

Effects of Neutralization on the Structure and Properties of an Ionomer

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ABSTRACT: The structure, morphology, and properties of an ionomer, poly(ethylene-acrylic-acid) neutralized by zinc salts (PI) depend on the free carboxylic acid content. In this work, metal acetates (Na, Zn, and Al acetates) were used to control the neutralization levels. A wide range of techniques were used, such as spectroscopic Fourier transform infrared spectroscopy (FTIR), thermal [thermogravimetric analysis, modulated differential scanning calorimetry (MDSC), and dynamic mechanical analysis (DMA)], mechanical (tensile measurement), and small angle neutron scattering (SANS). The melt rheological properties of the samples were also examined. The results show that metal acetate neutralizes free acrylic acid in the ionomer, which has the primary role in controlling ionic

association. The number of ionic groups in ionic domains and multiplets in the matrix is dependent on the neutralization level. Metal valence determines the ionic domain or multiplet structure (FTIR), further properties of PI. Dynamic mechanical properties, the ionic transition behaviour, and the mechanical properties are improved compared with PI using monovalent cation (Na^+), but decreased using trivalent cation (Al^{3+}) or shows less significant changes due to steric effects. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 2908–2918, 2012

Key words: ionomer; neutralization; thermal properties; rheology; mechanical properties

INTRODUCTION

The structure of ionomers is different from other polymers due to the presence of ionic groups. Extensive study has been carried out to determine the size and structure of these ionic domains and the correlation between molecular structure and properties,^{1–8} but there are still many open questions. Hirasawa et al.⁹ reported the effect of metal counterion type on the structure and properties of ethylene ionomer, where metal counterions were alkaline, alkaline earth, and transition metal salts. The results show that microphase separation exists using alkaline and alkaline earth metals, but not with transition metals. The authors found that the mechanical properties of poly(ethylene methacrylic acid) (EMAA) were dependent on the type of metal and the degree of the crystalline order of the ionic crystallites. The clusters formed by alkaline and alkaline earth metal salts were found to contain more carboxyl groups. Han and Williams¹⁰ investigated the Fourier transform infrared spectroscopy (FTIR) of EMAA ionomers with different degrees of neutralization with alkaline, alkaline earth, and transition metal ions. The

analysis of their results shows that the metal counterions play an important role in the structure of an ionomer. The two models illustrated for ionomers were the multiplet-cluster model found to be suitable for alkaline and alkaline earth metal ionomers, and the other one called the coordination complex model suitable for the transition metal ionomers. The study of the effects of ion type and content is meaningful not only to obtain the difference between materials neutralized with different metal counterions or the difference between neutralized and unneutralized (or ionic versus nonionic) polymers of similar backbone architecture, but also a greater range of properties can be obtained by varying the bound ion type or by expanding the counterion.^{11–16} Bonotto and Bonner¹² studied the effect of ion valence on the physical properties of poly(ethylene-co-acrylic acid) ionomers. They found that the physical properties of the ionomers were independent of the ion valence when the carboxyl groups were converted to equivalent degree of ionization. The modulus increased with increasing degree of neutralization up to about 33% conversion, at which a maximum modulus was obtained. The stiffness is also closely connected to the type of counter ionic species. In addition, the higher the neutralization level, the shorter the crystalline PE sequences become. Hirasawa et al.⁹ made a similar observation in stiffness behavior, which showed a maximum at 33% neutralization in both the alkaline and alkaline earth metal salts for salts of EMAA, while the

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maximum value of the stiffness was obtained up to 60% neutralization in the transition metal salts. Eisenberg et al.¹⁷ found that the choice of counterions and the ion concentration affected the viscoelastic properties of ethyl acrylate ionomers. The glass transition increased with increasing Na salt content. The studies on the effect of ion type on the melt rheology of EMAA found that the zero-shear viscosity of the ionomer depended strongly on the neutralization level and the type of counterion.¹⁸ The zero-shear viscosity of Zn ionomers was much higher than for Na ionomers. Weiss et al.¹⁹ demonstrated, using mono-, di-, and tri-substituted alkyl amines that the ionic interaction of sulphonated PS decreased drastically with the bulkiness of the substituent. The glass transition temperature and the melt viscosity were much lower than unionized PS.

In this study, the effects of various ion and neutralization levels on the structure, thermomechanical, and rheological behaviors of Poly(ethylene-acrylic acid) neutralized by zinc salts (PI) ionomer are evaluated. Various metal acetates have been used to neutralize PI, e.g., Na⁺, Zn²⁺, and Al³⁺ acetates. The neutralization can be shown as $3 \text{ PI-COOH} + \text{M}^{x+} \rightarrow (\text{PI-COO})_3\text{M}^{x+} + 3\text{H}^+$, where metal ion forms hexacoordination with carboxylate group after neutralization, and x is 1, 2, or 3. FTIR and small angle neutron scattering (SANS) were used to obtain the structure and morphology of the samples. The thermal properties were measured using thermogravimetric analysis (TGA), modulated differential scanning calorimetry (MDSC), and dynamic mechanical analysis (DMA) measurements. The rheological behavior of the samples was evaluated from elastic modulus and time-temperature superposition (TTS) master curves.

EXPERIMENTAL AND CHARACTERIZATION

Materials

PI (Iotek 4200) manufactured by EXXON was kindly donated by Kemocor Australia. Metal salts used were sodium acetate (E. Merck, Darmstadt, Germany), zinc acetate (The British Drug Houses, UK), and aluminum acetate (Aldrich, MO, USA). The melting points of Na acetate, Zn acetate, and Al acetate are >300, 237, and 154°C, respectively.

Sample preparation

PI was first melted in the mixer, and then mixed with various acetate salts for 3 min using a Brabender Plasticorder at 180°C and a rotor speed of 60 rpm. The mixture was then compression-moulded to make a sheet at 150°C under a pressure of 31 MPa, which was then cooled to room temperature under the same pressure. Various amounts of salts were used to achieve a wide range of neutralization level.

