

Preparation and Viscoelastic Behavior of Methacrylate Ionomers Crosslinked by Titanium(IV) and Zirconium(IV)

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ABSTRACT: Ionomers of poly(methyl methacrylate-co-methacrylic acid) crosslinked by titanium(IV) (Ti^{4+}) and zirconium(IV) (Zr^{4+}) ions were prepared, and their structures, optical absorption and viscoelastic properties were investigated. IR measurement revealed that tetravalent metal ions were coordinated by $-\text{COO}^-$ groups of deprotonated methacrylic acid and functioned as crosslinkers. The coordination of $-\text{COO}^-$ to the Ti^{4+} especially brought about strong UV absorption below 360–370 nm owing to charge transfer. Dynamic mechanical thermal analysis (DMTA) showed storage modulus (E') below glass transition temperature (T_g) and a peak temperature of $\tan \delta$ for every ionomer not to increase regardless of metal ion content. This was attributed to residual alcohols. E' above T_g increased with metal ions content, and DMTA for every ionomer was measured up to 350°C. Crosslinking by tetravalent metal ions thus greatly improves heat resistance of host polymers.

KEY WORDS Ionomer / Titanium(IV) / Zirconium(IV) / Crosslinking / Viscoelastic / Methacrylate /

Ionomers are crosslinked polymeric materials consisting of a hydrophobic backbone and small amounts of acid groups (e.g. carboxylic acid and sulfonic acid etc.) neutralized either partially or completely with metal cations. The structures and properties can be varied by types of counter ions, constitution of a matrix copolymer and degree of neutralization.^{1–3} Most investigations have dealt with ionomers containing mono- or divalent ions of alkali, alkaline earth and transition metals. Regarding ionomers containing tetravalent metal ions, some authors have studied polymers having titanium alkoxy groups which are self-polishing coating materials for ship,^{4,5} halato-telechelic polymers as elastomers crosslinked by titanium(IV) (Ti^{4+}) and zirconium(IV) (Zr^{4+}).^{6,7} However, studies on ionomers crosslinked by tetravalent metal ions are limited. Recently investigations of ionomers with colored multivalent metal ions are increasing because of their optically functional properties. Optical absorption materials were found on ionomers crosslinked by copper(II) and neodymium(III)^{8,9} and ion-cluster structures of ionomers were clarified using polymers containing lanthanide ions.^{10,11} We prepared methacrylate ionomers crosslinked by Ti^{4+} with excellent mechanical properties, heat resistance and optical characteristics.^{12,13}

The present study reports the preparation and structures of two ionomers containing tetravalent metal ions. That is, ionomers of Poly(methyl methacrylate-co-methacrylic acid) crosslinked by Ti^{4+} and Zr^{4+} were prepared and their structures were characterized by infrared absorption and wide angle X-Ray scattering measurement. Optical absorption properties and viscoelastic behavior were investigated from the viewpoint of differences in tetravalent metal ions.

EXPERIMENTAL

Reagents

Methyl methacrylate (MMA) and methacrylic acid (MAA) were purified by conventional methods. Tita-

ni-um(IV) tetraisopropoxide ($\text{Ti}(\text{O}-i\text{Pr})_4$) and 85 wt% zirconium(IV) tetrabutoxide ($\text{Zr}(\text{O}-\text{Bu})_4$) butanol solution were used without purification as Ti^{4+} and Zr^{4+} sources, respectively. Benzoyl peroxide (BPO) used as an initiator was recrystallized from benzene solution. All reagents were purchased from Wako Pure Chemical Co. Ltd.

Preparation of Ionomers

Preparation of Ti^{4+} or Zr^{4+} ionomer was carried out as follows. After mixing MMA and MAA in prescribed molar ratio, tetraalkoxide of titanium(IV) or zirconium(IV) equivalent to MAA (molar ratio $[\text{MAA}]/[\text{metal ion}] = 4$) was added to the mixture. Mixtures containing the metalalkoxides were allowed to stand at ambient temperature for 1 h, and BPO was dissolved in each solution. Each mixture containing metalalkoxide was poured into a mold made of two glass plates with a silicone spacer of 1 mm thickness, and bulk-polymerized at 70°C for 2 h and then at 95°C for 24 h under dry nitrogen atmosphere. After polymerization, all ionomers were dried at 95°C for 24 h under vacuum to remove residues in the specimens. In this paper, ionomers crosslinked by Ti^{4+} and Zr^{4+} are represented by P(MMA/MAA)-Ti and P(MMA/MAA)-Zr, respectively. Table I summarizes the codes and compositions of the ionomers.

