# Thermoplastic softening behavior of organically modified polyoxotitanates: Effects of the amount of water and benzoylacetone for hydrolyzing alkoxides

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**ABSTRACT:** Organically modified polyoxotitanates were prepared by hydrolyzing titanium tetra-*n*-butoxide in the presence of benzoylacetone (BzAc) in solution at $Ti(OC_4H_9)_4 : BzAc : H_2O : CH_3COCH_3$ mole ratios of $1 : (1 \text{ or } 2) : (1 \text{ or } 10) : 20$. The solutions were concentrated at 80°C and dried at 140°C in $N_2$ flow, producing transparent and yellow materials of BzAc-modified polyoxotitanate. The materials had refractive indices of $\sim$1.7 and exhibited thermoplastic softening at temperatures below 70°C. Low contents of BzAc and high contents of $H_2O$ in solution led to higher softening temperatures of the materials, indicating the tunability of the softening temperature. Gel permeation chromatographic analyses showed that the higher softening temperatures originated mainly from polymerized species of higher molecular weights that were generated by hydrolysis and condensation reactions promoted by the low BzAc and high $H_2O$ contents in solution. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42653.

## INTRODUCTION

Polyoxometalates are clusters that are composed of connected oxygen coordination polyhedra with centered metal atoms. They can possess a variety of functions such as magnetism, high refractive indices, and dielectric properties depending on the types of metal atoms and the structure of the polyhedra. Although the syntheses and structural analyses of polyoxometalates have been reported extensively in literature,[1–3] the properties of bulk materials composed of polyoxometalates have rarely been studied.

When polyoxometalates are organically modified, the organic species may hinder the development of spatially extended structures and only allow weak interactions between polyoxometalates. Then we expected that bulk materials that are composed of such organically modified polyoxometalates can exhibit thermoplasticity or melt-castability, which is an advantage from the viewpoint of processability. Accordingly, they would exhibit functions based on polyoxometalates as well as processability based on thermoplasticity. Such materials are different from the high refractive index organic–inorganic hybrid materials that have been reported to date such as $TiO_2$–polyimide[4,5] and ZnO–polystyrene nanocomposites,[6] whereby the organic polymers are responsible for the thermoplastic properties of the hybrid materials.

Based on the above concept, we prepared organically modified polyoxometalates in the absence of organic polymers by hydrolyzing titanium *n*-butoxide and zirconium *n*-propoxide in the presence of various types of *β*-diketones as chelating agents, followed by solvent evaporation.[7] Transparent materials displaying thermoplasticity were obtained when *β*-diketones with high boiling points were used. These materials were amorphous and exhibited no endothermic peaks owing to the melting of *β*-diketones, indicating that the thermoplasticity property does not originate from the melting of *β*-diketones but from the weak interactions among polyoxometalates. Additionally, we studied the effect of the drying temperature on the thermoplasticity of these materials.[8] As observed, the softening temperature increased with increasing drying temperatures. *β*-Diketones and alkoxyl groups were lost at higher temperatures, promoting condensation reactions and increasing the molecular weight of the polyoxometalates, consequently leading to increased softening temperatures.

Furthermore, the contents of the chelating agent and $H_2O$ in the starting solution may influence the softening temperature because they may alter the extent of hydrolysis and condensation reactions of the metal alkoxides and the molecular weight of the polymerized species. Thus, the softening temperature of
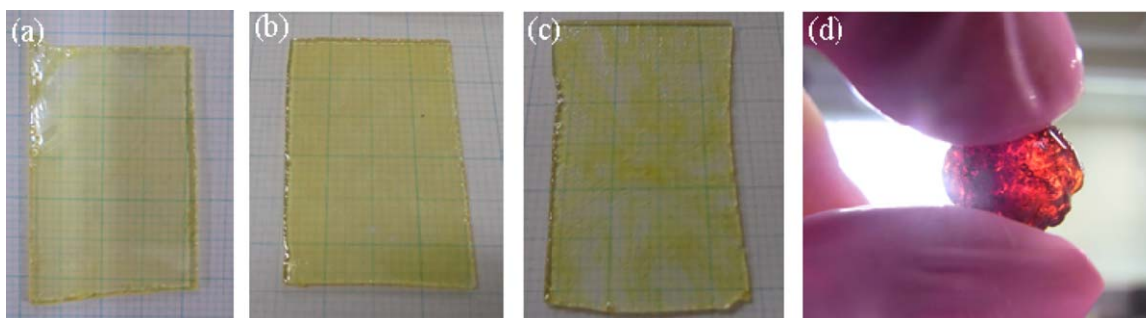
**Figure 1.** Appearance of the film samples prepared by spin-coating at (a) 6000, (b) 3000, and (c) 6000 rpm on $SiO_2$ substrates from concentrated solutions of Ti : BzAc : $H_2O$ at mole ratios of (a) 1 : 1 : 1, (b) 1 : 2 : 1, and (c) 1 : 2 : 10. (d) Appearance of the bulk sample prepared from solution of Ti : BzAc : $H_2O$ at a mole ratio of 1 : 2 : 1. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the hybrids can be tuned by varying these above-mentioned processing parameters.

