

Viscoelastic Properties of (Cellulose Oligo-Oxymethylene Ether) Acylates with Bulky Side Chain

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Synopsis

A series of (cellulose oligo-oxymethylene ether) acylates (COAs) are characterized by the presence of the micro-Brownian motion of the side chain (β process) which appears separately from that of the main chain (α process). Both the α and β processes are largely affected by the kind of acyl groups introduced in the side chain. To clarify the effect of the acyl group on these processes, we investigated the dynamic mechanical properties of newly prepared COAs with acyl side chain, bulky in chemical structure (iso-butyrate, privalate, and benzoate) in relation to those for COAs with linear acyl side chain (acetate, butyrate, and valerate). By substituting bulky acyl isomer for linear acyl group in COAs, we observed that the temperature region of both the α and β processes moved to higher temperature. Furthermore, with an increase in molecular size of bulky acyl group, the β region shifts were much larger than the α region, indicating that the mobility of the side chain became comparable to that of the main chain. Finally, when such a large bulky group, for example, benzoate was introduced, the micro-Brownian motion of the side chain prior to that of the main chain ceased. The apparent activation energy for a third process (γ) due to the motion of the oligo-oxymethylene parts in the side chain was estimated to be 10.3 kcal/mol.

INTRODUCTION

The homogeneous acylation of cellulose in paraformaldehyde/dimethyl sulfoxide medium is known to produce novel acylated cellulose called (cellulose oligo-oxymethylene ether) acylate, COA.¹ A series of COAs are different in chemical structure from the conventional cellulose acylates in that oxymethylene oligomers are bonded between a glucopyranose ring and an acyl side group (Fig. 1). Accordingly, physical properties of COAs are different from those of cellulose acylates.² They are controllable not only by altering the acyl group but also by changing the length of the intervening oxymethylene chain.³ In our previous work,⁴ dynamic mechanical properties of polymers in a series of COAs with linear side chain were studied, varying their side chain length in both the oxymethylene group and acyl group portion. In the dynamic mechanical data, three processes for all COAs and an additional process for higher homologue above the butylate were observed in the frequency and temperature ranges examined. These processes were labelled α , β , γ and δ in the order of decreasing temperature at which they were detected. These processes were respectively attributed to: micro-Brownian motion of the main chain (α), micro-Brownian motion of side chain (β), local

mode motion involving oxymethylene group (γ), and motion initiated by three or more methylene groups (δ). The COAs series are characterized by observing that the micro-Brownian motion in the side chain (β process) appears separately from that in the main chain (α process). The existence of the two kinds of micro-Brownian motion is interpreted as a result of the difference in flexibility between the side chain and the main chain: the former consists of the smaller and more flexible motional-units such as $-\text{CH}_2-$ or $-\text{O}-$ than the latter, namely, glucopyranose ring. If this is the case, a COA should exist without the β process. In that case side chains would involve such bulky motional-units as glucopyranose rings.

The present article describes viscoelastic properties of newly prepared COAs with acyl side chain bulky in chemical structure (isobutyrate, pivalate, and benzoate), in relation to those of COAs with linear acyl group, using dynamic mechanical measurements. All the COAs used were peracylated, and gave clear, transparent films.

EXPERIMENTAL

Preparation of (Cellulose Oligo-Oxymethylene ether) Acylates

The preparation method of (cellulose oligo-oxymethylene ether) acylates used in this study is similar to that reported in our previous article.² Dried cellulose powder (6 g) and paraformaldehyde (12 g) were well dispersed in dimethylsulfoxide (150 mL) at room temperature. The mixture was then kept at 120°C for 3 h in a 300 mL Erlenmyer flask equipped with a condenser to obtain cellulose solution. To the cooled cellulose solution, triethylamine (6 mol/anhydroglucose unit of cellulose) and an aliphatic anhydrides one (isobutyric, pivalic, and benzoic anhydride) were added (6 mol/anhydroglucose unit of cellulose) with continuous stirring. The reaction mixture was allowed to stand at room temperature for 5 h, and then poured into an excess amount of methanol to obtain precipitates. Hot methanol was used as precipitant for preparation of benzoate, and the precipitates were separated by filtration. After the crude product was purified by repeated dissolution and precipitation technique, it was dried under vacuum without heating. Infrared spectra of thus obtained products showed no significant contamination by any low molecular weight substances. Other COAs used were identical with those examined in our previous paper.²

Measurements of Thermal Deformation

Thermal deformation of samples was observed using a thermomechanical analyzer (TMA, Shinku Riko Co., Ltd., TM-1500). A column of the sample under a constant load of 3 kg/cm² collapsed under a plunger heated at a uniform rate of 1°C/min.

