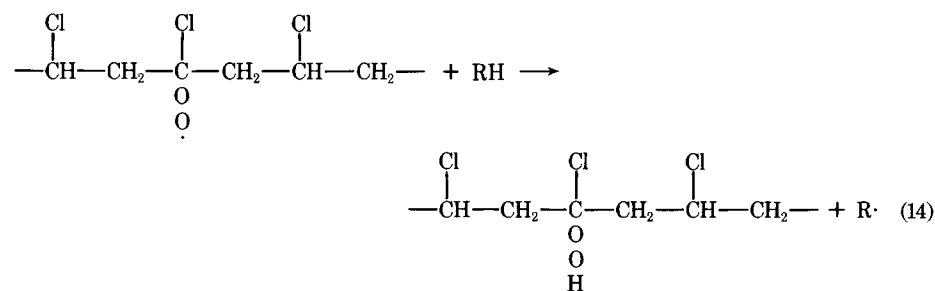
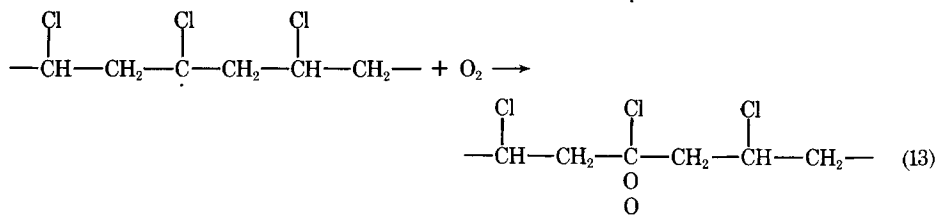
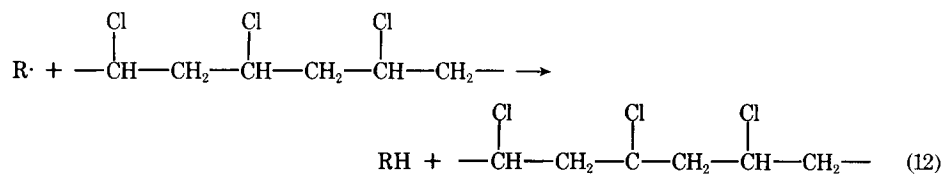


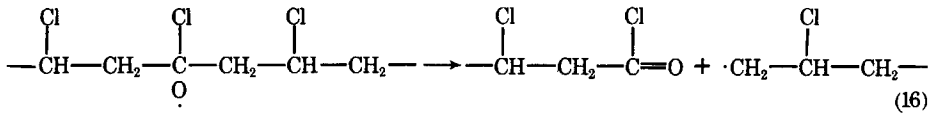
Fig. 12. Comparison of thermomechanical behavior in air and nitrogen.

in Figure 10. From the slope of each straight line, the rate constants k are calculated as listed in Table III. It is found that the increase in the rate of the relative rigidity is slower the higher the molecular weight of PVC.

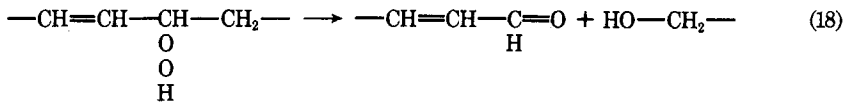
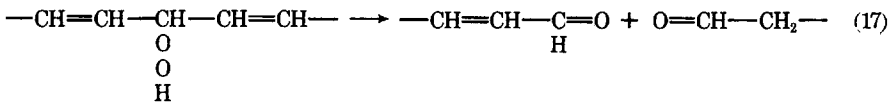
As shown in Figure 11, the plot of the rate constant against the reciprocal of the molecular weight gives a straight line as reported by Talamani and Pezzini³³ and Bataille and Van.¹⁶ This result agrees with the data shown in Figure 4 where the temperature of the minimum in G_r was plotted against the reciprocal of the molecular weights. It is concluded that the increase in rigidity measured by TBA is controlled by the dehydrochlorination rate of PVC.

In Figure 12, the thermomechanical behavior in air is compared with that in nitrogen for P-800. Measurement of the thermomechanical behavior in nitrogen was carried out flowing highly pure nitrogen gas (above 99.999% pure) at a rate of 200 ml/min. Changes in thermomechanical behavior in nitrogen are the same as those in air until 200°C. Above 200°C, G_r increases rapidly in air, while in nitrogen it increases gradually. At temperatures between 200° and 270°C, the rate of increase in G_r in nitrogen is faster than in air. However, between 270° and 340°C, the rate in air is faster than in nitrogen and the value of G_r in air is larger than in nitrogen. These are explained by the following mechanisms. Winkler²² proposed the following oxidative scission mechanisms:

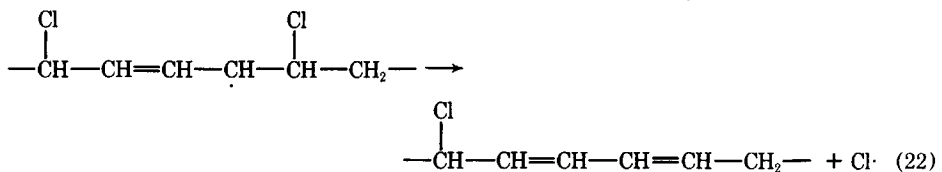
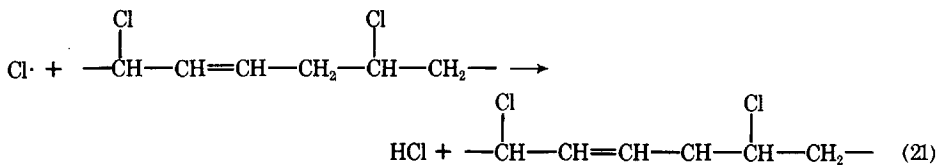
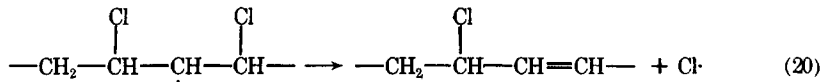
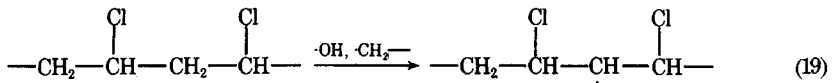




Sobue, Tabata, and Tajima¹¹ also proposed the following mechanisms:



Radicals formed during scission reactions abstract hydrogen atoms from other polymer chains and accelerate the formation of double bonds:⁹



According to these mechanisms, the scission reactions accompanied by dehydrochlorination occur at the initial stage of the thermal degradation of PVC in

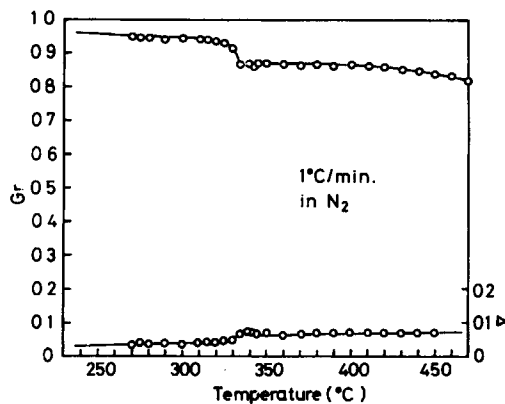
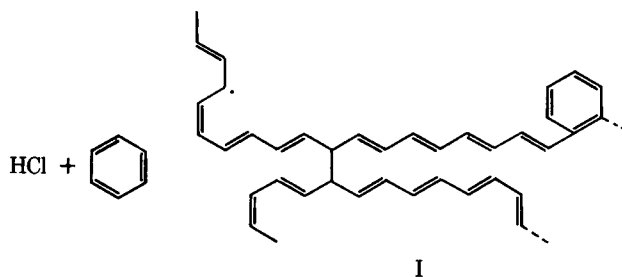


Fig. 13. Thermomechanical behavior of PVC (P-800) cooled from 480° to 30°C in nitrogen.

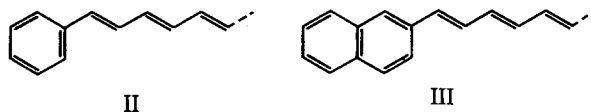
air.^{9,22} Abbās and Sörvik⁹ reported that weight-average molecular weights increased with progressing dehydrochlorination, but in air these decreased initially and then increased. Consequently, between 200° and 270°C, the rate of increase in G_r in air is slower than in nitrogen owing rather to the effect of scission in air than to formation of double bonds; and between 270° and 340°C, the formation of the double bonds which are accelerated according to eqs. (20), (21), (7), and (8) causes a marked increase in G_r . Above 340°C in air, G_r decreases owing to the formation of low molecular weight products, while in nitrogen the remarkable scission reaction of the molecular chain does not occur, as shown in the DTA curve (Fig. 5).

Shimokawa et al.³⁶ suggested that the structure of pyrolysis products in nitrogen by using NMR and ESR is as follows:

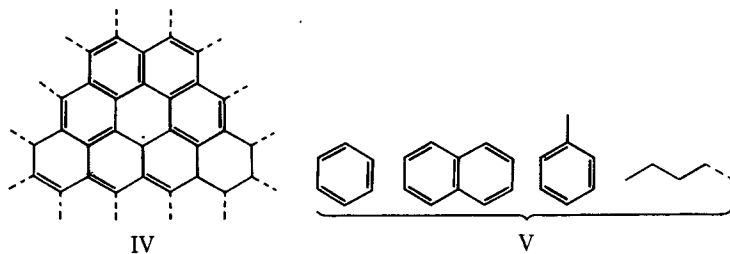
At 200–350°C:



At 350–410°C:



Above 420°C:



Increase in G_r above 200°C in nitrogen may be due to the formation of a structure such as I, which is produced by dehydrochlorination and crosslinking reactions. A small decrease in G_r at 470°C in nitrogen is considered to be due to the formation of structure II or III.

Changes in Δ in nitrogen are approximately the same as those in air up to 280°C, but a peak at about 300°C in air is not observed in nitrogen. This may be due to the gradual increase in G_r in nitrogen, and transition from a liquid state to a glassy state may not occur.

For a composite specimen heated to 480°C and allowed to cool to room temperature in nitrogen, the thermomechanical behavior is measured again as shown in Figure 13. The decrease in G_r and a small peak in Δ are observed at 335°C. This may be due to the melting transition of a dense structure such as IV. Shi-

mokawa et al.³⁶ and Otani³⁷ reported that when PVC was heated at a rate of 10°C/min, residues of thermally decomposed PVC melt rapidly at about 410°C. The difference between our results (335°C) and their results (410°C) may be due to the heating rate, i.e., 1°C/min in our measurements and 10°C/min in their measurements.

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