

# Viscoelastic Properties of Cellulose Acylates

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**Abstract**—Five kinds of cellulose acylates from propionate to caprate were prepared by trifluoro acetic anhydride-fatty acid esterification. The temperature variations of dynamic modulus, loss modulus and loss tangent for these acylates were measured at four frequencies of 3.5, 11, 35 and 110 Hz in the temperature range from  $-190^{\circ}\text{C}$  to  $200^{\circ}\text{C}$ . Four types of relaxation process were observed for the acylates from butyrate to caproate, being labelled  $\alpha$ ,  $\beta$ ,  $\beta'$  and  $\gamma$  in order of decreasing temperature at which they were detected. However, the  $\gamma$  process for propionate and the  $\beta'$  process for caprate were not observed. On the contrary, a relaxation process, labelled  $\gamma'$ , for propionate was detected. These  $\alpha$  to  $\gamma'$  processes were respectively attributed to; micro-Brownian motion ( $\alpha$ ), motion of the side chain ( $\beta$  and  $\beta'$ ), motion initiated by three or more methylene groups ( $\gamma$ ), and motion of two methylene groups ( $\gamma'$ ).

## Introduction

Fossil resources including petroleum have been widely used as industrial raw materials for synthetic polymers and other compounds, as well as for energy sources. However, their future availability is considered to be limited and the countermeasures for compensating for the shortage of oil and natural gas are being investigated in various fields. As an approach to this problem, further developments in the use of renewable resources are desired. Cellulose is a renewable resource which is produced in the largest quantities on the earth. In recent years, several types of organic solvents for dissolving cellulose have been developed, and various kinds of homogeneous reactions of cellulose in these solvents have been attempted<sup>1)</sup>. This suggests that cellulose is one of the industrial raw materials which is readily handled. Accordingly, it is expected that the utilization of cellulose derivatives as plastic materials would increase still more in future. Therefore, systematic studies on their physical properties, especially viscoelastic properties are necessary. However, so far little work has been reported on the viscoelastic properties of cellulose derivatives as compared with those of synthetic polymers.

The present paper describes the viscoelastic properties of homologue of cellulose esters from propionate to caprate over a wide temperature range. All the samples

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employed in this experiment are prepared by trifluoro acetic anhydride-fatty acid esterification, which is considered to be suitable for our experiments, since it induces no notable cellulose degradation and results in pure and colorless products<sup>2)</sup>.

## Experimental

### Materials

The cellulose used was Whatman cellulose powder CF-11. Special grade trifluoro acetic anhydride (TFAA) and n-fatty acids; propionic acid, n-butyric acid, n-valeric acid, n-caproic acid and n-capric acid, were used for the esterification of cellulose powder. Reagent grade methanol was used as a precipitant.

### Preparation of cellulose acylates

TFAA (16.7 ml/g of cellulose) and the corresponding fatty acids from propionic acid to n-capric acid (mole ratio of the fatty acids to TFAA was 1.23:1) were mixed together and stirred mildly at 50°C for 20 min for increasing solvation of TFAA and fatty acid and aging. This solution was added to dried cellulose powder (6 g) placed in a 300 ml Erlenmyer flask equipped with a condenser and stirred mildly at 50°C for 5 hr. The reaction mixture was poured into an excess amount of methanol. The precipitate was filtered and washed with methanol repeatedly. The samples prepared were peracylated.

### Measurement of dynamic mechanical properties

Dynamic mechanical properties for filmed specimens were measured with a direct reading viscoelastometer (Toyo Baldwin Co., Ltd., Rheovibron DDV II-C). Complex modulus and loss tangent were measured in the temperature range from -190°C to 200°C at four constant frequencies of 3.5, 11, 35 and 110 Hz. The programmed heating rate was about 1°C/min. The size of specimens was 0.2 mm thick × 2 mm wide × 4 cm long for measurements in the temperature range from -190°C to 30°C and 1 mm thick × 2 mm wide × 2 cm long in the range from 30°C to 200°C.