TABLE I
PI Neutralization by Various Metal Acetates

Sample	Moles of metal ions per 100 g PI (mol)	Degree of neutralization (mol %)	—COOH after neutralization from FTIR (%)
PI	—	— ^a	84.77
PI-NaAC-1	0.0132	10	56.76
PI-NaAC-2	0.0230	17	50.50
PI-NaAC-3	0.0461	35	41.14
PI-NaAC-4	0.0656	50	36.27
PI-ZnAC-1	0.0065	10	64.82
PI-ZnAC-2	0.0114	17	58.01
PI-ZnAC-3	0.0232	35	53.03
PI-ZnAC-4	0.0328	50	50.00
PI-AlAC-1	0.0044	10	81.74
PI-AlAC-2	0.0077	17	81.08
PI-AlAC-3	0.0154	35	81.09
PI-AlAC-4	0.0219	50	95.09

^a Degree of neutralization in PI is taken as zero, mole of —COOH per 100 g PI is 0.13.

Table 1 summarizes the amount of the salts used for neutralization. The samples are transparent at lower salt proportions, but are opaque at 50%, indicating the existence of microlevel phase separation between the polymer matrix and the ionic groups. All samples were tested after 24 h of preparation.

Characterization

Photo-acoustic Fourier transform infrared spectroscopy (PA-FTIR) was performed on a Nicolet Magna Spectrometer (Model 750) equipped with a photoacoustic detector (MTEC 300, MTECH Photoacoustics, USA). The resolution was 8 cm⁻¹. The run consisted of 256 scans with mirror velocity of 0.158 cm s⁻¹.

TGA measurements were done using TA 2950 thermal analyzer (TA Instruments) under nitrogen atmosphere. The samples were heated from 30 to 600°C at 10°C min⁻¹ heating rate. The maximum degradation and the residue remaining at 600°C were evaluated.

MDSC was conducted using differential scanning calorimetry (DSC) 2920 from TA Instruments to analyze the melting/crystallization behavior of the samples. The sample was first heated from 30 to 120°C at 20°C min⁻¹ in DSC mode, then cooled from 120 to 30°C at 0.5, 2, and 5°C min⁻¹ cooling rates respectively, and finally heated again from 30 to 120°C at 2°C heating rate under a heat only condition with an amplitude of modulation ±0.2°C and period of 40 s in MDSC mode. The heat flow associated with the transitions in the materials as a function of time and temperature was measured.

Dynamic mechanical properties of the samples were measured using DMA 2980 (TA Instruments). The sample size used was 15 × 2 × 0.5 mm³ (Length × width × thickness). The module DMA multifrequency-tension mode was used with a static force of

1 N and frequency 1 Hz. The sample was heated from -150 to 100°C at $3^{\circ}\text{C min}^{-1}$ heating rate.

SANS measurements can provide information on microstructure evolution in a sample. The measurement time for each sample was 4 h on a 10 m SANS instrument. The collimation length was 5000 mm, and the sample-to-detector distance was also 5000 mm. The neutron beam with wavelength 3 \AA had a diameter of 10 mm at the sample position and a flux of approximately 2×10^4 neutrons per $\text{cm}^2 \text{ s}^{-1}$. The q -range used was from 0.012 to 0.14 \AA^{-1} . The intensity as a function of q for each sample was obtained.

The melt flow properties of the sample were investigated using AR 1000N (TA Instruments) under oscillation mode. Isothermal measurements were taken in the temperature range of 115 – 155°C over the frequency range 0.1 – 50 Hz. The sample (20×1 mm [diameter \times thickness]) was put between the parallel plates to be heated to the desired temperature under a nitrogen atmosphere. The quantities measured were the in-phase and out-of-phase components of the shear stress, from which the shear storage (G') and loss (G'') moduli were obtained.

The relationship between force and fractional deformation was measured following the ASTM D 882-97 specific counterion. The stress-strain behavior of the materials is studied.

RESULTS AND DISCUSSION

Effect of metal acetate neutralization on the structure of the ionomer

FTIR technique was used to study the structure change after adding metal salts. The measurement range is between 400 and 4000 cm^{-1} , but the peaks change only in the region from 1300 to 1800 cm^{-1} . Figure 1 shows the FTIR spectra of the ionomer with various ions at 10% neutralization. In general, the band at 1700 cm^{-1} , ascribed to C=O stretching mode peak from the $-\text{COOH}$ group, does not shift with increasing salt proportion, but the intensity decreases. This observation indicates that the neutralization takes place on introducing metal acetates, and the number of $-\text{COOH}$ groups is reduced, but no hydrogen bonding is formed between $-\text{COOH}$ groups and metal salts. The $-\text{COOH}$ group remains after the neutralization. The $-\text{COOH}$ group intensity decreases with increasing Na and Zn acetate contents; however, the percentage of $-\text{COOH}$ group does not change with the Al acetate content.

Two distinct peaks in the range of 1500 – 1660 cm^{-1} appear for Zn acetate system: one at 1630 cm^{-1} and the other at 1560 cm^{-1} . These two peaks do not shift position with increasing Zn acetate content, but the intensity of the peaks increases. This means that the ionic domain structure does not change with the

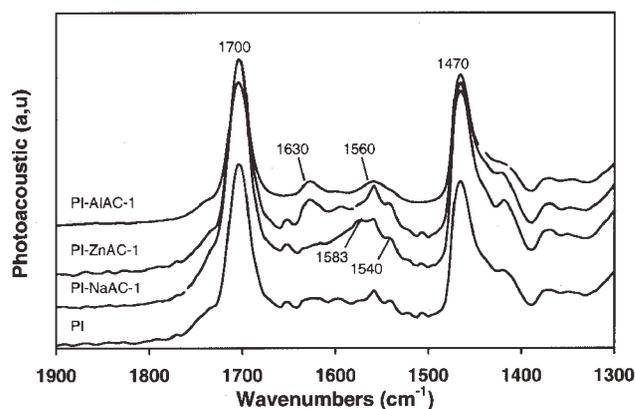


Figure 1 FTIR spectra of PI with various degrees of neutralization in Zn acetate system.

