# A Study of the Thermal Degradation of Several Halogen-containing Polymers by Torsional Braid Analysis

Noboru Furusho, Tsuyoshi Komatsu, and Tsurutaro Nakagawa
*Department of Polymer Science, Faculty of Science, Hokkaido University, Sapporo 060*

(Received October 20, 1973)

The thermal degradation of several halogen-containing polymers in air was studied by means of the TBA (Torsional Braid Analysis) method and IR spectroscopy. The samples were poly(vinyl chloride)(PVC), vinylidene chloride-vinyl chloride copolymer(PVdC-VC), poly(vinyl fluoride)(PVF), poly(vinylidene fluoride)(PVdF), poly(vinyl bromide)(PVB), and poly(vinylidene bromide)(PVdB). The dynamic mechanical properties of these polymers are complicated at higher temperatures because of the thermal degradation, by, for example, dehydrohalogenation. The relative shear modulus ($G_r$) increases and then decreases through a maximum, accompanied by changes in the logarithmic decrement. The temperatures at which the changes in $G_r$ occur become higher in the order of PVdB$<$PVB$<$PVdC-VC$<$PVC$<$PVdF$<$PVF. This order agrees with that of the bond energy in carbon-halogen bonds. The apparent activation energies of these reactions were obtained from the changes in $G_r$ and from the relative absorbance ratio of the carbon-carbon double bond with time, respectively. In general, the values estimated by these two procedures agreed well in each case.

The thermal degradation of polymers has been studied widely by various methods, by, for instance, thermogravimetric analysis and pyrolysis gas chromatography. On the other hand, relatively few studies have been carried out on the basis of measurements of the mechanical properties, which are much more sensitive to the changes in the state of the material. This situation may be attributed to the difficulties in the measurements of the mechanical properties of polymers at higher temperatures because of softening and fluidity. Gillham and Lewis[1] have established a new procedure, called the Torsional Braid Analysis (TBA) method, in which a composite system composed of a polymer and a mechanically-inactive supporting material (usually glass braids) is used.

Previously, using this TBA method, we have studied the change in the dynamic mechanical properties of several polymers during the thermal degradation and concluded that the TBA method can be used as a convenient tool for the kinetic study of the thermal degradation of polymers.[2,3]

In the present paper, we will report some results on the thermal degradation of several halogen-containing polymers: poly(vinyl halide) and poly(vinylidene halide). The halides are chloride, fluoride, and bromide. We will also report on the correlation between the changes in the dynamic mechanical behavior at higher temperatures and the chemical reactions with the aid of the results of the thermogravimetric analysis and the IR spectra.

The purpose of this work is to elucidate the effects of the various halogens and the types of substitution on the thermal stabilities of polymers on the basis of the measurements of the mechanical properties. Also, we intend to examine the applicability of these mechanical procedures to the kinetic studies by comparing the data obtained from the mechanical measurements with the values obtained from the IR spectra.

## Experimental

The poly(vinyl chloride)(PVC), vinylidene chloride-vinyl chloride copolymer(PVdC-VC), poly(vinyl fluoride)(PVF), and poly(vinylidene fluoride)(PVdF) were commercial materials. The poly(vinyl bromide)(PVB) and poly(vinylidene bromide)(PVdB) were obtained as the starting materials from the 1,2-dibromoethane in the ordinary way;[4] the polymers were identified by elementary analysis and by IR spectroscopy. The known parameters relating to the molecular dimensions of the present samples are as follows. The viscosity-average molecular weights are $1.0\times10^5$ for PVC and $1.2\times10^5$ for PVB. The intrinsic viscosity in *N,N*-dimethylformamide at 20 °C is 1.8 (dl/g) for PVdF. The number-average degree of polymerization is 1000 for PVdC-VC, and the weight ratio of the components is 82:18.

