A Torsional Braid Analysis of Polymethacrylates, Polyacrylate, Poly(vinyl alcohol), and Their Related Polymers during the Thermal Degradation

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The torsional braid analysis (TBA), thermogravimetry, and IR spectroscopy of polymethacrylates, polyacrylate, poly(vinyl alcohol), and their related polymers were carried out in air. The chemorheological properties of these polymers are markedly dependent on their chemical structures. First, the α-hydrogen atom plays an important role. In poly(methyl acrylate), the chemorheological behavior is similar to that of the polymers which have tendency to crosslink, whereas poly(methyl methacrylate) does not show any such behavior. A similar situation was found when comparing poly(acrylic acid) with poly(methacrylic acid). At the same time, the influence of the functional groups was examined. Second, the change in the mechanical properties due to crosslinking becomes more noticeable with an increase in the side-chain length of the methacrylate polymers. Furthermore, in addition to procedures used in the previous work, a new method of kinetic analysis of the heating-rate dependence was carried out in the case of poly(acrylic acid). The apparent activation energies estimated by this treatment are in good agreement with those estimated by other procedures.

Studies of the thermal degradation of polymers have been carried out by various methods—for example, pyrolysis gas chromatography, and thermogravimetry. Among those studies, relatively few studies have been done on the basis of the measurements of mechanical properties. Previously, we have reported some results of a thermal-degradation study of polymers by the measurement of their dynamic mechanical properties using the TBA method.[1,3] We found some interesting features not observable by other methods and proposed to use this method as a convenient tool for kinetic studies.

In the present paper, we wish to report some results of the TBA of polymethacrylates, polyacrylate, poly (vinyl alcohol) and their related polymers. Moreover, with the aid of the results of the thermogravimetry and IR spectroscopy, we will discuss the correlation between the chemorheological behavior and the chemical processes.

The purpose of this work is to elucidate the effects of the α-hydrogen atom, the side-chain length of the alkyl methacrylate polymers, and the character of the functional group on the chemorheological properties during the thermal degradation. We also intended to examine the applicability of the kinetic treatment usually used in thermogravimetry to the TBA studies.

Experimental

The poly(methyl acrylate)(PMA), poly(methyl methacrylate)(PMMA), poly(vinyl alcohol)(PVA), poly(acrylamide) (PAAm), poly(methyl vinyl ether)(PVME), and poly(vinyl acetate)(PVAc) were all commercial materials. The poly(acrylic acid)(PAA), poly(methacrylic acid)(PMAA), poly(ethyl methacrylate)(PEMA), poly(butyl methacrylate) (PBMA), poly(hexyl methacrylate)(PHMA), and poly(2-ethyl hexyl methacrylate) (PEHMA) were synthesized in the ordinary way.

The procedures of the torsional braid analysis(TBA) have been described in a previous paper.[1] The relative shear modulus ($G_r=(P_0/P)^2$) is calculated from the periods of oscillations, P, where the values of P_0 are the period of oscillation 10 min after the setting of the specimen under isothermal conditions or that at room temperature under the conditions of a constant heating rate (and where the values of P are the period at the time t or that at the temperature T). 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 where A_1 and A_{2n+1} are the amplitudes of the first and nth oscillations. The studies of the heating-rate dependence of the mechanical properties were carried out using an automatic TBA apparatus made by Takahashi *et al.*[2]

The IR measurements and the thermogravimetry(TG) were carried out in the same way as in a previous work.[3]

Results and Discussion

Chemorheological Behavior and Its Relation to the Chemical Process. The mechanical properties of these polymers are shown in the following figures. Each curve consists of several regions. The lower-temperature regions correspond to the physical process (glass transition, fusion, *etc.*). Their details will not be discussed here.

PMA and PMMA: In order to clarify the effect of the α-hydrogen atom on the chemorheological behavior, TBA measurements of PMA and PMMA, which both have ester groups and which differ each other in the point of whether the α-hydrogen atom exists or not, were carried out. As is shown in Fig. 1, the chemorheological properties of PMA and PMAA are very different from each other. In PMA, the gradual increase in G_r, its abrupt increase and the corresponding maximum of λ are observed above 150 °C. This situation resembles that in systems in which crosslinking occurs.[4]. However, for PMMA, no significant change is observed other than the glass transition at about 120 °C and the fusion at about 240 °C, in spite of the occurrence of a considerable weight loss above 200 °C; this weight loss is the result of the depolymerization. This mechanical behavior will be discussed below.