Therefore, based on the concept mentioned above, in this study, titanium tetra-*n*-butoxide (Ti($OC_4H_9^n$)$_4$) was hydrolyzed in the presence of benzoylacetone (BzAc), a $\beta$-diketone, to obtain hybrid materials, and the effect of the amounts of BzAc and $H_2O$ in the starting solution on the thermoplasticity of the hybrid materials was examined. The effect of such processing parameters on the molecular weight of the polymerized species was also studied to determine the relationship between the molecular weight and softening temperature.

## EXPERIMENTAL

### Preparation of Samples

Ti($OC_4H_9^n$)$_4$, BzAc, and acetone ($CH_3COCH_3$) were purchased from Wako Pure Chemical Industries, Osaka, Japan. Starting solutions with molar compositions of Ti($OC_4H_9^n$)$_4$ : BzAc : $H_2O$ : $CH_3COCH_3$ = 1 : (1 or 2) : (1 or 10) : 20 were prepared by the following procedure. BzAc was dissolved in acetone to which Ti($OC_4H_9^n$)$_4$ and $H_2O$ were successively added under magnetic stirring. After stirring at room temperature for 1 h, the solutions were concentrated at 80°C for 50 min. Film samples were deposited on Si(100) or $SiO_2$ glass substrates using the concentrated solutions by spin-coating at 3000 or 6000 rpm, dried at 140°C for 30 min, and cooled to room temperature; both drying and cooling were conducted under dried $N_2$ flow. Bulk samples were prepared by placing a drop of the concentrated solution on Si(100) substrates in a flask at 140°C, dried at 140°C for 30 min, and cooled to room temperature; the entire process was conducted under dried $N_2$ flow. The prepared bulk samples are referred to as "dropped samples."

A bulk sample of a larger size was also prepared by the following procedure. The concentrated solution was dropped on soda-lime glass substrates and dried at 120°C for 23 min for sample softening. Then, the softened sample was infused in a syringe that was maintained at 120°C for 3 min and injected into a silicon rubber mold at 120°C, after which the temperature was maintained for 10 min. The resulting product was refrigerated in dry $N_2$ gas and then removed from the mold at room temperature.

### Measurements

The ultraviolet–visible (UV–vis) absorption spectra of the films on $SiO_2$ glass substrates were recorded on a UV–vis spectrophotometer (V-570, Jasco, Tokyo, Japan) using a bare $SiO_2$ glass substrate as the reference. The thickness of the samples on the $SiO_2$ glass substrates was measured by a contact probe surface profilometer (SE-3500, Kosaka Laboratory, Osaka, Japan); part of the samples was scraped off with a surgical knife to make the level difference to be measured as the thickness.

The infrared (IR) absorption spectra of the films on Si(100) substrates were recorded on a Fourier transform IR spectrophotometer (FT/IR-410, Jasco, Tokyo, Japan) using a bare Si(100) substrate as the reference.

Refractive index measurements, thermomechanical analysis (TMA), thermogravimetry and differential thermal analysis (TG–DTA), and gel permeation chromatography (GPC) of the dropped samples prepared on Si(100) substrates were conducted. The TMA measurements were performed on each sample in duplicate. The refractive index was measured by a prism coupler (2010, Metricon Corporation, NJ) using a prism with a refractive index of 1.9648 and a He/Ne laser with a wavelength of 632.8 nm. TMA was conducted using a thermomechanical analyzer (TMA8310, Rigaku, Tokyo, Japan) at a heating rate of 5°C min$^{-1}$ under a load of 98 mN in flowing $N_2$ gas. To prevent adhesion of the sample to the detection rod, an aluminum lid was placed between the two components. TG–DTA curves were obtained on a thermal analyzer (TG8120, Rigaku). For analysis, the crushed and powdered samples were heated at a rate of 5°C min$^{-1}$ in flowing air. The GPC analyses were performed on the samples dissolved in tetrahydrofuran using a GPC apparatus (TDA305, Viscotek, TX) equipped with two columns (TSKgel GMHXL-L, Tosoh, Tokyo, Japan) that were maintained at 35°C; tetrahydrofuran was used as an eluent at a flow rate of 1.0 mL min$^{-1}$. The molecular weight, $M$, of the polymerized species was calculated from the ratio of the intensity of the signal obtained from the right angle light scattering (RALS) detector, RALS$_{sig}$, to that obtained from the refractive index (RI) detector, RI$_{sig}$, using the following equations:[9]

