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THE STRUCTURES AND IONIC CONDUCTIVITY OF COMPLEXES FORMED BY POLY(TETRAMETHYLENE SUCCINATE) AND ALKALI METAL SALTS

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ABSTRACT

The relationship between the structures and properties of solid polymer electrolytes formed by poly(tetramethylene succinate) and alkali metal salts is investigated in this article. The complexation between ions and polar groups, e.g., ester groups in the polymer chains, is determined by FT-IR and XPS techniques. The complexes are semicrystalline materials with the crystallites similar to pure polyester. Inorganic salts do not enter the crystal lattice of the polymer, whereas they do mainly dissolve in the amorphous domains of the polymer. The addition of salts depresses the melting temperature and crystallinity of the polyester. On the contrary, it increases the glass transition temperature. The conductivity of the polyester complexes varies with the concentration, species, solubility of salts in the polyester, temperature, etc. Ionic migration in the amorphous regions of the polymer contributes to the conduction of the electrolytes to a great extent. The conductive behavior could not simply be described either by the Arrhenius equation based on classical theory or by the WLF equation based on free volume theory.

INTRODUCTION

The polymeric electrolytes have aroused considerable interest because polymers have advantageous mechanical properties, they are easy to fabricate in large thin films or sheets, and they retain excellent contact with an electrode. After Wright et al. [1] first reported high ionic conductivity for the complexes of poly(ethylene oxide) and alkali metal salts, and extensive investigations on the polyether complexes were made by Armand et al. [2], many laboratories began to explore solid polymeric electrolytes [2–5]. Up to now, much work has focused on the polyether complexes, including studies on their properties, structures, and ion transport mechanism [2, 6–8]. At the same time, many reports have concerned flexible chain polymers for solid electrolytes, e.g., aliphatic polyesters [9–11], polyphosphazene [12], polyethleneimine [13], and poly(ethylene oxide-*co*-dimethylsiloxane) [14]. There has also been intense attention to the potential application of polymer materials as solid electrolytes in electrochemical solid-state primary or secondary generators [15–17]. A general investigation of complexes formed by an aliphatic polyester and inorganic salts is made in the present paper.

EXPERIMENTAL

Poly(tetramethylene succinate) (PTS-4,4) was prepared from freshly distilled dimethyl succinate and butanediol by ester-exchange reactions at an elevated temperature [11]. Dimethyl succinate, excess butanediol (2–3-fold molar amount of the diester), antimony trioxide (0.03–0.05 wt% of the diester), and calcium acetate (0.15–0.30 wt%) were mixed by stirring and heating in a nitrogen atmosphere. After reacting at 180°C for 4 h, the product methanol was distilled out. The mixture was then elevated to 240°C to distill excess diol. Finally, vacuum (3–5 torr) was used at 240°C for 4–8 h for the ester-exchange polycondensation. The polymer obtained was purified by reprecipitation using trichloromethane and methanol followed by washing, respectively, with water and methanol, and then dried in a vacuum stove at 60°C. The inherent viscosity of the polymer in chloroform solvent at 25°C was 0.361 dL/g (concentration: 0.5 g/dL).

Analysis. Calculated: C, 55.81; H, 6.98; O, 37.21%. Found: C, 55.78; H, 7.09; O, 37.13%.

All alkali metal salts were dehydrated or dried at 160°C for over 8 h in a vacuum stove.

Polymer PTS-4,4 and stoichiometric inorganic salts (in molar ratio: [salt]/[unit]) were mixed and heated to ~140°C in a dry nitrogen stream in a dry box. When the mixture was melted, it was stirred in order to promote salt dissolution. After the melt became optically homogeneous, it was cooled to ambient temperature and finely crushed. This procedure was repeated several times to achieve a homogeneous dissolution of the salts in the polymer.

The PTS-4,4-salt complexes were pressed into cyclindrical pellets (13 mm in diameter, 1-2 mm in thickness) under a pressure of ~6 ton/cm^2 for the conductance measurement. Special care must be taken to exclude traces of water during the preparation of PTS-4,4-salt complexes and sample preparation. The conductance of an electrolyte was measured at a frequency of 3 kHz with a TR-10T dielectrical loss instrument, Ando Co., Japan. The measuring instrument was filled with dry, inert gas to protect the electrolyte against atmospheric humidity.

