

STUDY ON LIGHTLY SULFONATED SYNDIOTACTIC POLYSTYRENE IONOMERS

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Abstract Sulfonated syndiotactic polystyrene ionomers (SsPS) with 1.8 mol% degree of sulfonation have been studied. WAXD shows that the crystallinity of SsPS ionomers was decreased with increasing diameter size of the counter ions and $sPS > SsPS-H > SsPS-K > SsPS-Zn$. Moreover, SsPS ionomers only have α crystal form, while original sPS has two crystal forms: α and β crystal form. TGA shows that the thermal stability of SsPS ionomers is higher than that of the original sPS and $SsPS-Zn > SsPS-K > SsPS-H$. DSC shows that all the glass transition temperatures (T_g) of SsPS ionomers are higher than that of the neat sPS and $SsPS-Zn > SsPS-Na > SsPS-K > SsPS-H$. However, the melting temperature (T_m) and crystallization peak temperature (T_p) of SsPS ionomers are lower and $SsPS-H > SsPS-Zn > SsPS-K > SsPS-Na$, while the crystallinity (X_c) of SsPS-Zn is the lowest. Nonisothermal crystallization kinetics shows that the Avrami index of sPS and SsPS-H are both about 4, suggesting the nucleation growth of SsPS-H with lower degree of sulfonation still keeps its three-dimension form. FTIR spectra of SsPS ionomers show a splitting absorption band for asymmetric stretching vibration of sulfonation group. The CH in-plane bending vibration of benzene ring shifted to higher wavenumber and the symmetric stretching vibration of sulfonation group changed slightly with different counter ion neutralized SsPS ionomers.

Keywords Sulfonated syndiotactic polystyrene, Ionomer, Sulfonation, Thermal behavior

INTRODUCTION

Syndiotactic polystyrene (sPS) is a semicrystalline polymer, as compared with atactic polystyrene (aPS). sPS not only keeps the good properties of aPS but also possesses some other specific properties, e.g., high heat deformation temperature, rapid crystallization rate and high crystallinity, which endow it with desirable heat resistance, chemical resistance and processability. Especially at elevated temperature, it still maintains good mechanical performance^[1-3]. Recently, since the successful development of ionomers, many studies have been carried out. It was found that the desirable chemical and physical properties of these materials were strongly dependent on the size, quantity and distribution of ionic groups and crystalline domains in the polymer^[4]. In addition, thermal properties of these ionomers were also influenced by the extent of ionic interactions and ionic aggregation.

Sulfonated syndiotactic polystyrene ionomers have many different characteristics compared with sPS and can be used as the compatibilizer for blends of sPS and other polar polymers, such as PA, PET, PC^[5]. However, few researchers have investigated the SsPS ionomers. This paper will focus on the properties, such as thermal properties, nonisothermal crystallization kinetics and crystallinity, of the SsPS ionomers with 1.8 mol% degree of sulfonation.

EXPERIMENTAL

Materials

sPS with syndiotactic units greater than 96% and an average molecular weight of 30×10^4 g/mol was obtained

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Sulfonation Procedure

*s*PS was sulfonated using acetylsulfate as sulfonating reagent in chloroform^[6]. The amount of acetylsulfate required was determined by the desired degree of sulfonation. The degree of sulfonation was determined by nonaqueous titration, using methanolic KOH solution as titrant and phenolphthalein as the indicator. After sulfonation, the SsPS samples were neutralized by dissolving 0.5 g of the polymer in 100 mL of chloroform and adding a stoichiometric amount of methanolic NaOH, KOH or ZnAc₂ solution. After neutralization, the samples were precipitated, filtered and then dried in a vacuum oven at 70°C for more than 72 h.

Measurements

WAXD analysis

A D/MAX-3AX Wide Angle X-ray Diffraction Spectrometer (WAXD) made in Japan was used to study the crystallinity of SsPS ionomers. CuK α and Ni targets were used and the scanning range was from 0 to 50 degrees under 25°C.