Measurement of Dynamic Mechanical Properties

Dynamic mechanical properties for film 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

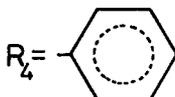
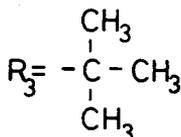
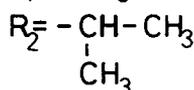
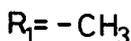
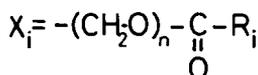
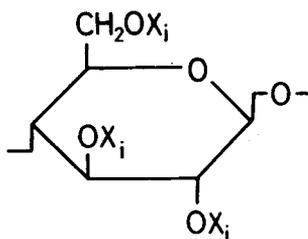


Fig. 1. Chemical structures of several (cellulose oligo-oxymethylene ether) acylates. $i = 1$: acetate(CAcOM), 2: isobutyrate(CiBOM), 3: pivalate(CPiOM), 4: benzoate(CBzOM).

range from -190°C to 200°C at frequencies of 11, 35, and 110 Hz. The programmed heating rate was about $1^\circ\text{C}/\text{min}$. Specimen size was $40 \times 2 \times 0.2$ mm (length \times width \times thickness) for measurements in the temperature range from -190 – 30°C and $20 \times 2 \times 1$ mm in the range from 30 – 200°C .

RESULTS AND DISCUSSION

Thermal analysis using TMA gives useful information on glass transition or melting of polymer samples as described in our previous paper.^{2,5} One of the resulting diagrams of thermal deformation (D) versus temperature is illustrated in Figure 2 for (cellulose oligo-oxymethylene ether) pivalate, CPiOM. In the diagram, D is normalized: D is zero at room temperature and unity at the temperature at which the plunger in TMA reached the bottom of the glass capillary, indicating completion of liquid flow of the sample. All the COAs examined gave a deformation thermodiagram pattern similar to that for CPiOM, showing two transition regions above room temperature.

Figure 2 shows that the higher temperature range transition proceeds gradually. In contrast, highly crystalline polymers are known to exhibit a well-defined transition point from solid to liquid state in the thermodiagram.⁶ Because COAs examined do not exhibit such a well defined transition point in

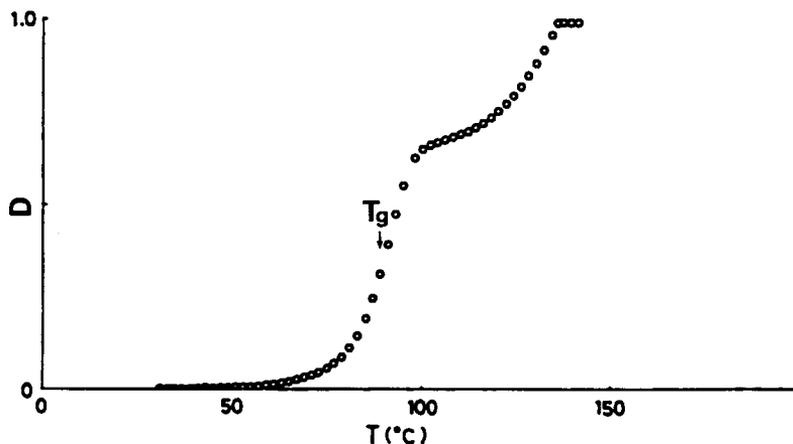


Fig. 2. Diagram of thermal deformation, D , versus temperature for (cellulose oligo-oxymethylene ether) pivalate, CPiOM.

the thermodiagram, they are considered to be amorphous in nature. This is consistent with the results of X-ray diffraction measurements reported earlier.²