DSC analyses were conducted with a Dupont 1090 analyzer at a heating rate of 15°C/min. Wide-angle x-ray diffraction patterns were measured with a Siemens D-500 automatic diffractometer. XPS spectra were obtained from a XSAM 800 Krate polyfunctional surface analyzer with an AlK$_\alpha$ source at 12 kV/15 mA under 10^{-8} torr. FT-IR spectral measurements were completed with the aid of a 5DX spectrometer.

RESULTS AND DISCUSSION

The Complexation between Ions and PTS-4,4

FT-IR Analyses

The FT-IR spectrum of PTS-4,4-LiClO$_4$ is shown in Fig. 1. As compared with PTS-4,4, the peaks at 1720 cm^{-1} ($\nu_{-C=O}$), 1340 cm^{-1} ($\nu_{-\underset{\underset{O}{\|}}{C}-C-}$), 1155 cm^{-1} ($\nu_{-O-C-}$ or $\nu_{as(-\underset{\underset{O}{\|}}{C}-O-C-)}$), and 1045 cm^{-1} ($\nu_{s(-\underset{\underset{O}{\|}}{C}-O-C-)}$), for the complex change in strength. The peaks at 1720 and 1155 cm^{-1} become narrower and sharper, which seems similar to

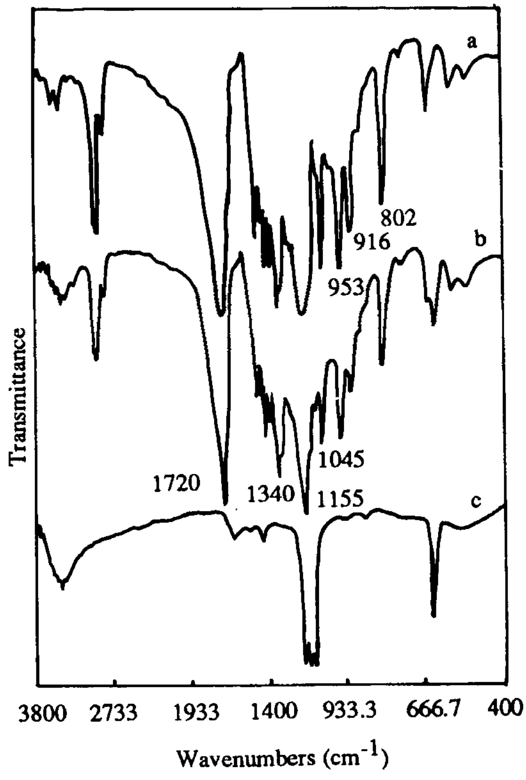


FIG. 1. FT-IR spectra of (a) PTS-4,4; (b) PTS-4,4-$LiClO_4$ ([$LiClO_4$]/[unit] = 1/10); and (c) $LiClO_4$.

Raman spectrum analyses [18]. The relative strength of peaks at 1045 and 1340 cm^{-1} decreases. Obviously, these changes are related to interactions among ions and the ester groups of polymer chains. As seen from Fig. 1, the complexation between ions and oxygen atoms also causes the peaks at 802, 916, and 953 cm^{-1} to change.

XPS Analyses

Figure 2 shows the XPS spectrum of the PTS-4,4-$NaClO_4$ complex. All elements in the electrolyte appear in this spectrum. The electron-orbit-binding energy for various complexes is tabulated in Table 1. As seen from this table, the binding energy of elements for polymeric elec-

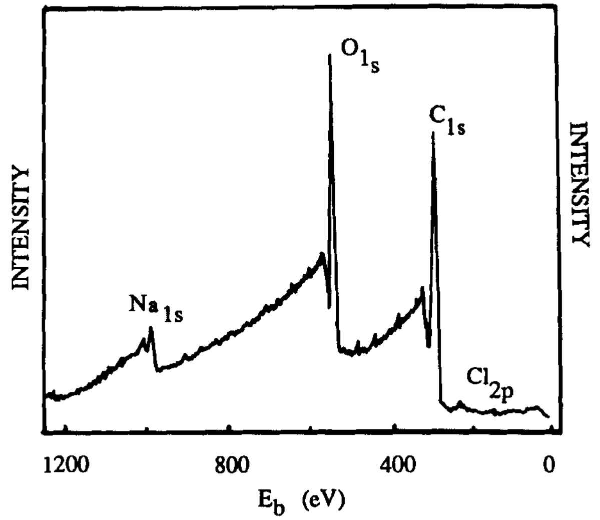


FIG. 2. Scan XPS spectrum of PTS-4,4-$NaClO_4$ complex with [$NaClO_4$]/[unit] = 1/10.