level of salt but the number of ionic groups in the ionic domains increases. With increasing degree of neutralization, more and more carboxylate groups are formed. These carboxylate groups extend to aggregate as closely as possible resulting in electrostatic forces due to their opposite charge. So the number of ion pairs in the ionic regions increases with the degree of neutralization. The ionomer neutralized by Zn acetate mainly has zinc acid salt and hexacoordinated zinc carboxylate structures in the multiplets and clusters. These two peaks indicate the existence of hexacoordinated zinc carboxylate (1560 cm^{-1}) and zinc acid salt (1630 cm^{-1}). In Na acetate system, one broad peak (1560 cm^{-1}) with a shoulder (1583 cm^{-1}) is seen in the range of 1500 – 1660 cm^{-1} . The peak becomes broader and the intensity of the peak increases with increasing the neutralization level, indicating that the local structure becomes more complex. The wavenumber from low to high value demonstrates the local structure change from multiplets to clusters, and a neutralization process with the addition of Na acetate. The ratio of the peak area at 1583 cm^{-1} to the peak area at 1560 cm^{-1} increases with increasing salt content, indicating that the number of clusters increases with the degree of neutralization. One peak with shoulders indicates the existence of various kinds of ionic aggregation. The local structure around zinc changed on changing the Zn/Na ratio. At low Zn/Na ratio, the cluster was mainly contributed by zinc aggregates, and sodium ions just filled in the cluster.²⁰

In Al acetate system, two peaks at 1630 and 1560 cm^{-1} are observed, which has the similar results as the ionomer containing zinc salt (Fig. 1). The peaks do not shift and the intensity of the peaks does not change with increasing salt proportion. This indicates that the local structure with the Al counterion is independent of the neutralization level. Tsujita et al.¹⁵ reported similar observation that the radius and distance of the aggregates of ionomers with trivalent counterion did not change with the ion content. As the two peaks have the same wavenumbers as the

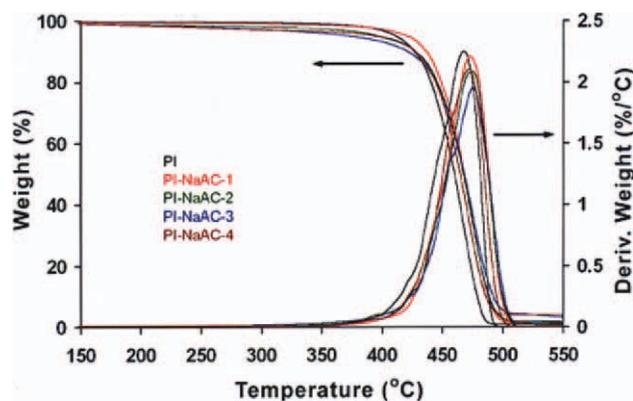


Figure 2 TG and DTG curves of the ionomer with various amounts of Na acetate. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

ionomer containing zinc ions, the cluster is mainly composed of zinc ions. The number of Al ions in the cluster is limited due to the size of Al carboxylate and does not change with the degree of neutralization.

Comparison of the FTIR results of the samples using various metal salts shows that the ionic domain structure of the ionomer is strongly dependent on ion valence. Two local environments exist using Al^{3+} counterion, which do not change with the ion content. For Na/Zn systems, the ionic structure is more complex and it changes with the salt proportion. The ionic groups with Na counterion are mainly multiplets and clusters. The concentration of the ionic groups is directly proportional to the size of the cluster. However, there is a limit after which the clusters cannot persist, and leading to multiplet formation.

Thermal stability of the ionomer with various metal salts

Figure 2 shows weight-temperature (TG) and derivative weight loss (DTG) curves of PI at various Na ace-

tate proportions. In all the cases, weight loss occurs with increasing temperature, and the weight loss occurs between 350 and 500°C mainly due to the decomposition of the ionomer plus decomposing of the acetic salts. The results show that the curves of the samples with Na acetate shift to higher temperatures. Table II lists the maximum decomposition temperature of all the samples. The thermal stability of the ionomer increases marginally after adding Na acetate, but changes marginally with the Na acetate proportion. At high salt content, the sample is opaque, indicating microphase separation. The onset decomposition temperature of the samples in the Na acetate system is lower than that of PI due to decomposition of the metal acetate (a shoulder on the left-hand side of the peak). The weight loss rate is in line with the Na acetate proportion. It is clear from Table II that the addition of monovalent and divalent ion increase the thermal stability of PI, but is independent of the neutralization level. Trivalent ion (Al) changes the PI thermal stability marginally, but decreases the onset temperature of the decomposition due to Al acetate low decomposition temperature.

Dynamic mechanical properties

The effect of neutralization on the viscoelastic behavior of the samples was studied using DMA. The cluster transition behavior was obtained from $\tan\delta$ curves. The values of storage modulus at 50°C and temperature for ionic transition are listed in Table II. Figure 3 shows the storage modulus and $\tan\delta$ versus temperature curves of PI with various Zn acetate proportions. The glass transition of polyethylene occurs at -130°C and does not change in all the samples, indicating that the degree of neutralization does not affect the polyethylene phase.

In Figure 3, the $\tan\delta$ curves show that the cluster transition peak shifts to higher temperatures with

TABLE II
Effect of Neutralization on the Thermal and Mechanical Properties of PI

Sample	T_{max} from TGA ($^\circ\text{C}$)	Mechanical tests			DMA results	
		Stress at yield point (MPa)	Elongation at break (%)	E' (MPa) 50°C	T_i ($^\circ\text{C}$)	
PI	468.0	11.7	852.6	51.0	32.0	
PI-NaAC-1	472.2	12.9	706.5	109.7	42.1	
PI-NaAC-2	475.7	15.8	426.4	187.5	53.1	
PI-NaAC-3	474.4	16.5	485.3	301.8	59.9	
PI-NaAC-4	472.8	17.2	572.6	50.1	59.5	
PI-ZnAC-1	474.4	11.8	702.4	103.0	35.7	
PI-ZnAC-2	473.6	13.1	719.5	139.8	37.2	
PI-ZnAC-3	474.4	–	–	203.9	43.3	
PI-ZnAC-4	474.4	16.4	553.6	228.3	46.3	
PI-AlAC-1	465.4	10.6	817.2	79.3	37.2	
PI-AlAC-2	471.4	10.1	773.6	95.0	38.7	
PI-AlAC-3	467.6	11.1	673.8	86.6	32.3	
PI-AlAC-4	466.1	10.1	710.5	105.9	34.1	