The details of the TBA method have been described elsewhere.[2] The relative shear modulus ($G_r=(T_0/T)^2$) and the logarithmic decrement ($\lambda=(1/n)\ln(A_{2n+1}/A_1)$) are obtained from the frequencies and the amplitudes of the damped oscillations. The measurements of $G_r$ and $\lambda$ are carried out under the conditions of a constant heating rate and under isothermal conditions. In the former case, the moduli at room temperatures, and in the latter case, the values 10 min after the setting of the specimen, were used as standards of the relative shear moduli. The test specimens were prepared by the impregnation of the polymer solutions into the glass braids and by the subsequent evaporation of the solvents. The frequency range is about 0.13—0.35 Hz.

The measurements of the IR spectra were carried out as follows. At first, KBr pellets with a known concentration of these polymers were prepared and then heated in air for the desired periods under isothermal conditions. The pellets were made again from those heat-treated materials and then used in the IR experiment. The relative absorbance ratios for the C–C double bond and the C–H group were calculated from the heights of the absorption peaks.

The thermogravimetric analysis(TGA) and the differential thermal analysis(DTA) were carried out in the air at a constant heating rate by using an apparatus made by the Rigaku Denki Co.

## Results and Discussion

*Temperature Dependence of $G_r$ and $\lambda$.* The dynamic mechanical properties of these polymers are shown in Figs. 1, 2, and 3. In these figures, the ordinates are arbitrarily shifted in order to avoid the overlapping of the curves. As is shown in Fig. 1, the $G_r$ and $\lambda$ of PVC behave in a complicated way. The curves of the

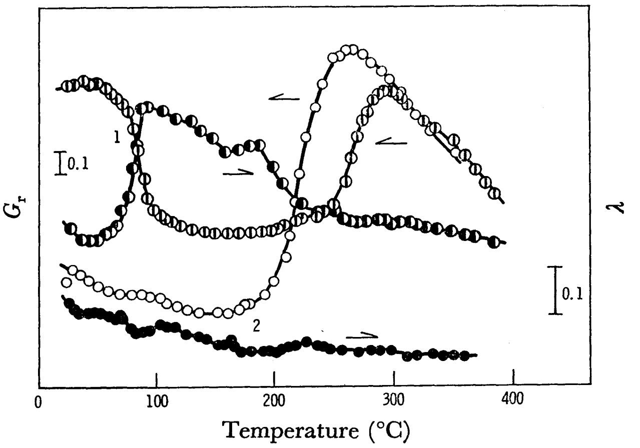

Fig. 1. $G_r$, λ *vs*. T plots of PVC and PVdC–VC heated in air. Heating rate: 1 °C/min. (1): PVC, (2): PVdC–VC.
◑ ○: $G_r$, ◐ ●: λ.

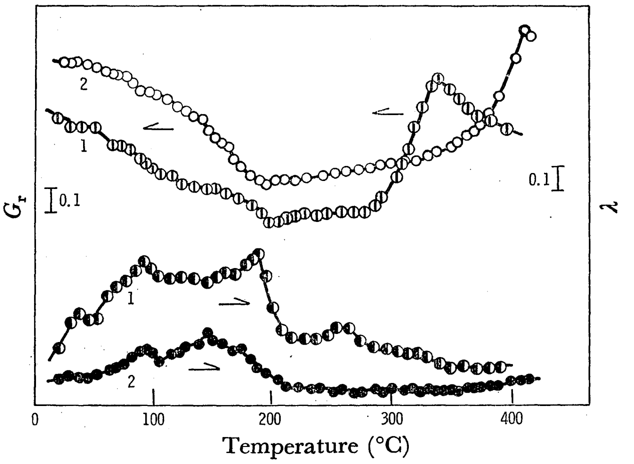

Fig. 2. $G_r$, λ *vs*. T plots of PVF and PVdF heated in air. Heating rate: 1 °C/min. (1): PVF, (2): PVdF.
◑ ○: $G_r$, ◐ ●: λ.