trolytes is lower than that for PTS-4,4 and salts. It is quite possible for a salt to dissolve and ionize in the polyester. Meanwhile, ions interact with oxygen in the polymer chains and/or carbonyl groups. The electron cloud density on oxygen atoms increases due to the induced action of cations. When the salt ionizes in the polyester, the radius of the atoms decreases. Therefore, the binding energy of the elements in the complexes also decreases.

The Structures and Properties of Polyester Complexes

The Solubility of Inorganic Salts in PTS-4,4

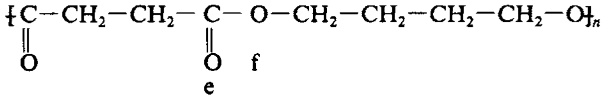
As mentioned above, alkali metal salts can be dissolved in PTS-4,4. However, the solubility of salts is different and limited. When the concentration [$LiClO_4$]/[unit] reaches ¼, the salt crystallites can be detected by observation with a hot-stage polarization microscope. The dissolution of some salts in PTS-4,4 is recorded in Table 2. The solubility of a salt in the polymer is probably related to the lattice energy and melting point of the salt. As shown in Table 2, the higher the lattice energy of a salt,

TABLE 1. The Electron-Orbit-Binding Energy of Elements in XPS for PTS-4,4-Salt Complexes

	O_{1s}[b]		I_{3d}			
Sample[a]	e	f	1	2	Na_{1s}	Cl_{2p}
PTS-4,4	532.50	531.10				
PTS-4,4-$LiClO_4$	532.05	530.75				206.50
$LiClO_4$	532.35					207.60
PTS-4,4-NaSCN	532.30	530.80			1071.45	
PTS-4,4-NaI	531.95	530.60	629.42	617.95	1071.45	
NaI			630.65	618.75	1072.15	
PTS-4,4-$NaClO_4$	532.25	530.85			1071.70	206.55
$NaClO_4$	532.20				1072.25	207.35
PTS-4,4-$KClO_4$	532.05	530.70				207.60
$KClO_4$	532.65					207.65

[a] Molar ratio: [salt]/[unit] = 1/10.

[b] Position of atoms:



$$\left[\underset{\underset{O}{\|}}{C} - CH_2 - CH_2 - \underset{\underset{\underset{e}{O}}{\|}}{C} - \underset{f}{O} - CH_2 - CH_2 - CH_2 - CH_2 - O \right]_n$$

TABLE 2. The Lattice Energy and Melting Temperature of Inorganic Salts [19] and Their Solubility in PTS-4,4

Salt	Lattice energy, kJ/mol	mp, °C	Solubility[a]
$LiClO_4$	709	236	+
$NaClO_4$	643	482	+
$KClO_4$	599	610	×
NaSCN	682	173	+
KSCN	623	287	−
NH_4SCN	605	150	+
NaI	682	661	−
KI	632	681	×
NaCl	769	801	×
NaBr	732	747	×

[a] Concentration: [salt]/[unit] = 1/10; +, dissolution; −, partial dissolution; ×, minor dissolution (by observation with a microscope).

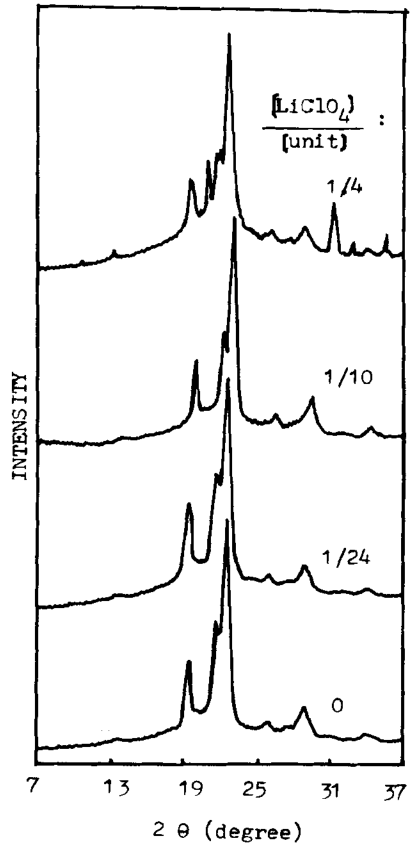


FIG. 3. X-ray diffraction diagrams of PTS-4,4-LiClO$_4$ complexes with different ratios.

the less the solubility; the higher the melting point of a salt, the worse the dissolution of the salt in the polyester.