Thermal analysis and nonisothermal crystallization kinetics

Thermal properties of *s*PS and SsPS ionomers were determined by using a Perkin-Elmer DSC 7 Differential Scanning Calorimeter under nitrogen atmosphere.

To eliminate previous thermal history, all samples were first heated to 290°C and kept for 10 min and then cooled to 30°C. The second heating and cooling curves were used to study the melting and crystallization behavior and all at a rate of 10 K/min.

Crystallinity (X_c) = $\Delta H_m / \Delta H_o \times 100$, $\Delta H_o = 53.6 \text{ J/g}$ ^[7].

To study the nonisothermal crystallization kinetics of *s*PS and SsPS ionomers, all annealed samples were cooled at a rate of 5, 7.5, 10, 15, 20 K/min from 290°C to 30°C.

Nonisothermal crystallization kinetics was treated using the Mandelkern method^[8]. Supposing the temperature during polymer crystallization was not changed, the process could be described by the Avrami equation:

$$1 - X(t) = \exp(-Z_t \times t^n) \quad (1)$$

where $X(t)$ is the comparative crystallinity at time t , Z_t is the kinetics constant which was associated with crystallization temperature, diffusion and nucleation rate, n is the Avrami index, which was associated with the nucleation mechanism and crystallization growth form. From (1) we obtain:

$$\lg[-\ln(1 - X(t))] = \lg Z_t + n \lg t \quad (2)$$

where $t = (T_o - T)/R$, T_o is the terminal crystallization temperature, R is the cooling rate. Then a nonisothermal crystallization kinetics parameter Z_c was defined as follows:

$$\lg Z_c = \lg Z_t / R \quad (3)$$

Thermal gravimetric analysis: A Perkin-Elmer TGA-2 was used to study the thermal stability of samples at a heating rate of 20 K/min to 600°C under nitrogen atmosphere.

FTIR spectra analysis

A Nicolet 205 Spectrometer (FTIR) was used with KBr pelleted samples.

RESULTS AND DISCUSSION

WAXD Analysis

Figure 1 shows the WAXD spectra of *s*PS and SsPS ionomers. The WAXD spectrum of *s*PS has strong diffraction peaks at diffraction angles of 6.14, 11.52, 13.44 and 20.52, which are the special diffraction peaks for the α crystal form. There are also strong diffraction peaks at angles of 12.32 and 18.75, which are the special

diffraction peaks for the β crystal form. Therefore, the *s*PS sample has two crystal forms^[9, 10].

For S*s*PS ionomers, the intensity of diffraction peaks decreases with increasing the diameter size of counter ions, and the diffraction peaks at angles of 6.14, 11.52, 12.32, 18.75 disappear. These results indicate that the crystallinity of S*s*PS ionomers decreases and only α crystal form exists. For S*s*PS-H, there are broad diffraction peaks at angle of 10.04, 15.88, 20.10, while for S*s*PS-K and S*s*PS-Zn, the intensity of the diffraction peak at an angle of 10.04 is very weak and the peak at an angle of 20.52 becomes broader. As we know, hydrogen bond of interaction, ionic interaction and complexation ability of S*s*PS ionomers make the motion of molecular chains more difficult, the crystallinity of S*s*PS ionomers decreases accordingly.

Thermal Stability

Figure 2 shows the thermograms of *s*PS and S*s*PS ionomers. The initial thermal decomposition temperature (T_{ini}) and the thermal decomposition equalization temperature (T_{equ}) are the temperature at point of tangent of the maximum thermal decomposition temperature (T_{max}) with initial and terminal line respectively. T_{ini} is used to indicate the thermal stability of samples.

