The Heating-rate Dependence of the Mechanical Properties of Several Polymers at Higher Temperatures

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Measurements of the mechanical properties of various polymers at higher temperatures under the conditions of several heating rates were carried out in the air using the torsional braid analysis (TBA) method. It has become apparent that the examples of the dependence of the mechanical properties upon the heating rate at higher temperatures are classified into two groups. The first is characterized by the fact that the temperature of the maximum in the logarithmic decrement remains unchanged, irrespective of any changes in the heating rate. This situation is related to the physical process. On the other hand, in the case of the second group, the TBA curves are shifted to higher temperatures with an increase in the heating rate; this is the results of chemical processes. A kinetic treatment of thermal analysis, in which kinetic parameters can be calculated from the heating-rate dependence of the characteristic point in the observed curves, was used in the present study. From this analysis, the apparent activation energies of the thermal degradation of polymers were obtained, and comparisons of these values with those from the isothermal measurements were made.

Previously, we measured the chemorheological properties of a series of polymers during thermal degradation using the torsional braid analysis (TBA) method and discussed the relationship between the mechanical behavior and the chemical processes with the aid of the results of IR spectroscopy, thermogravimetry, and calorimetric measurements. From these studies, it has become apparent that the TBA method can be used for the studies of the thermal degradation of polymers and can also be used as a convenient kinetic tool, and that the shapes of the TBA curves of the polymers can be classified into three groups according to their degradation mechanisms. Moreover, it was found that the isothermal TBA curves were superposed into one composite curve by shifting them along the axis of the logarithms of time and that activation energies were obtained from the shift factor which agree well with those estimated from the slopes of the curves of the moduli *versus* the time.[1,2)]

Furthermore, from the study of the heating-rate dependence of the TBA curves of poly(acrylic acid), we found that the mechanical behavior due to the glass transition is scarcely affected at all by the heating rate and that the chemorheological behavior is shifted to higher-temperature region with an increase in the heating rate. Using the kinetic treatment in thermal analysis, in which the kinetic parameters can be derived from the plots of the logarithmic heating rate *versus* the reciprocal temperature at the characteristic point in the curves observed, the apparent activation energies of the thermal degradation of polymers were obtained. These values agree well with those obtained from the isothermal measurements.[3)]

In the present study, we will report the results of studies of the heating-rate dependence of the TBA curves of several polymers at higher temperatures. For these polymers, the isothermal mechanical measurements had previously been carried out.

The purpose of this work is to examine the possibility and the validity of the classification of the mechanical properties into one group resulting from chemical processes and another resulting from physical processes on the basis of measurements of the heating-rate dependence. It was also intended to examine the general applicability of the kinetic treatment in thermal analysis, in which the kinetic parameters can be obtained from the heating-rate dependence of the characteristic point in the curves observed, and to compare the activation energies obtained from this non-isothermal analysis with those obtained from the isothermal measurements.

Experimental

The poly(methyl methacrylate) (PMMA), the poly(vinyl fluoride) (PVF), the poly(vinyl chloride) (PVC), the vinylidene chloride–vinyl chloride copolymer(PVdC-VC) with the weight ratio of 82: 18, the poly(vinyl acetate) (PVAc), the poly(methyl acrylate) (PMA), the polyacrylonitrile(PAN), and the polyacrylamide(PAAm) were all commercial materials. The polystyrene(PSt), the poly(α-methyl styrene) (PMSt), and the poly(methacrylic acid) (PMAA) were, on the other hand, synthesized in our laboratory.

The procedure of the torsional braid analysis (TBA) has been described in previous papers.[1—3)] Measurements of the mechanical properties were carried out in the air using a modified TBA apparatus made by the addition of a Shinku Riko model HPC-5000 programed temperature controller. The relative shear moduli, $(1/P)^2$, were calculated from the periods, P, of damped oscillations. . The logarithmic decrement [$\lambda = (1/n)\ln(A_{2n+1}/A_1)$] is calculated from the amplitudes of the damped oscillations, where n is the number of oscillations and A_1, A_{2n+1} are amplitudes of the first and n-th oscillations respectively.

Results and Discussion

Heating-rate Dependence of the Mechanical Properties. The results of the dependence of the TBA curves of several polymers upon the heating rate are shown in Figs. 1—6. As is shown in the figures, the heating-rate dependences of the mechanical properties can be classified into two types. The first type is characterized by the fact that little change occurs in the temperature of the maximum in λ, which is accompanied by an abrupt or slight drop in the modulus. In the second type, the TBA curves are shifted to higher temperatures as the heating rate increases.