The lower temperature range transition can be attributed to the segmental motion of the main chain,² i.e., micro-Brownian motion (α process). Thus, the temperature corresponding to the dD/dT maximum in the region can be regarded as about equal to the glass transition point T_g of the sample. Table I shows T_g for six kinds of COAs examined in the present work. It can be seen that the values of T_g for COA with linear side chain decreases regularly with increasing molecular weight of the side chain: 83, 65, and 49°C for (cellulose oligo-oxymethylene ether) acetate (CAcOM), butyrate (CBuOM), and valerate (CVaOM), respectively. However, as was observed in early work for polyalkyl methacrylate or acrylate with bulky side chain,^{7,8} such regularity in T_g disappears when the molecular weight of the side chain increases by introducing bulky acyl group in the order of acetate, isobutyrate, pivalate, and benzoate. In this case, the lowest T_g value of the four is given in (cellulose oligo-oxymethylene ether) isobutyrate, CiBOM.

The dynamic mechanical properties of COAs with bulky side chain (CiBOM, CPiOM, and CBzOM) were compared to those of COAs having linear side chain with corresponding molecular weight. Figure 3 shows the dynamic

TABLE I
Glass Transition Point T_g for (Cellulose
Oligo-oxymethylene Ether) Acylates

Samples	T_g (°C)
CAcOM	83
CBuOM	65
CVaOM	49
CiBOM	74
CPiOM	90
CBzOM	88

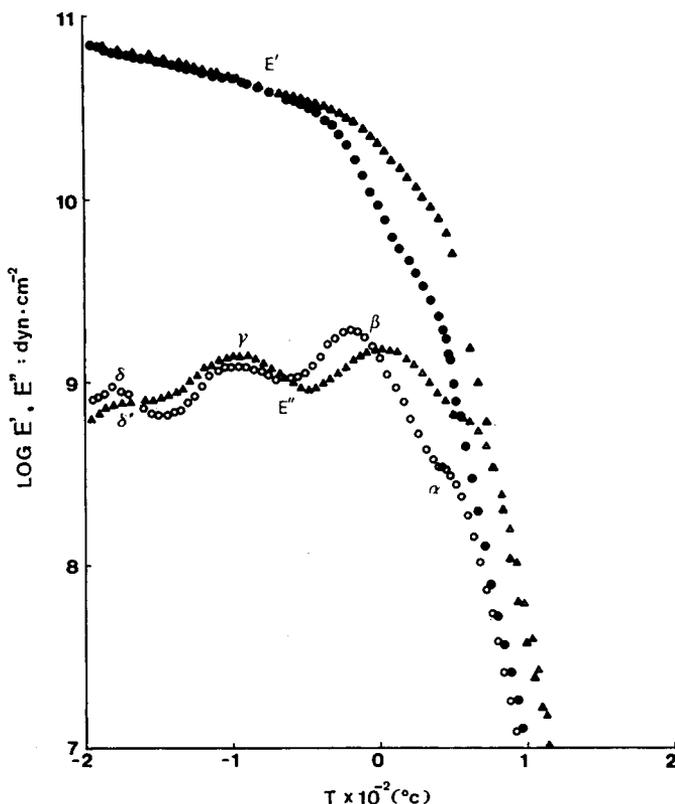


Fig. 3. Temperature dependence of dynamic modulus E' , loss modulus E'' at 110 Hz for (\circ , \bullet) (cellulose oligo-oxymethylene ether) butyrate (CBuOM), and (Δ , \blacktriangle) isobutyrate, (CiBOM).

modulus E' and loss modulus E'' at 110 Hz as a function of temperature for both CBUOM and CiBOM.

Regarding E'' temperature curves, CiBOM reveals three processes above -150°C , each of which is considered to be similar in molecular mechanism to the corresponding processes in CBUOM. These can also be labelled α , β , and γ , respectively. The γ peak for CiBOM is located at the same temperature as that for CBUOM, while both the β and α peaks for CiBOM shift to higher temperatures compared to CBUOM. Since the motion of the oligo-oxymethylene portion is responsible for the γ process, these data show that the kind of acyl group has little effect on temperature-frequency locations of the γ process.