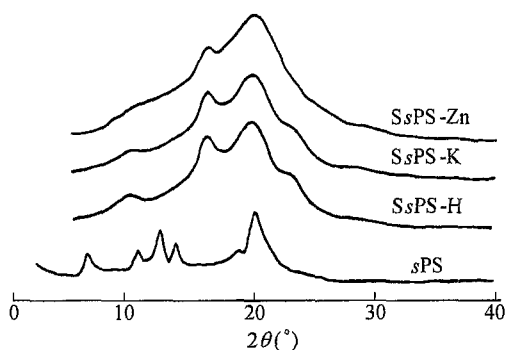


Fig. 1 WAXD spectra of *s*PS and S*s*PS ionomers

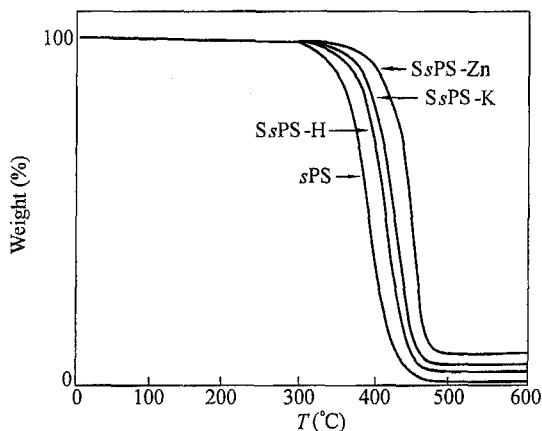


Fig. 2 TGA thermograms of *s*PS and S*s*PS ionomers

It shows that T_{ini} , T_{equ} , T_{max} and the ash content of S*s*PS ionomers are all higher than those of *s*PS, and the bivalent-ion neutralized ionomer is better than the univalent-ion neutralized ionomers, i.e. S*s*PS-Zn > S*s*PS-K > S*s*PS-H > *s*PS. This means that the thermal stability increases. This result can easily be explained by the counter ion diameter size, molecular polar and the ionic interaction. The results of Fig. 2 are listed in Table 1.

Table 1. TGA data of *s*PS and S*s*PS ionomers*

	SPS	S <i>s</i> PS-H	S <i>s</i> PS-K	S <i>s</i> PS-Zn
T_{ini} (°C)	379.6	386.3	400.3	416.5
T_{max} (°C)	409.7	417.1	421.4	432.2
T_{equ} (°C)	413.1	425.8	435.7	446.8
Weight loss (%)*	97.5	95.5	90.3	88.4

*Measured at T_{equ}

Thermal Analysis

Figures 3 and 4 show the thermal behavior of *s*PS and S*s*PS ionomers. T_g of the ionomers is higher than that of *s*PS, but their T_m , T_p and X_c are all lower. These results are understandable since strong interactions existed in S*s*PS ionomers, e.g., hydrogen bonding in S*s*PS-H and ionic interactions between the ion pairs in the neutralized samples. All these may restrict the motion of the polymer chains and raise the T_g of the ionomers. On the other hand, it may suppress crystallization and the size of crystals, resulting in the decreasing of T_m and T_p of the ionomers.

The results of DSC measurements are listed in Table 2. Compared with SsPS-H, the T_g of SsPS ionomers with metal counter ions are all higher than that of SsPS-H, while T_m , T_p and X_c are lower. As we know, the interaction of hydrogen bonding in SsPS-H is far weaker than the ionic interaction in SsPS ionomers with metal counter ions. For the neutralized samples, T_g of SsPS-Na is only slightly higher than that of SsPS-K, while T_m , T_p , X_c of SsPS-Na are a bit lower. Previous investigation of SsPS ionomers has found that the ionic interaction of ionomers decreases with increasing diameter of metal counter ion^[11]. Since the diameter of Na^+ is smaller than that of K^+ , it is therefore expected that the ionic interaction in the Na^+ ionomer is stronger than that of K^+ ionomer. With the strength of the ionic interaction increasing, the amount of thermal energy required to disrupt the ionic interaction for aggregation and to provide the sulfonated chain mobility increase, which makes T_g increase. Since the strong interaction leading to large size of ionic aggregation in noncrystalline phase suppresses the crystal growth and the formation of perfect crystals, T_m , T_p and X_c of SsPS-Na decrease. Since SsPS-Zn has the ability to undergo complexation, the ionic interaction is much stronger, which leads to a remarkable decrease of the molecular chain motion. Therefore, the thermal behavior of SsPS-Zn is different from that of alkali metal ionomers. T_g of SsPS-Zn is much higher. However, T_p , T_m of SsPS-Zn are much higher than those of SsPS-Na and SsPS-K, which are close to SsPS-H. X_c of SsPS-Zn is much lower.

