Mechanical and dielectric relaxations of poly(hydroxy ethers): 1. Low-temperature relaxations

Mitsukazu Ochi, Hiroyuki Kageyama and Masaki Shimbo
Department of Applied Chemistry, Faculty of Engineering, Kansai University, Suita-shi, Osaka 564, Japan
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Mechanisms for the low-temperature relaxations were investigated for poly(hydroxy ethers) prepared by the polyaddition reaction of diglycidyl ethers with diphenols. Two relaxations, denoted β and β', are observed at -70 and $+40$°C (for a frequency of ~ 1 Hz), respectively. It is revealed by comparing the mechanical relaxation with the dielectric relaxation that the β relaxation is a complex relaxation, that is, the overlap of the relaxation of hydroxy ether segment with that of other parts in the polymer chain, and that the β' relaxation is due to the motion of the phenylene group in the polymer chain. In the acetylated poly(hydroxy ethers), the relaxation of the hydroxy ether segment disappears and a new relaxation due to the motion of the acetylated segment appears near 0°C. This new relaxation is superimposed upon the β' relaxation.

(Keywords: poly(hydroxy ethers); mechanical relaxation; dielectrics)

INTRODUCTION

Epoxide resin is a typical network polymer. It is well known that cured epoxide resin has some low-temperature relaxations, and their mechanisms have been studied to analyse segmental motions of network polymers[1-8]. We have also investigated the mechanisms for the mechanical and dielectric relaxations in epoxide resins cured with various agents[9-15]. It was reported in the previous papers that the β relaxation observed near -40°C in amine-cured systems could be interpreted as the sum of relaxations of hydroxy ether groups and of other parts of the networks[9,10], and that the β' relaxation based on the motion of the aromatic ring appears in the range from 50 to 100°C[14,15].

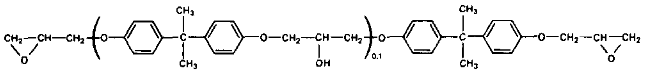
On the other hand, linear polymers, i.e. poly(hydroxy ethers), are obtained by the reaction of epoxide resins with diphenols[16-27]. The relaxation behaviour of these polymers has not been studied sufficiently[17,22], and there has been no investigation on the mechanisms for the low-temperature relaxations.

In the present paper, the relationship between mechanical relaxation behaviour and chemical structure of poly(hydroxy ethers) is studied, and the effect of acetylation on the relaxation behaviour of these polymers is investigated in detail. The mechanisms for the low-temperature relaxations of poly(hydroxy ethers) are discussed on the basis of these data and the dielectric relaxation behaviour of these polymers.

EXPERIMENTAL

Materials

The epoxide resins used were liquid bisphenol A type epoxide resins (DGEBA; Epikote 828, epoxy equivalent 190±5):



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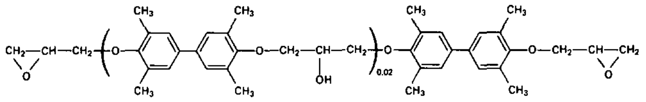
and biphenyl type resin (DGEBP; Epikote YX-4000, epoxy equivalent 180±5):



4,4′-Isopropylidenediphenol (BA) and 3,3′,5,5′-tetramethylbiphenyldiol (BP) were used as diphenols to be reacted with epoxide resins. Tetramethylammonium hydroxide was used as a catalyst for the polyaddition reaction of diphenols with diglycidyl ethers.

These epoxide resins and diphenols were commercial-grade materials and were purified by recrystallization from organic solvents. The catalyst was EP-grade material and was used without further purification.

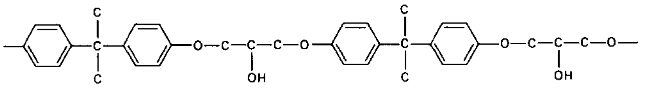
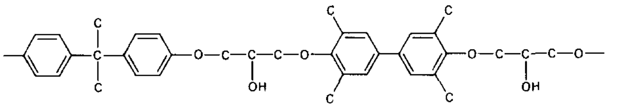
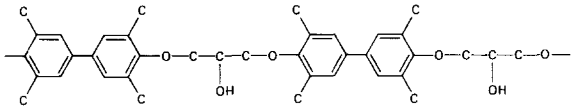
Polymer preparation

A detailed description of polymer preparation is outside the scope of this paper, but we may mention the outline of the polymerization procedure. The bisphenol A and biphenyl type epoxide resins with bisphenols in a 1:1 molar ratio were dissolved in xylene and chlorobenzene, respectively, under reflux with stirring. Catalyst (0.99 mol%) was added to these solutions. The time of catalyst addition was taken as time zero. The polymerization was carried out at the reflux temperature of each solvent for 8 h with stirring in a flowing stream of N_2 gas.