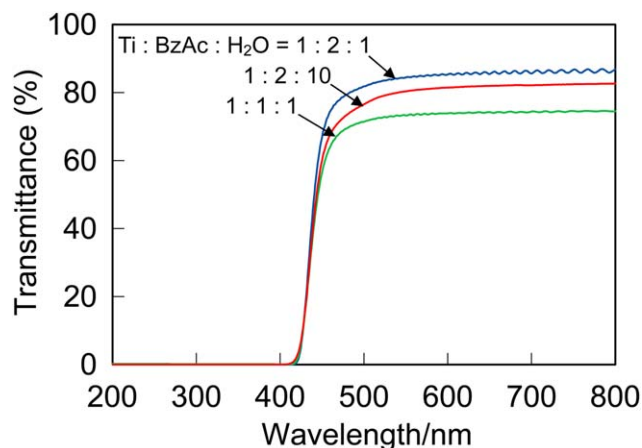$$RALS_{sig} = \left(\frac{dn}{dc}\right)^2 \times M \times c \times K_1, \quad (1)$$

**Figure 2.** UV–Vis absorption spectra of the samples prepared by spin-coating on SiO$_2$ substrates from concentrated solutions of Ti : BzAc : H$_2$O at mole ratios of 1 : 1 : 1, 1 : 2 : 1 and 1 : 2 : 10. The thickness of the films was ∼10 μm. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$$RI_{sig} = \frac{dn}{dc} \times c \times K_2, \qquad (2)$$

$$M = \frac{RALS_{sig}}{RI_{sig}} \times \left(\frac{dn}{dc}\right)^{-1} \times \frac{K_2}{K_1}, \qquad (3)$$

where $n$ is the refractive index, $c$ is the concentration of the polymerized species, and $K_1$ and $K_2$ are the instrumental constants.

## RESULTS

### Appearance and Refractive Index of the Samples

Both the starting and concentrated solutions were transparent and yellow regardless of the amount of BzAc and H$_2$O used. The appearance and UV–vis absorption spectra of the films on SiO$_2$ glass substrates are shown in Figures 1(a–c) and 2, respectively. The films were ∼10-μm-thick and had absorption edges of ∼425 nm. Additionally, fine cracks that were formed during cooling in the flask were observed.

The dropped samples were also transparent and yellow. They were hard at room temperature and soft at 140°C. The softened material featured solidified skins on the surface when heated in air. However, such features were not observed when the material was heated in flowing N$_2$. The appearance of the bulk sample prepared by casting is shown in Figure 1(d). The sample exhibited a cone-like shape of ∼10 mm in diameter and 5 mm in height. It was deep brown in appearance while it looked red and transparent through light transmission.

The refractive indices of the dropped samples were comparable at 1.68–1.70 regardless of the amount of BzAc and H$_2$O used.

### Samples Prepared with Different Amounts of BzAc

The effect of the amount of BzAc on the thermoplastic softening behavior was studied on the samples that were prepared from solutions at BzAc/Ti molar ratios of 1 and 2 and a constant H$_2$O/Ti molar ratio of 1. The TMA curves of the dropped samples are shown in Figure 3. The curves obtained on the first
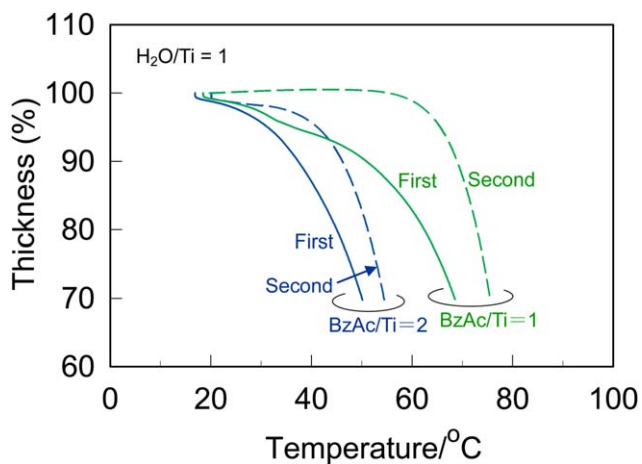


**Figure 3.** TMA curves of the samples prepared by dropping concentrated solutions of Ti : BzAc : H$_2$O at mole ratios of 1 : (1 or 2) : 1 on Si(100) substrates. The two successive TMA measurements: first (solid line) and second (broken line) are shown. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

and second measurements are denoted as "First" and "Second," respectively. In both measurements, a decrease in thickness was observed that was indicative of the softening of the samples. However, the second measurement generated a softening temperature that was higher than that obtained in the first measurement regardless of the amount of BzAc used. It is also noticed that the sample prepared at a BzAc/Ti molar ratio of 2 exhibited a decrease in thickness at a lower temperature than that at a BzAc/Ti molar ratio of 1.