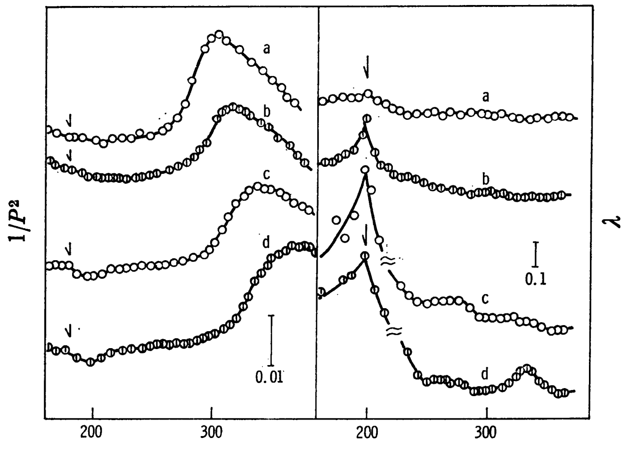

Fig. 1. The plots of $(1/P)^2$, λ *vs.* T of PVF under the several heating rates.
The arrows indicate the mechanical changes due to the melting. (a): 0.5 °C/min, (b): 1 °C/min, (c): 2 °C/min, (d): 5 °C/min.

First, the mechanism of the mechanical changes classified as the first type will be discussed. In the case of PVF, as is shown in Fig. 1, the temperature at which a slight drop in the moduli and the corresponding maximum in λ were found does not alter, irrespective of the change in the heating rate. Situations similar to that in PVF were found in the cases of PMSt and PMMA. That is, in PMSt (Fig. 2), the maximum in λ and the abrupt drop in the moduli at about 180 °C remain unaltered, and also in PMMA, an intense peak of λ and the slight drop in the moduli at about 230 °C are not shifted. Such phenomena, which have been discussed in our previous papers, too, may be interpreted as follows by the aid of the results of the calorimetric and other results reported by us and by other workers. First, the mechanical change at about 200 °C in PVF may be assigned to the melting.[2,4,5] Second, that at about 180 °C in PMSt is attributed to the glass transition.[6,7] Lastly, that at about 230 °C in PMMA is due to the melting.[1,8]

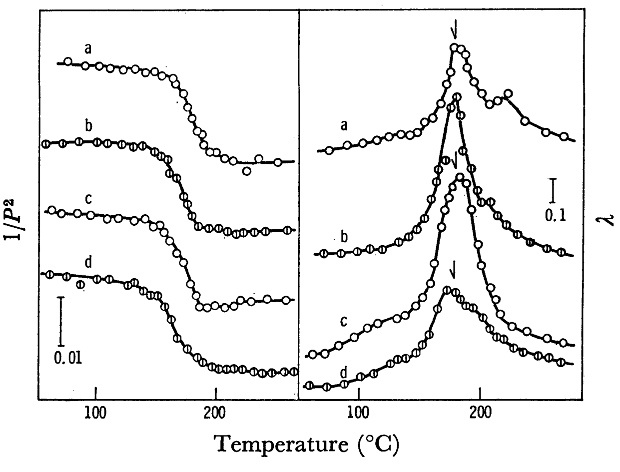

Fig. 2. The plots of $(1/P)^2$, λ *vs.* T of PMSt under the several heating rates. The arrows indicate the maximum in λ due to the glass transition.
(a): 0.5 °C/min, (b): 1 °C/min, (c): 2 °C/min, (d): 5 °C/min.

Wunderlich *et al.* have studied the heating-rate dependence of the glass-transition temperature (T_g) of polystyrene by means of dynamic differential thermal analysis.[9] In their results, the increase in T_g is only a few degrees in the heating-rate region from 1 to 7.6 K/min in a system in which the sample has been cooled slowly above 400 K. They compared their experimental data with the results of the theoretical considerations derived from the hole theory of liquids and calculated the activation energy at 160 kcal/mol (669 kJ/mol) from the plots of the logarithmic heating rate against the reciprocal glass-transition temperature. In PMSt, assuming that the value of the activation energy is analogous to that in PSt (probably larger than