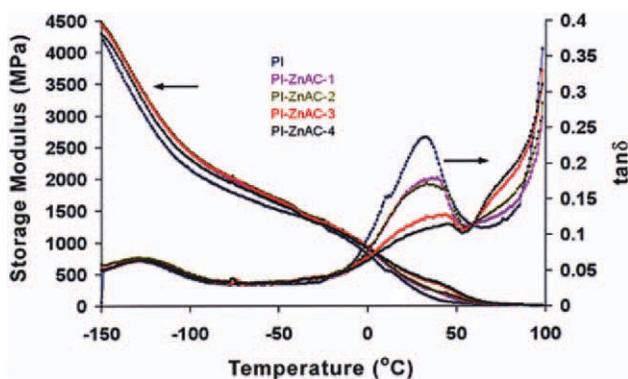


Figure 3 Storage modulus and $\tan\delta$ curves as a function of temperature for the ionomer with various Zn acetate content. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

increasing Zn acetate content. In addition, the storage modulus of this material indicates a degree of ionic association as evidenced by the elevated rubbery plateau. This indicates that the neutralization of free acid takes place by adding Zn acetate, and the ordered structure of ionic groups in a relaxation process is increased with the degree of neutralization. The transition peak becomes broader, and the intensity decreases with increasing Zn salt proportion, which indicates that the number of ionic groups increases with the addition of Zn salt and the local structure changes. This result is in-line with the FTIR results. Table II shows that the cluster transition temperature (T_i) increases significantly with increasing Na acetate content. The increase in T_i is due to the restriction of the molecular mobility of the chains as a result of ionic complexation. A marginal change is observed in the case of the counterions Zn^{2+} and Al^{3+} . Thus, it is clear that there is a competition between degree of neutralization to form ionic crosslinks that reduce the molecular motions and the steric hindrance of the counterion that increases the free volume of the polymer and decreases the T_i . This result indicates that neutralization occurs with the addition of Na acetate, and the local structure is affected by the neutralization level. However, a large excess of NaAC in PI-NaAC-4 appears to form micro-sized but phase separated crystallites, which then acts as melt flow promoter. The $\tan\delta$ value in Al systems is slightly higher than that of PI, but shows minor change with the neutralization level. This indicates that the local structure of the ionomer is not affected very much by the addition of Al acetate. The $\tan\delta$ curve of the ionomer shows an upturn after the ionic transition, which is due to the onset of melt flow for polyethylene. At 10% and 17% Na acetate and Zn acetate, respectively, the upturn can be seen after the ionic transition which is slightly higher than that of PI. This

means that the melting temperature of PE increases with the addition of Na/Zn acetate. New local structure restricts polymer chain motion. However, at 35% and 50%, the transition peak and the upturn overlay and the upturn shifts to lower temperature compared to PI. This could be because the neutralization happens between unneutralized Na/Zn acetates and acrylic acid at high temperature, and/or the volatiles cause a decrease of the upturn. The clarity of the sample reveals the existence of phase separation at a particular salt proportion. This phenomenon is not observed in the Al acetate system, indicating that no further neutralization occurs. The cluster transition of the counterion demonstrates that in the case of bulky or trivalent counterions, the counterion is added in excess, and therefore, no effective intermolecular interaction occurs.

In all cases, the storage modulus decreases with increasing temperature. Figure 3 shows that at a particular temperature, the storage modulus increases with the addition of Zn acetate, indicating an improvement of the elastic properties of the ionomer. The modulus value increases with increasing neutralization level. The increase in storage modulus was ascribed to the formation and buildup of an ordered structure of ionic groups during the relaxation process.⁹ The storage modulus values do not change with Na acetate content except at 50% neutralization and at 50°C (not shown). This indicates that the storage modulus is independent of the neutralization level at low salt proportion. The modulus value at 50% is lower than those at other proportions. The DMA results show that monovalent and divalent counterions have the same effect on the mechanical properties of the ionomer. The samples with Al acetate show the storage modulus to decrease marginally with increasing Al acetate below 50°C, but increase slightly at 50°C. The effect of the metal valence on the storage modulus is more significant at 50°C rather than other temperatures. This is in-line with the cluster transition: $\text{Na}^+ > \text{Zn}^{2+} > \text{Al}^{3+}$. The difference in dynamic mechanical properties with different type and size of metal counterion is ascribed to the different number of carboxyl groups in the ionic domains, and the different extent of ion-dipole interaction.⁹ Thus, a counterion can be selected to control ionic association by either increasing its T_i or as internal plasticizer by keeping T_i constant or decreasing.

Morphological studies of the ionomer with various metal salts

The SANS technique was used to obtain the morphology of the ionic domains of the ionomer and the neutralized polymers. Figure 4 is the superimposed SANS profiles of PI, PI-NaAC-2, and PI-AlAC-2. An

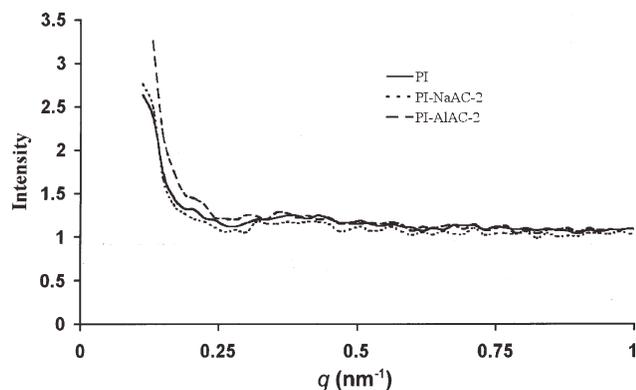


Figure 4 SANS profiles of PI, PI-NaAC-2 and PI-AlAC-2.

upturn is observed at $q = 0.11 \text{ nm}^{-1}$ ($d = 57 \text{ nm}$) for PI, but at $q = 0.13 \text{ nm}^{-1}$ ($d = 49 \text{ nm}$) for PI-NaAC-2 and PI-AlAC-2. The intensity of PI-NaAC-2 is higher than that of PI, indicating an increase in the number of ionic aggregations. The broadness of PI-NaAC-2 is similar to that of the ionomer, indicating that the size of the ionic domains does not change with the addition of Na acetate. Grady²⁰ reported that there was only one type of zinc-containing aggregate at low Zn/Na ratios, in which zinc counterions form the clusters, and sodium counterions appear in the clusters. The PI-AlAC-2 upturn becomes broader, and the intensity is higher than that of PI, indicating an increase in the number of ionic aggregations with various sizes. This behavior is different from that of Na^+ , for which the peak moves to a lower angle and the intensity is also lower. The primary reason for such difference is the strength of interaction between Na^+ and the carboxylate unit compared with the Al-carboxylate unit, while Na^+ binds to the multiplet much more strongly than Al^{3+} . A consequence of this difference is the drop in modulus accompanying the cluster transition in Al acetate systems as evidenced by DMA. Also, because the interaction in the Al^{3+} is weaker than in the Na^+ carboxylate due to its bulky nature, the addition of Al^{3+} to the region surrounding multiplets is more effective in disrupting clusters, by introducing additional free volume in its immediate vicinity. It must be pointed out here that one trivalent counterion interacts with 3 anions; therefore, the ion pair is a quartet, if it is to remain uncharged. The preliminary SANS results thus reveal that the local structure of the ionomer depends on ion valence.