## Results and Discussion

The results of dynamic modulus  $E'$ , loss modulus  $E''$  and loss tangent  $\tan \delta$  at 110 Hz as a function of temperature for cellulose butyrate are presented in Figure 1. With respect to  $E''$ , four relaxation processes were detected within the experimental frequency and temperature ranges, being labelled  $\alpha$ ,  $\beta$ ,  $\beta'$  and  $\gamma$  processes in order of decreasing temperature at which they were detected. These four processes were also observed for the valerate and the caproate in the temperature range between -190°C and 150°C at 110 Hz. However, the  $\gamma$  process for the propionate and the

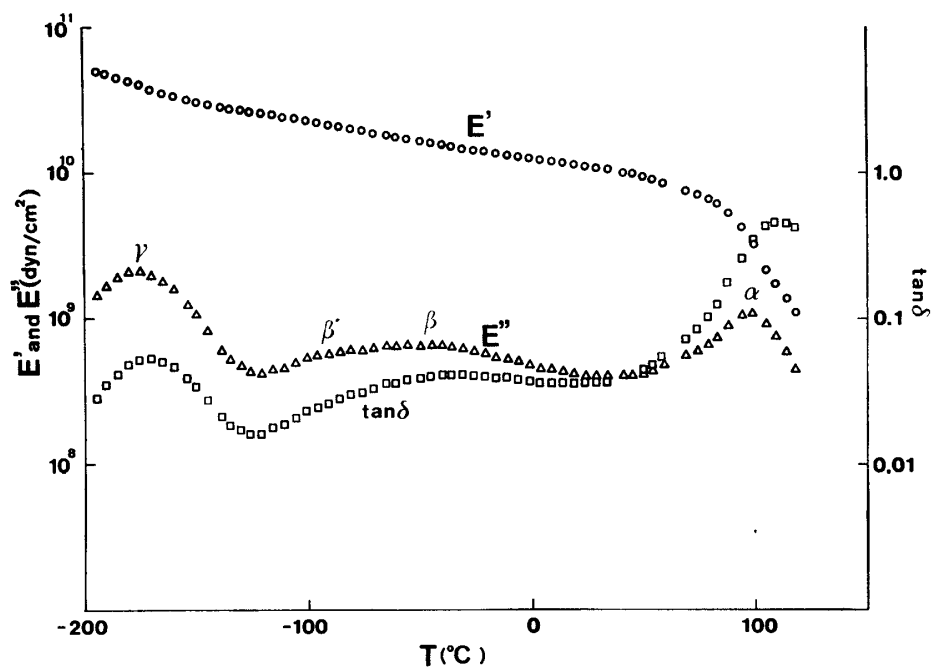


Fig. 1. Temperature dependence of dynamic modulus  $E'$ , loss modulus  $E''$  and loss tangent  $\tan \delta$  at 110 Hz for cellulose butyrate.