The IR absorption spectra of the films prepared from the solutions at BzAc/Ti molar ratios of 1 and 2 at a constant H$_2$O/Ti molar ratio of 1 are shown in Figure 4, and the peak assignment is summarized in Table I after Refs. 10–17. Both samples displayed the peaks assigned to the C═C and C═O stretching vibrations in the BzAc chelate rings and to the breathing mode of the chelating rings as well as those assigned to the C─H
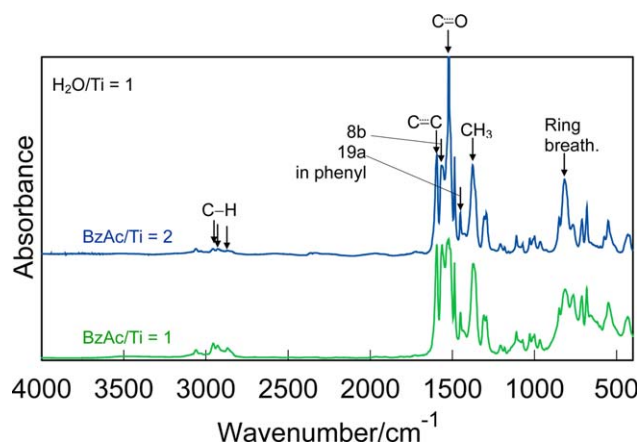


**Figure 4.** IR absorption spectra of the film samples prepared by spin-coating at 6000 and 3000 rpm on Si(1 0 0) substrates from respective concentrated solutions of Ti : BzAc : H$_2$O at mole ratios of 1 : 1 : 1 (green line) and 1 : 2 : 1 (blue line). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

**Table I.** Assignments of the Infrared Absorption Peaks

| Wavenumber (cm$^{-1}$) | Assignment | Reference |
|---|---|---|
| 400-900 | Ti—O—Ti stretching | 17, 18 |
| 810 | Ring breathing in chelating rings of bidentate BzAc | 13 |
| 1371 | CH$_3$ bending in butoxy groups and BzAc | 14, 15 |
| 1487 | 19a mode in the phenyl group of BzAc | 15, 16 |
| 1520 | C=O stretching in chelating rings of bidentate BzAc | 10-12 |
| 1556 | (8b + $v_{C=O}$ + $\delta_{OH}$) and (8b + $v_{C=C}$ + $\delta_{OH}$) mode in the phenyl group of BzAc | 15, 16 |
| 1590 | C—C stretching in chelating rings of bidentate BzAc | 10-12 |
| 2870 | C—H stretching in butoxy groups | 14, 17 |
| 2930 | C—H stretching in butoxy groups | 14, 17 |
| 2975 | C—H stretching in butoxy groups | 14, 17 |

stretching vibrations, the CH$_3$ bending vibrations, and the 8b + $v_{C=O}$ + $\delta_{OH}$, 8b + $v_{C=C}$ + $\delta_{OH}$ and 19a vibration modes in the phenyl group. With increasing amounts of BzAc, the C=O stretching vibration and ring breathing peaks increased in intensity, whereas the C—H stretching vibration peaks decreased. The sample prepared at a BzAc/Ti molar ratio of 1 displayed a broad band assigned to Ti—O—Ti vibrations in the TiO$_2$ network.

The TG–DTA curves of the dropped samples prepared from the solutions with BzAc/Ti molar ratios of 1 and 2 at an H$_2$O/Ti molar ratio of 1 are shown in Figure 5. Both samples exhibited significant weight losses with exothermic peaks at 200–400 and 400–500°C following a slight weight loss at temperatures below 200°C. The sample prepared at a BzAc/Ti molar ratio of 1 showed a more gradual weight loss at ~200–400°C, and the onset temperature of weight loss was lower than that of sample prepared at a BzAc/Ti molar ratio of 2. Both samples showed a steep weight loss at 460–470°C associated with an exothermic peak. The sample prepared at a BzAc/Ti molar ratio of 2 displayed a smaller residual weight following heating to 1000°C (24%) when compared with that of sample prepared at a BzAc/Ti molar ratio of 1 (33%).
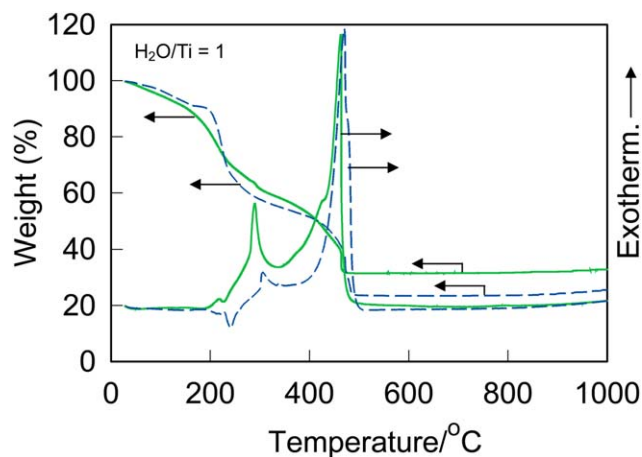
The GPC profiles of the samples are shown in Figure 6. Both samples displayed two peaks, as generated from the RI and RALS detectors. The molecular weight of the polymerized species calculated from RI$_{sig}$ and RALS$_{sig}$ using eq. (3) is also shown in Figure 6. As observed, $M$ of the sample prepared at a BzAc/Ti molar ratio of 1 was higher than that of sample prepared at a BzAc/Ti molar ratio of 2 at either of the two peaks of the RI and RALS signal profiles.