Measurements

Infrared absorption measurements (IR) were performed by the KBr method with a Perkin-Elmer 1640 fourier transform infrared (FT-IR) spectrometer. Measurement conditions were 16 scans and resolution of 4 cm^{-1} . Ultraviolet-visible region absorption spectroscopy (UV/VIS) was conducted with a Hitachi U-3500 UV/VIS/NIR recording spectrophotometer. Light-path length of all specimens was 1 mm. Wide angle X-Ray scattering (WAXS) experiments were performed with a Rigaku Geigerflex 2028 diffractometer using Ni-filtered $\text{Cu}-K_\alpha$ radiation. Voltage and current of the X-Ray source were 40 kV and 150 mA, respectively. Dynamic mechanical

Table I. Composition of P(MMA/MAA)-Ti and P(MMA/MAA)-Zr

Code	MMA/MAA mol/mol	MMA	MAA	$\text{Ti}(\text{O-}i\text{Pr})_4$	$\text{Zr}(\text{O-Bu})_4^a$	BPO
Ti-91	9/1	9.0 g (90 mmol)	0.861 g (10 mmol)	0.7106 g (2.5 mmol)	—	0.0986 g
Ti-82	8/2	8.0 g (80 mmol)	1.722 g (20 mmol)	1.4212 g (5 mmol)	—	0.0986 g
Ti-73	7/3	7.0 g (70 mmol)	2.583 g (30 mmol)	2.1317 g (7.5 mmol)	—	0.0986 g
Ti-64	6/4	6.0 g (60 mmol)	3.444 g (40 mmol)	2.8423 g (10 mmol)	—	0.0986 g
Zr-91	9/1	9.0 g (90 mmol)	0.861 g (10 mmol)	—	1.129 g (2.5 mmol ^b)	0.0986 g
Zr-82	8/2	8.0 g (80 mmol)	1.722 g (20 mmol)	—	2.257 g (5 mmol ^b)	0.0986 g
Zr-73	7/3	7.0 g (70 mmol)	2.583 g (30 mmol)	—	3.385 g (7.5 mmol ^b)	0.0986 g
Zr-64	6/4	6.0 g (60 mmol)	3.444 g (40 mmol)	—	4.514 g (10 mmol ^b)	0.0986 g

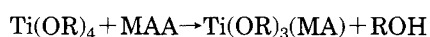
^a 85 wt% $\text{Zr}(\text{O-Bu})_4$ butanol solution. ^b Molar quantity of $\text{Zr}(\text{O-Bu})_4$ content in 85 wt% $\text{Zr}(\text{O-Bu})_4$ butanol solution.

thermal analysis (DMTA) was carried out to obtain storage modulus (E') and $\tan \delta$ using a ITK Co. DVA-200 in a stretching mode with frequency of 10 Hz and heating rate of 5°C min^{-1} . 20 mm \times 4 mm \times 1 mm strips were used for the measurements. Density was obtained by a pycnometer (liquid paraffin system, at 30°C).

RESULTS AND DISCUSSION

Formation of Metal Complexes and Preparation of Ionomers

$\text{Ti}(\text{O-}i\text{Pr})_4$ and $\text{Zr}(\text{O-Bu})_4$ are strong bases and may rapidly react with MAA, an acidic monomer, and are neutralized. At $[\text{MAA}]/[\text{Ti}^{4+}] = 1$ the following reaction proceeds, and a Ti^{4+} complex and alcohol are generated.⁴



R and MA denote alkyl group and deprotonated MAA ($\text{CH}_2 = \text{C}(\text{CH}_3)\text{COO}^-$), respectively.

The above neutralization reaction is expected. Actually, when alkoxides of Ti^{4+} and Zr^{4+} were added to mixtures of MMA and MAA, the color immediately changed and exothermic reaction occurred. Hence, it is considered that neutralization rapidly proceeds between MAA and metalalkoxide. Consequently, the complexes of the metal ions with MA are generated accompanied by alcohols as impurities. All mixture solutions including metal ions were transparent and no precipitate was generated during several months. After polymerization all ionomers were transparent, although alcohols were contained in the specimens. In the absence of MAA, mixtures of MMA and metal alkoxides became opaque after polymerization because of phase separation of the metal alkoxides from PMMA. The above results indicate that the MA coordinates to the tetravalent metal ions and helps complexes of metal ions to be soluble in MMA even after polymerization. Thus, our method for preparing ionomers is good to introduce tetravalent metal ions into a hydrophobic polymer matrix.

Figures 1a and 1b show IR spectra of P(MMA/MAA)-Ti and P(MMA/MAA)-Zr, respectively. For coordination states of Ti^{4+} complexes with methacrylate, two absorption peaks at 1548 cm^{-1} and 1580 cm^{-1} were observed in Figure 1a. Both absorptions were assigned to C=O asymmetric stretching band ($\nu_a(\text{C=O})$) for $-\text{COO}^-$ group of carboxylate combined with Ti^{4+} .^{4,14,15} The literature shows three coordination modes of carboxylate combined with metal ions, monodentate, bidentate