X-Ray Diffraction Analyses of PTS-4,4-Salt Complexes

Wide-angle x-ray diffraction patterns from different concentrations are shown in Fig. 3. The diagrams of complexes are similar to or the same as that of the polymer. This indicates that the electrolytes formed by PTS-4,4 and LiClO$_4$ are semicrystalline materials with the crystallites similar to PTS-4,4; LiClO$_4$ doesn't enter the crystalline lattice of PTS-

4,4. The salt only dissolves in the amorphous regions of the polymer. On the other hand, the crystal diffraction peaks of the salt occur as the concentration of the salt reaches ¼. This also suggests that the complex has been saturated with the salt.

Experimental results by x-ray diffraction analyses for various ionic conductors are tabulated in Table 3. The data show that some electro-

TABLE 3. X-Ray Diffraction Analyses for Complexes Formed by PTS-4,4 and Salts with a Molar Ratio of [salt]/[unit] = 1/10[a]

Sample	Spacings, Å				
PTS-4,4	6.47(vs),	4.55(s),	4.06(s),	3.93(vs),	3.62(vw),
	3.42(vw),	3.25(vw),	3.08(m),	2.86(vw),	2.66(w).
PTS-4,4-$LiClO_4$	6.34(vw),	4.46(s),	3.99(s),	3.86(vs),	3.58(vw),
	3.36(w),	3.20(w),	3.03(m),	2.62(w).	
PTS-4,4-$NaClO_4$	6.44(vw),	4.53(s),	4.05(s),	3.92(vs),	3.60(vw),
	3.42(w),	3.24(vw),	3.08(m),	2.86(vw),	2.65(vw),
	2.52(vw).				
PTS-4,4-$KClO_4$	6.54(vw),	4.53(s),	4.06(s),	3.91(vs),	3.41(w),
	3.25(w),	3.07(m),	2.84(w),	2.65(m),	2.52(m),
	3.81(m),	*3.64*(m),	*3.49*(w),	*3.36*(w),	*3.14*(m),
	2.96(w),	*2.89*(m).			
PTS-4,4-NaSCN	6.55(vw),	4.55(s),	4.06(s),	3.92(vs),	3.66(vw),
	3.56(vw),	3.26(w),	3.05(w),	2.86(vw),	2.65(m).
PTS-4,4-KSCN	6.59(vw),	4.55(s),	4.08(s),	3.92(vs),	3.62(vw),
	3.42(m),	3.25(w),	3.08(m),	2.85(vw),	2.66(m),
	2.98(vw).				
PTS-4,4-NH_4SCN	6.27(vw),	4.53(s),	4.05(s),	3.92(vs),	3.42(m),
	3.25(vw),	3.08(m),	2.84(vw),	2.64(w).	
PTS-4,4-NaI	6.39(vw),	4.53(s),	4.06(s),	3.91(vs),	3.59(vw),
	3.41(w),	3.24(w),	3.06(m),	2.88(vw),	2.64(w),
	2.51(vw),	*3.19*(s).			
PTS-4,4-NaBr	6.47(vw),	4.53(s),	4.05(s),	3.91(vs),	3.60(vw),
	3.40(m),	3.25(w),	3.08(m),	2.87(vw),	2.65(m),
	3.45(m),	*2.99*(s).			

[a] *Italic* data are for the salts.

TABLE 4. Estimated Crystallinity of PTS-4,4-$LiClO_4$ Complexes

$\frac{[LiClO_4]}{[unit]}$	0	1/24	1/10	1/4
Crystallinity (%)	56.4	53.8	54.1	44.9

lytes are similar to the polymer and others are not. The differences are caused by the presence of salt crystallites in the complexes. This demonstrates that the solubility of some salts is better than that of others, which corresponds to the microscope results.