**Samples Prepared with Different Amounts of H$_2$O**
The effect of the amount of H$_2$O on the thermoplastic softening behavior was studied on the samples that were prepared from solutions of H$_2$O/Ti molar ratios of 1 and 10 at a constant BzAc/Ti molar ratio of 2. The TMA curves of the dropped samples are shown in Figure 7. As observed, the softening temperature was higher in the second measurement when compared with that obtained in the first measurement regardless of the amount of H$_2$O. The sample prepared at an H$_2$O/Ti molar ratio of 10 exhibited a decrease in thickness at a higher temperature than that at an H$_2$O/Ti molar ratio of 1.



**Figure 5.** TG–DTA curves of the samples prepared by dropping concentrated solutions of Ti : BzAc : H$_2$O at mole ratios of 1 : 1 : 1 (solid lines) and 1 : 2 : 1 (broken lines) on Si(100) substrates. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
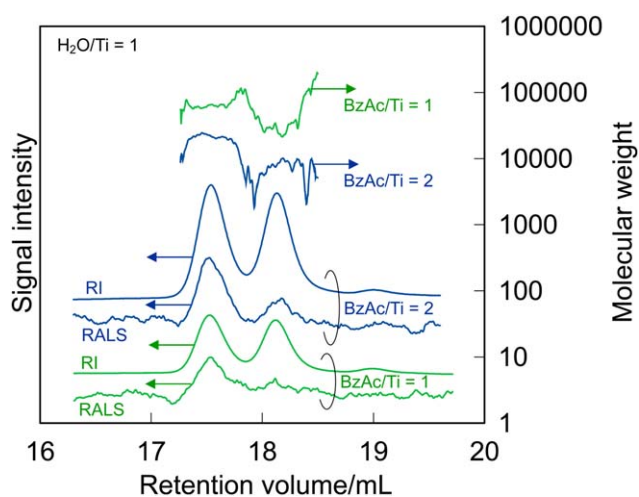


**Figure 6.** GPC profiles of the samples prepared by dropping concentrated solutions of Ti : BzAc : H$_2$O at mole ratios of 1 : (1 or 2) : 1 on Si(100) substrates. The intensity of the RALS signals is magnified by 200×. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
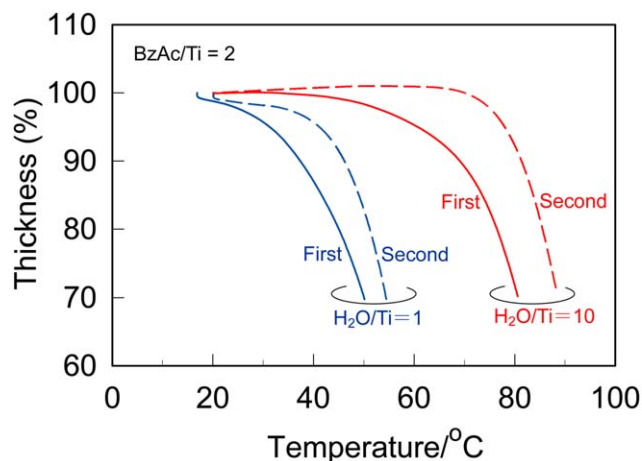
**Figure 7.** TMA curves of the samples prepared by dropping concentrated solutions of Ti : BzAc : $H_2O$ at mole ratios of 1 : 2 : 1 and 1 : 2 : 10 on Si(1 0 0) substrates. The two successive TMA measurements: first (solid line) and second (broken line) are shown. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



**Figure 9.** TG–DTA curves of the samples prepared by dropping concentrated solutions of Ti : BzAc : $H_2O$ at mole ratios of 1 : 2 : 1 (broken line) or 10 (solid line) on Si(1 0 0) substrates. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The IR absorption spectra of the films prepared from solutions of $H_2O$/Ti molar ratios of 1 and 10 at a constant BzAc/Ti molar ratio of 2 are shown in Figure 8. Both samples displayed peaks corresponding to chelate rings and butoxy groups similarly to the results in Figure 4. However, the sample prepared at an $H_2O$/Ti molar ratio of 10 displayed a peak at 1720 cm$^{-1}$ (C═O stretching vibrations), and the intensity of the peak at 1520 cm$^{-1}$ (C═O vibrations in the chelating rings) was weaker than that of the sample prepared at a $H_2O$/Ti molar ratio of 1.