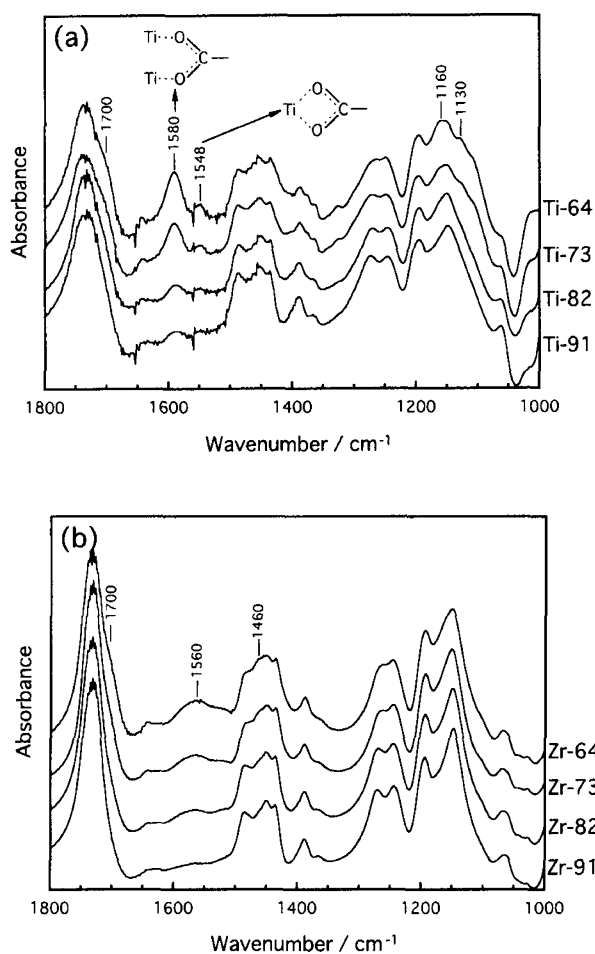
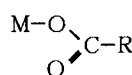
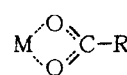


Figure 1. IR spectra of P(MMA/MAA)-Ti(a) and P(MMA/MAA)-Zr(b).

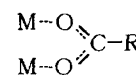
chelating and bidentate bridging.^{4,15,16}



Monodentate



Bidentate chelating



Bidentate bridging

These coordination modes can be identified by $\Delta\nu = \nu_a - \nu_s$ ¹⁶ where $\Delta\nu$ is the frequency separation and ν_s is frequency of a C=O symmetric stretching band. Two $\nu_a(\text{C=O})$ peaks of P(MMA/MAA)-Ti are considered to

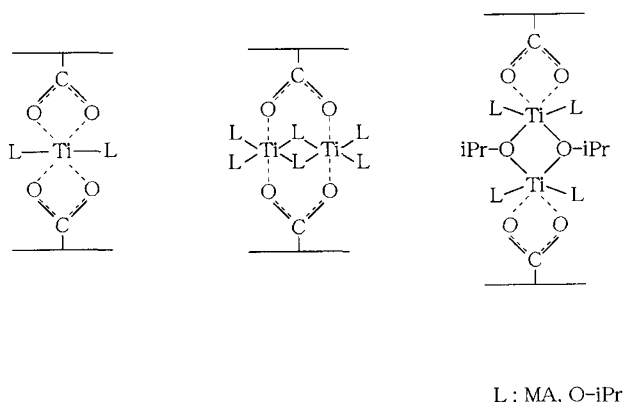


Figure 2. Possible coordination structures of P(MMA/MAA)-Ti.

originate from bidentate chelating (1548 cm^{-1}) and bidentate bridging (1580 cm^{-1}).^{4,14,15} Thus, there are two coordination states in P(MMA/MAA)-Ti. For P(MMA/MAA)-Zr, a broad absorption band of $\nu_a(\text{C}=\text{O})$ was observed at 1560 cm^{-1} shown in Figure 1b. $\nu_a(\text{C}=\text{O})$ and $\nu_s(\text{C}=\text{O})$ of P(MMA/MAA)-Zr were 1560 cm^{-1} and 1460 cm^{-1} , respectively, so that $\Delta\nu = 100\text{ cm}^{-1}$. In general, $\Delta\nu$ of monodentate is much larger than those of bidentate chelating and bidentate bridging ($\Delta\nu(\text{monodentate}) > 200\text{ cm}^{-1}$).¹⁶ This indicates that the coordination state of the carboxylate is either bidentate bridging or bidentate chelating, but not monodentate. Intermediary states of the two bidentate coordination modes of P(MMA/MAA)-Zr may be formed, because widths of the bands for $\nu_a(\text{C}=\text{O})$ are broader than that of P(MMA/MAA)-Ti.

Regarding the number of MA coordinated to metal ions, we can expect that a maximum of four MAA molecules may react with Ti^{4+} or Zr^{4+} , because these metal ions are tetravalent cations, MAA is a monovalent acid and the molar ratio $[\text{MAA}]/[\text{metalalkoxide}]$ is four in all specimens. However, $\nu_a(\text{C}=\text{O})$ of unreacted MAA was observed in Figure 1a at 1700 cm^{-1} as a shoulder. Absorptions assigned to skeletal vibration of isopropoxy group were observed at 1130 cm^{-1} and 1160 cm^{-1} . Neutralization thus does not perfectly proceed between MAA and $\text{Ti}(\text{O}-i\text{Pr})_4$, and some isopropoxy groups kept coordinating to Ti^{4+} as they were. In Figure 1b, P(MMA/MAA)-Zr has the absorption of $\nu_a(\text{C}=\text{O})$ of unreacted MAA as the shoulder. Thus, all MAAs do not react with metalalkoxides, and some alkoxy groups continue coordinating to metal ions, though MAA equivalent to metal ions was added in this study. Sayilkan *et al.* prepared titanium(IV) alkoxide methacrylates and investigated molar ratio dependence of the reactivity of titanium(IV) tetraethoxide and zirconium(IV) tetraisopropoxide with MAA.¹⁷ They showed that a part of MAA was unreacted with metal ions at $[\text{MAA}]/[\text{Ti}^{4+}] > 1.2$ and $[\text{MAA}]/[\text{Zr}^{4+}] > 2$. This supports the existence of the unreacted MAA in this study because both molar ratio $[\text{MAA}]/[\text{Ti}^{4+}]$ and $[\text{MAA}]/[\text{Zr}^{4+}]$ were 4. The absorption intensity of the shoulder at 1700 cm^{-1} of P(MMA/MAA)-Zr was obviously smaller than that of P(MMA/MAA)-Ti. Hence, the number of MA coordinated to Zr^{4+} is considered larger than that of Ti^{4+} . MAA may coordinate to Zr^{4+} more