The β process, however, is initiated by the micro-Brownian motion of the side chain. The high temperature shift of this region for CiBOM is thought to be caused by decreasing mobility of the segment along the side chain. This comes from an increase in steric hindrance of the bulky isobutyrate group as compared with that of the linear butyrate group.

Comparing the relaxation magnitude in the β region for CiBOM with that for CBUOM in E' temperature curve, it is found that the lowering of the side-chain mobility for CiBOM results in the decrease of relaxation magnitude. Both COAs reveal the same E' value at temperatures below the β

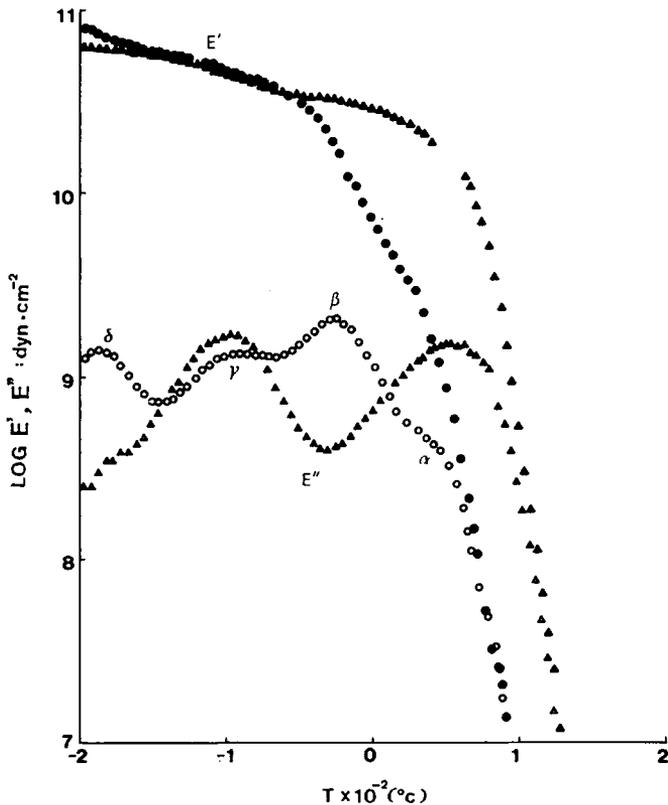


Fig. 4. Temperature dependence of dynamic modulus E' , loss modulus E'' at 110 Hz for (○, ●) (cellulose oligo-oxymethylene ether) valerate (CVaOM) and (△, ▲) pivalate (CPiOM).

region. We further observe that the α region for CiBOM shifts to higher temperature, indicating that the mobility of the side chain affects that of the main chain.

In addition to these three processes (α , β , and γ) commonly observed for both COAs, CBUOM exhibits an additional process labelled δ below -150°C . The δ process has been thought to arise from the twisting motion involving at least three or more methylene groups in a row in the side chain. The E'' temperature curve for CiBOM reveals a relaxation process (labelled δ') as a shoulder in the region comparable to that of the δ process for CBUOM, though CiBOM lacks $-\text{CH}_2-\text{CH}_2-\text{CH}_2-$ parts. On the basis of the findings concerning polymers in a series of cellulose acylates,⁹ the δ' process can be assigned to the motion initiated by $-\text{CH}_2-\text{CH}_2-$ parts in the side chain.

The difference observed in the relaxation process between CBUOM and CiBOM is even greater when comparisons are made between CVaOM and CPiOM. In these, acyl parts in the side chain are larger than those of CBUOM or CiBOM. Figure 4 shows the dynamic modulus E' and loss modulus E'' at 110 Hz against temperature for both CVaOM and CPiOM.

Concerning E' values, CPiOM has lower E' in the range below -50°C than those of CVaOM. This lowering in E' is not observed when the butyrate

group is replaced by the isobutyrate groups in the side chain (Fig. 3). The introduction of a bulky acyl side chain (pivalate) substantially reduces inter-chain cohesive force in COA as compared with that in COA having linear side chains of equal molecular weight.