The crystallinity of various complexes is estimated by calculating the areas which contributed to crystalline or noncrystalline regions of the polymer in diffraction diagrams [20] (Table 4). As seen from Table 4, the crystallinity decreases with an increase in the concentration of $LiClO_4$. The crystallinity drops particularly rapidly at high molar ratios of $[LiClO_4]/[unit]$. This implies that the salt mainly dissolves in the amorphous domains of PTS-4,4. When the amorphous domains are saturated with the salt, the effect of the salt on polymer crystallization becomes notable. At this point the salt evidently prevents crystallization of the polymer, so the crystallinity of the electrolyte largely decreases.

DSC Analyses for Various Complexes

DSC analyses of the complexes formed by PTS-4,4 and $LiClO_4$ are shown in Table 5. The glass transition temperature (T_g) increases with a rise in $LiClO_4$ concentration. The reason is that interactions take place between ions and polymer chains. However, the melting temperature of PTS-4,4 decreases with an increase in the concentration, and the relationship between the melting point and the salt concentration agrees with the Flory-Huggins theory [21] (see Fig. 4), i.e.,

$$\frac{1}{T_m} - \frac{1}{T_{mo}} = \frac{RX'd_EM}{\Delta H_u d_s} C \tag{1}$$

where d_E and d_s are the densities for the electrolyte and the salt, respectively; T_m and T_{mo} are the melting temperatures for the electrolyte and the polymer respectively; R is the universal gas constant; X' is the ratio of the partial molar volume of the polymer repeat unit to that of the

TABLE 5. DSC Analyses for PTS-4,4-$LiClO_4$ Complexes in the Second Run (15°C/min)[a]

$\frac{[LiClO_4]}{[unit]}$	0	1/24	1/20	1/16	1/12	1/10	1/8	1/6	1/4
T_g (°C)	−34.0	−31.7		−24.5	−24.8	−23.4	−16.3	−16.2	−18.3
T_m (°C)	113.5	112.2	112.2	112.0	111.0	109.5	108.9	107.7	98.7
ΔH_m (J/g)	64.3	64.1		68.5	68.3	61.0			53.7

[a] All samples were quenched from 160°C to liquid nitrogen temperature.

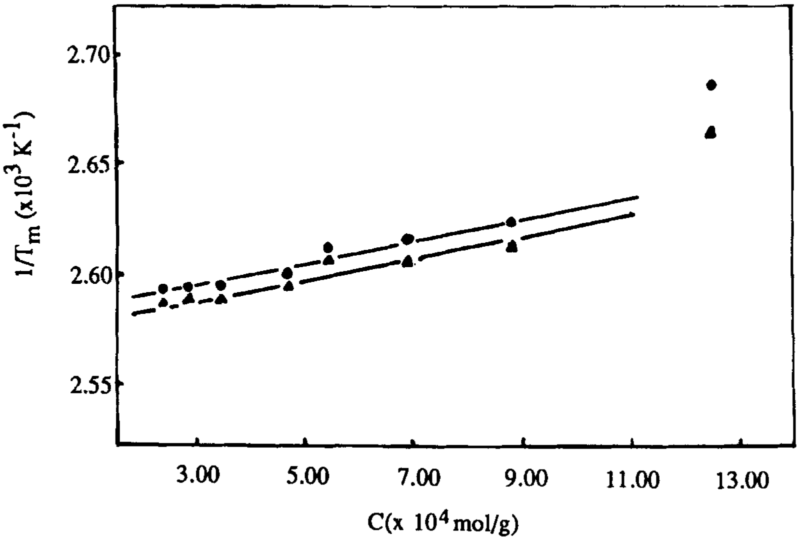


FIG. 4. The inverted melting temperature of PTS-4,4-$LiClO_4$ complexes as a function of $LiClO_4$ concentration (▲) in the first heating run and (●) in the second run.

salt; M is the molecule weight of the salt; ΔH_u is the heat of fusion for the polymer; and C is the concentration of the salt. The complex is considered to be a mixture, and the addition of a salt increases the crystal defects of the polymer. Therefore, the melting point of the polymer is depressed. The values in the ΔH_m column of Table 5 decrease with the addition of $LiClO_4$. This also verifies that the crystallinity of PTS-4,4 drops. DSC analyses for various complexes with different salts manifest similar results.