The IR spectra of these two heat-treated polymers remained essentially unchanged. The TG curve (Fig. 2) and the TBA curve (Fig. 1) show that, in PMA, the increase in G_r above 150 °C is not accompanied by any weight loss and that the decrease in G_r near 400 °C is closely connected with the large weight loss. Those observations are quite different from those of

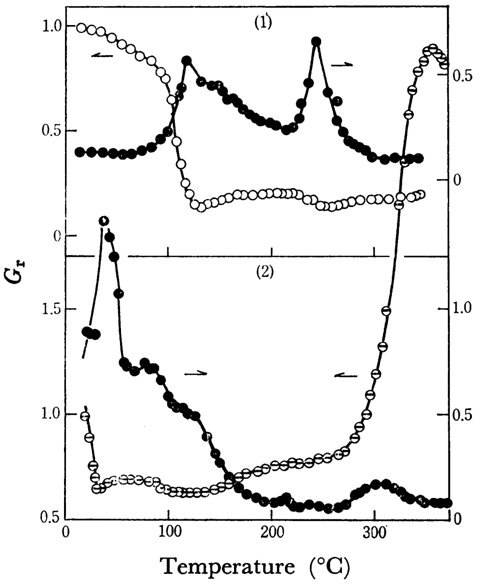

Fig. 1. G_r, λ *vs.* T plots of PMA and PMMA heated in air.
Heating rate: 1 °C/min. (1): PMMA, (2): PMA, G_r: ○⊖, λ: ●.

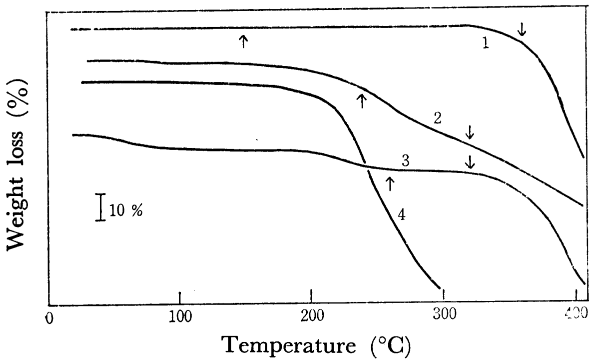

Fig. 2. TG curves of PMA, PMAA, PAA and PMMA in air.
Heating rate: 10 °C/min(1), 3 °C/min(2, 3 and 4). (1): PMA, (2): PAA, (3): PMAA, (4): PMMA. The arrows indicate the point at which G_r begins to increase (↑) and to decrease (↓).

the halogen-containing polymers, in which the chemorheological behavior is closely related to the weight loss resulting from the dehydrohalogenation.[3]

From the above discussion it may be concluded that, in PMA, the increase in G_r is attributable to the cross-linking caused by the α-hydrogen atom removal, while the decrease in G_r is due to the destruction of the network structure by the chain scission of the polymers, as is suggested by the large weight loss at higher temperatures. However, the nature of the slowing down of the rate of the increase in G_r just above 200 °C is not clear at present.

PAA and PMAA: From the study of PMA and PMMA, it has been made clear that the ester group does not affect the chemorheological behavior. Therefore, TBA measurements of PAA and PMAA were made. The PAA and PMAA are different from PMA and PMMA in only the point that PAA and PMAA have carboxyl groups instead of methyl ester groups.