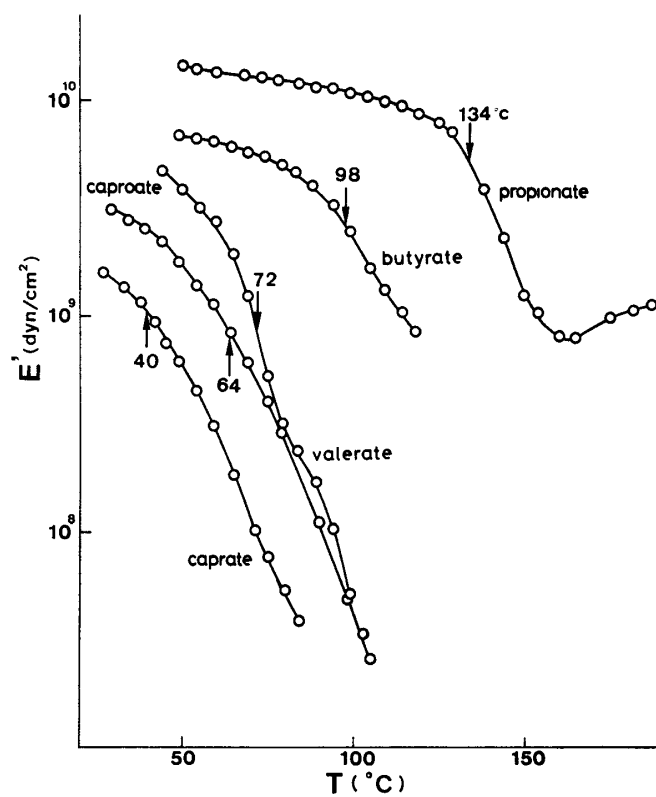


Fig. 2. Temperature dependence of dynamic modulus  $E'$  at 35 Hz for the acylates from propionate to caprate.

$\beta'$  process for the caprate were not observed. On the contrary, a relaxation process, labelled  $\gamma'$ , for the propionate in the temperature range below  $-150^{\circ}\text{C}$  was detected, which was not recognized for the other acylates.

Figure 2 shows the changes in  $E'$  at 35 Hz above room temperature for the acylates from propionate to caprate. In the temperature range of the  $\alpha$  process, a remarkable drop in  $E'$  was recognized. Especially, that for the acylates from valerate to caprate extended by three orders in magnitude. Furthermore, the maximum  $\tan\delta$  values in the  $\alpha$  process for all the acylates were nearly equal to unity. These facts mean that this process is related to the glass-rubber transition, and so the  $\alpha$  process is assigned to a micro-Brownian motion of the main chain of the acylates. The apparent activation energy  $\Delta E$  for the  $\alpha$  process was 55 to 121 kcal/mol, which is of the order of the principal dispersion. The temperature locations of  $E''$  maxima in the  $\alpha$  process, which is considered to be almost equal to the glass transition points  $T_g$ , are denoted by arrows in Figure 2. The  $T_g$  for the acylates apparently shifted to lower temperature region with increasing the number of carbon  $n$  in the introduced acyl group. This phenomena can be interpreted as follows: the increase in the molecular size of non-polar  $n$ -alkyl groups causes decreased interaction of dipolar ester group, thus facilitating the chain back bone motion. This effect is similar to that produce by the addition of a plasticizer. However, the  $T_g$  seems to level off when  $n$  reached to about 6. In connection with the dynamic mechanical properties, the dielectric properties for the acylates were also studied and it was clarified that these polymers exhibited a dielectric process in the temperature and frequency ranges comparable to those of the mechanical  $\alpha$  process<sup>3)</sup>. As was observed in the mechanical  $\alpha$  process, the temperature of the dielectric loss maximum decreased markedly with increasing  $n$  up to 6, but it remained almost constant for  $n$  above 7. These trends recognized for  $T_g$  were parallel to those for the melting points.<sup>3)</sup> On the other hand, it is noted that the  $T_g$  for poly  $n$ -alkyl methacrylates decreases continuously with increasing  $n$ , reaching  $-65^{\circ}\text{C}$  for poly  $n$ -dodecyl methacrylate.<sup>4)</sup> This difference between cellulose acylates and poly  $n$ -alkyl methacrylates, both involving long  $n$ -alkyl groups in the side chain, may be attributed to the different structure of the frame work; the former being bulkier than the latter. Klarman et al.<sup>5)</sup> studied the mechanical relaxation for a series of cellulose acylates with the aid of dilatometry and reported that the  $T_g$  decreased abruptly from  $133^{\circ}\text{C}$  for the propionate to  $-69^{\circ}\text{C}$  for the decanoate. However, the samples employed by Klarman et al. were supplied by three different companies and seems to be somewhat different in nature. As is well known, the  $T_g$  of polymers is strongly dependent of their molecular weights. Therefore, the comparison of  $T_g$  for the acylates should be made for the samples having same order of molecular weight. All the samples