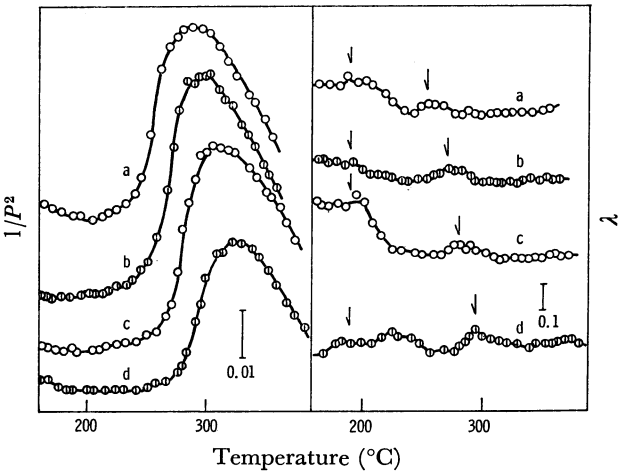

Fig. 3. The plots of $(1/P)^2$, λ *vs.* T of PVC under the several heating rates. The arrows at about 200 °C indicate the mechanical changes due to the physical process and those at higher temperatures indicate the maximum in λ due to the chemical process.
(a): 0.5 °C/min, (b): 1 °C/min, (c): 2 °C/min, (d): 5 °C/min.

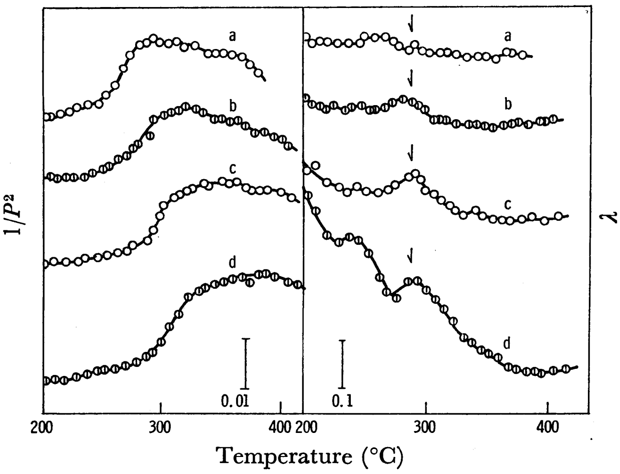

Fig. 4. The plots of $(1/P)^2$, λ *vs.* T of PAN under the several heating rates. The arrows indicate the maxima in λ due to the physical process.
(a): 0.5 °C/min, (b): 1 °C/min, (c): 2 °C/min, (d): 5 °C/min.

that in PSt), the change in T_g is calculated at a few degrees from the analysis described just above. Therefore, our experimental data in PMSt are reasonable.

The above discussions have demonstrated that the slight dependence of the TBA curves upon the heating rate is a characteristic feature in the physical processes: glass transition, melting, *etc.* In order to make clear the mechanical changes in polymers in the higher-temperature region, an inspection of the heating-rate dependence of the TBA curves of PAN, PVC, PAAm, PMAA, and PSt will be made on the basis of this consideration. The nature of the processes (physical or chemical) has not yet been fully elucidated.[1-3]

In PVC, as is shown in Fig. 3, it was found that the increase in the moduli begins at about 200 °C and that the broad maximum in the λ curve at around 200 °C does not shift. In the previous paper, the origin of this change in λ (the fusion or the result of the formation of conjugated carbon–carbon double bonds) was not determined. From its slight dependence upon the heating rate in the present study, it may be concluded that this broad maximum in the λ curve is due to a physical process, presumably the fusion. This consideration agrees with the results of the measurements in the fusion of PVC by other workers.[9-11] We found, in PVC (Fig. 3), that both the increase in the moduli and the corresponding maximum in λ in the region of temperatures higher than those discussed above are shifted to higher temperatures with an increase in the heating rate. In PAN (Fig. 4), in contrast to this, slight dependence of λ at about 290 °C upon the heating rate was observed irrespective of the existence of a considerable increase in the moduli. Gillham and Schwenker have mentioned that these mechanical changes (the considerable increase in the moduli and the maximum in λ at about 290 °C) coincide in position with a exothermic peak in the differential thermal analysis.[12] This exothermic peak is assigned by Thompson to the formation of the ladder structure.[13] However, in view of the slight dependence of this maximum in λ upon the heating rate in this study, it may be concluded that the change in λ at about 290 °C is attributed to a physical process. This conclusion is supported by our finding that this exothermic peak shifts to higher temperatures with an increase in the heating rate. However, considering that this exothermic peak temperature moves below or just above the temperature of the maximum in λ according to the heating rate, it is not clear whether this change in λ is a characteristic feature in the original PAN or in the so-formed ladder polymer from PAN.