Melting and crystallization behaviors of the ionomer with various salts

DSC was used to get quantitative information about the thermal transitions of materials. Table III lists two transition temperatures of all samples from DSC runs. Approximately 50°C is the ionic transition tem-

perature, while the PE melting temperature is approximately 96°C .²¹ In all samples, these two temperatures are observed. The ionic transition temperature shifts to lower temperature by introducing Na acetate, but changes little with the degree of neutralization. This indicates that neutralization occurs with the addition of Na acetate, and the ionic groups formed after the neutralization appear in the ionic domains, which cause the reorganization of the clusters and multiplets. The local structure changes due to the appearance of Na counterions in the clusters. The ionic transition of PI does not change with the addition of Zn acetate and the salt proportion. FTIR results show that the local structure of the ionomer with Zn acetate is the same as that of the ionomer. Adding Zn salt only affects the number of aggregates, but not the local structure. The transition temperature of the ionomer decreases with the addition of Al acetate, indicating that the steric effect of the Al^{3+} ion allows ionic aggregates to reorganize in a fashion with more free volume. However, the transition temperature remains invariant to the level of neutralization. The ionic transition is affected by the ion valence due to different size and structure. The results (Table III) show that the PE melting temperature remains invariant with the addition of metal salts.

MDSC measurement was carried out to investigate the effect of neutralization on the transition behavior of the ionomers. Figure 5(a) shows the reversing heat flow versus the degree of neutralization curves for the ionomer with metal salts, and the nonreversing and total heat flow curves as a function of the degree of neutralization are shown in Figure 5(b). The PE melting in all cases happens in both reversing and nonreversing heat flows. The reversing heat flow of the ionomer in Na acetate systems first slightly increases at low salt content, then decreases

TABLE III
Ionic Transition, PE Melting Temperatures and Crystallinity for Various Samples from MDSC

Sample	Ionic transition temperature ($^\circ\text{C}$)	Crystallinity from MDSC (%)	PE melt temperature ($^\circ\text{C}$)
PI	53.2	20.9	96.2
PI-NaAC-1	49.8	21.9	99.5
PI-NaAC-2	50.9	22.8	99.5
PI-NaAC-3	51.7	21.8	99.0
PI-NaAC-4	50.2	21.2	99.1
PI-ZnAC-1	52.1	21.3	98.4
PI-ZnAC-2	52.2	20.3	98.0
PI-ZnAC-3	54.6	20.6	98.2
PI-ZnAC-4	53.3	20.2	97.7
PI-AlAC-1	50.7	22.0	99.0
PI-AlAC-2	49.6	22.6	98.4
PI-AlAC-3	49.1	22.0	98.4
PI-AlAC-4	51.9	21.1	98.4

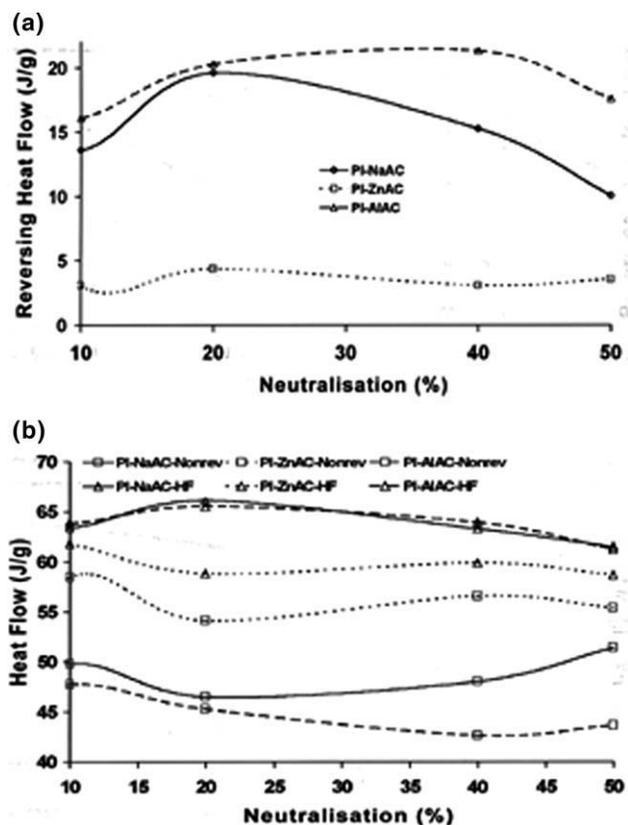


Figure 5 Reversing heat flow (a), nonreversing and total heat flow curves (b) versus neutralization level for the ionomer with metal salts (PI-NaAC-Nonrev: nonreversing heat flow of PI-NaAC; PI-NaAC-HF: total heat flow of PI-NaAC).

at higher degree of neutralization. This indicates that the entanglement density of linear PE depends on the degree of neutralization. The reversing heat flow shows minor changes with the Zn salt content. The results for Al system are similar to Na one at low neutralization, but at higher salt concentration the values drop faster in Na samples than in Al ones. The above results indicate that the metal valence affects the morphology of PE crystals in the ionomer. The reversing heat flow values in Zn acetate systems are much lower than those in Na/Al acetate systems, because the reversing behavior includes an endothermic transition at low temperature and an exothermic transition at high temperature. This means that not only melting of PE but also some structural reorganization occurs. The reversing component is only a small fraction of the total heat flow.