In the cases of PAA and PMAA (Fig. 3), in contrast to the cases of their ester analogues, the chemorheological properties resemble each other. The IR spectra shown in Fig. 4 give important information on the mechanism of the mechanical change. In PAA, the peaks were observed at about 1050 and 1150 cm^{-1}, and a small shoulder, at about 1800 cm^{-1}. The former is probably due to the oxidative cross-linking, as has been suggested by Otani,[5] and the latter, to the formation of the anhydride structure.[6]

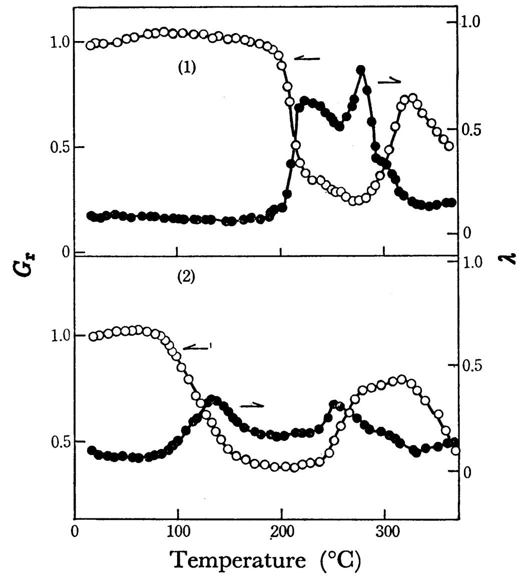

Fig. 3. G_r, λ *vs.* T plots of PMAA and PAA heated in air.
Heating rate: 1 °C/min. (1): PMAA, (2): PAA, G_r: ○, λ: ●.

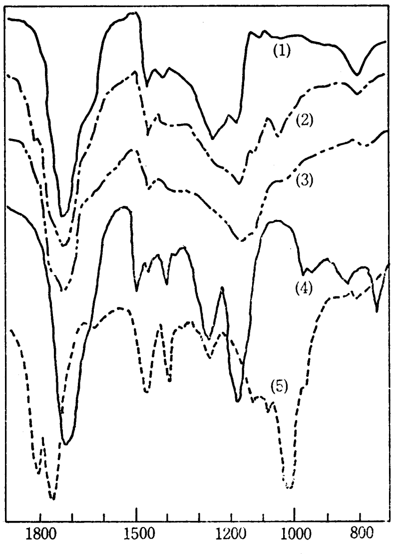

Fig. 4. IR spectra of PAA and PMAA heated in air. (1): original PAA, (2): PAA heated at 210 °C for 165 min, (3): PAA heated at 246 °C for 70 min, (4): original PMAA, (5): PMAA heated at 246 °C for 40 min.

On the other hand, the formation of the anhydride structure is slight. In PMAA, on the other hand, very intense peaks were found at about 1760 and 1810 cm^{-1}, shifted from 1720 cm^{-1}; these peaks can be assigned to the vibrations of the carbonyl group in the acid anhydride and the acid form. This finding suggests the formation of a typical acid-anhydride structure. Grant and Grassie have pointed out that this occurs both intramolecularly and intermolecularly.7) Moreover, quite different behavior was found in the change in mechanical properties due to the chemical process by means of isothermal TBA measurements of the two polymers, as will be discussed below.

These results indicate that, in PAA, the α-hydrogen atom, not the carboxyl group, is the principal factor in determining the chemorheological behavior in air. On the other hand, in PMAA, the formation of both intermolecular and intramolecular anhydride structures is the predominant factor. From the viewpoint of weight loss, in both PAA and PMAA the weight loss occurs with the chemorheological change; this weight loss is presumably related to the formation of the anhydride structure. This situation is different from that in the case of PMA, in which only the α-hydrogen atom plays an important role in the chemorheological behavior.

PVA, PVME, PVAc, and PAAm: From a comparison of the results on PMA and PAA, it can be expected that the chemorheological properties of the polymers with the α-hydrogen atom will be greatly influenced by the functional group in the side chain. Therefore, TBA studies of PVA, PVME, PVAc and PAAm, which all have the α-hydrogen atom, just as PAA and PMA have, were carried out. The results for these polymers are shown in Figs. 5 and 6. It should be pointed out here that the increase in G_r at lower temperatures in PVME is due to the evaporation of the residual solvent used for the specimen preparation. The fact that an ordinary decrease in G_r is observed by heating it up to 100 °C supports this consideration (see Curves A—B—C in Fig. 5).