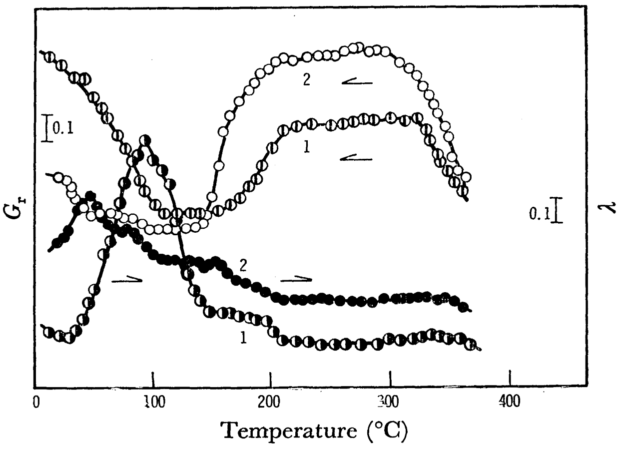

Fig. 3. $G_r$, λ *vs*. T plots of PVB and PVdB heated in air. Heating rate: 1 °C/min. (1): PVB, (2): PVdB.
◑ ○: $G_r$, ◑ ●: λ.

temperature dependence of $G_r$ and λ consist of several parts. These features can be explained by assuming the following mechanism. The first abrupt decrease in $G_r$ and the corresponding maximum of λ at about 90 °C are due to the glass transition. The gradual decrease in $G_r$ and, presumably, the corresponding maximum of λ at about 180 °C may be due to the flow or the fusion. The successive increase in $G_r$ (and the corresponding shoulder of λ at about 250 °C) and the last decrease in $G_r$ through the maximum at about 300 °C may be attributed to the thermal degradation. The assumption about the last stage of the thermo-mechanical change is supported by the results of the thermogravimetric analysis shown in Fig. 4. In the case of PVC, as is shown in the figure, the weight loss accompanied by the dehydrochlorination reaction begins at about 230 °C and becomes intense between 250 and 290 °C; this temperature range is the same as that in which the values in $G_r$ increase considerably. Considering the difference in the heating rates, it is reasonable to assume that these results correspond to each other.

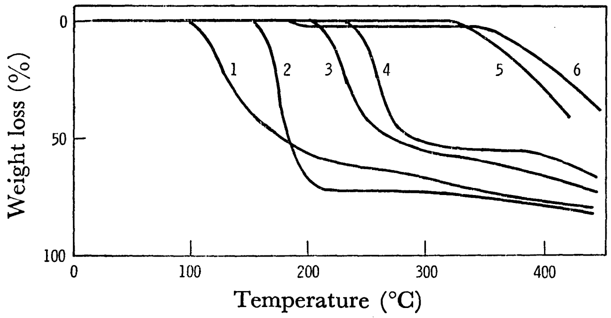

Fig. 4. TGA thermograms of halogen-containing polymers in air. Heating rate: 2.5 °C/min (1,2), 3 °C/min (3,4,5,6). (1): PVdB, (2): PVB, (3): PVdC–VC, (4): PVC, (5): PVF, (6): PVdF.

In the cases of the other polymers, the features in the dynamic mechanical properties can be also explained in the same way as in the case of PVC. For PVdC-VC, as is shown in Fig. 1, the decrease in $G_r$ at the lower temperatures, the shoulder of λ at about 70 °C, and the successive decrease in $G_r$ accompanied by the small peak (110 °C) and the shoulder (160 °C) of λ may be attributed to the physical relaxations. Such a situation is in agreement with the results obtained by Schmieder and Wolf.[5] The successive increase in $G_r$ (and the corresponding small peak of λ at about 230 °C) and the last decrease in $G_r$ through the maximum at about 270 °C are the results of the thermal degradation. It may be noticed that the values of $G_r$ sharply decrease through a maximum in spite of the relatively slight loss of weight. Similar behavior is observed in the other systems. This result may be attributed to the destruction of the network structure by the oxidative chain scission, because the mechanical properties are very sensitive to the change in the network structure.

In the case of PVF, as is shown in Fig. 2, the decrease in $G_r$, the corresponding shoulder of λ at 40 °C, and the maximum of λ at 90 °C may be attributed to the molecular motions in the amorphous region and to those in the crystalline region, respectively. Considering our finding that the endothermic peak exists at about 190 °C, the small drop in $G_r$ and the maximum of λ at 190 °C are due to the melting. These considerations are supported by the results of Kawasaki and Hashimoto,[6] and Nielsen[7] with regard to its mechanical dispersion. The successive increase in $G_r$ (and the corresponding shoulder of $\lambda$ at about 320 °C) and the decrease in $G_r$ through the maximum at 360 °C come from the thermal degradation. The nature of the small peak of $\lambda$ at 260 °C has not been elucidated.