In a similar manner, the mechanism of the mechanical change above 200 °C in PAAm and PMAA is determined by the aid of the calorimetric analysis to be due to the following physical processes. First, in PAAm, the maximum of λ at about 200 °C is due to the glass transition, and that of λ at about 240 °C is due to some physical process, the details being not yet clear. Second, in PMAA, the maximum in λ at about 220 °C is attributable to the glass transition, while the peak in λ at about 270 °C is presumably due to the melting.

In the case of PSt (Fig. 5), in contrast to the cases of PVC, PAN, PAAm, and PMAA, it was found that the small maximum in λ and the corresponding drop in the moduli shift from 220 °C to 280 °C with an increase in the heating rate. On the basis of the above discussions of the heating-rate dependence of the TBA curves, this mechanical change is considered to be attributable to the chemical process, not to the physical process. Considering that the weight loss during heating is slight in this temperature region, as has been reported in a previous paper,[1] and that the abrupt drop in the molecular weight at an early stage of the thermal

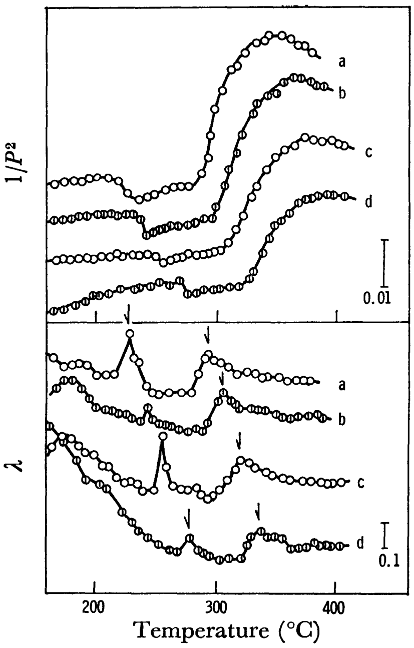

Fig. 5. The plots of $(1/P)^2$, λ *vs.* T of PSt under the several heating rates.
The arrows in left-hand side and right-hand side indicate the maxima in λ due to the chemical processes.
(a): 0.5 °C/min, (b): 1 °C/min, (c): 2 °C/min, (d): 5 °C/min.

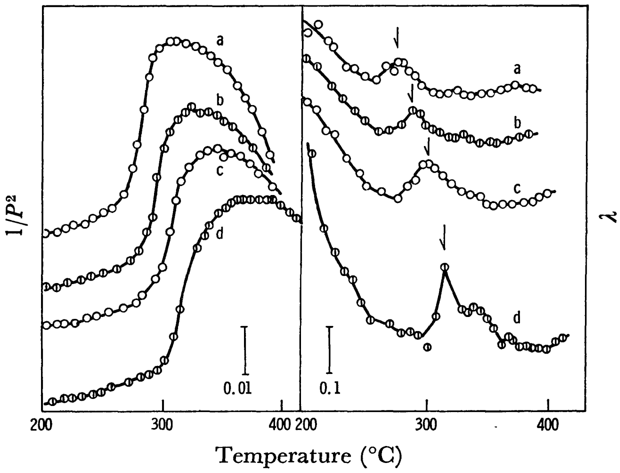

Fig. 6. The plots of $(1/P)^2$, λ *vs.* T of PVAc under the several heating rates.
The arrows indicate the maxima in λ due to the chemical process. (a): 0.5 °C/min, (b): 1 °C/min, (c): 2 °C/min, (d): 5 °C/min.

degradation of PSt was observed by Jellinek,[14] the mechanism of this mechanical change seems to be related to the abrupt drop in the molecular weight.