Ionic Conductivity of Various Electrolytes

The Dependence of Salt Content

Conductivity changes for PTS-4,4-$LiClO_4$ complexes with the $LiClO_4$ content is shown in Fig. 5. There is a maximum conductivity at the salt concentration $[LiClO_4]/[\text{unit}] = \sim 1/4$, and the logarithm of conductivity varies linearly with the salt content in the lower concentration range

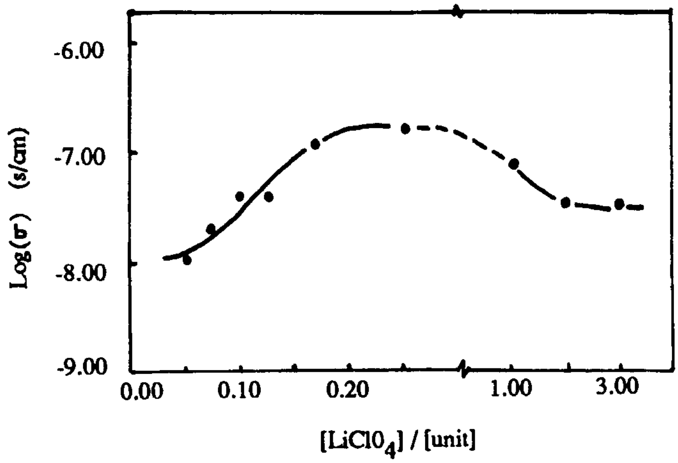


FIG. 5. The conductivity of PTS-4,4-LiClO$_4$ complexes as a function of LiClO$_4$ concentration at 40°C. (- - -) Hypothetical.

(see Fig. 6) at the same temperature, $T - T_g$. The inorganic salt could ionize in the polyester:

$$\begin{array}{ccccc} MX & \rightleftharpoons & M^+ & + & X^- \\ C_0(1-\alpha) & & \alpha C_0 & & \alpha C_0 \end{array}$$

where C_0 is the initial concentration of a salt and α is the degree of ionization. If the salt doesn't fully ionize, i.e., is not equal to unity, the conductivity of the electrolyte could be expressed by

$$\sigma = \mu ZF\sqrt{K}\sqrt{\frac{C_0}{\gamma_+\gamma_-}} \tag{2}$$

in which μ is the mobility of the charge carriers, Z is their valence, γ_+ and γ_- are their activity coefficient, K is the equilibrium constant for ionization, and F is the Faraday constant. According to Eq. (2), log (σ) versus C_0 should be a straight line if μ and γ do not depend on C_0. Although log (σ) changes linearly with the original concentration of the salt in this system, the slope of the straight lines is about 2, which is different from that previously reported [22]. This is probably caused by

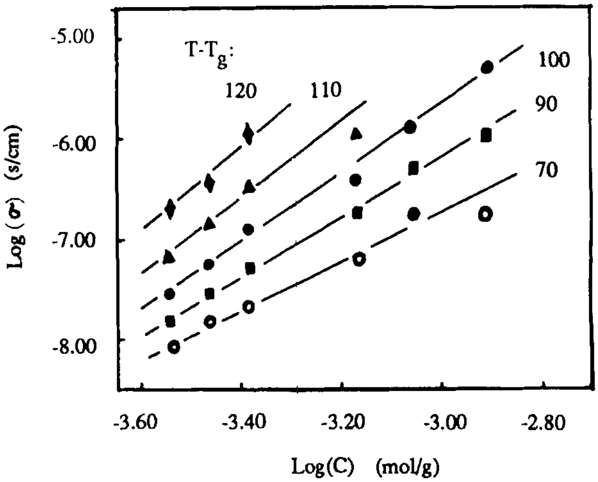


FIG. 6. Conductivity of PTS-4,4-$LiClO_4$ complexes as a function of $LiClO_4$ at different $T - T_g$.

the presence of the crystalline domains and ion aggregates like triplets and quartets in the complexes. The result could not be described by Eq. (2) based on classical solution theory. As the content of salt rises, the concentration of ions would increase and the conductivity of the electrolyte would also be enhanced. When the concentration of ions rises to such an extent that ions could easily associate with each other, the migration of ions becomes more difficult. As mentioned above, the solubility of the salt in the polyester is limited, so not all salt molecules are solvated by the polymer and ionize. Therefore, conductivity would be expected to decrease as the salt content increases.