After completion of polymerization, the products were washed to remove the low-molecular-weight fraction and unreacted monomer by a reprecipitation method: the products were first dissolved in tetrahydrofuran (THF) and then reprecipitated by addition of acetone–methanol (2:1 volume ratio) mixed solvent. The reprecipitation was repeated three times.

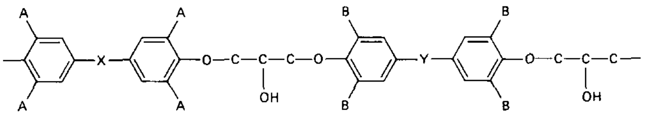
The resulting polymers may be represented by the

Table 1 Structures and molecular weights of a series of poly(hydroxy ethers)

Abbreviation	Polymer structures	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	n^a
DGEBA-BA		36500	1.63	60.0
DGEBA-BP		32800	1.58	52.7
DGEBP-BP		34500	1.35	56.9

^{a}Number of repeat units

general formula of the repeating segment:



where the ring substituents A and B are hydrogen or methyl, and the bisphenol bridge groups X and Y are isopropyridene or nothing.

The molecular weight $\bar{M}_w$ was determined by g.p.c. analysis calibrated with standard polystyrene to be roughly 3×10^4. *Table 1* lists the molecular weight $\bar{M}_w$ and the number of repeat units n of the polymers with their abbreviations and structures.

Acetylation of poly(hydroxy ethers)

Acetylation of poly(hydroxy ethers) was carried out according to the method described by Reinking[17]. Polymer (25.0 g) and pyridine (15.8 g) were dissolved in 250 ml of dioxane and 10.3 g of acetyl chloride was added. The mixture was refluxed for 1.5 h. The acetylated polymers were precipitated into 2-propanol containing a small amount of ice and washed with 2-propanol, dilute HCl and water, and finally dried at about 60°C for 16 h under reduced pressure. The acetylation of polymers was confirmed by the appearance and disappearance of the adsorptions for the ester group (1730 cm^{-1}) and the hydroxy group (3470 cm^{-1}), respectively, in i.r. spectroscopy.

Measurements

Dynamic mechanical properties were investigated using an inverted, free-oscillation torsion pendulum (RD-110, Rhesca Co. Ltd) according to ASTM D 2236-70. The frequency of oscillation was adjusted to be within the range 0.3–3.0 Hz. The temperature range from −160 to +250°C was studied. Samples were heated at 0.7°C min^{-1} *in vacuo*.

Dielectric measurements were performed at a frequency of 3 kHz and a temperature range from −70 to +200°C using an inductive ratio arm bridge (TRS-10T, Ando Electric Co. Ltd).

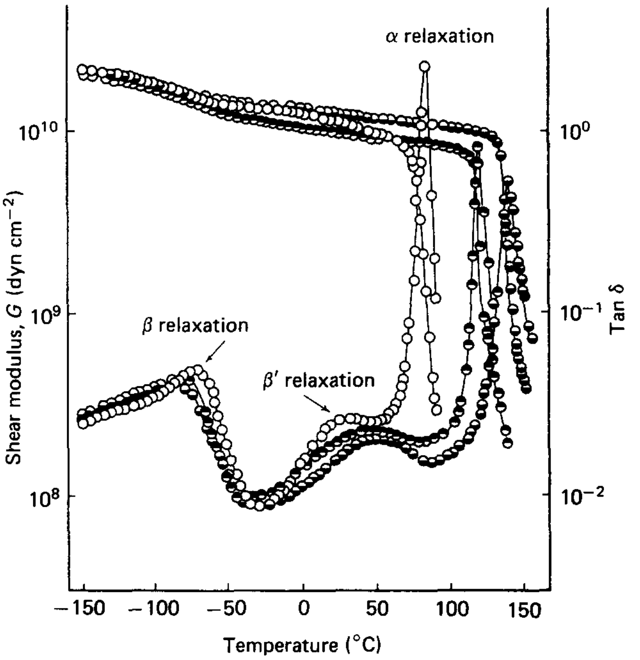


Figure 1 Dynamic mechanical properties for a series of poly(hydroxy ethers): (○) DGEBA-BA, (●) DGEBA-BP, (◒) DGEBP-BP