The nonreversing component in Na and Zn systems decreases slightly below 17%, and then increases with increasing salt proportion [Fig. 5(b)]. The effect of metal valence on the nonreversing heat flow is in the order: $Zn^{2+} > Na^+ > Al^{3+}$. However, the total heat flow and the crystallinity (Table II) do not change with the salt content. The heat flow curves in Figure 5(b) show minor differences between the

samples and with salt content. The ionic transition peak does not appear in the MDSC run. This is because the ionic crystallites are not formed during cooling from the melt, but they gradually develop on aging by a relaxation mechanism. Thus, during cooling after the DSC run, they primarily remain in a disordered state. Over time clustering of the polar group can occur due to rejection of the polar groups from the hydrophobic matrix.²²

Melt rheology

The ability of the ionic groups to interact with each other can have a significant effect on the melt viscosity of the ionomer. The melt viscosity of the ionomer with various salts at 1.089 Hz as a function of temperature is shown in Figure 6(a). The melt viscosity drops with increasing temperature, showing shear thinning behavior. In Al acetate system, the viscosity decreases with increasing salt content. PI-AIAC-1 shows similar viscosity to PI due to the low salt proportion. This result indicates that adding Al acetate promotes the melt flow of the ionomer. The ionic interaction of the ionomer is reduced with the addition of Al acetate. The viscosity behavior of the Na acetate samples shows the reducing of the viscosity

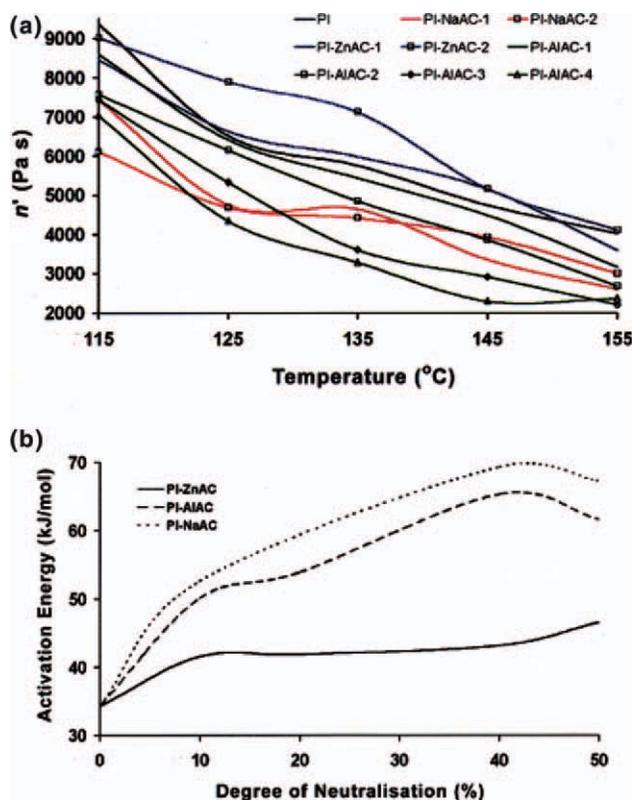


Figure 6 (a) Plots of n' versus temperature for the samples at 1.089 Hz; (b) activation energy curves as a function of degree of neutralization for the ionomer with various metal acetates. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