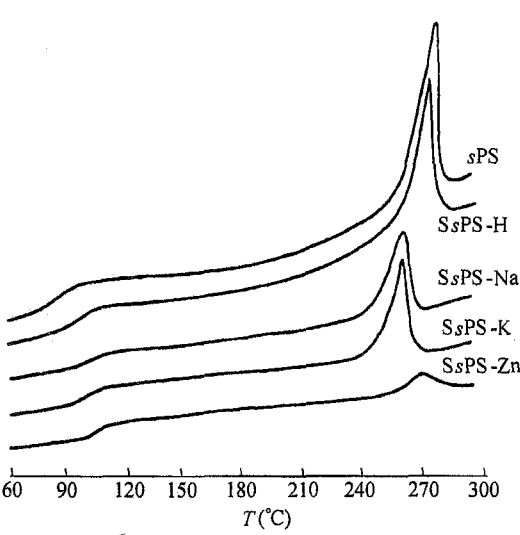


Fig. 3 DSC fusion thermograms of sPS and SsPS ionomers

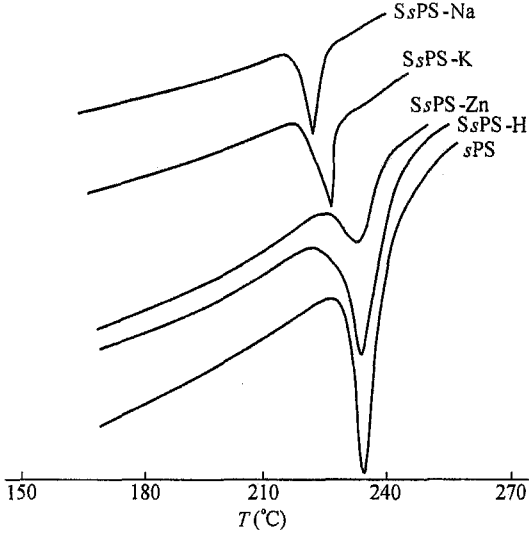


Fig. 4 DSC crystallization thermograms of sPS and SsPS ionomers

Table 2. DSC data of sPS and SsPS ionomers

Sample	$T_g(^{\circ}C)$	$T_m(^{\circ}C)$	$\Delta H_m(J/g)$	$X_c(\%)$	$T_p(^{\circ}C)$	$\Delta H_c(J/g)$
sPS	96.2	271.3	24.3	45.3	236.5	24.80
SsPS-H	99.0	266.8	18.67	31.1	234.0	17.28
SsPS-Na	101.4	261.2	16.06	29.9	223.6	15.86
SsPS-K	100.2	262.5	17.12	31.9	225.5	16.72
SsPS-Zn	103.6	266.0	4.69	8.75	233.2	5.40

Nonisothermal Crystallization Kinetics

Figure 5 shows the DSC thermograms of sPS and SsPS-H at different cooling rates and their results are tabulated in Table 3.

As we know, crystallization peak temperature (T_p) is the temperature at which the crystallization rate is the fastest and T_c is the initial crystallization temperature, which could be used to describe the crystallization behavior. As the cooling rate is increased, T_p and T_c all shift to lower temperature because the molecular chains

could easily enter the crystal lattice. At the same cooling rate, T_p and T_c of SsPS-H are lower than that of sPS , indicating that the crystallinity and the crystal rate of SsPS-H are lower than those of sPS . This result can be expected because the hydrogen bonding of SsPS-H restricts the motion of molecular chain remarkably.