prepared in this experiment gave molecular weight of the order of  $10^5$ , and so the results obtained are considered to be reasonable. In Figure 2, a rise in  $E'$  with temperature in the region just above  $T_g$  was recognized for the propionate. This rise in  $E'$  means the development of a structure which could support stress elastically, i.e. the crystallization of the sample<sup>5,6)</sup>. This phenomenon was also observed for the other acylates. The results of the temperature dependence of  $E'$  for the valerate at respective frequencies are illustrated in Figure 3. The crystallization process which was clearly visible at 3.5 Hz became less distinct as the frequency increased.

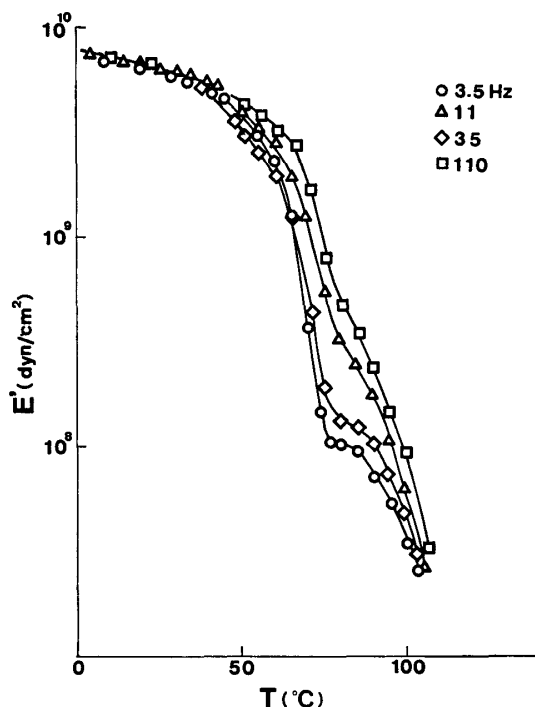


Fig. 3. Temperature dependence of dynamic modulus  $E'$  for the valerate at respective frequencies.

The  $\beta$  process for the butyrate appeared in the temperature region at around  $-50^\circ\text{C}$  in the  $E''$  versus temperature curves shown in Figure 1. To compare the absorption magnitude in the  $\beta$  process among the acylates,  $\tan \delta$  curves should be used instead of  $E''$  curves, because it is considered that  $\tan \delta$  corresponds to the specific loss, the ratio of the energy dissipated to the energy stored per quarter cycle, while  $E''$  correspond to the absolute energy dissipated. The plots of  $\tan \delta$  and  $E'$  at 11 Hz against temperature for the acylates in the temperature region of the  $\beta$  process are shown in Figures 4a and 4b, respectively. The  $\beta$  peak increased in height with increasing  $n$ . Corresponding to this, the relaxation magnitude increased with increasing  $n$  as shown in Figure 4b. In particular,  $E'$  value for caprate fell from  $1.5 \times 10^{10}$  dyn/cm<sup>2</sup> to  $1.8 \times 10^9$  dyn/cm<sup>2</sup> as the temperature rose from  $-100^\circ\text{C}$  to  $-20^\circ\text{C}$ .