The TG–DTA curves of the dropped samples prepared from the solutions of $H_2O$/Ti molar ratios of 1 and 10 and a BzAc/Ti molar ratio of 2 are shown in Figure 9. Both samples showed the same weight losses, that is, significant weight losses with associated exothermic peaks at 200–400 and 400–500°C following a slight weight loss at temperatures below 200°C were
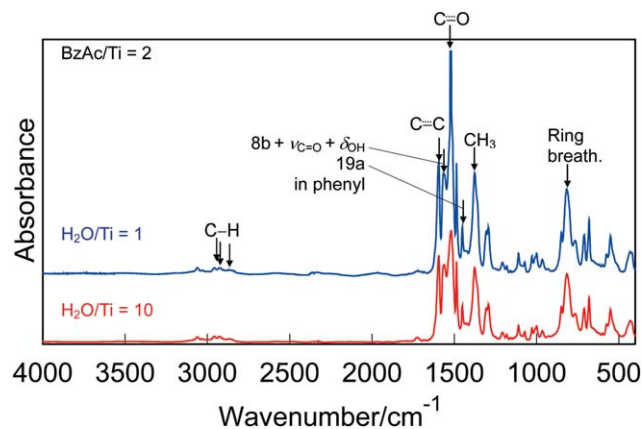
observed. The residual weight following heating to 1000°C was the same (24%) for both samples.

The GPC profiles of the samples are shown in Figure 10. The RI and RALS signal profiles of both samples each displayed two peaks. The molecular weights of the polymerized species, calculated from $RI_{sig}$ and $RLAS_{sig}$, were, respectively, higher and lower at the smaller and larger retention volume peaks and were comparable for the samples prepared at $H_2O$/Ti molar ratios of 1 and 10 (Figure 10). However, the RI and RALS signal profiles indicate that the sample prepared at a $H_2O$/Ti molar ratio of 10 consisted of a high proportion of higher molecular species. The sample prepared at an $H_2O$/Ti molar ratio of 10 displayed larger and smaller peaks at smaller and larger retention volumes, respectively, in the RI and RALS signal profiles, whereas the



**Figure 8.** IR absorption spectra of the film samples prepared by spin-coating at 3000 and 6000 rpm on Si(100) substrates from respective concentrated solutions of Ti : BzAc : $H_2O$ at mole ratios of 1 : 2 : 1 (blue line) and 1 : 2 : 10 (red line). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
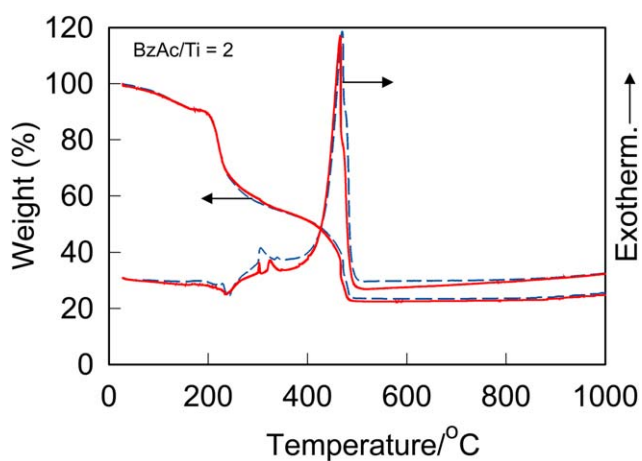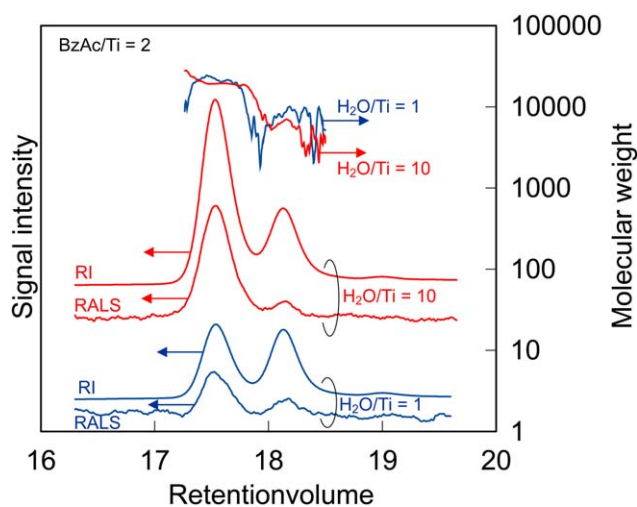