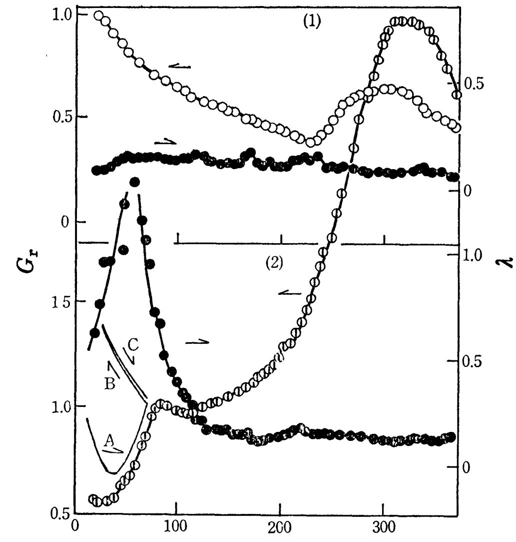

Fig. 5. G_r, λ *vs.* T plots of PVA and PVME heated in air.
The solid line shows the change in G_r of PVME during the repeated run (A-B-C). Heating rate: 1 °C/min. (1): PVA, (2): PVME, G_r: ○◐, λ: ●.

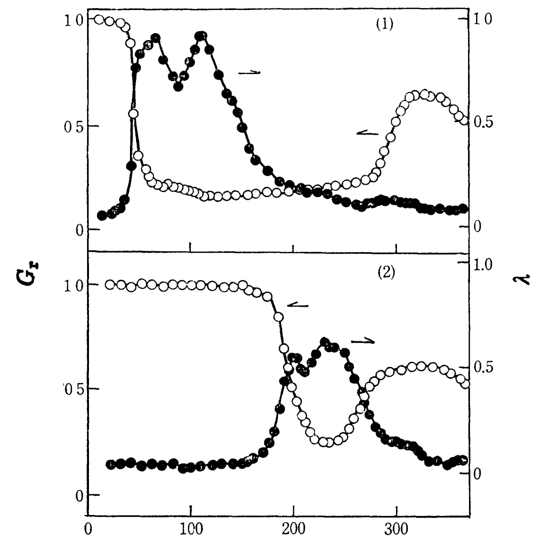

Fig. 6. G_r, λ *vs.* T plots of PVAc and PAAm heated in air.
Heating rate: 1 °C/min. (1): PVAc, (2): PAAm, G_r: ○, λ: ●.

In these four polymers, as in PMA and PAA, a considerable increase in G_r is observed at higher temperatures. In the IR measurements and thermogravimetry, we found the formation of the carbon-carbon double bond and the imide group, and also a close relation between the increase in G_r and the weight loss. Moreover, in these polymers, it is known that such reactions as the dehydration in PVA,8) the deacetylation in PVAc,9) and the imidization in PAAm10) occur at higher temperatures. Considering this, it may be concluded that the increase in G_r in these four polymers is closely connected to such reactions as dehydration, which involve the functional group in the side chain.

This situation resembles to some extent that in the halogen-containing polymers, in which the dehydrohalogenation is a dominant factor in their chemorheological properties. However, the findings that the IR absorptions of the double bond and of the imide group are not very intense and that the G_r increases without any weight loss from 120 to 180 °C in PVME suggest an undeniable role of α-hydrogen atom.

The order of the temperatures at which G_r begins to increase is; PVME<PVAc<PVA<PAAm. However, it is not clear that this order of temperatures corresponds to the order of the reactivities of the methoxyl, acetyl, hydroxyl, and amide groups because of the difference in the glass-transition temperatures and the undeniable effect of the α-hydrogen atom.

Polymethacrylates: The role of the α-hydrogen atom has been demonstrated in the above discussions. Furthermore, we compared poly(alkyl methacrylate)s, with a large number of hydrogen atoms in the side chain, with poly(methyl methacrylate), in which no