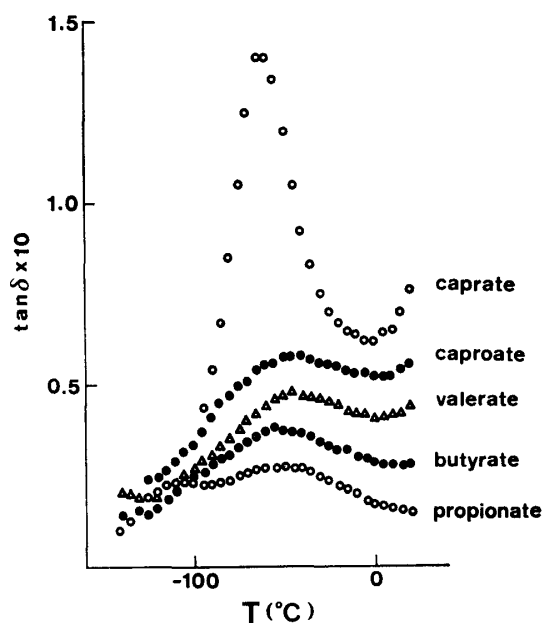


Fig. 4a. Temperature dependence of  $\tan \delta$  at 11 Hz for the acylates from propionate to caprate.

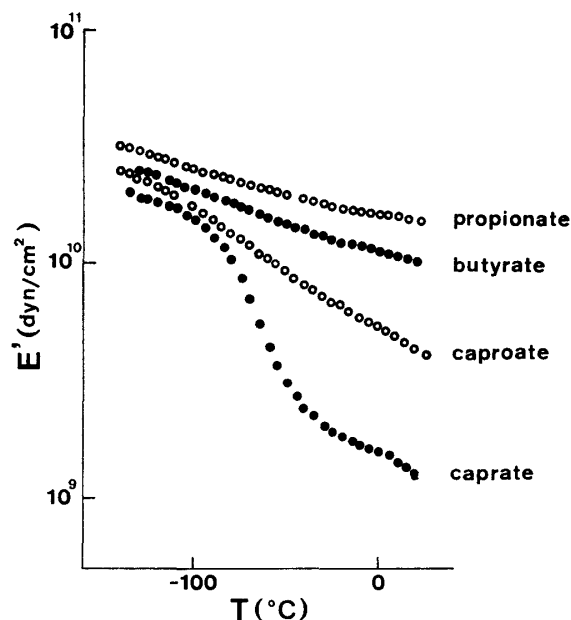


Fig. 4b. Temperature dependence of  $E'$  at 11 Hz for the acylates from propionate to caprate.

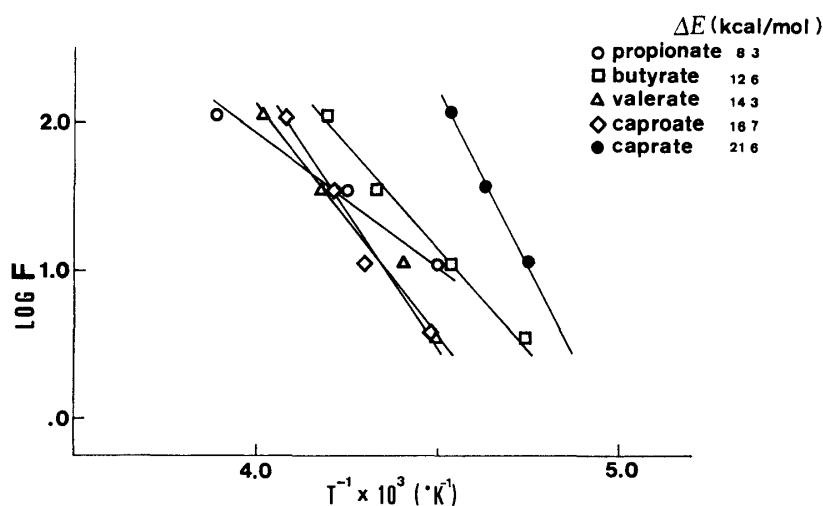


Fig. 5. Plots of logarithm of the frequency at  $\tan \delta$  maximum against the reciprocal of absolute temperature for the  $\beta$  process.