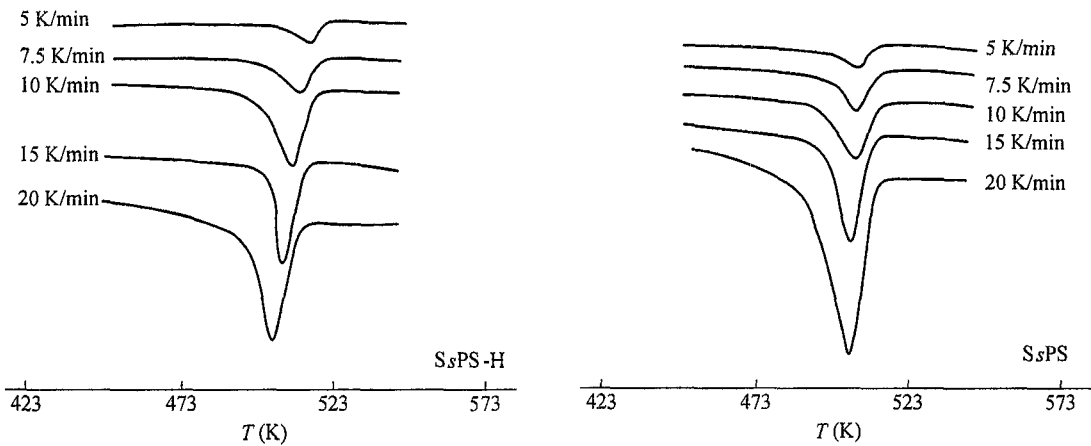


Fig. 5 DSC thermograms of sPS and SsPS-H at different cooling rates

Table 3. DSC results of sPS and SsPS-H at different cooling rates					
Rate (K/min)	5.0	7.5	10	15	20
sPS					
T_p (K)	515.3	510.5	509.5	505.2	503.8
T_o (K)	517.1	514.8	513.2	510.5	508.6
ΔH_c (J/g)	24.34	24.73	24.80	24.82	25.11
SsPS-H					
T_p (K)	514.8	510.3	507.0	504.5	502.3
T_o (K)	523.4	521.8	521.2	513.1	512.0
ΔH_c (J/g)	16.60	16.88	17.28	18.01	18.58

Figure 6 is $X(t)$ versus temperature plot of sPS and SsPS-H and Fig. 7 is $\lg [-\ln(1 - X(t))]$ versus $\lg t$ ($T_o - T)/R$) plot of sPS and SsPS-H. Their results are listed in Table 4.

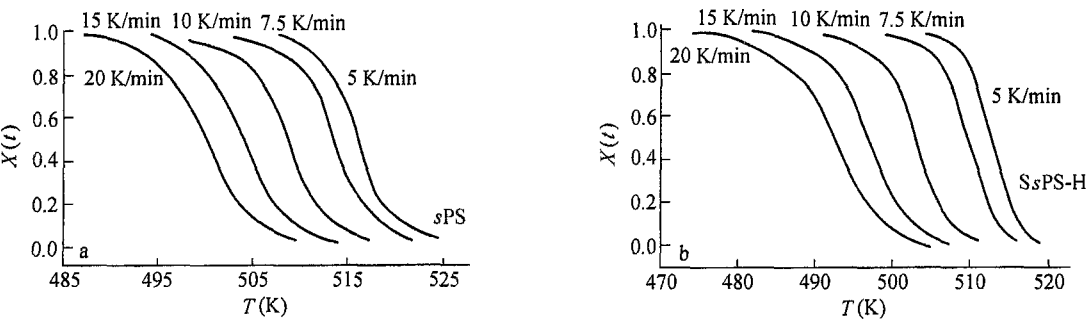


Fig. 6 $X(t)$ versus T plot of sPS and SsPS-H

With increasing cooling rate, Z_i and $t_{1/2}$ of SsPS-H change remarkably as compared with sPS , suggesting that the cooling rate has a considerable effect on the crystallization of ionomers. At a lower cooling rate, the crystallization rate is slow and it increases with increasing cooling rate. The initial crystallization temperature

decreases with increasing cooling rate. Moreover, the Avrami indices of *s*PS and S*s*PS-H are both about 4, suggesting that nucleation form was three-dimensional. Since the size of the sulfonic acid group is large and has difficulty in entering the crystal lattice, it can only exist in noncrystalline phase, which restricts the crystal growth.