With respect to E'' , the two curves are quite different in shape except for those in the γ region. At about -180°C , the δ process clearly observed for CVaOM disappears for CPiOM because of the absence of $-\text{CH}_2-\text{CH}_2-\text{CH}_2-$ parts in the side chain. While CiBOM do not exhibit the δ process because of lacking $-\text{CH}_2-\text{CH}_2-\text{CH}_2-$ parts, it shows the δ' process due to the motion of $-\text{CH}_2-\text{CH}_2-$ parts in the side chain. This indicates that for CPiOM, even the twisting of $-\text{CH}_2-\text{CH}_2-$ parts do not occur because of the steric hindrance caused by $-\text{CH}_3$ branch around $-\text{CH}_2-\text{CH}_2-$ parts within the pivalate group.

In the temperature region of the overlapping β and γ processes for CVaOM, CPiOM shows one distinct process. From its temperature frequency locations, we assign it to the γ process. In our previous work,² because of the overlapping of the γ region to the β region in COAs with linear side chain, we evaluated the apparent activation energy ΔE for the γ process from resolved E'' temperature curve, assuming that both γ and β have Gaussian distribution. As is seen in Figure 4, however, the γ peak for CPiOM is distinct without any influence of other processes. Thus, the ΔE value for the γ process can be estimated more precisely for CPiOM than for other COAs, being 10.5 and 10.1 kcal/mol from E' and $\tan \delta$ curves, respectively.

A broad peak for CPiOM is observed in the higher temperature range. For elucidating the relaxation mechanism in this region, variation of E'' temperature curves for CPiOM with frequency are shown in Figure 5. The broad peak at 110 Hz splits, indicating the existence of the two kinds of processes in the

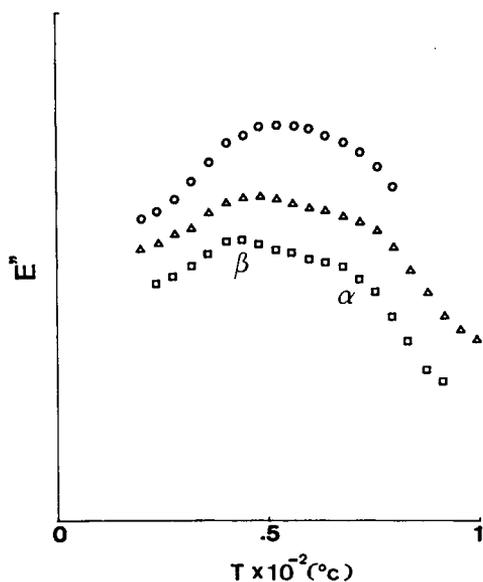


Fig. 5. Variation of E'' temperature curve with frequency for (cellulose oligo-oxymethylene ether) pivalate, CPiOM. (○) 110; (Δ) 35; (□) 11 Hz.

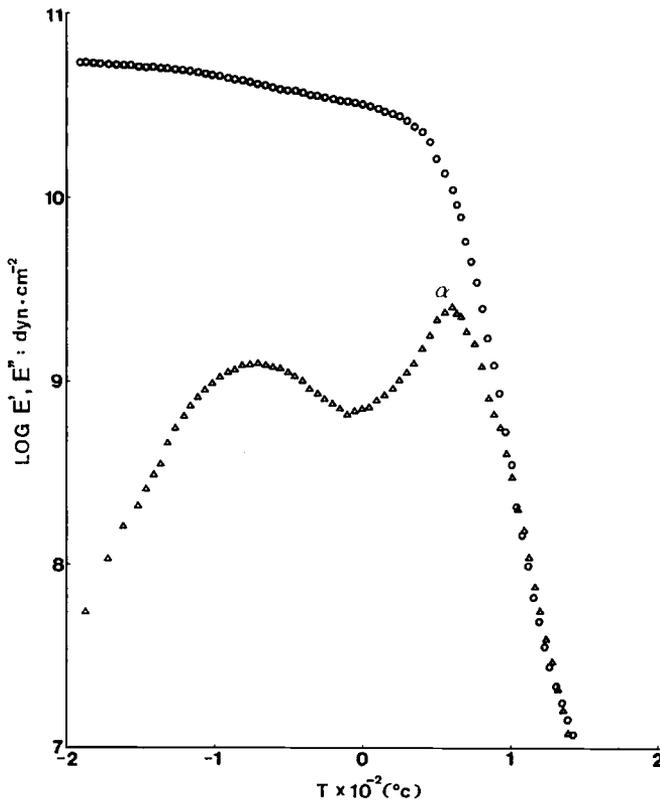


Fig. 6. Temperature dependence of dynamic modulus E' and loss modulus E'' at 110 Hz for (cellulose oligo-oxyethylene ether) benzoate, CBzOM.