The plots of logarithm of the frequency at  $\tan \delta$  maximum against the reciprocal of absolute temperature are shown in Figure 5. There was a linear relationship between them. The values of  $\Delta E$  calculated from the slopes are also shown in the Figure. Obviously, the value increased with increasing  $n$  and that for cellulose caprate seemed to be somewhat larger compared to that quoted usually for polymers in the glassy state. It should be emphasized that  $\tan \delta$ ,  $\Delta E$  and relaxation magnitude,

increase with increasing the side chain length. From these findings, it is considered that the  $\beta$  process is due to the side chain motions of the acylates. A possible explanation for the motion of the side chain is as follows: when the side chain length is short as in cellulose propionate, the motion of molecular segment responsible for the  $\beta$  process may be restricted only to the hindered rotation or the twisting. In this case,  $\Delta E$  for the motions is considered to be fairly small. On the other hand, when the side chain length is long enough as in the caprate, a short range diffusional motion of the segments along the side chain, similar to a micro-Brownian motion along the main chain, may result in the  $\beta$  process, which requires large  $\Delta E$ . Therefore, it may be considered that the motion of the side chain responsible for the  $\beta$  process shifts from the hindered rotation or the twisting to the short range diffusional motion with increasing the side chain length.

In Figure 4a, a shoulder at about  $-100^\circ\text{C}$  occurred in  $\tan \delta$  versus temperature curve. This process labelled  $\beta'$  has appeared more distinctly in  $E''$  versus temperature curves than in  $\tan \delta$  versus temperature curves as shown in Figure 6, in which  $E''$  is plotted in arbitrary scale over the temperature range from  $-150^\circ\text{C}$

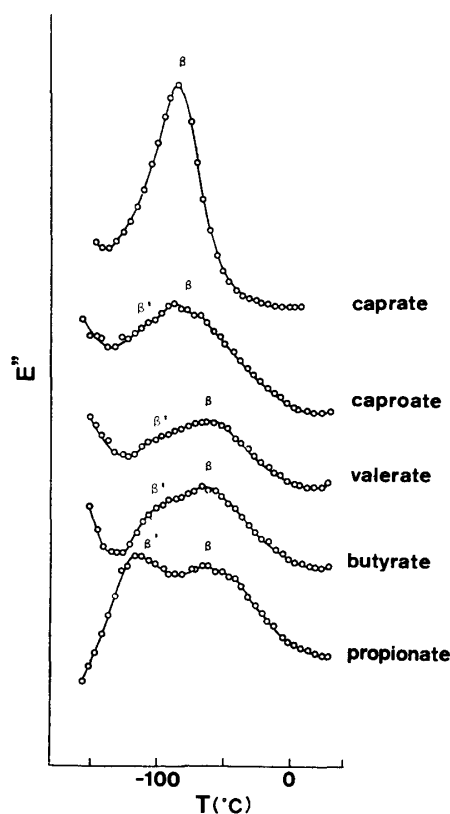


Fig. 6. Temperature dependence of loss modulus  $E''$  at 11 Hz for the acylates from propionate to caprate.

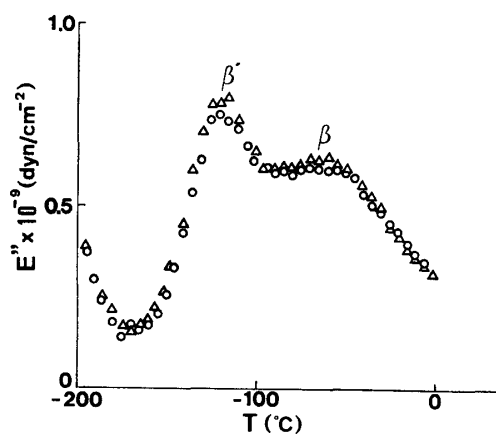


Fig. 7. Temperature dependence of loss modulus  $E''$  at 11 Hz for cellulose propionate.  
 $\triangle$ : immersed in water  
 $\circ$ : dried at  $80^\circ\text{C}$  for 40 hr in vacuo