The activation energy ΔE of the low-temperature relaxations was calculated from the temperature dependences of the storage and loss moduli by using the equation[2]:

$$\Delta E = \frac{\pi k (G_u^{T_{max}} - G_r^{T_{max}})}{2\int G'' \, d(1/T)}$$

where $G_u^{T_{max}}$ and $G_r^{T_{max}}$ are the values of the unrelaxed and relaxed shear moduli at the peak temperature of the relaxation, respectively, and k is Boltzmann's constant. There may be some uncertainty in the value of ΔE estimated from this equation, because the equation is derived by assuming a single relaxation time. Therefore only relative values of ΔE are discussed in this paper.

RESULTS AND DISCUSSION

Mechanical and dielectric relaxations of poly(hydroxy ethers)

Dynamic mechanical properties of three poly(hydroxy ethers) are shown in *Figure 1*. In all systems, three well

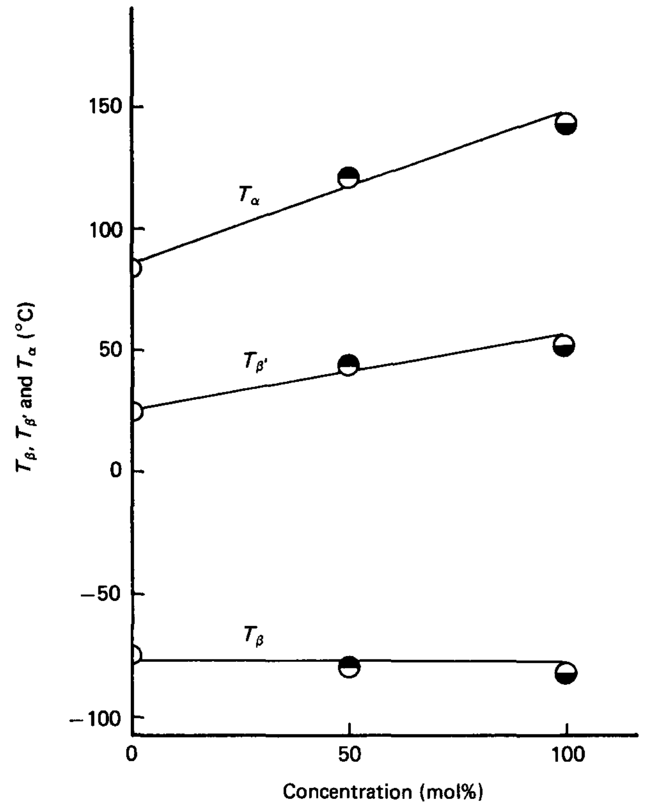


Figure 2 Relaxation temperatures vs. concentration of tetramethylbiphenyl units in poly(hydroxy ethers): symbols as in *Figure 1*

defined relaxation peaks are observed from 80 to 140°C, 20 to 60°C and at about −70°C, and denoted by α, β' and β relaxations as in previous papers[14,28].

It is well known that the α relaxation corresponds to the glass–rubber transition and is due to micro-Brownian motion of polymer chains. The peak temperature of the relaxation, T_α, is successively increased on introducing biphenyl segments into the polymer chains. This shows that the mobility of a biphenyl segment is lower than that of a bisphenol A segment.

The β' relaxation shifts considerably to high temperature as the concentration of biphenyl units is increased; this relaxation is affected by the mobility of the phenylene groups in the polymer chains. The peak height and temperature of the β relaxation are influenced little by the change in chemical structure of phenylene groups. Therefore the β relaxation is not due to the motion of the chain segments including the phenylene ring.

The effect of the concentration of biphenyl units on the relaxation temperatures of the poly(hydroxy ethers) is shown in *Figure 2*. The α relaxation temperature T_α is increased with increase in the concentration of tetramethylbiphenyl units. As the chemical structure of the aromatic ring changes from bisphenol A type to tetramethylbiphenyl type, the specific volume of polymers is increased from 0.79 to 0.87 $\mathrm{cm^3\,g^{-1}}$. Thus, it is reasonable to consider that the free volume of the polymers is increased with introduction of the methyl branch of the phenylene ring. The increase in free volume usually decreases T_α of a polymer[22]. Nevertheless, T_α of these polymers shifts to high temperature with increase in the concentration of biphenyl units. This should mean that the mobility of the phenylene ring in the biphenyl unit is remarkably lower than that in the bisphenol A unit.