For PVdF (Fig. 2), the decrease in $G_r$ and the corresponding peaks of $\lambda$ at 90 and 150 °C may be attributed to the molecular motion in the crystalline region and to the melting, respectively. These assumptions are supported by the results of Kakutani[8] and Ota *et al.*[9] and by our finding that the endothermic peak exists at about 150 °C. The successive increase in $G_r$ is due to the thermal degradation. However, the correlation between the gradual increase in $G_r$ at about 200 °C and the chemical process is not clear at present. A slight weight loss is observed at about 180 °C. Ishii found a similar weight loss and stated that it was the result of the dehydrofluorination.[10] It should be pointed out here that the increase in $G_r$ is greater than that to be expected from the curve of the weight loss; moreover, $G_r$ continues to grow without showing any plateau.

For PVB (Fig. 3), the decrease in $G_r$ and the corresponding maximum at 100 °C in $\lambda$ relate to the glass transition. This agrees with the results obtained by Zutty and Whitworth.[11] The successive increase in $G_r$ (and the corresponding shoulder of $\lambda$ at 180 °C) and the decrease in $G_r$ above 300 °C through the high plateau arise from the thermal degradation.

For PVdB (Fig. 3), the decrease in $G_r$, the corresponding maximum at 50 °C, and the shoulder at about 80 °C in $\lambda$ are the results of the physical relaxation. The successive increase in $G_r$ (and the corresponding shoulder of $\lambda$ at 160 °C) and the decrease in $G_r$ above 280 °C through a high plateau come from the thermal degradation. It may be noted that the values of $G_r$ remain constant at a high plateau, irrespective of the continuous weight loss. This fact can be explained by assuming that the crosslinked network is formed at the first stage of the thermal degradation and that the so-formed polymeric structure remains unchanged in spite of the escape of small molecules, resulting in a continuous weight loss. In the case of epoxy resins during the curing process, the changes in $G_r$ with time are similar to those of the present case (Fig. 6), and so an analogous mechanism of the formation of crosslinkage may be proposed.

These results concerning the thermal degradation are summarized in Table 1. The temperatures at which the values of $G_r$ begin to increase become higher in the order of PVdB<PVB<PVdC-VC<PVC<PVdF<PVF. This order agrees well with that of the bond energy in the carbon-halogen bonds. Considering these features, together with the relation between the dynamic mechanical and the thermogravimetric results, and considering the appearance of the peak of the C-C double bond in the IR spectra, the increase in $G_r$ seems to be attributable mainly to the dehydrohalogenation and the crosslinking reaction. The temperatures of the maximum of $G_r$ become higher in the order of PVdB≈PVB<PVdC-VC<PVC<PVF<PVdF. In the cases of PVB and PVdB, those of the left-hand side of the plateau were taken as the maxima. The order of the temperatures at which $G_r$ begins to decrease is PVdC-VC≈PVdB<PVC<PVB<PVF<PVdF.

These features are attributable to the difference in the stability of the dehydrohalogenation products against the oxidation which proceeds at the relatively higher temperatures, though the details have not been elucidated.

*Time Dependence of $G_r$ and $\lambda$.* In order to study the kinetics of the thermal degradation, the $G_r$ and $\lambda$ are measured under isothermal conditions. Two typical results are shown in Figs. 5 and 6. Assuming that the

Table 1. THE TEMPERATURES AT WHICH THE CHANGES IN THE MECHANICAL PROPERTIES AND THE WEIGHT LOSS OCCUR

| Sample | $G_r$ (in)[a] | $W$ (loss) | $G_r$ (max) | $G_r$ (de)[a] |
|---|---|---|---|---|
| PVC | 190 °C | 230 °C | 300 °C | 300 °C |
| PVdC-VC | 160 | 210 | 280 | 280 |
| PVF | 280 | 310 | 340 | 340 |
| PVdF | 200 | 180 | 400 | 400 |
| PVB | 150 | 150 | 200—320 | 320 |
| PVdB | 130 | 100 | 200—280 | 280 |

a) $G_r$ begins to increase or decrease.