**Figure 10.** GPC profiles of the samples prepared by dropping concentrated solutions of Ti : BzAc : $H_2O$ at mole ratios of 1 : 2 : (1 or 10) on Si(100) substrates. The intensity of the RALS signals is magnified by ×200. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
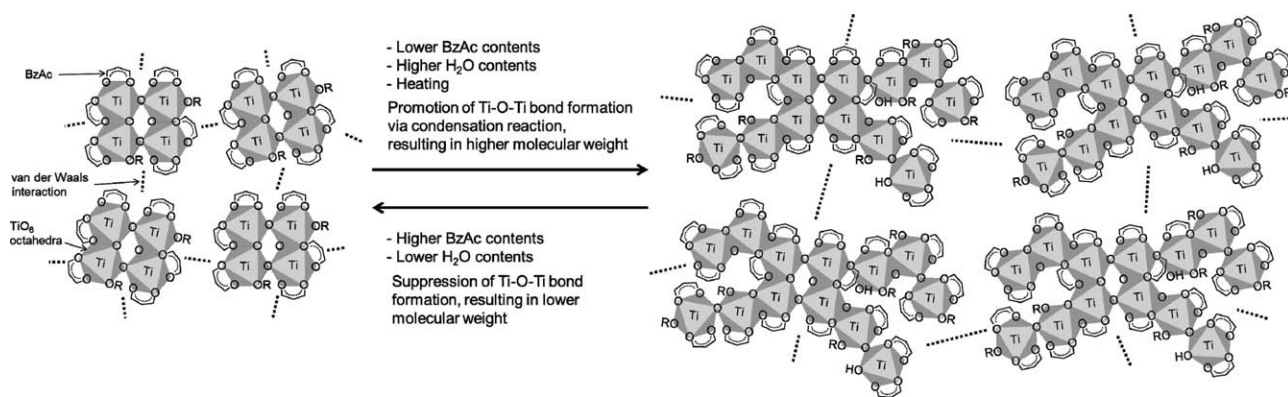
**Figure 11.** Schematic illustration of the structure of the products, showing that the lower BzAc contents and the higher $H_2O$ contents in solutions, and the heating of the dried materials promote the Ti—O—Ti bond formation via condensation reaction, which leads to an increase in molecular weight. The illustration also demonstrates that the polymerized species have van der Waals interaction between themselves.

sample prepared at an $H_2O/Ti$ molar ratio of 1 displayed peaks of comparable intensity at smaller and larger retention volumes.

## DISCUSSION

### Hydrolysis and Condensation of the Alkoxide

Before discussing the effects of the amounts of water and BzAc on the thermoplastic softening behavior, the chemical reactions in solutions and the products obtained thereby are briefly described. When the titanium butoxides with titanium atoms chelated by BzAc are hydrolyzed, either butoxyl or BzAc ligands are replaced by hydroxyl groups as represented by the following formula;
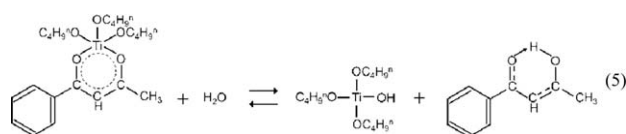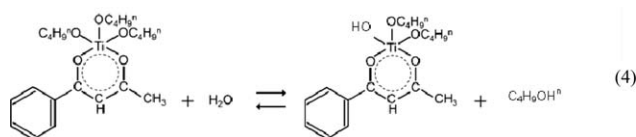


Then the hydrolyzed species undergo condensation reaction to form Ti—O—Ti bonds with water molecules as the by-product;
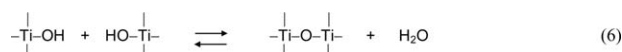


These hydrolysis and condensation reactions proceed successively and concurrently to form polyoxotitanate clusters, oligomers, or polymers, depending on the degree of polymerization, as schematically illustrated in Figure 11, where how the products are changed by BzAc and $H_2O$ contents and by heating, which will be mentioned later. The products thus obtained

consist of $TiO_n$ polyhedra where Ti atoms are chelated by BzAc and the polyhedra are linked together via Ti—O—Ti bonds. The polyoxotitanate clusters, oligomers, or polymers may have van der Waals interaction between them as is represented by broken lines in Figure 11.

### Effect of Drying in Flowing $N_2$

In previous studies, the concentrated solutions were dried in an ambient atmosphere.[7,8] In contrast, in this study, the solutions were dried under dry $N_2$ flow. The products featured solidified skins on the surface when dried in an ambient atmosphere. In contrast, such a feature was not observed when the products were dried under a dry $N_2$ flow. The solidified skins could form basically by gelation induced by solvent evaporation. The above experimental observations, however, suggest that the formation of the skins was promoted by hydrolysis reactions [eqs. (4) and (5)] owing to the presence of moisture in the air, followed by condensation reaction [eq. (6)].

The skins could inhibit evaporation of the solvent during drying. Under such a scenario, the bottom regions of the product may not be dry and exhibit a viscous solution-type texture. However, this feature was not observed for samples that were dried at 140°C under a dry $N_2$ flow—solvent evaporation occurred because of the absence of such skins. Therefore, the softening observed at temperatures considerably lower than the drying temperature can be attributed to the thermoplastic property of the dried and solidified materials rather than the residual solvent.

All samples that were dried in flowing $N_2$ softened at higher temperatures, as observed from the second TMA measurement relative to those observed from the first TMA measurement (Figures 3 and 7). As clarified in the previous study by GPC analyses,[8] such an increase in the softening temperature was due to an increase in molecular weight of the polymerized species that resulted from the progress of the condensation reaction in the first run of the TMA measurements as is schematically illustrated in Figure 11.