While the β' relaxation temperature $T_{\beta'}$ increases, the β relaxation temperature T_β remains nearly constant as the aromatic ring changes from bisphenol A to biphenyl type. Therefore, the reduction of the mobility of phenylene group affects the β' relaxation behaviour but does not influence the β relaxation behaviour. In a strict examination, T_β is slightly decreased with increase in the concentration of biphenyl units. This decrement of T_β seems to be due to the increase in the free volume as mentioned above.

The activation energy ΔE for the β' and β relaxations of the poly(hydroxy ethers) is shown in *Figure 3*. The values of ΔE for β' relaxation are increased with increase in the concentration of biphenyl units. On the other hand, the ΔE for β relaxation is nearly constant regardless of the structure of the phenylene group. It is also shown from this result that the β' relaxation depends on the mobility of the phenylene group, and the β relaxation is independent of the structure of the phenylene group.

The mechanical and dielectric relaxations of the poly(hydroxy ethers) are shown in *Figure 4*. The β relaxation is clearly observed in both the dynamic mechanical and dielectric measurements. However, the β' relaxation definitely appears in the former, but could not be observed in the latter. It is well known that in dielectric measurements the motion of a polar group is detected and that of a non-polar group cannot be detected[29,30]. Thus, it is clear that the β relaxation is due to the motion of the segment including the polar group and the β' relaxation is attributed to that of the non-polar segment. For the poly(hydroxy ethers) studied in this work, the non-polar segment is only the phenylene group. In addition, the peak temperature and the activation energy of the β' relaxation were affected by the mobility of the phenylene group (*Figures 2* and *3*). Accordingly, we conclude that the β' relaxation of the poly(hydroxy ethers) is due to the motion of the phenylene group in the polymer chain.

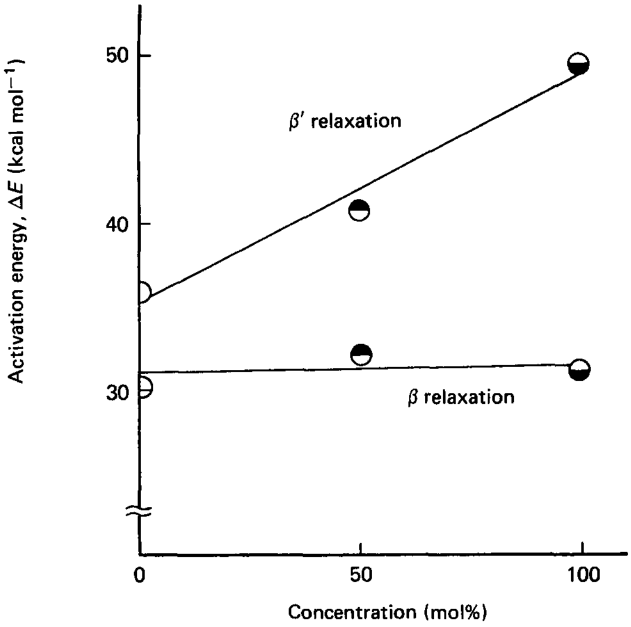


Figure 3 Activation energy for the β and β' relaxations vs. concentration of tetramethylbiphenyl units in poly(hydroxy ethers)