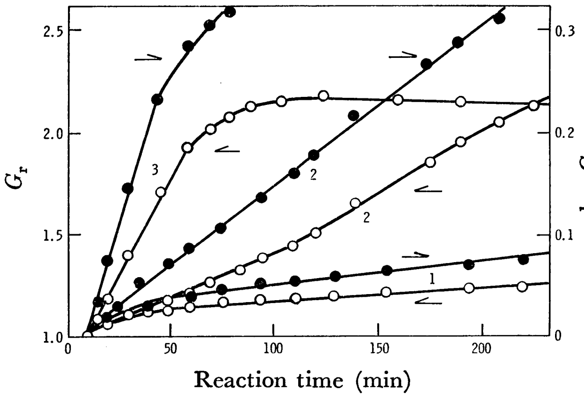

Fig. 5. $G_r$ *vs.* $t$ and log $G_r$ *vs.* $t$ plots of PVC during degradation in air at various temperatures. (1): 196 °C, (2): 221 °C, (3): 246 °C.
○: $G_r$, ●: log $G_r$.

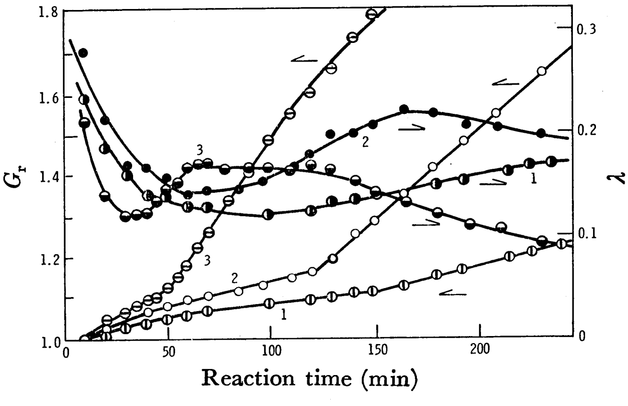

Fig. 6. $G_r$, $\lambda$ *vs.* $t$ plots of PVdB during degradation in air at various temperatures. (1): 102 °C, (2): 110 °C, (3): 122 °C.
⦶ ○ ⊖: $G_r$, ◑ ● ◒: $\lambda$.

Table 2. The apparent activation energies obtained from the several ways of analysis

| Sample | Temp. range (°C) | $G_r$[a] | The apparent activation energies (kcal/mol) From $G_r$ | $A_r$ | log $G_r$ | log $A_r$ | shift | t (λ-max) |
|---|---|---|---|---|---|---|---|---|
| PVC | 170—250 | in | 24.7 | 26.4 | 29.6 | 12.4 | 29.7 | |
| | 250—340 | de | 21.7 | | 28.6 | | 21.7 | |
| PVdC-VC | 150—250 | in | 26.0 | 27.5 | 26.5 | 20.7 | 26.5 | |
| | 250—300 | de | 29.5 | | 29.5 | | 17.5 | |
| PVF | 190—300 | in | 22.7 | 20.7 | 22.3 | 17.0 | 26.3 | |
| | 270—370 | de | 10.8 | | 16.0 | | 18.0 | |
| PVdF | 250—300 | in | 10.6 | | 10.0 | | 23.5 | |
| | 300—390 | in | 30.2 | 36.6 | 30.5 | 18.2 | 31.1 | |
| | 350—420 | de | 27.9 | | 31.6 | | 31.1 | |
| PVB | 120—200 | in | 12.8 | 47.9 | 11.7 | 30.2 | 12.8 | |
| | 250—320 | de | 29.8 | | 34.7 | | 28.6 | |
| PVdB | 110—170 | in | 18.2 | 19.1 | 16.0 | 18.4 | 15.7 | 18.2 |
| | 250—300 | de | 17.7 | | 21.8 | | 21.6 | |

a) $G_r$ increases or decreases.