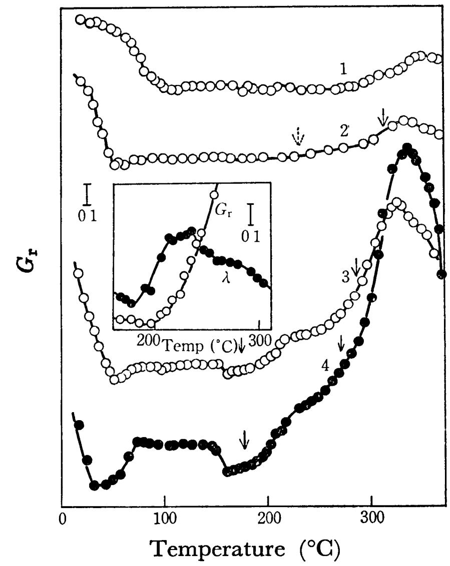

Fig. 7. G_r *vs.* T plots of the alkyl methacrylate polymers heated in air.
Inside figure: G_r, λ *vs.* T plots of polyethylene. Heating rate: 1 °C/min. (1): PEMA, (2): PBMA, (3): PEHMA, (4): PHMA. The arrows indicate the direction of the increase in G_r.

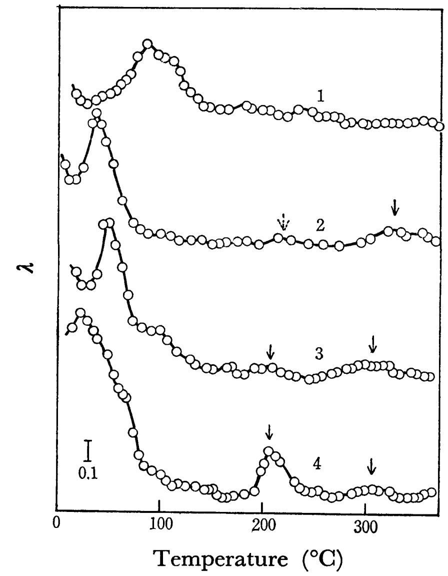

Fig. 8. λ *vs.* T plots of the alkyl methacrylate polymers heated in air. Heating rate: 1 °C/min. (1): PEMA, (2): PBMA, (3): PEHMA, (4): PHMA. The arrows indicate the maxima of λ which correspond to the increase in G_r.

significant mechanical change other than the glass transition and fusion is observed. In the alkyl methacrylate series, as is shown in Figs. 7 and 8,* the chemorheological properties approach those in polyethylene, which has a tendency to crosslink, with an increase in the alkyl side-chain length. The feature that λ shows a maximum corresponding to the increase in G_r becomes perceptible from PBMA. Considering the absence of the significant mechanical change due to the chemical process in PMMA, the resemblance between the TBA curves of polyethylcne and polyalkyl methacrylates, and the results of other workers, which will be discussed later, this increase in G_r and the corresponding maximum of λ can be explained by assuming that the crosslinking occurs between the hydrocarbon parts of the side chains.** However, the details of the relation of the mechanical change to the chemical process and the nature of the fact that the change in λ in polyalkyl methacrylates is smaller than that in polyethylene are not clear at present.

Graham found that gelation occurs in poly(heptyl methacrylate) and higher alkyl methacrylate polymers, and not in the polymers with a branched alkyl side-chain including longer ones. He pointed out that the length of the alkyl side chain is important and that the crosslinking probably occurs between side chains, but that the apparent relationship between the glass transition temperature and the behavior on γ-irradiation *in vacuo* is absent.[11] Burlant *et al.* have also found a similar role of hydrocarbon parts in the side chain during the γ-irradiation of polyalkyl acrylates.[12] On the other hand, in their study by UV irradiation in air, Morimoto and Suzuki observed gelation in PBMA and crosslinking without gelation in poly(lauryl methacrylate); they concluded that the degree of the crosslinking, estimated from the distribution of the molecular weight, increases with the increase in the glass transition temperature.[13] The results in the present study agree partially with those of the above two investigations. That is, they agree with Graham's suggestion of the importance of the side chain length, on the one hand, and with Morimoto's finding of the crosslinking in PBMA and higher alkyl methacrylate polymers, on the other hand. A systematic investigation is a subject in the future.

Relation of the Shapes of TBA Curves to the Degradation Mechanism. From the above discussions, the relation of the chemorheological behavior to the chemical process and the effect of the difference in chemical structure on the mechanical properties have been elucidated. Here, turning to the viewpoint of the relation of the shapes of the TBA curves to the degradation mechanism, it is possible to classify the curves into several types.