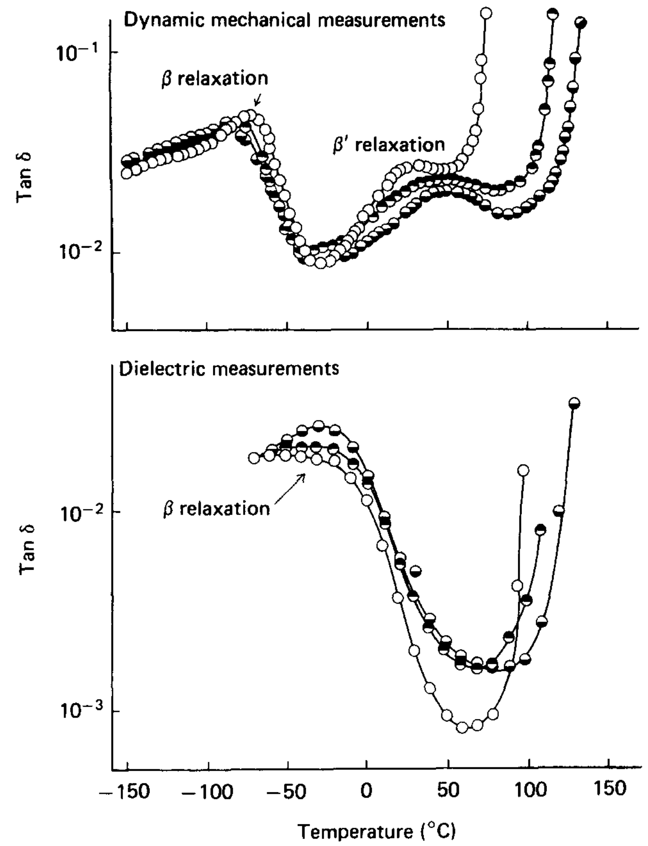


Figure 4 Mechanical and dielectric relaxations of poly(hydroxy ethers): symbols as in *Figure 1*. Measuring frequency ~1 Hz and 3 kHz for dynamic mechanical and dielectric measurements, respectively

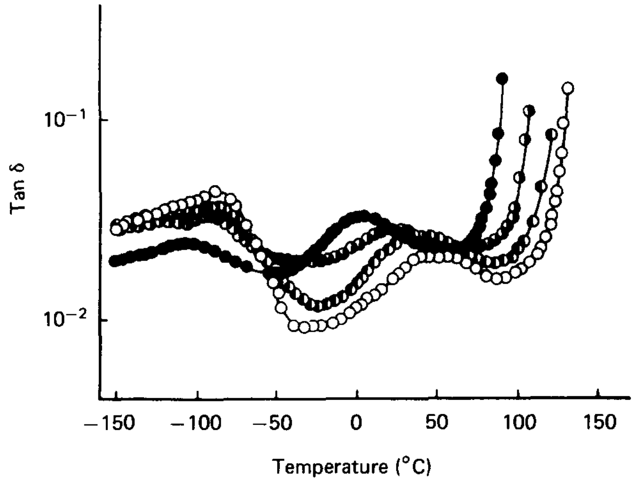


Figure 5 Effect of degree of acetylation on the mechanical relaxations of poly(hydroxy ethers). Degree of acetylation (%): (○) 0, (◐) 15, (◑) 50, (●) 93. Sample DGEBP–BP

Effect of acetylation on the β and β' relaxations of poly(hydroxy ethers)

Effect of acetylation on the β and β' relaxations of the biphenyl type poly(hydroxy ether) is shown in *Figure 5*. The intensity of the β relaxation is rapidly decreased and a broad relaxation appears near −100°C with increasing degree of acetylation. In the acetylation of this polymer, acetyl groups should be added to hydroxy groups on the hydroxy ether segments and decrease the mobility of these segments. Thus, it is natural to consider that the disappearance of the β relaxation with acetylation is related to the change in the mobility of the hydroxy ether portion. In addition, it has been mentioned that the β relaxation is attributed to the motion of the polar segment and is not affected by the change in the structure of the aromatic ring (*Figures 2*, *3* and *4*). Accordingly, it is apparent that the motion of the hydroxy ether portion contributes to the β relaxation. However, an additional relaxation is observed at lower temperature in the completely acetylated system. We conclude from these results that the β relaxation of the poly(hydroxy ethers) is a complex relaxation which is due to the overlap of the relaxation of hydroxy ether segment with that of other parts in the polymer chain. Such a complex relaxation has been reported for the β relaxation in amine-cured epoxide resins[9,10]. This similarity of the β relaxation mechanism in poly(hydroxy ethers) to that in cured epoxide resins is reasonable, because the poly(hydroxy ethers) correspond to linear high-molecular-weight epoxide resins.

Moreover, the β' relaxation seems to shift to low temperature and increases in peak height with increase in the degree of acetylation. These phenomena could be interpreted as the overlap of a new relaxation (which has a peak near 0°C) on the β' relaxation for the unacetylated polymer. The magnitude of this relaxation increases with the progress of acetylation. Thus, it is considered that the new relaxation is due to the motion of the segment produced by the acetylation, that is, the acetylated hydroxy ether segment.

To confirm the mechanism for this new relaxation, the dielectric relaxation of the acetylated poly(hydroxy ethers) is measured (*Figure 6*). In the non-acetylated system, only the β relaxation is observed at about −30°C as mentioned in *Figure 4*. With increasing degree of acetylation, a new relaxation develops at about 60°C. This result shows that the new relaxation is due to the motion of the polar segment which is caused by the acetylation. Accordingly, it is concluded that this relaxation is related to the motion of the acetylated hydroxy ether portion.