order of the reaction is zero or first, the plots of the $G_r$ *versus* the time and of the log $G_r$ *versus* the time were made. In the case of PVC (Fig. 5), these two curves are linear at the initial stage. The order of the reaction has not yet been determined. At any rate, the slopes of these curves are a measure of the velocity constants, irrespective of the order of the reactions. The time dependence of $\lambda$ is very slight and has been omitted from the figure. For other polymers, behavior was observed similar to that in the case of PVC. In the case of PVdB (Fig. 6), on the other hand, the curves are each composed of the two stages, and, at the same time, there exists a maximum in $\lambda$ corresponding to the transition between the two stages. These phenomena have been found for polystyrene in our previous work[2] and for many cases of epoxy resins during the curing process. The time corresponding to the maximum of $\lambda$, therefore, may be regarded as a measure inversely proportional to the velocity constants.

The logarithms of the initial slopes and the time of the maximum $\lambda$ were plotted against the reciprocal temperature ($K^{-1}$). From this analysis, the apparent activation energies are obtained as is shown in Table 2. These values agree well with those obtained by the other methods. For example, in the case of PVC, the value estimated from $G_r$, 24.7 kcal/mol, agrees well with 24 kcal/mol obtained by Talamini and Pezzin by TGA method.[12]

Furthermore, as was done in the previous work, a superposition procedure for the temperature dependence of $G_r$-reaction time curves was made. A typical composite curve is shown in Fig. 7. As was pointed out by Tobolsky[13] and shown in our previous work, the apparent activation energies can be obtained from the Arrhenius plot of the so-called shift factor in this procedure. The values are shown in Table 2. Except for a few cases, the agreement of the values estimated by various procedures is excellent; this fact confirms the validity of the analysis mentioned above.

*The Changes in the Relative Absorbance Ratio.* In order to substantiate the above discussion about the correlation between the changes in the dynamic mechanical properties and the chemical processes, and also in order to carry out the kinetic study, the IR spectra were measured. The change proceeds as follows; first, the peak of C-X bond disappears and the peak of C-C double bond appears in consequence of the dehydrohalogenation; second, the peaks of the carbonyl and ether groups resulting from the oxidation reaction appear. Otani suggested that the appearance of the peak of the ether group is the result of a crosslinking formation by the oxidation reaction.[14] These features support the considerations mentioned above of the mechano-chemical processes.

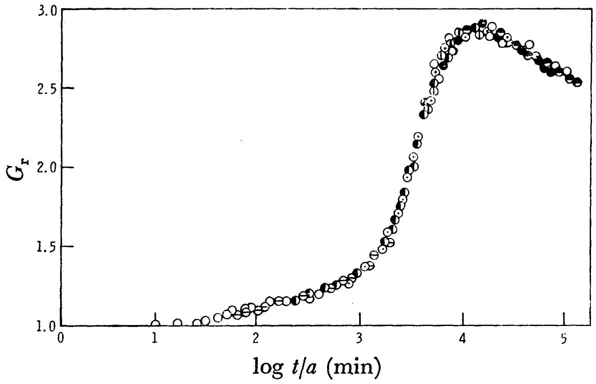

Fig. 7. Composite curve for relative shear modulus of PVC. ($T_0$=172 °C)
○: 172 °C, ⊖: 196 °C, ◐: 221 °C, ⊙: 246 °C, ⦶: 271 °C, ●: 294 °C, ○: 319 °C, ◓: 343 °C.

A typical example of the changes in the relative absorbance ratio ($A_r$) is shown in Fig. 8. A procedure of kinetic study similar to that used in the time dependence of $G_r$ was used. The $A_r$ *vs.* time and log $A_r$ *vs.* time curves are linear at the initial stage. The slopes of these curves are, therefore, a measure of the velocity constant.