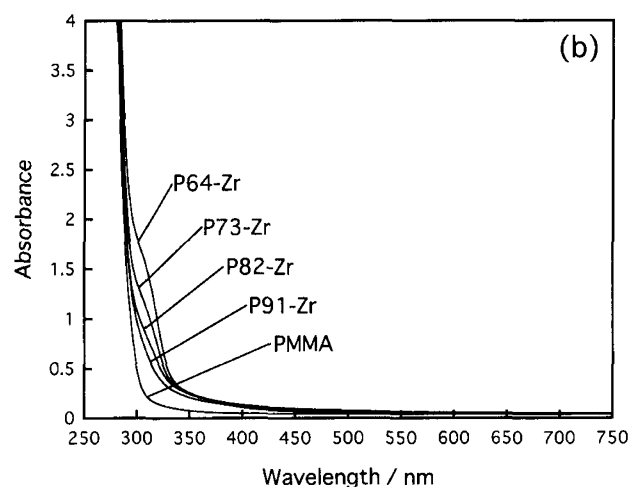
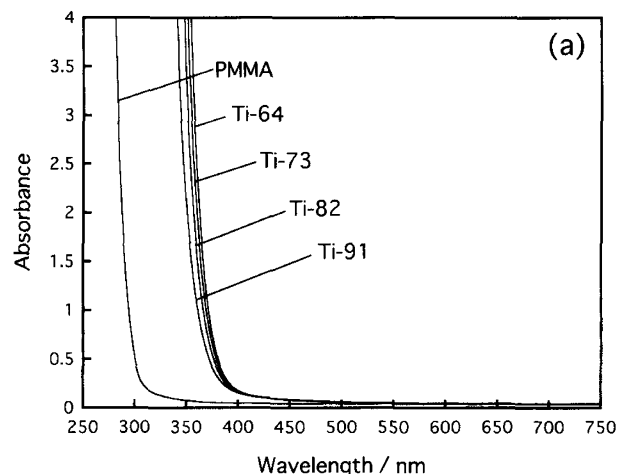


Figure 3. UV-VIS spectra of P(MMA/MAA)-Ti(a) and P(MMA/MAA)-Zr(b).

easily than Ti^{4+} , because the ionic radius and coordination number of Zr^{4+} are larger than those of Ti^{4+} (ionic radius, Ti^{4+} : 0.68 \AA , Zr^{4+} : 0.80 \AA).¹⁸

From the results of IR, possible coordination structures of P(MMA/MAA)-Ti can be proposed as shown in Figure 2 on an assumption that molecular chains are crosslinked by Ti^{4+} . It is considered that actual coordination structures are not simple like these. The coordination structures of P(MMA/MAA)-Zr are probably more complicated, because the absorption band of $\nu_a(\text{C}=\text{O})$ around 1560 cm^{-1} was broader and the coordination number of Zr^{4+} was larger than that of Ti^{4+} in comparison with P(MMA/MAA)-Ti.

Figures 3a and 3b show UV/VIS spectra of P(MMA/MAA)-Ti and P(MMA/MAA)-Zr, respectively. The spectrum of PMMA is shown in the figures for comparison. The color of P(MMA/MAA)-Ti was pale yellow or yellow, and P(MMA/MAA)-Zr was colorless. By introduction of metal ions the absorption edge of every ionomer shifted to the long wavelength side from PMMA. The absorption edges of the Ti^{4+} and the Zr^{4+} ionomers were at 400 nm and 340 nm, respectively, and wavelengths were independent of concentration of metal ions in the ionomers. In particular, P(MMA/MAA)-Ti exhibited strong absorption below 360–370 nm, which is useful for UV cut-off