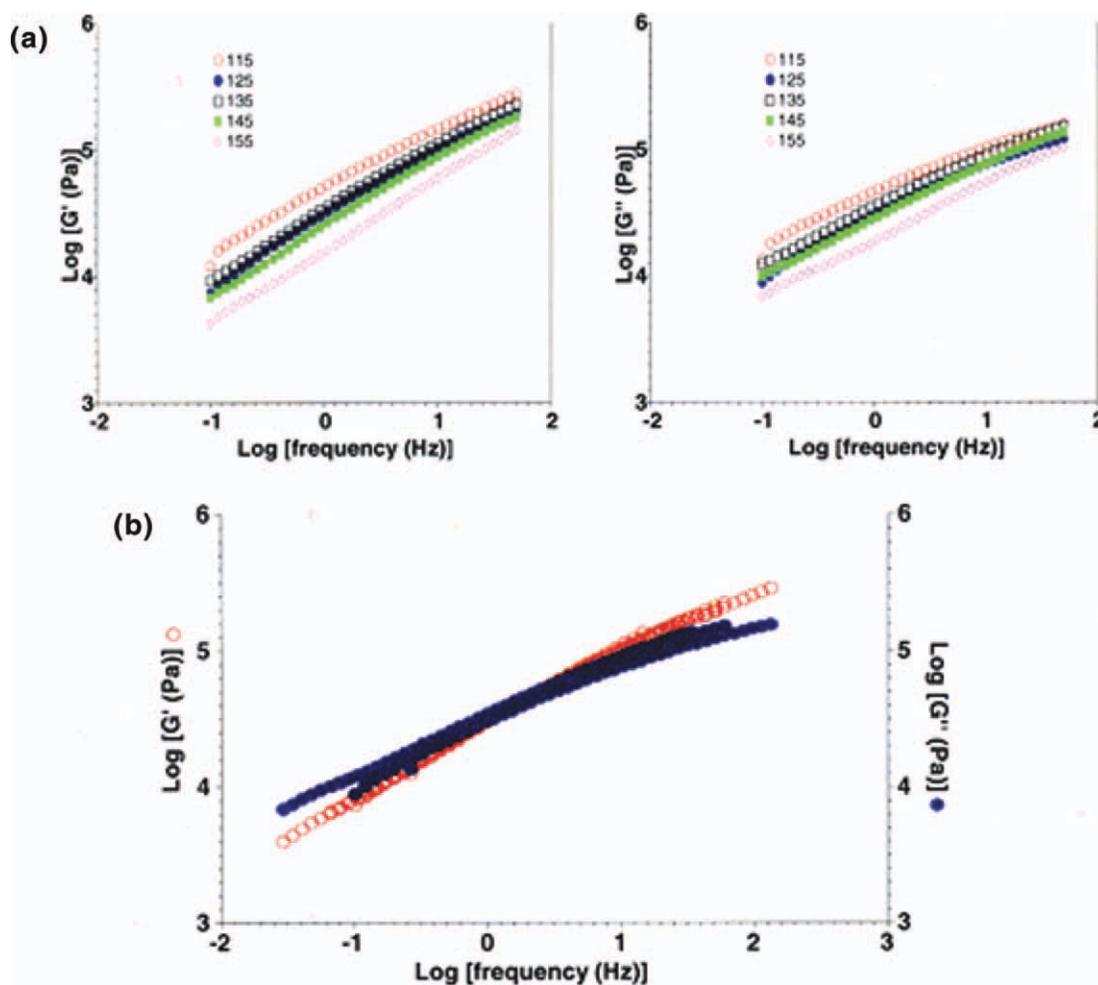


Figure 7 (a) G' and G'' versus angular frequency curves of PI-NaAC-2 at various temperatures; (b) G' and G'' master curves from (a). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of PI, but the viscosity change with salt content is minor. PI-ZnAC-1 shows similar viscosity behavior to that of PI due to low Zn acetate content. However, the viscosity of the ionomer increases at high Zn acetate proportions. In general, the increase in melt viscosity with neutralization is larger for alkaline metal salts than for transition metal salts.⁹ In our case, the viscosity of the ionomer is lower with the addition of Na acetate than with Zn acetate. This is because two types of metal counterion appear in the ionic domains to form different ionic aggregates from PI.

Activation energy of the melt flow processes at a constant frequency can be calculated using $n' = A \times \exp(E/RT)$, where n' is the viscosity at a constant frequency, E is activation energy, A is a constant, R is the gas constant, and T is temperature. Figure 6(b) shows the activation energy as a function of degree of neutralization for the ionomer with various metal acetates. The curves show that the activation energy increases with increasing neutralization level in Na and Al acetate systems, but changes are minor in the

Zn acetate samples. The effect of metal valence on activation energy is obvious. The activation energy curves in Na and Al systems are similar, and the values are slightly higher in the Na acetate system than the Al acetate system due to higher ionic interaction.

The shear storage and loss moduli for isothermal experiments as a function of angular frequency are shown in Figure 7(a) for PI-NaAC-2. This figure is typical results found for most of the samples in this study. At a constant temperature, G' and G'' increase with the angular frequency, and display a linear log-log relationship over the temperature range investigated. Master curves, corresponding to Figure 7(a) with the horizontal shifts normalized to the 125 °C curve in all cases, are shown in Figure 7(b). Excellent superposition for PI-NaAC-2, for which both G' and G'' obey TTS, indicates the thermorheological simplicity of the system. The modulus curves for the samples at low neutralization levels show excellent superposition, and the curves of both moduli (G' and G'') are superimposable by applying the

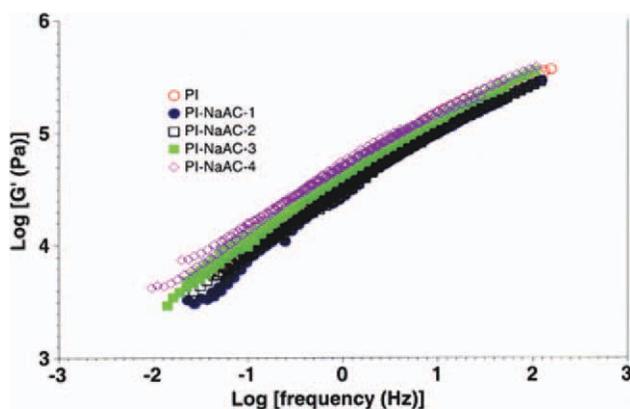


Figure 8 G' master curves of the ionomer with various Na acetate proportions. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

same shift factors. Thus, the presence of the ions does not introduce additional major relaxation processes in the melt region. These particular systems do not contain microphase-separated regions that influence their rheological properties. However, the master curves fail for the samples at higher salt contents. The microphase separation in those systems affects their dynamic rheological properties. Bonotto and Bonner¹² explained that during melt mixing, redistribution of counterions among carboxylate groups occurred when free acid groups were present. When the salt proportion is higher, phase separation occurs.

The G' and G'' master curves using various ionic contents can show different features. Figure 8 superimposes the master curves of Na acetate at various proportions. At low proportion, the samples' G' and G'' curves all obey TTS, indicating thermorheologically simple materials. The melt rheology behavior is similar to PI. With increasing content of Na acetate, the G' and G'' master curves partially or totally deviate TTS. The results of the sample at 35% show that superposition of G' and G'' fails at 155°C. This phenomenon is due to the different relaxations of polyethylene in PI and Na acetate in the sample on account of their incompatibility. The sample at 50% does not follow superposition, which again indicates that the material becomes thermorheologically complex at high-level salt proportion. Eisenberg and Navratil,²³ Eisenberg et al.,¹⁷ and Greener et al.²⁴ studied the systems with ion content as the parameter. The authors found that departures from TTS became more noticeable with increasing ion content. TTS usually does not hold at a certain functionalization level. The G' curves follow the order: PI > PI-NaAC-4 > PI-NaAC-3 > PI-NaAC-2 = PI-NaAC-1. The G' and G'' master curves in Na acetate systems are just below the PI curve, but have the similarity in their slopes. All Zn acetate samples are found to

obey TTS at low salt proportion and deviate from TTS at high salt content. However, G' and G'' curves show a different trend on changing the salt proportion. G' and G'' values are slightly higher than those of PI. This indicates that increasing the neutralization level increases the ionic interaction at high proportion, but does not necessarily affect the flow behavior of PI at low content. The master curves of the samples using Zn acetate are higher than that of the ionomer. This is simply because the ionic crosslink is high enough to allow as much migration of the ionic bonds and concomitant chain diffusion as in other samples. The increase in G' and G'' values with Zn content was also observed by Duvdevani et al.²⁵ and Jackson et al.²⁶ The Al acetate system shows a similar trend to the Na acetate system, with the G' and G'' master curves being lower than those of the ionomer, indicating that the ionic crosslinking is reduced with the appearance of Al counterions. These systems also exhibit a greater variation of their elastic component with changing frequency.