The logarithmic initial slopes in their curves were plotted against the reciprocal temperature ($K^{-1}$). From this analysis, the apparent activation energies were obtained as is shown in Table 2. These values agree well with the values obtained from the several other procedures of analysis. For example, in the case of PVdC-VC, the values are 26.0 kcal/mol from the $G_r$

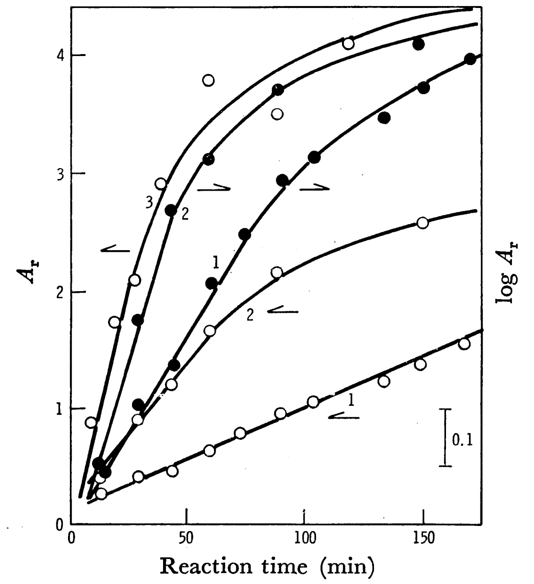

Fig. 8. $A_r$ vs. $t$ and log $A_r$ vs. $t$ plots of heat-treated PVdC–VC. (1): 184 °C, (2): 201 °C, (3): 221 °C. ○: $A_r$, ●: log $A_r$.

*vs. t* curves, 26.5 from log $G_r$ *vs. t*, 26.5 from the shift factor of the composite curve, 27.5 from $A_r$ *vs. t* curves, and 20.7 from log $A_r$ *vs. t*. These agreements support also the considerations mentioned above of the correlation between the mechanical processes and the chemical reactions. There are, however, some deviations in several cases in the table. The problem of these deviations remains unsolved.

## Conclusion

The changes in the mechanical properties at higher temperatures are associated with such chemical reactions as dehydrohalogenation, crosslinking and oxidation. The effect of the different halogen species on the thermal stability was elucidated. The stability of the polymers studied lies in the order of PVdB<PVB<PVdC-VC<PVC<PVdF<PVF.

Kinetic studies of these reactions were carried out, and the apparent activation energies were obtained by several ways of analysis. These values agree well each other except for a few cases. Finally, composite curves for the relative shear modulus were obtained for all the polymers studied.

The authors wish to thank Mr. Yoshio Takahashi (Electrotechnical Laboratory) and Associate Professor Yoshio Shibazaki (Saitama University) for affording the facilities for the use of the TGA and DTA apparatus.

## References

1) J. K. Gillham and A. F. Lewis, *J. Appl. Polym. Sci.*, **7**, 685 (1963).

2) N. Furusho, T. Komatsu, and T. Nakagawa, *Nippon Kagaku Kaishi*, 1166 (1973).

3) N. Furusho, T. Komatsu, and T. Nakagawa, *Repts. Progr. Polym. Phys. Japan*, **16**, 335 (1973).

4) W. W. Korshrk and N. G. Matwejewa, *C. Zentralbl.*, **127**, 3317 (1956); G. Blauer, M. Shenblat, and A. Katchalsky, *J. Polym. Sci.*, **38**, 189 (1959).

5) K. Schmieder and K. Wolf, *Kolloid-Z.*, **134**, 149 (1953).

6) N. Kawasaki and T. Hashimoto, *J. Polym. Sci., Part A-2*, **9**, 2095 (1971).

7) L. E. Nielsen, "Mechanical Properties of Polymers," Reinhold Publishing Co., New York (1953), pp. 17, 34.

8) H. Kakutani, *J. Polym. Sci., Part A-2*, **8**, 1177 (1970).

9) M. Ota, S. Nishida, and H. Ishii, *Kobunshi Kagaku*, **27**, 785 (1970).

10) H. Ishii, *ibid.*, **27**, 858 (1970).

11) N. L. Zutty and C. J. Whitworth, *J. Polym. Sci., Part B*, **2**, 709 (1964).

12) G. Talamini and G. Pezzin, *Makromol. Chem.*, **39**, 26 (1960).

13) A. V. Tobolsky, "Properties and Structure of Polymers," John Wiley & Sons, Inc., New York (1960), p. 226.

14) S. Otani, *Kogyo Kagaku Zasshi*, **61**, 447 (1958).