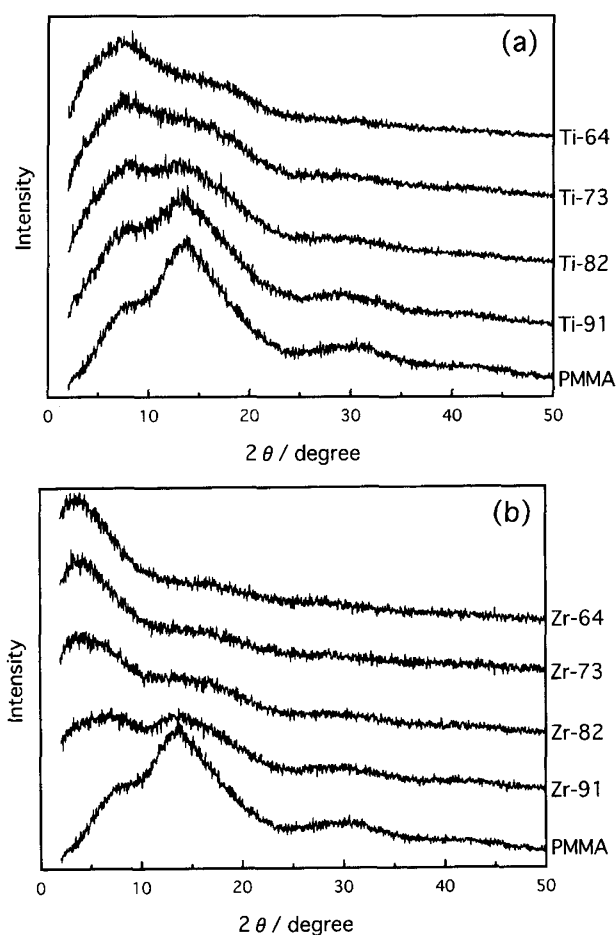


Figure 4. WAXS patterns of P(MMA/MAA)-Ti(a) and P(MMA/MAA)-Zr(b).

filter. The absorptions of both ionomers may be caused by charge transfer between metal ions and $-\text{COO}^-$ groups in MAA.¹³

Figures 4a and 4b show WAXS patterns of P(MMA/MAA)-Ti and P(MMA/MAA)-Zr, respectively. WAXS of PMMA appears in each figure. No sharp reflection by metal complexes was observed, and thus crystalline components do not exist in all ionomers. Characteristic amorphous patterns depending on the quantity and metal ions were noted. For WAXS of PMMA the broad peak at $2\theta = 13.8^\circ$ originated from interferences between neighboring chains of PMMA component.^{19,20} Instead of decrease of peak intensity at $2\theta = 13.8^\circ$ the peak intensity below $2\theta = 10^\circ$ increased with metal ion content. Thus, considerable conformational change of molecular chains may occur by introduction of metal ions, although we have no definite information on origin of change in WAXS.

Viscoelastic Behaviors of Ionomers

Figure 5 shows temperature dependence of E' and $\tan \delta$ of P(MMA/MAA)-Ti. In spite of increase of Ti^{4+} content, E' slightly decreased at room temperature and the peak temperature of $\tan \delta$ at 145°C , representing α relaxation (segmental motion related to glass transition temperature (T_g)), hardly changed. In general, the higher crosslinking density is, the higher modulus and

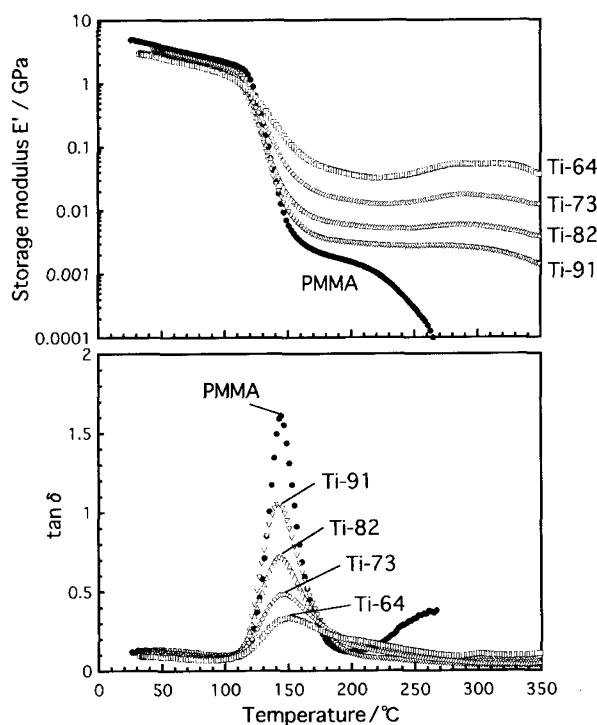


Figure 5. Temperature dependence of storage modulus E' and $\tan \delta$ of P(MMA/MAA)-Ti.

T_g are.²¹ However, our ionomers did not show such tendency below T_g . Above 120°C viscoelastic behavior showed considerable difference between specimens. For PMMA E' abruptly decreased above 250°C owing to melt-flow, and many bubbles were generated in the specimen, probably caused by depolymerization of MMA sequences by elevation in temperature. DMTA measurements for P(MMA/MAA)-Ti could be carried out up to 350°C , and a rubbery state continued from 150°C to 350°C . E' of P(MMA/MAA)-Ti above T_g was heightened with increase of Ti^{4+} content, which indicates that Ti^{4+} effectively crosslinked molecular chains of the polymethacrylates. Even after heating till 350°C the shape of the every specimen crosslinked by Ti^{4+} did not change and no bubbles were generated in the specimens. When all P(MMA/MAA)-Tis were compressed at 250°C , 30MPa, thermoplasticity was not exhibited. This compression temperature is high enough to exhibit thermoplasticity of ethylene ionomers, the most conventional ionomers of poly(ethylene-co-methacrylic acid) crosslinked by metal ions such as Na^+ and Zn^{2+} .^{1,2} Ethylene ionomers melt above 100°C ^{1,2}; thus, their heat resistance is not so high. From the results of DMTA for our ionomers, Ti^{4+} strongly crosslinked molecular chains and brought about high heat resistance of host polymer.