Here, turning the viewpoint to the mechanical changes grouped into the second type, in which the increase or decrease in the moduli and the corresponding change in the λ are shifted to higher temperatures with an increase in the heating rate (a typical example is shown in Fig. 6, the case of PVAc), the mechanism of these mechanical changes will be discussed. For PVC, it was found that the IR absorption peak of the carbon-carbon double bond becomes more intense with the progress of the reaction and that the temperature at which the weight loss occurs is near to that at which the moduli begin to increase. From these findings, it has been concluded that the increase in the moduli is attributable to the formation of the C–C double bond resulting from dehydrochlorination and the cross-linking through the double bond, while the decrease in the moduli is due to the chain scission.[2] In a similar way, in PAN, it has been shown that the formation of the ladder structures leads to an increase in the moduli.[1] For other polymers, the relationship between the mechanical change and the chemical process was demonstrated in the previous works by the aid of the results of IR spectroscopy, thermogravimetry, calorimetric study, and the results of other workers. From the above discussions, it may be concluded that a distinct dependence of the mechanical behavior upon the heating rate in these polymers is a peculiar feature of the chemorheological processes.

The considerations in this section suggest that the inspection of the heating-rate dependence of the mechanical properties can be used as a convenient tool for the identification of the nature of mechanical changes in higher-temperature regions in which not only physical processes but also chemical reaction can simultaneously occur.

Kinetic Analysis of Chemorheological Properties during Thermal Degradation. In the preceding sections, it has become clear that the heating-rate dependence of the mechanical properties can be classified into two groups. In the second group, the observed chemorheological curves shift to higher temperatures with an increase in the heating rate. A similar heating-rate dependence has been found in several kinds of thermal analysis: the thermogravimetry,[15] the mass spectrometric thermal analysis,[16] the electric thermal analysis,[17] *etc.* In these measurements, the procedures derived from the isothermal kinetic equation were used to obtain the kinetic parameters. In these procedures, the following assumptions are made. That is, the observed quantity characterizing some properties, y, is a function of a structural quantity, $x; y=f(x)$, and the change in the structural quantity obeys the Arrhenius equation; $\mathrm{d}x/\mathrm{d}t=A\cdot\exp(-E/RT)\cdot g(x)$, where A, E, and R are the frequency factor, the activation energy, and the gas constant respectively. Also, the same degree of change in the structural quantity leads to an equal degree of change in the properties observed. Here, a linear temperature change is also assumed; $T=T_0+ht$, where T_0 and h are the initial temperature and the heating rate respectively, and then x is integrated. The details of this calculation have been shown in the works by Ozawa and other workers.[18,19]

From the final solution of this calculation, a linear relationship between the logarithmic heating rate and the reciprocal of the temperature at the characteristic point in the observed curves is derived, and then the activation energies can be estimated from the slope of their plots. Also, it has been concluded that the superposition of the TBA curves into one composite curve is possible by their shift along the axis of the reciprocal temperatures. This kinetic treatment is extended to the systems in which the exact quantitative correlation between the observed properties and the structural quantities is not clear, assuming that conditions similar to those presented above are satisfied in such systems.[20]

In the previous paper, we attempted to apply this kinetic treatment to the chemorheological behavior in PAA and obtained reasonable activation energies, which agree well with those from the isothermal measurements. Moreover, the superposition of the isothermal TBA curves into one composite curve was successfully carried out by shifting them along the axis of the logarithmic time in all the polymers studied. In both procedures, it was assumed that the mechanical properties depend only upon their chemical structure and that the same extent of reaction leads to an equal degree of mechanical change. These assumptions are the same as those used in the kinetic procedure in thermal analysis. The success of the application of the non-isothermal kinetic treatment to the chemorheological behavior in PAA and the superposition procedure of the isothermal curves suggest that the TBA method can be used as a convenient kinetic tool in thermal analysis, despite a lack of information about the exact quantitative relationship between the mechanical properties and the chemical structures.

Below, the results of the examination of the application of this non-isothermal kinetic procedure to the chemorheological behavior during the thermal degradation of various polymers will be discussed. This was

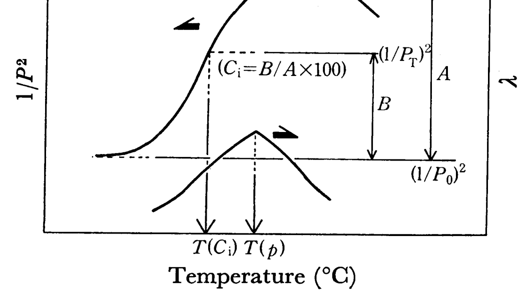

Fig. 7. The schema of the kinetic procedure.
The $(1/P_T)^2$, $(1/P_0)^2$, and $(1/P_\infty)^2$ are the values at temperature T, at minimum point, and at the maximum point in moduli, respectively.
The $T(C_i)$, $T(p)$ are the temperatures at conversion C_i and of maximum in λ.