Differences in rheological behavior certainly exist when different counterions are employed. Figure 9 shows the G' and G'' master curves of PI, PI-NaAC-2, PI-ZnAC-2, and PI-AlAC-2. The results show that G' and G'' values follow the trend: PI-ZnAC-2 > PI > PI-AlAC-2 > PI-NaAC-2. This phenomenon demonstrates that Na acetate and Al acetate promote the melting behavior of PI, but not PI-ZnAC-2. Adding Zn acetate increases the viscosity of the ionomer. Comparing the samples at 10% proportion of metal acetate shows the same trend, except that the G' and G'' values of PI and PI-ZnAC-1 are similar. Vanhoorne and Register¹⁸ studied the melt rheology of a partially neutralized system using either Na or Zn EMAA ionomers. They observed that the free acid groups preferred to interact with Na carboxylates than with the Zn carboxylates. These differences were also observed in their infrared spectrum

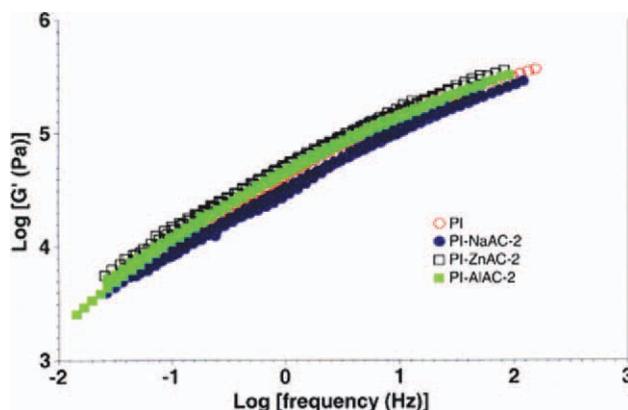


Figure 9 G' master curves of the ionomer with metal salt at 17%. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

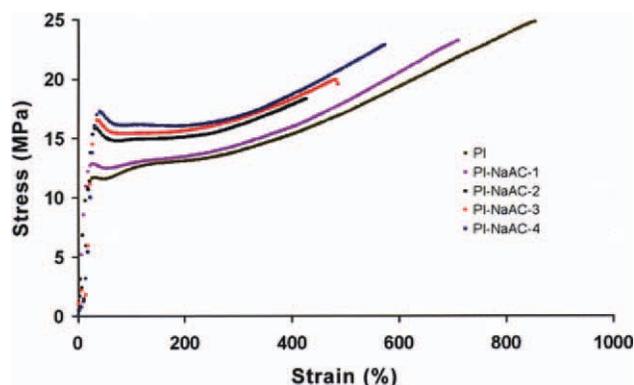


Figure 10 Stress-strain curves of the ionomer with various amounts of Na acetate. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

results. The C=O stretch peak for COOH groups (at 1700 cm^{-1}) maintained its position and became broader as the neutralization level was increased for Zn ionomer. However, in the Na ionomers the peak became broader and shifted toward lower wave number as the Na level was increased (1685 cm^{-1} in an 83% neutralized sample). These changes indicated that the local environment of the acid groups in Na ionomers changed continuously as the neutralization level was increased (as would be expected if the acid groups are associated with the ionic aggregates); the lack of change in the Zn ionomer spectra as the neutralization level increased suggested that the unneutralized acid groups were dispersed in the polymer matrix.

At higher Na, Zn, and Al acetate proportions, the TTS curves fail. It is possible that the metal salts increase the rates of relaxation. There are two relaxation processes in ionomers (ionic domain and PE crystal relaxations), but one of them may be too rapid or not sufficiently rapid to be apparent in the time scale studied. Metal acetate salts may change the rate of the second relaxation process and the ability to capture in the experimental time scale. Also the addition of metal acetate salts to ionomers leads to a greater extent of microphase separation, thereby increasing the importance of the second relaxation process.

Mechanical properties

The mechanical properties of the samples were evaluated from stress-strain measurements. Figure 10 shows the overlaid stress-strain curves of PI with various Na acetate contents. All the curves show a linear stress increase at low strain value following an appearance of a yield point, and then successive strain-hardening behavior before fracture. The linear relationship between stress and strain at low strain

value does not show any difference between the samples, indicating that it is independent of the degree of neutralization. Table II lists the mechanical properties of the samples. It is clearly seen that the yield stress increases with increasing Na acetate content. The concentration of Na acetate is directly proportional to the yield point. For small ions, strong ionic interaction predominates. This is due to an increase in interchain attraction.¹² Hirasawa et al.⁹ observed an increase in yield stress with increasing neutralization level. The results are in agreement with the DMA one. After the yield point, the stress of the samples increases with increasing the degree of neutralization, indicating that the mechanical properties of PI are improved by the neutralization level of Na acetate. Particularly after 17% neutralization, the increase of the stress compared to PI at the same strain is quite obvious. However, the difference in the stress between 35% and 50% is very minor. The elongation at break of PI is reduced after introducing Na acetate, indicating that the samples with Na acetate are more brittle than the ionomer. Lee et al.²⁷ studied the effect of addition of dodecylbenzene sulfonic acid tetra-*n*-butyl phosphonium salt (DSP) into polycarbonate (PC) on the mechanical properties of PC. The authors reported that the elongation at break decreased with increasing the DSP content and finally brittle fracture took place.

In the Zn acetate system, the same trend can be observed (Table II). The yield stress increases with increasing Zn acetate content. However, the elongation at break gradually diminishes, indicating that PI becomes more brittle with increasing Zn acetate. The results of tensile tests conducted on PI with various degrees of neutralization imply that PI is also capable of undergoing a ductile-brittle transition as the metal salt content is varied.

In the Al acetate system, the stress-strain results show that the yield stress decreases by adding Al acetate, but the stress value of the samples with various Al acetate proportions is quite similar. The ionomer with Al acetate shows different mechanical behavior from the ionomer with Zn acetate and Na acetate. This result indicates that the valence of the metal and the steric hindrance play a major role in determining the mechanical properties of the ionomer. This is primarily due to different local structure of the ionic groups. The elongation at break for the samples is slightly lower than that of the ionomer. The mechanical properties of the ionomer are enhanced markedly in Na/Zn acetate systems, but less significantly so with the addition of Al acetate.

CONCLUSION

A wide range of ionomer properties can be achieved from the ionomer by changing the type of

counterion and proportion. The number of clusters and multiplets are affected by the neutralization level. The modulus, cluster transition temperature, and stress at yield increase compared to those properties of the ionomer, when a small monovalent counterion such as Na⁺ is used. However, trivalent counterion shows decrease in these properties or shows less significant changes due to steric effects.

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