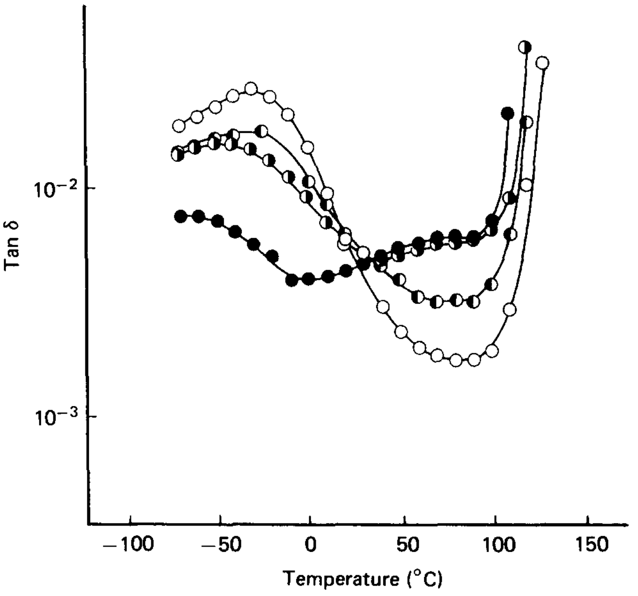


Figure 6 Effect of degree of acetylation on the dielectric relaxations of poly(hydroxy ethers): symbols as in *Figure 5*. Sample DGEBP–BP. Measuring frequency 3 kHz

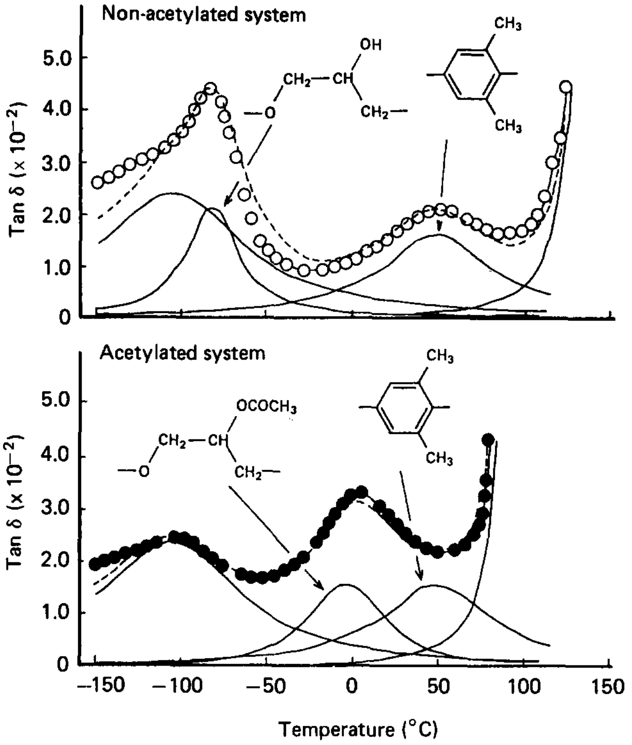


Figure 7 Schemes for overlap of mechanical relaxations in poly(hydroxy ethers): symbols as in *Figure 5*

CONCLUSIONS

A series of poly(hydroxy ethers) were prepared by the reaction of epoxide resins with diphenols. The mechanisms of some low-temperature relaxations in these polymers were investigated in detail by comparing the mechanical and dielectric relaxations with the chemical structure of the non-acetylated and acetylated polymers.

The conclusions of this investigation are summarized in *Figure 7*. In this figure, the plotted points show the experimental loss tangent curves; the full curves correspond to the individual low-temperature relaxations found in this work. These full curves were estimated from the experimental curves, assuming that the single relaxation is characterized by a Lorentz function and the additive law is applicable to the relaxations. The broken curves show the total sum of the individual relaxations given by the full curves. These broken curves are in fair agreement with the experimental loss tangent curves except in the low-temperature region below −130°C. In the non-acetylated poly(hydroxy ethers), the β relaxation can be interpreted by the sum of the relaxation of the hydroxy ether group, which is observed near −70°C, and that of the other parts of the polymer chain. The β' relaxation is observed at about 50°C and is due to the motion of the phenylene group in the polymer chain.

In the acetylated poly(hydroxy ether), the relaxation near −70°C disappears, because the motion of the hydroxy ether segment is restricted by acetylation of the hydroxy group. Instead of this relaxation, a new relaxation appears at about 0°C and is attributed to the motion of the acetylated hydroxy ether segment. The relaxation of the acetylated segment is superimposed upon that of the phenylene group.

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