to 20°C at 11 Hz. The  $\beta'$  peak, which was clearly observed for the propionate, becomes less distinct as  $n$  increased and at last merged completely into the  $\beta$  peak for the caprate. In order to assign the  $\beta'$  process, the effect of water on the process for cellulose propionate was investigated and the results are shown in Figure 7. As is evident from the figure, it can be seen that the  $\beta'$  process is independent of water absorbed. In this connection, it was found that the  $\beta$  process was also independent of water. From this fact, the cause of  $\beta'$  process should be attributed to the molecular motion of the acylates themselves. It can be considered that there is a remarkable difference in the degree of freedom of the motion of the side chains introduced at C-6 and C-2 or C-3 positions of a glucopyranose ring. Therefore, it is plausible that the side chains attached to the different positions cause substantially different relaxation mechanisms with each other. If the difference in the relaxation time

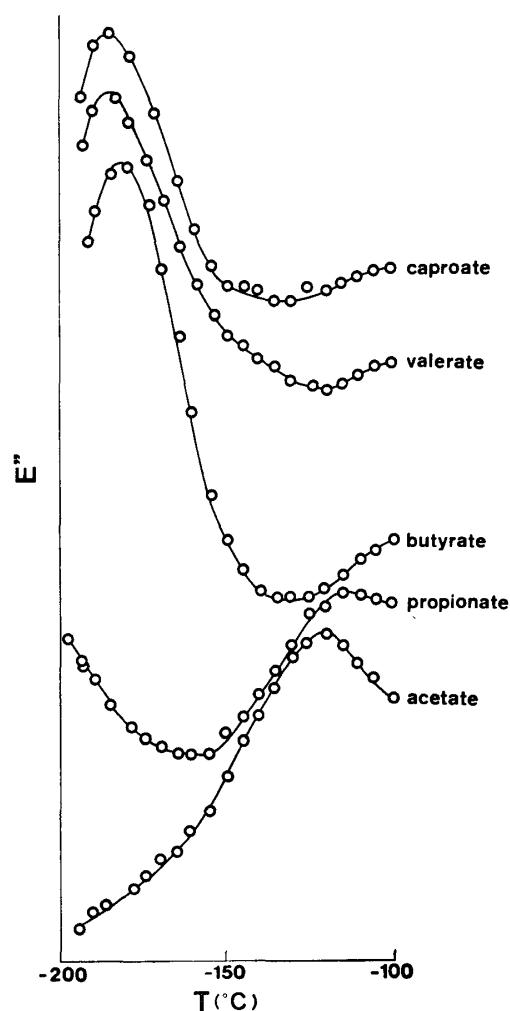


Fig. 8. Temperature dependence of loss modulus  $E''$  at 11 Hz for the acylates from acetate to caprate.



among these side chain motions exists, then the resulting relaxation process ought to be different. Therefore, the  $\beta'$  process as well as  $\beta$  process may be due to the motion of the side chain.