range noted. Since the shoulder at about 70°C at 11 Hz corresponds to the glass transition region, this process can be regarded as the α process. Because the mobility of the bulky pivalate group is considered to be reduced by its steric hindrance as compared with that of the valerate group, the β region shifts to markedly higher temperatures, and appears slightly below the α region. The process just below the α region can be classified as the β process for CPiOM. It is also found that for CPiOM, the α region moves to higher temperatures with the higher temperature shift of the β region.

When the bulky acyl group is changed from isobutyrate to larger pivalate, bigger shifts in the β region occur at higher temperature as compared to the α region. This indicates the mobility of the side chain segment approaches that of the main chain segment. Thus, we expect that if the bulky acyl group in the side chain of COA were large enough (i.e., glucopyranose ring or benzene ring) the mobility of the segment in the side chain would be reduced and become similar to that in the main chain. This would result in the extinction of the β process.

To examine this point, Figure 6 displays the variation of E' and E'' at 110 Hz with temperature for CBzOM where the acyl portion in the side chain involves a benzene ring. The figure shows that two processes occur. The process appearing at about 70°C is sharp in contrast to the corresponding

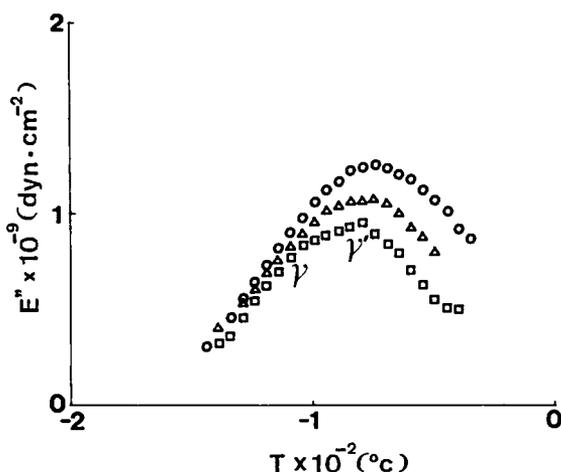


Fig. 7. Variation of E'' temperature curve with frequency for (cellulose oligo-oxymethylene ether) benzoate, CBzOM. (○) 110; (△) 35; (□) 11 Hz.

process for CPiOM. In this region, E' values decrease markedly from 2.05×10^{10} dyn/cm² to less than 10^7 dyn/cm² as the temperature rises from 40 to 140°C. Furthermore, ΔE values for this process calculated from E'' and $\tan \delta$ curves are, respectively, 53.5 and 55.3 kcal/mol. From these findings, the process can be regarded as a micro-Brownian motion along the main chain (α process). It should be emphasized that the β process having been observed for all other COAs examined disappears for CBzOM. Accordingly, we conclude that for CBzOM, the micro-Brownian motion along the side chain, independent of that along the main chain, cannot occur because of the similarity in the molecular size of both the benzene ring in the side chain and glucopyranose ring in the main chain.

In addition to the α process, the γ process (due to the motion of the oxymethylene portion) should appear at about -100°C at 110 Hz regardless of whether the acyl group in the side chain is bulky or not. As is seen in Figure 6, however, the temperature location of the process detected in the lower temperature apparently differs from that of the γ process for other COAs. This discrepancy can be interpreted by considering the existence of an additional process in the vicinity of the γ process.

Figure 7 illustrates the variation of E'' temperature curves for CBzOM with frequency at temperatures between -150 and -20°C . From the plots at 11 Hz, two processes are clearly recognized. The process at the lower temperature can be ascribed to the γ process because of its location. The process at the higher temperature (which is labelled γ') may correspond to the motion involving benzyl groups which was observed in benzyl cellulose in the corresponding region.¹⁰

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