Figure 6 shows the densities of P(MMA/MAA)-Ti and PMMA at 30°C plotted as open circles against MAA composition. Although content of Ti^{4+} , a large atomic weight component, increased, the densities of the specimens did not. The density of polymer is decreased by low-density components and voids in specimens. These also lower both modulus and T_g of glassy polymers. In the case of our ionomers there were few voids; they had high transparency. Thus, we consider the existence of low-density components. Isopropanol, a low-density component,

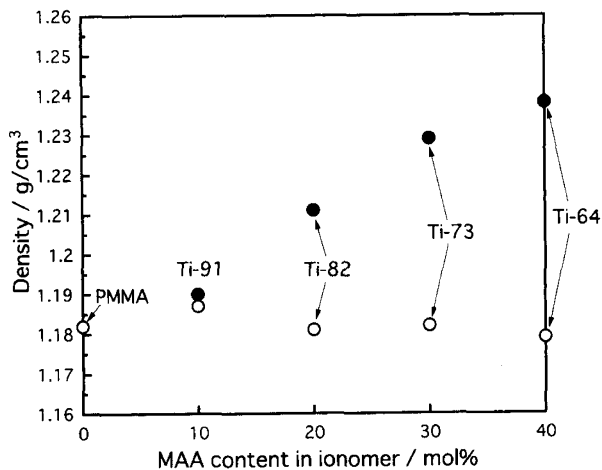


Figure 6. Density of P(MMA/MAA)-Ti (○ : non annealed, ● : annealed at 200°C for 1 h under vacuum).

would remain as impurity in the specimens, although the specimens were dried as described in the experimental section (at 95°C for 24 h under vacuum). Residual isopropanol would be reduced by annealing at higher temperature than 95°C. After annealing of P(MMA/MAA)-Ti at 200°C for 1 h under vacuum the densities increased depending on Ti^{4+} content shown as closed circles in Figure 6. The annealing may thus reduce the residual isopropanol in the specimens. The residual isopropanol would lower density and suppress the rise both E' at room temperature and α relaxation temperature in spite of increase of the crosslinking density.

To examine the influence of reduction of the residual isopropanol on viscoelastic behaviors, DMTA measurements were carried out after annealing of the specimens. Figure 7 shows the temperature dependence of E' and $\tan \delta$ of P(MMA/MAA)-Ti annealed at 200°C for 1 h under vacuum. For all annealed P(MMA/MAA)-Tis, E' from room temperature to 300°C and peak temperature of $\tan \delta$ increased, and peak magnitude of $\tan \delta$ decreased considerably in comparison with non-annealed P(MMA/MAA)-Ti. In particular, E' of annealed Ti-64 monotonously decreased with increase of temperature and the peak of $\tan \delta$ around 150°C almost disappeared. Thus, relaxation of the molecular chains of methacrylate up to 300°C may be suppressed by reduction of residual isopropanol after annealing. E' below T_g and the peak temperature of $\tan \delta$ did not surpass those of PMMA, a non-crosslinked polymer, even after annealing. These results are in contrast to acrylate ionomers, poly(ethyl acrylate-co-acrylic acid) crosslinked by Ti(IV) and Zr(IV) with lower T_g , as shown in another paper.²² That is, E' below T_g and the peak temperature of $\tan \delta$ for the acrylate ionomers increase with metal ion content without annealing.²² With increasing ion content of poly(ethyl acrylate-co-acrylic acid) crosslinked by Ti^{4+} , E' at -100°C and peak temperature of $\tan \delta$ rose from 1.9 GPa to max. 6.4 GPa and from -1°C to max. 47°C, respectively. The difference between methacrylate and acrylate is probably attributed to the relationship between polymerization temperature and T_g of the ionomers. The polymerization temperature was higher than T_g of acrylate ionomers (polymerization temperature:

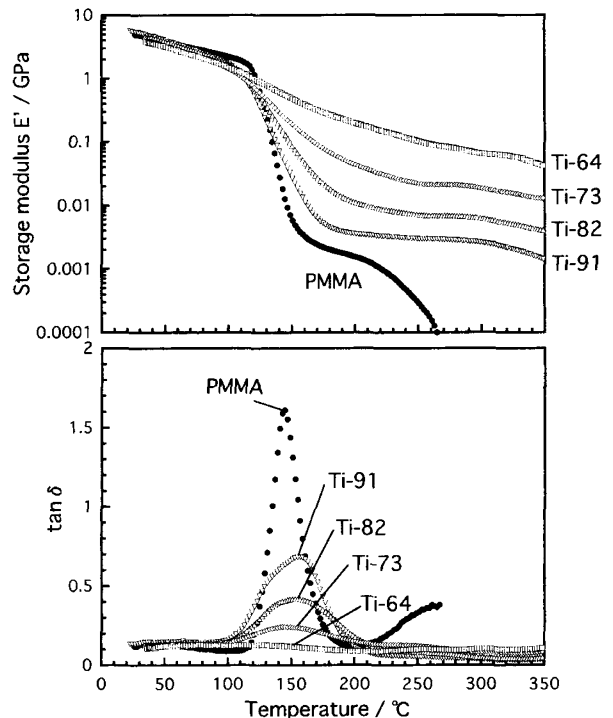


Figure 7. Temperature dependence of storage modulus E' and $\tan \delta$ of P(MMA/MAA)-Ti annealed at 200°C for 1 h under vacuum.

95°C, $T_g(\text{acrylate ionomers}) < 50^\circ\text{C}$). Therefore, acrylate ionomers show Brownian motion and relaxation of molecular chains at 95°C, so that small molecules such as isopropanol move about in the specimens. Consequently, isopropanol would evaporate during polymerization. As proof of this consideration, the densities of the as-polymerized acrylate ionomers increased with Ti^{4+} content. Polymerization temperature was lower than T_g of P(MMA/MAA)-Ti. Hence, polymerization restricts the molecular motion of methacrylate ionomers. Isopropanol would be inhibited to evaporate by restriction of molecular motion and remain in methacrylate ionomers. Lowering of E' at room temperature and T_g of P(MMA/MAA)-Ti may thus be prevented by removal of alcohol from the mixture of MMA and MAA containing metalalkoxides before polymerization.

Figure 8 shows temperature dependence of E' and $\tan \delta$ of P(MMA/MAA)-Zr. All P(MMA/MAA)-Zr exhibited a rubbery state up to 350°C, and E' above T_g increased with Zr^{4+} content as well as P(MMA/MAA)-Ti. Thus, P(MMA/MAA)-Zr have high heat resistance up to 350°C. E' at room temperature slightly decreased in comparison with that of PMMA, as also noted for P(MMA/MAA)-Ti. Peak temperatures of $\tan \delta$ for P(MMA/MAA)-Zr were ca. 120°C, considerably lower than those of P(MMA/MAA)-Ti and PMMA. This would be caused by huge residual butanol, because purchased zirconium(IV) tetrabutoxide contained butanol as solvent so that the quantity of residual alcohol in the specimens was much larger than that of P(MMA/MAA)-Ti. Characteristic odor of butanol could be confirmed when P(MMA/MAA)-Zr was scratched by a file. Therefore, butanol was not completely removed in drying at 95°C for 24 h under vacuum. Consequently, butanol acted as a

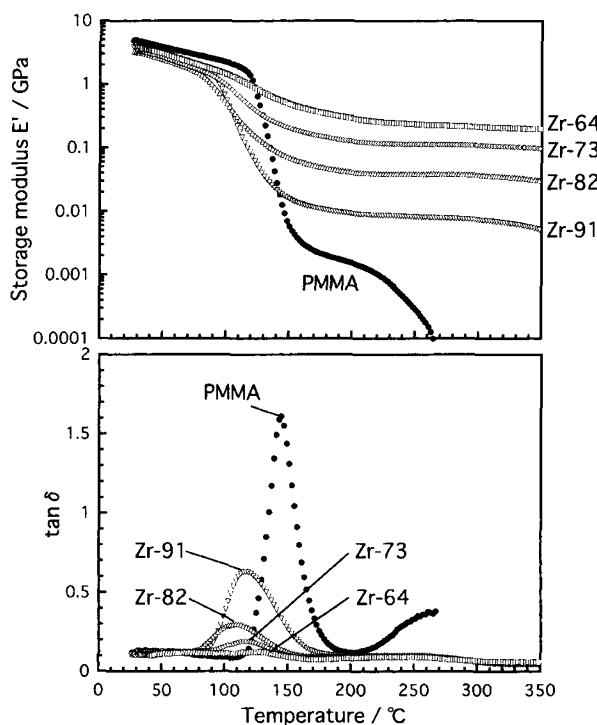


Figure 8. Temperature dependence of storage modulus E' and $\tan \delta$ of P(MMA/MAA)-Zr.