The first type is found in the case of PMMA, in which no significant mechanical change due to the chemical process is observed. Considering the PMMA and poly(α-methyl styrene), which are known to depolymerize mostly to monomers, behave chemorheologically in the same way,[14] it may be suggested that the flatness in the TBA curve can be explained by assuming that the modulus of the unchanged glass braid was observed as a result of the formation of substances with a lower mechanical reactance and/or the evaporation of such substances from the braid.

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* In these figures, the ordinates are arbitrarily shifted in order to avoid the overlapping of the curves.

** It should be pointed out here that the scission of the main chain and other reactions occur simultaneously with the crosslinking.

In the second type, G_r increases considerably at higher temperatures, but the change in λ is slight; especially the change in λ due to the chemical process in the isothermal measurements was negligibly small. The PVA, PVME, PVAc, PAAm, and PMAA belong to this type. Halogen-containing polymers, reported in the previous paper,[3] also belong to this type. In these polymers, reactions which involve the functional group in the side chain, such as dehydration, deacetylation, and dehydrohalogenation, are closely connected with the chemorheological behavior.

The third type is characterized by a maximum of λ which corresponds to the considerable increase in G_r on the curves of the temperature dependence and by one of λ found at the transition between the two stages of increase in G_r in the isothermal measurements (Fig. 10). The PMA, PAA, and other samples, which have a tendency to crosslink, belong to this type. Probably, higher alkyl methacrylate polymers can also be classified into this type. On the relation of the shapes of the TBA curves to the degradation mechanism, further extensive work is necessary.

Kinetic Studies. In the previous work,[3] a kinetic approach was carried out, in which the measurements of the relative shear modulus due to the chemical process under isothermal conditions and the superposition of G_r *vs.* time curves were tested. In addition to these procedures, two new approaches were undertaken in this study. One was the superposition of the λ *vs.* time curves, while the other was the application of the kinetic treatment used in such thermal analysis as thermogravimetry.

The curves of the changes in the mechanical properties due to the chemical process under isothermal conditions are classified into two categories in Figs. 9 and 10. No kinetic studies of the polyalkyl methacrylates were made. The PMAA, PVA, PVME, PVAc, and PAAm, in which the role of the functional group is important, as has been stated above, belong to the type shown in Fig. 9 (the case of PVME), where λ is omitted because of its slight change with the reaction time. On the other hand, the PMA and PAA belong to the other type, shown in Fig. 10 (PMA). A situation similar to that in the latter case, in which λ shows a maximum corresponding to the transition between the two stages of the increase in G_r, has been found in the samples in which crosslinking mainly occurs.[15] In all cases, the linearity of the curves was observed at the initial stage. As in a previous work,[3] the logarithms of the initial slopes and the time of the maximum, λ, were each plotted against the reciprocal temperature (K^{-1}). The apparent activation energies estimated from this analysis are listed in Table 1.

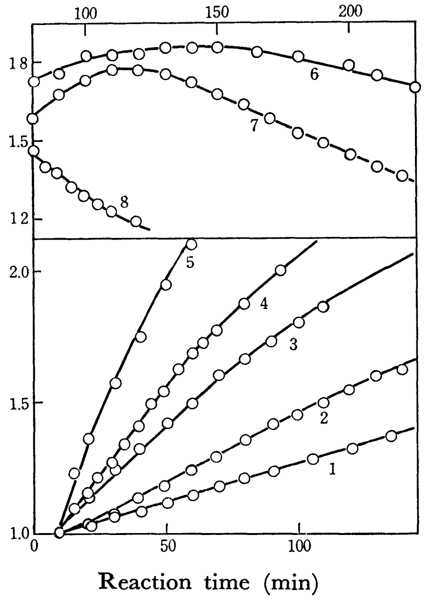

Fig. 9. G_r *vs. t* plots of PVME during degradation in air at various temperatures.
(1): 172 °C, (2): 196 °C, (3): 221 °C, (4): 246 °C, (5): 270 °C, (6): 343 °C, (7): 356 °C, (8): 370 °C.