made by noting whether or not the following conditions are satisfied. (1) The plot of the logarithmic heating rate *versus* the reciprocal of the temperature of the maximum in λ, $T(p)$, is linear. (2) The plot of the logarithmic heating rate *versus* the reciprocal of the temperature to the same degree of conversion in the chemorheological change, $T(C_i)$, is linear. (3) The superposition of the curves of the chemorheological properties, plotted as a function of the reciprocal temperature, is possible. A schema of this procedure is shown in Fig.7.

The obvious maxima in λ which correspond to the increase or decrease in the moduli were found in PSt, PVC, PVdC–VC, PVAc, and PMA. The plots of the logarithmic heating rate against the reciprocal of the temperature of the maximum in λ are shown in Fig. 8. As is clear in the figure, these plots are linear in all the polymers mentioned above. From the slopes of these plots, the activation energies were obtained as listed in Table 1. Here, these values will be compared with those calculated from the isothermal measurements. In general, the values from these two procedures roughly agree with each other for the individual polymer.

In PMA, a good agreement similar to that in PAA reported previously[3] was found. However, in PSt, in which the increase in the moduli was controlled by the cross-linking, as in PAA and PMA, the agreement is not so satisfactory as in the above two polymers. Also, in the cases of PVC, PVdC–VC, and PVAc, in which the cross-linking is undeniable but is not the main factor affecting the chemorheological properties, as was discussed in the preceding paper, the situation is not simple. That is, a good agreement was found in PVdC–VC, but the agreement in PVC and PVAc is not so good as in PVdC-VC. This suggests that these discrepancies can not be explained by only the difference in the degradation mechanisms. In order to make clear the nature of these facts, further work is necessary.

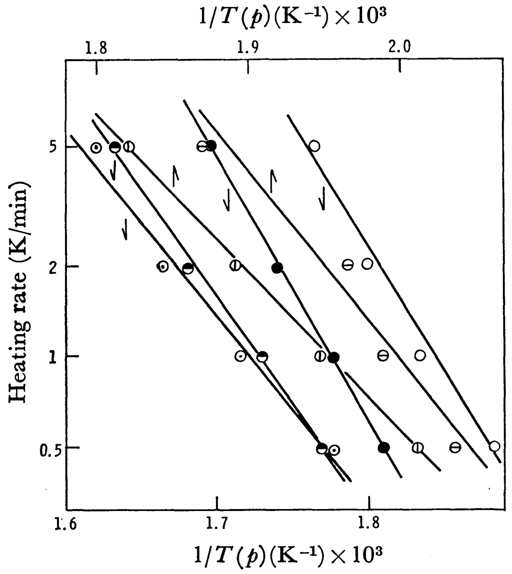

Fig. 8. The plots of the logarithmic heating rates *versus* the reciprocal of the temperatures of the maximum in λ of several polymers. ○: PVC, ⊖: PVdC–VC, ●: PVAc, ⦶: PSt(L) (the maximum in λ at lower temperatures), ◓: PSt (H) (the maximum in λ at higher temperatures), ⊙: PMA.

Table 1. The apparent activation energies estimated from the various procedures of analysis

Sample	The apparent activation energy (kJ/mol)[a]					
	From this work[b]	From isothermal measurements				
		initial slope[c]			shift factor $(1/P)^2$	time of max. λ
		G_r *vs. t*	log G_r *vs. t*	A_r *vs. t*		
PVC	151	103	124	110	124	—
PVdC–VC	113	109	111	115	111	—
PSt(H)[d]	140	102	102	—	129	104
PVAc	168	118	118	—	103	—
PMA	101	92	90	—	77	67
PSt(L)[e]	96	—	—	—	—	—

a) 1J=1/4.184 cal. b) The value is estimated from the slope of the plot of the logarithmic heating rate *versus* the reciprocal of the temperature of maximum in λ. c) Assuming $dG_r/dt=k_0$, $dA_r/dt=k'_0$, and $d(\log G_r)/dt=k_{1st}$, where k_0, k'_0, and k_{1st} are the apparent rate constants of the zero order and first order reactions, respectively. The value of A_r are the relative absorbance ratio for C–C double bond and C–H group in IR spectra. d, e) In PSt(H) and PSt(L), the maxima in λ were found in the relatively higher temperature side and relatively lower temperature side, respectively.