The Relation between the Conductivity and the Solubility of a Salt

The conductivity of PTS-4,4-salt complexes as a function of salt species is shown in Fig. 7, which indicates that the conductivity of the electrolytes formed by PTS-4,4 and $LiClO_4$, $NaClO_4$, NaSCN, NH_4SCN, NaI, and KSCN is higher than that formed by PTS-4,4 and $KClO_4$, KI, NaCl, and NaBr. The gap between the two groups is as high as two to three orders of magnitude. This is mainly due to the difference of solubility of these salts in PTS-4,4. The better the dissolution of a salt, the higher the conductivity of the electrolyte.

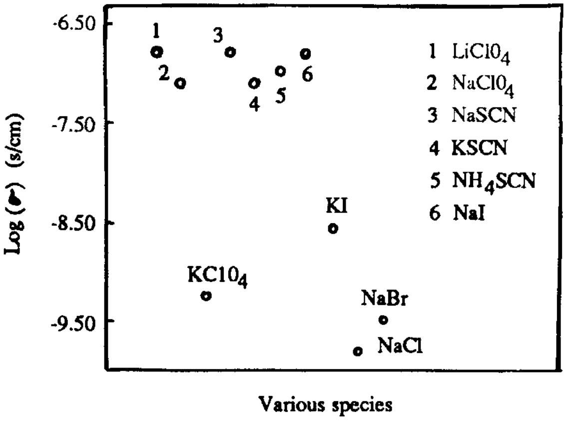


FIG. 7. Ionic conductivity for PTS-4,4-salt complexes at 60°C ([salt]/[unit] = 1/10).

The Effect of Cation Properties on the Conduction of an Electrolyte

The conductivity of the complexes comprising PTS-4,4 and alkali metal perchlorate salts is shown in Fig. 8. The order of their conductivity is

$LiClO_4 > NaClO_4 > KClO_4$

As compared in Table 6, we found that the smaller the radius of a cation, the higher its conductivity. Figure 9 shows the conductivity of the complexes formed by PTS-4,4 and thiocyanate salts. The order is

$NaSCN > NH_4SCN > KSCN$

The size of these ions is

$Na^+ < K^+ < NH_4^+$

The conductivity of PTS-4,4-NH_4SCN complex is higher than that of PTS-4,4-KSCN although the radius of NH_4^+ is higher than that of K^+. This seems to be contradictory. The fact is that NH_4^+ is easily transported because of its higher polarizability; more importantly, the solubility of NH_4SCN is greater than that of KSCN in PTS-4,4.

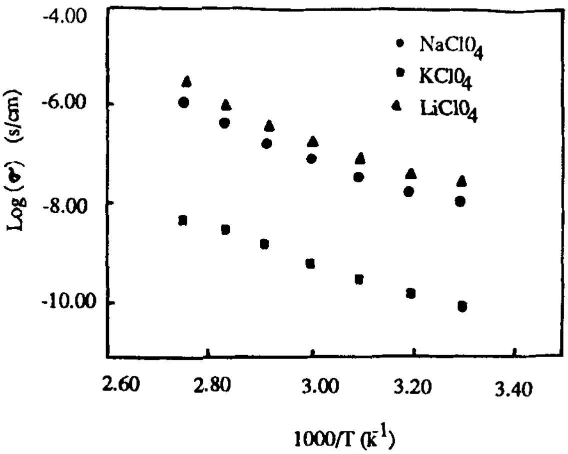


FIG. 8. Temperature dependence of conductivity for various PTS-4,4-salt complexes with molar ratio [salt]/[unit] = 1/10.

The Effect of Anion Properties on the Conductivity of an Electrolyte

Figure 10 shows the conductivity of Na^+ salts of polymeric conductors. The order of their conductivity is

$$NaSCN > NaI > NaClO_4 > NaBr > NaCl$$

The size of these anions is

TABLE 6. The Radius and Polarizability of Ions [19]

Ion	Radius, Å	Polarizability, $Å^3$	Ion	Radius, Å	Polarizability, $Å^3$
Li^+	0.60	0.031	ClO_4^-	*2.45*	
Na^+	0.95	0.179	SCN^-	*2.04*	
K^+	1.33	0.83	I^-	2.16	7.10
NH_4^+	1.48		Br^-	1.95	4.77
			Cl^-	1.81	3.66

[a]The *italic* values were calculated by the atomic valence radius.