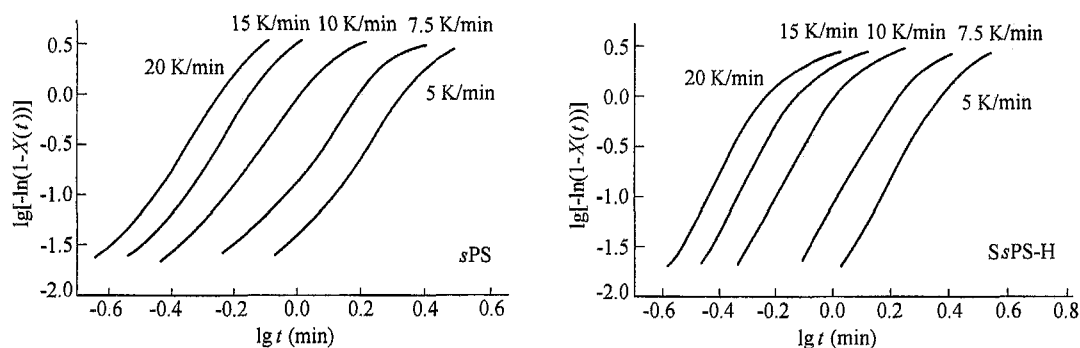


Fig. 7 $\lg[-\ln(1-X(t))]$ versus $\lg t$ plot of *s*PS and S*s*PS-H

Table 4. Parameters of *s*PS and S*s*PS-H at different cooling rates

Rate (K/min)	5.0	7.5	10	15	20
<i>s</i> PS					
Z_t	0.0181	0.0862	0.4725	0.7369	2.4631
Z_c	0.0036	0.0115	0.0473	0.0491	0.1232
N	4.37	4.15	4.11	4.05	4.26
$t_{1/2}(\text{min})$	2.3029	1.6525	1.0977	0.9850	0.7426
S <i>s</i> PS-H					
Z_t	0.0368	0.1548	0.5119	0.8004	3.4552
Z_c	0.0074	0.0206	0.0512	0.0534	0.1428
N	3.87	3.59	4.01	3.92	4.18
$t_{1/2}(\text{min})$	2.1353	1.5183	1.0785	0.9640	0.6809

FTIR Spectrum Analysis

The FTIR spectra of S*s*PS ionomers are shown in Fig. 8. The $\sim 1097\text{ cm}^{-1}$ and $\sim 1125\text{ cm}^{-1}$ bands are attributed to the in-plane skeletal vibration of the di-substituted benzene ring^[12] and the $\sim 825\text{ cm}^{-1}$ band is assigned to CH out-of-plane vibration for *para*-di-substituted benzene^[13]. The $\sim 570\text{ cm}^{-1}$ and $\sim 537\text{ cm}^{-1}$ bands are indicative of the presence of a helical crystalline phase^[1, 14–16]. All the wavenumbers of the above characteristic bands are slightly affected by counter ions.

Table 5. Some principal IR bands of S*s*PS ionomers

Sample	CH in-plane bending vibration of benzene ring (cm^{-1})	Split of asymmetric stretching vibration of sulfo group (cm^{-1})	Symmetric stretching vibration of sulfo group (cm^{-1})
S <i>s</i> PS-H	1007	1179, 1192	1030
S <i>s</i> PS -Na	1013	1196, 1220	1032
S <i>s</i> PS -K	1012	1193, 1218	1032
S <i>s</i> PS -Zn	1018	1198, 1226	1031