The examination of the second point—that the plot of the logarithmic heating rate *versus* the reciprocal of the temperature to the same degree of conversion in the chemorheological change is linear—was carried out in the following manner. The degree of conversion in the chemorheological change was defined as follows:

$$C = [(1/P_T)^2 - (1/P_0)^2]/[(1/P_{00})^2 - (1/P_0)^2]$$

where $(1/P_T)^2$ is the value at a cetain temperature, T, and where $(1/P_0)^2$ and $(1/P_\infty)^2$ are the values of the minimum and maximum in the moduli respectively. Then the temperature in the degree of the conversion C_i was determined from the figure. The schema of this treatment is shown in Fig. 7. Finally, the plot of the logarithmic heating rate *versus* the reciprocal of the temperature at C_i was made. It should be added here that the determination of the value of $(1/P_0)^2$ is approximative because of the lack of a wide and flat base line of the modulus.

Some typical plots of log h *vs.* $1/T(C_i)$ are shown in Fig. 9. As is clear in the figure, in PVC the plots are linear. In the other polymers, also, similar straight lines were obtained. By means of the analysis described above, the activation energies are also obtained, as is listed in Table 2.

In PVC, the values are scarcely affected by the degree of conversion. On the other hand, in PVAc, it was found that the activation energies below $C=70$ % are analogous to each other, while above $C=80$ % the values become smaller. This fact suggests that some reaction which probably leads to the decrease in the moduli occurs simultaneously at a high degree of conversion. Similar situations have been found in

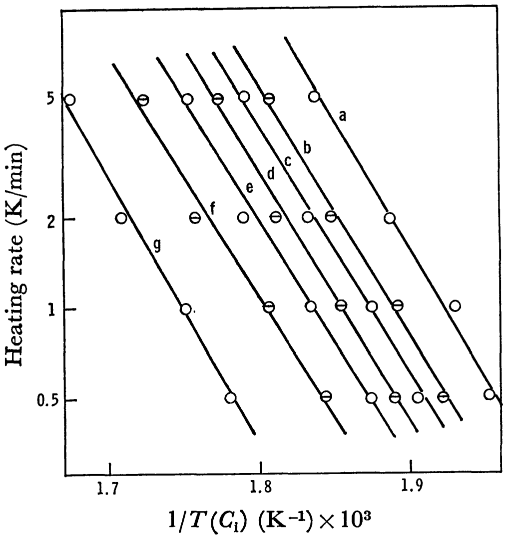

Fig. 9. The plots of the logarithmic heating rates versus the reciprocal temperatures at conversion C_i of PVC. (a): 10%, (b): 20%, (c): 30%, (d): 50%, (e): 70%, (f): 90%, (g): 100%.

Table 2. The apparent activation energies estimated from the slope of the plot of the logarithmic heating rate versus the reciprocal temperature at the same degree of conversion

Sample	The apparent activation energy (kJ/mol)[a] Degree of conversion (%)									
	10	20	30	40	50	60	70	80	90	100
PVC	161	158	158	161	160	159	156	155	156	176
PVdC-VC	126	125	143	140	149	151	141	139	139	120
PSt	152	156	156	147	146	140	132	131	159	159
PMA	—	109	93	86	83	78	75	73	71	37
PVAc	—	168	173	169	173	170	157	142	134	116
PVF	147	137	135	135	139	137	124	123	114	105
PAN	93	87	112	112	114	116	116	111	104	76
PAAm	169	153	146	136	133	124	118	111	103	100
PMAA	209	190	178	168	155	151	141	133	127	114

a) 1J=1/4.184 cal.

some other polymers. However, the nature of the decrease in the activation energies at an early stage in PAAm and PMAA is not yet clear. The values at the relatively lower degrees of conversions estimated by this analysis also roughly agree with those from the isothermal kinetic treatment and agree well those from the first non-isothermal kinetic treatment described above.