Figure 8 shows the variation of  $E''$  with temperature for the acylates from acetate to caprate in the temperature range from  $-190^\circ\text{C}$  to  $-100^\circ\text{C}$  at 11 Hz. The relaxation process labelled  $\gamma$  was detected for from the butyrate to the caprate at around  $-180^\circ\text{C}$ . However, the process was not recognized for both the acetate and the propionate in the temperature range examined. By using the mechanical experiments, many investigators have reported that a relaxation process occurs in the temperature range from  $-100^\circ\text{C}$  to  $-200^\circ\text{C}$  at low frequencies for polymers involving at least three methylene groups ( $-\text{CH}_2-$ ) in a row. The  $\Delta E$  for the  $\gamma$  process calculated from the relaxation map shown in Figure 9 is about 6.3 kcal/mol which is comparable to the values obtained for the polymers mentioned above. From these facts, the  $\gamma$  process can be ascribed to the motions initiated by  $-\text{CH}_2-\text{CH}_2-\text{CH}_2-$  parts of the side chain. It is of interest to note that  $E''$  for the propionate increased with decreasing temperature in the range from  $-150^\circ\text{C}$  to  $-190^\circ\text{C}$ . For the propionate, the  $\gamma$  process can occur no longer due to the absence of  $-\text{CH}_2-\text{CH}_2-\text{CH}_2-$  portion in the side chain. However, in this case, the motion due to  $-\text{CH}_2-\text{CH}_2-$  part may exist. Supposing that the  $\gamma'$  process results from the motion of  $-\text{CH}_2-\text{CH}_2-$  parts in the side chain, then it may occur in lower temperature region compared to that for the  $\gamma$  process, since the relaxation time for the motions of  $-\text{CH}_2-\text{CH}_2-$  segments is considered to be shorter than that for the  $-\text{CH}_2-\text{CH}_2-\text{CH}_2-$  motions. Such being the case, the  $\gamma'$  process will not be observed for the acetate which lacks  $-\text{CH}_2-\text{CH}_2-$  parts. In fact, no relaxation process similar to the  $\gamma'$  process could be observed

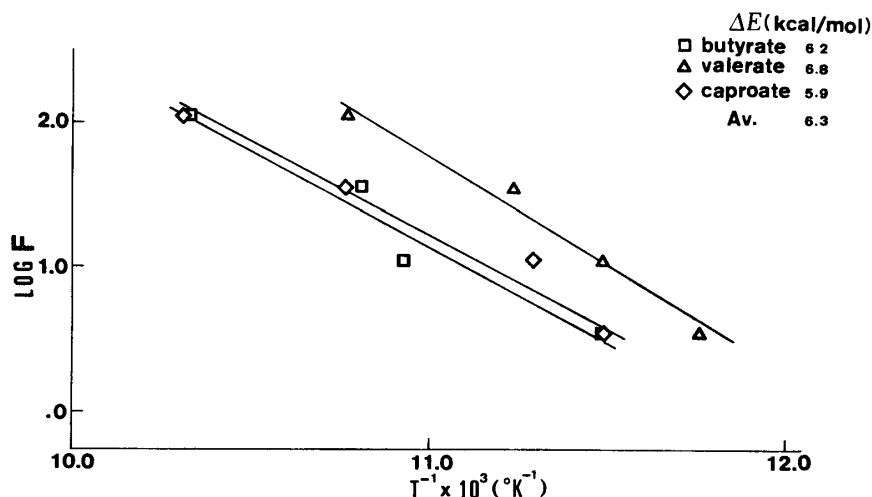


Fig. 9. Plots of logarithm of the frequency at  $E''$  maximum against the reciprocal of absolute temperature for the  $\gamma$  process.

for the acetate in the corresponding temperature range. Accordingly, it can be concluded that the  $\gamma'$  process is due to the motion initiated by  $-\text{CH}_2\text{-CH}_2-$  parts of the side chain.

### References

- 1) K. MATSUZAKI and K. UDA: SEN-I Gakkaishi, **38**, P-156 (1982).
- 2) M. TSUZUKI, N. SHIRAISHI and T. YOKOTA: J. Appl. Polymer Sci., **25**, 2567 (1980).
- 3) Y. HIRABAYASHI, M. NORIMOTO, T. AOKI, T. YAMADA and N. SHIRAISHI: Abstracts of Papers Presented at 29th. National Meeting, Japan Wood Research Soc., Sapporo, P. 290 (1979).
- 4) S. S. ROGERS and L. MANDELKERN: J. Phys. Chem., **61**, 985 (1957).
- 5) A. F. KLARMAN, A. V. GALANTI and L. H. SPERLING: J. Polymer Sci., **7**, 1513 (1969).
- 6) R. E. BOY, R. M. SCHULKEN, Jr. and J. W. TAMBLYN: J. Appl. Polymer Sci., **11**, 2453 (1967).