The $\sim 1007\text{ cm}^{-1}$ band, the CH in-plane bending vibration of benzene ring, is remarkably affected by electrostatic field, e.g., it shifts to $\sim 1018\text{ cm}^{-1}$ for S*s*PS-Zn, $\sim 1012\text{ cm}^{-1}$ for S*s*PS-K. The $\sim 1179\text{ cm}^{-1}$ and the $\sim 1030\text{ cm}^{-1}$ bands are attributed to the asymmetric and symmetric stretching vibration of the sulfonic acid group^[17]. When S*s*PS-H is neutralized, the electrostatic field associated with the cation polarizes the anion and induces the splitting of the asymmetric stretching vibration of sulfonic acid groups into a doublet. With

increasing ionic interaction, the wavenumber of these split bands shifts to higher values. For SsPS-Zn, one band appears at around 1198 cm^{-1} and the other at around 1226 cm^{-1} , while for SsPS-K, one band appears at 1193 cm^{-1} , the other at 1218 cm^{-1} . The 1030 cm^{-1} band is slightly affected by counter ions. The results of Fig. 8 are listed in Table 5.

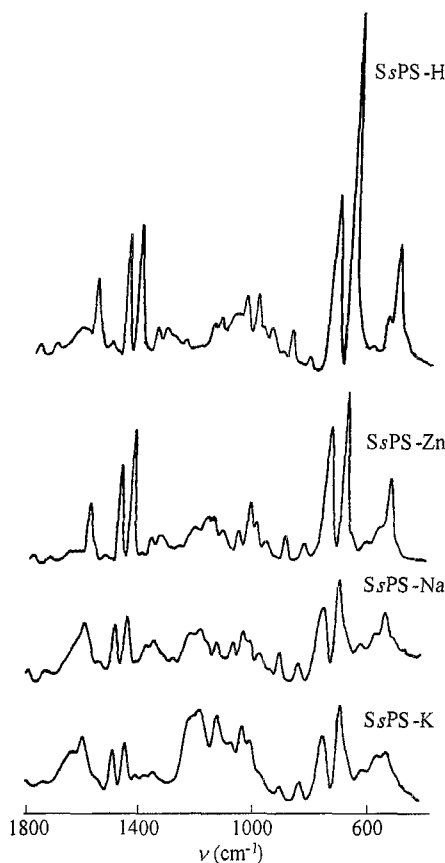


Fig. 8 FTIR spectra of SsPS ionomers

CONCLUSIONS

The properties of sulfonated syndiotactic polystyrene ionomers (SsPS) with a sulfonation degree of 1.8 mol% have been investigated. Results of WAXD show that the crystallinity of SsPS ionomers is lower than that of *s*PS and its crystal form (two crystal forms: α and β) changes into a single α form. The TGA results demonstrate that the thermal stability of SsPS ionomers is higher than that of *s*PS, and the stability is higher for ionomers with bivalent ions than for those with univalent ions, i.e., SsPS-Zn > SsPS-K > SsPS-H > SsPS. The DSC results show that the T_g of SsPS ionomers are all higher than that of *s*PS, i.e., SsPS-Zn > SsPS-Na > SsPS-K > SsPS-H > SsPS, but the T_m and T_p of SsPS ionomers are all low, and *s*PS > SsPS-H > SsPS-Zn > SsPS-K > SsPS-Na. The X_c of SsPS ionomers is also lower than that of *s*PS, and *s*PS > SsPS-H > SsPS-K > SsPS-Na > SsPS-Zn. For the alkali metal neutralized ionomers, the strength of ionic interaction is governed by the size of the neutralizing counter ion. When SsPS is neutralized with small alkali metal counter ions, the strength of ionic interaction is stronger than that with larger counter ions. Therefore, the polymer chain of SsPS-Na is difficult to move and has higher T_g and lower T_m , T_p and X_c as compared with SsPS-K. Since SsPS-Zn has complexation ability, therefore, the ionic interaction is much stronger and has the highest T_g . Nonisothermal crystallization kinetics indicates that the Avrami indices of *s*PS and SsPS-H ionomer are both about 4. The FTIR spectra indicate that the sulfonation

group is introduced into the *para*-position of the benzene ring, and the asymmetric stretching vibration of sulfonic acid groups splits into a doublet for SsPS ionomers with metal counter ions, and with the increase of ionic interaction, the splitting shifts to higher wavenumbers.

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