Furthermore, we attempted to superpose the TBA curves plotted against the reciprocal temperature for all the polymers studied. As is shown in Fig. 10, the procedure in PVAc was carried out successfully. In the other polymers, composite curves were also obtained. The quantities of the shift along the axis of the reciprocal temperature in the two temperature regions, where the moduli increase, or decrease, do not always coincide. This situation corresponds to the fact that the relationships of a shift factor to the reciprocal temperature in the two regions, where the moduli increase or decrease, are different in the superposition procedures of the isothermal TBA curves. The quantity of the shift in this procedure was not analyzed further in the present study.

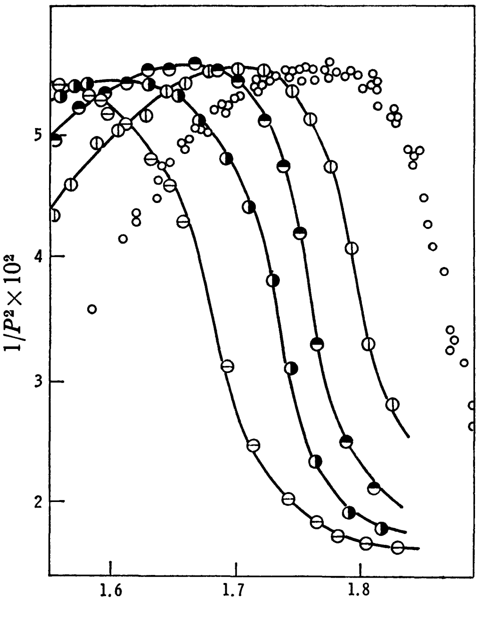

Fig. 10. The composite curve and the plots of $(1/P)^2$ *vs.* $1/T$ of PVAc under the several heating rates.
○: composite curve, ⦶: 0.5 °C/min, ◓: 1 °C/min, ◑: 5 °C/min, ⦶: 2 °C/min.

In the preceding sections, it has been demonstrated that the plots of the logarithmic heating rate *versus* the reciprocal of the temperature of the maximum in λ or at the conversion, C_i, are linear, and that the TBA curves observed under several heating rates can be superposed into one composite curve by means of their shift along the axis of the reciprocal temperature. These facts suggest that this kinetic treatment, in which the assumption that the same degree of change in the structural quantity leads to an equal degree of change in the observed properties was made, can be used in the kinetic studies of chemorheological behavior. However, the problem of the nature of the discrepancies between the activation energies obtained from this non-isothermal analysis and those obtained from the isothermal methods remains unsolved.

References

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

2) N. Furusho, T. Komatsu, and T. Nakagawa, This Bulletin, **47**, 1573 (1974).

3) N. Furusho, T. Komatsu, and T. Nakagawa, *ibid.*, **48**, 396 (1975).

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

5) D. I. Sapper, *J. Polym. Sci.*, **43**, 383 (1960).

6) R. F. Boyer, *Rubber Chem. Technol.*, **36**, 1303 (1963).

7) W. G. Barb, *J. Polym. Sci.*, **37**, 515 (1959).

8) L. E. Nielsen, "Mechanical Properties of Polymers," Reinhold Publishing Co., New York (1953), p. 34, 35.

9) B. Wunderlich and D. M. Bodily, *J. Polym. Sci.*, *Part C*, **6**, 137 (1964).

10) J. A. Juijn, J. H. Gisolf, and W. A. de Jong, *Kolloid-Z.*

Z. Polym., **235**, 1157 (1969).

11) C. E. Anagnostopoulus, A. Y. Coran, and H. R. Gamrath, *J. Appl. Polym. Sci.*, **4**, 181 (1960).

12) J. K. Gillham and R. F. Schwenker, Jr., *Appl. Polym. Symposia*, **2**, 59 (1966).

13) E. V. Thompson, *J. Polym. Sci., Part B*, **4**, 361 (1966).

14) H. H. G. Jellinek, *J. Polym. Sci.*, **3**, 850 (1948).

15) T. Ozawa, This Bulletin, **38**, 1881 (1965).

16) R. Sakamoto, Y. Takahashi, and T. Ozawa, *J. Appl. Polym. Sci.*, **16**, 1047 (1972).

17) T. Takamatsu and E. Fukada, *Bussei*, **12**, 513 (1971).

18) T. Ozawa, *J. Thermal Analysis*, **2**, 301 (1970).

19) L. Reich and S. S. Stivala, "Elements of Polymer Degradation," McGraw-Hill Book Co., New York (1971), Chapter 2.

20) T. W. Dakin, *AIEE Trans.*, **67**, 113 (1948).