### Effect of the Amount of BzAc

The weight losses at 200–400 and 400–500°C in the TG curves were attributed to the oxidation of BzAc and residual carbon,

respectively. Upon oxidation of BzAc, the softening behavior disappeared, as observed in the previous study involving BzAc-modified polyoxotitanates that were heated at 250°C.[8] It should be pointed out that the content of acetone, 1-butanol, and water in the BzAc-modified polyoxotitanates was negligible, as evidenced from the absence of C═O and O─H vibration peaks (1730 and 3400 cm$^{-1}$) in Figure 4. The slight weight loss observed below 200°C may be attributed to the evaporation of water and 1-butanol that were produced upon condensation reactions during heating.

TMA showed that at a given $H_2O$/Ti molar ratio of 1, the sample prepared at a BzAc/Ti molar ratio of 2 displayed a softening temperature that was lower than that of the sample prepared at a BzAc/Ti molar ratio of 1 (Figure 3). Furthermore, the sample prepared at a BzAc/Ti molar ratio of 2 displayed a smaller $M$ than that prepared at a BzAc/Ti molar ratio of 1 (Figure 6). The latter observation was believed to be the cause of the lower softening temperature observed. Generally, $\beta$-diketones, such as acetylacetone, chelate metal atoms in solution, inhibiting hydrolysis and condensation reactions of metal alkoxides.[19,20] As observed, the intensity of the IR absorption peaks corresponding to the chelating rings increased, and the band corresponding to Ti─O─Ti disappeared when the molar ratio of BzAc/Ti used during synthesis increased from 1 to 2 in this study (Figure 4). This finding indicates the presence of higher degrees of chelation and suppression of condensation reactions when a BzAc/Ti molar ratio of 2 was used, which is also schematically represented in Figure 11.

### Effect of the Amount of $H_2O$

TMA studies revealed that at a given BzAc/Ti molar ratio of 2, the sample prepared at an $H_2O$/Ti molar ratio of 10 displayed a higher softening temperatures than that of the sample prepared at an $H_2O$/Ti molar ratio of 1 (Figure 7). The sample prepared at an $H_2O$/Ti molar ratio of 10 had a larger $M$ than that prepared at an $H_2O$/Ti molar ratio of 1 (Figure 10), which is schematically illustrated in Figure 11 and is believed to be the cause of the higher softening temperature observed for this sample. The larger $M$ of the sample prepared at an $H_2O$/Ti molar ratio of 10 was due to the higher degree of hydrolysis that was evidenced in the following experimental observation. When the $H_2O$/Ti ratio increased from 1 to 10, the intensity of the IR absorption peaks corresponding to chelating rings decreased, and the peak corresponding to C═O vibrations in free BzAc (keto form) appeared (Figure 8). Such a decrease in the intensity of the chelating rings-associated peak and appearance of the free BzAc-associated peak may be due to hydrolysis reactions, as represented by eq. (5). The higher amount of free BzAc suggests the occurrence of a higher degree of hydrolysis reactions in solution prepared at an $H_2O$/Ti molar ratio of 10.

As discussed above, at a given BzAc/Ti molar ratio of 2, the sample prepared at an $H_2O$/Ti molar ratio of 10, which featured a higher $M$ than that of sample prepared at an $H_2O$/Ti molar ratio of 1, softened at higher temperatures relative to sample prepared at an $H_2O$/Ti molar ratio of 1. When comparison is made between samples prepared at Ti : BzAc : $H_2O$ molar ratios of 1 : 1 : 1 and 1 : 2 : 10 (with different BzAc and $H_2O$

contents), however, $M$ and the softening temperature display an inverse relationship. The latter sample, which featured a smaller $M$, softened at higher temperatures relative to the former sample. This indicates that the molecular weight of the polymerized species is not the sole factor governing the softening temperature. Furthermore, the structures of the polyoxometalate and polyhedra, the nature of the polyhedra linkage, and the degree of cross-linking may influence the softening temperature. Structural analysis of the components of the prepared samples is required to further clarify this issue.

## CONCLUSIONS

The thermoplastic properties were studied on optically transparent, organically modified polyoxotitanates that were prepared from solutions of $Ti(OC_4H_9)_4$ : BzAc : $H_2O$ : $CH_3COCH_3$ at mole ratios of 1 : (1 or 2) : (1 or 10) : 20 via concentration, spin-coating or dropping, and drying processes. All the products displayed thermal softening properties on TMA curves, where lower BzAc and larger $H_2O$ contents in solutions resulted in higher softening temperatures. The higher softening temperatures were attributed mainly to the formation of polymerized species with larger molecular weights upon hydrolysis and condensation reactions. This work thus demonstrates that the thermoplastic performance of polyoxometalate-based bulk materials can be controlled by manipulating the polymerization degree via reaction control.

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