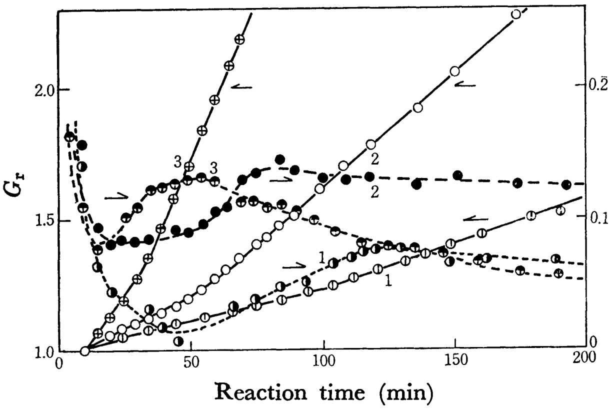

Fig. 10. G_r, λ *vs. t* plots of PMA during degradation in air at various temperatures.
(1): 246 °C, (2): 270 °C, (3): 294 °C. G_r: ⦶○⊕, λ: ◑●⊕.

A typical superposed curve is shown in Fig. 11, where the relative shear moduli were plotted on the scale of $(1/P)^2$ instead of G_r $((P_0/P)^2)$, because P_0 varies considerably as a result of the progress of the reaction after the setting of the specimen at higher temperatures. The superposition procedure for the shear moduli was satisfactorily used except for the temperature region of about 200 °C in PAAm. Superposition was done in the following manner; first plot the values of $(1/P)^2$ and λ as a function of log t, and then shift their isothermal curves along with the axis of log t until they overlap the superposed curve. The quantities of the shift in relation to the reference curve are the shift factor, a. For the logarithmic decrements, only in the cases of PMA and PAA, which belong to the type shown in Fig. 10, was the superposition successful. In other polymers, the superposition was difficult because of the absence of any significant mark in the change in λ due to the chemical process in the isothermal curve. The apparent activation energies were estimated from the Arrhenius plot of the shift factor. Table 1 shows that the values obtained from the superpositions of λ's agree well with those from the moduli.

In PMAA, the activation energy estimated from the increase in G_r agrees well with that obtained by Grant

TABLE 1. THE APPARENT ACTIVATION ENERGIES ESTIMATED FROM THE VARIOUS PROCEDURES OF ANALYSIS

Sample	Temp. range (°C)	Mech.[a] process	The apparent activation energy (kJ/mol)[b]					
			From intial slope[c]		shift factor		time of max. λ	log(h) *vs.* $(1/T_m)$
			G_r *vs.* t	$\log G_r$ *vs.* t	$(1/P)^2$	λ		
PMA	190—320	in.	92	90	77	64	67	
	290—360	de.	143	167	99	101		
PAA	170—270	in.	92	107	110	97	102	99[d]
	270—360	de.	119	135	78	69	—	126[e]
PMAA	250—320	in.	142	142	126			
	270—340	de.	97	134	126			
PVA	170—240	in.	92	105	105			
	240—340	de.	71	115	67			
PVME	170—270	in.	39	42	44			
	315—370	de.	172	260	96			
PVAc	190—280	in.	118	99	103			
	290—360	de.	109	146	70			
PAAm	210—270	in.	110	110	92			
	270—350	de.	64	69	59			

a) G_r increases or decreases. b) 1J = 1/4.184 cal. c) Assuming $dG_r/dt = k_0$ and $d(\log G_r)/dt = k_{1st}$, where k_0 and k_{1st} are the apparent rate constants of the zero-order and first-order reactions, respectively. d), e) The ranges of T_m are 250—290 °C and 380—420 °C, respectively.

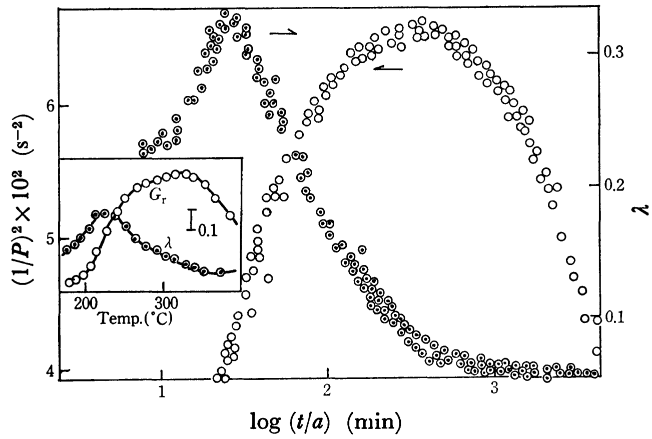

Fig. 11. Superposed curves for shear moduli, $(1/P)^2$, and λ of PAA. (T_0 = 246 °C) Inside figure: G_r, λ *vs.* T plots of PAA. G_r: ○, λ: ⊙.