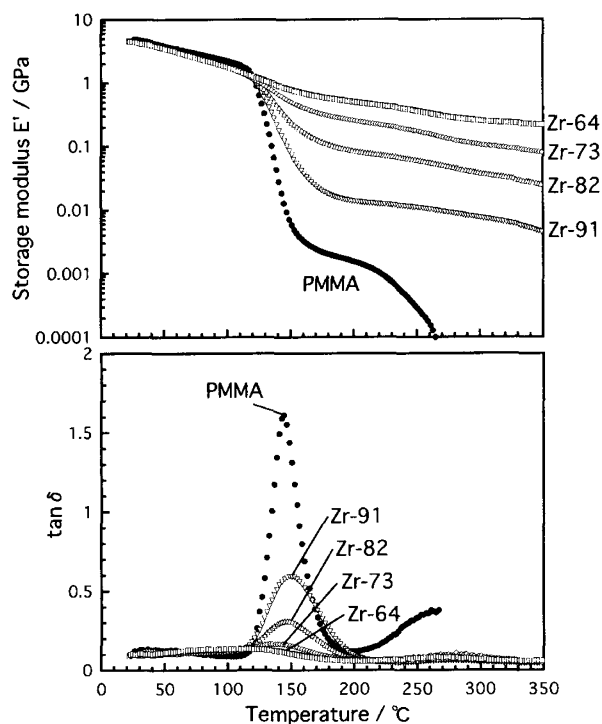


Figure 9. Temperature dependence of storage modulus E' and $\tan \delta$ of P(MMA/MAA)-Zr annealed at 200°C for 1 h under vacuum.

plasticizer and affected physical properties and T_g of the specimens. Figure 9 shows the temperature dependence of E' and $\tan \delta$ of P(MMA/MAA)-Zr annealed at 200°C for 1 h under vacuum. E' from room temperature to 270°C and peak temperature of $\tan \delta$ increased after annealing. These results are similar to those of P(MMA/MAA)-Ti. The degree of increase of E' and peak temperature of $\tan \delta$ was greater than that of P(MMA/MAA)-Ti. Therefore, the quantities of residual alcohols in P(MMA/MAA)-Zr were more and greatly affected mechanical and thermal properties.

Differences in E' above 150°C between P(MMA/MAA)-Ti and P(MMA/MAA)-Zr were noted. E' for P(MMA/MAA)-Zr surpassed that of P(MMA/MAA)-Ti compared at the same MAA content, as shown in Figures 7 and 9, owing to differences of crosslinking density of the two ionomers. Thus, molecular weight between crosslink points of each ionomer was estimated. According to the statistical theory of rubbery elasticity, the number-average molecular weight between crosslinks (M_c) is related to tensile modulus (E) in a rubbery state as,²¹

$$M_c = (3\rho RT) / E$$

where ρ is the density of specimen, R gas constant (8.314 J K⁻¹ mol⁻¹), and T absolute temperature. M_c was calculated by inserting E' at 300°C ($T=573.15$ K) in Figures 7 and 9 and ρ of annealed specimens at 30°C, into the equation. In this case, change of ρ at high temperature was ignored. Figure 10 shows M_c of P(MMA/MAA)-Ti and P(MMA/MAA)-Zr against MAA composition. With increase of metal ion content M_c of all ionomers decreased, namely, crosslinking density increased. M_c of P(MMA/MAA)-Zr was smaller than that of

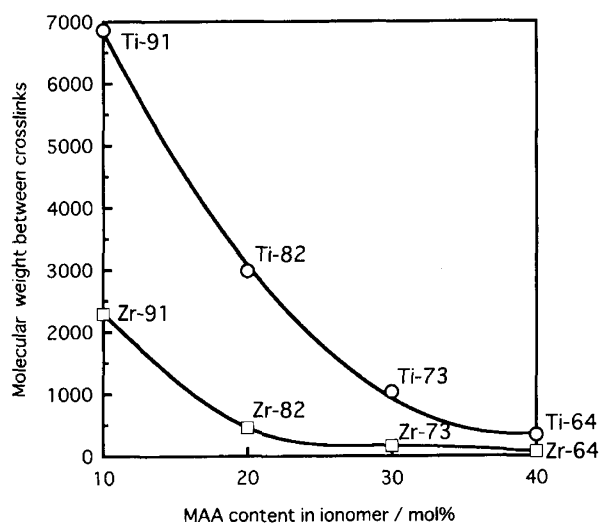


Figure 10. Number-average molecular weight between crosslinks of P(MMA/MAA)-Ti (○) and P(MMA/MAA)-Zr (□) annealed at 200°C for 1 h under vacuum.

P(MMA/MAA)-Ti, which means that crosslinking density of P(MMA/MAA)-Zr was larger, because larger radius and coordination number of Zr^{4+} ions caused many MA to coordinate with Zr^{4+} compared to Ti^{4+} . This agrees with the results of IR measurements.

From viscoelastic measurements, crosslinking by the tetravalent metal ions effectively promotes heat resistance of methacrylate polymers composed of conventional components such as MMA and MAA.

CONCLUSIONS

We prepared two ionomers of poly(methyl methacrylate-*co*-methacrylic acid) crosslinked by Ti^{4+} and Zr^{4+} . Tetravalent metal ions combined with $-\text{COO}^-$ of methacrylic acid and formed crosslink points between intermolecular chains. The combination of Ti^{4+} with $-\text{COO}^-$ brought about strong UV absorption below 360–370 nm. As a result of DMTA, E' above T_g increased with metal ion content but not below T_g . According to E' above T_g , P(MMA/MAA)-Zr had higher crosslinking density compared to P(MMA/MAA)-Ti, because both ionic radius and coordination number of Zr^{4+} were larger than those of Ti^{4+} . For all ionomers, a rubbery state continued up to 350°C. This indicates that the introduction of tetravalent metal ions greatly enhances heat resistance of host polymers.

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