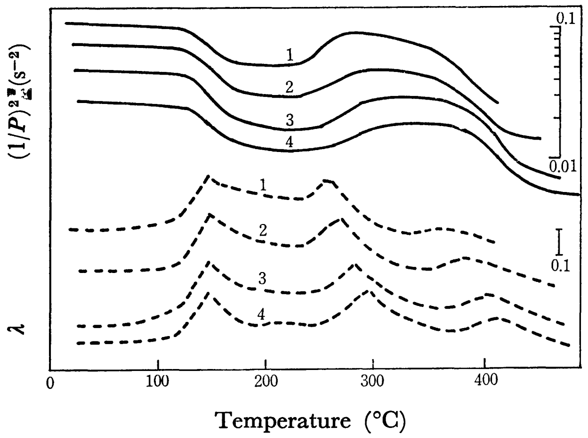

Fig. 12. The heating rate dependence of the chemorheological properties of PAA.
Heating rate, (1): 1.04 °C/min, (2): 2.04 °C/min, (3): 3.13 °C/min, (4): 4.24 °C/min. Solid line: relative shear moduli, dotted line: λ.

and Grassie, 37±3 kcal/mol (155±13 kJ/mol),[7] but the value in PVA is lower than that determined by Yamaguchi *et al.* by thermogravimetry, 35—55 kcal/mol (146—230 kJ/mol).[8] Popa *et al.* have pointed out that the apparent activation energies in PVA change greatly with the degree of conversion on the basis of the heating-rate dependence of the weight loss.[16] The values calculated by them become analogous to that estimated from the decrease in G_r as the conversion grows higher. Perhaps, this situation can be explained by considering that, at relatively lower conversions, in addition to the dehydration, the α-hydrogen atom affects the mechanical properties through crosslinking, which does not bring about any significant weight loss, whereas at higher conversions, the decrease in G_r is due to the chain scission, which leads to a weight loss.

The heating-rate dependence of the chemorheological behavior of PAA is shown in Fig. 12, where the shear moduli are plotted on the scale of $(1/P)^2$ and where the ordinates are shifted arbitrarily in order to avoid the overlapping of the curves. The glass transition temperature at about 140 °C remained unchanged. However, in the higher temperature region, the curves are displaced to higher temperatures as the rate becomes faster. These findings suggest that the inspection of the heating-rate dependence aids in the identification of the physical processes and the chemorheological processes.

It is known that the kinetic parameters can be determined by a study of the heating-rate dependence of the TG curve. Ozawa pointed out that the apparent activation energy can be obtained from the slope in the plot of the logarithm of the heating rate (log h)

against the reciprocal of temperature, T_m(K), at which certain reactions with various heating rates reach the same extent.[17)] In the present study, the temperature at which λ shows a maximum corresponding to the increase or decrease in G_r was taken as T_m, assuming that the reactions reached the same extent at this point. From the linear plot of log h *vs.* $(1/T_m)$, the activation energies were estimated. As is shown in Table 1, the two values are both in excellent agreement with those from initial slopes. The nature of the discrepancy between the values (78 and 69 kJ/mol) from the shift factor and those from other means (119 and 135 kJ/mol from the slopes and 126 kJ/mol from log h *vs.* $(1/T_m)$) in the range from 270 to 360 °C in PAA is not clear at present.

It is noteworthy that the kinetic method used in the thermal analysis can be successfully applied for the chemorheological measurements, in which chemical processes are investigated through the change in structure that controls the mechanical properties. The examination of the application of this procedure to the other polymers, especially to the polymers grouped in Fig. 9 or to the halogen-containing polymers, is a subject for future study.

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