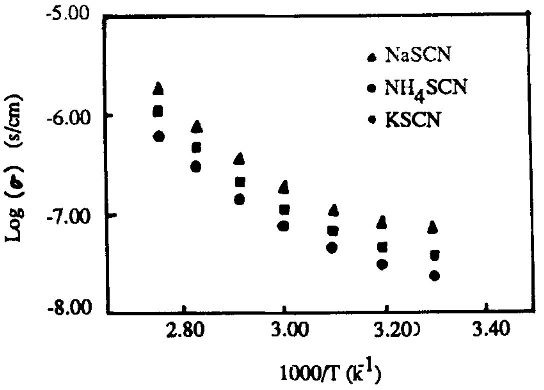


FIG. 9. Temperature dependence of conductivity for PTS-4,4-salt complexes with molar ratio [salt]/[unit] = 1/10.

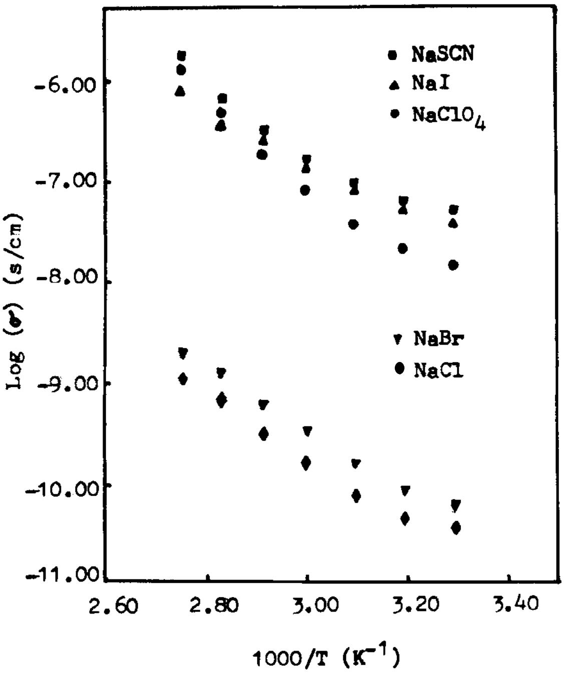


FIG. 10. Temperature dependence of the conductivity for PTS-4,4-Na salt complexes with molar ratio [salt]/[unit] = 1/10.

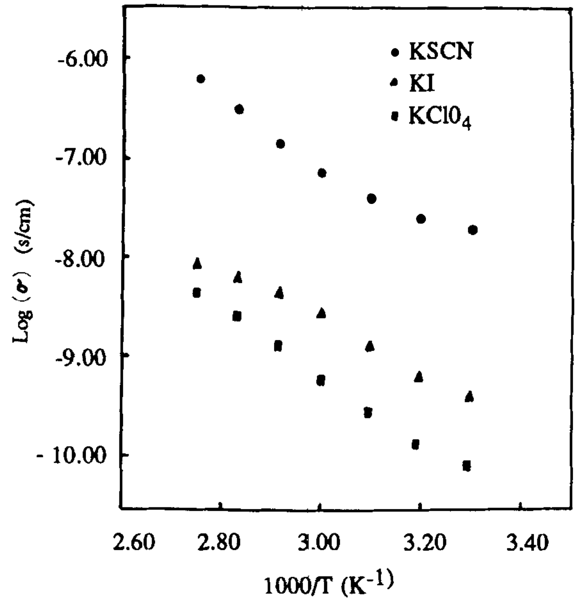


FIG. 11. Temperature dependence of the conductivity for various PTS-4,4-K salt complexes with molar ratio [salt]/[unit] = 1/10.

$ClO_4^- > I^- > SCN^- > Br^- > Cl^-$

It was again anticipated that the smaller the radius of an anion, the higher the conductivity. However, the conductivity of the electrolytes made of PTS-4,4 and NaBr and NaCl is lower than that of the others by as much as three orders of magnitude. The main reason is that the solubility of NaCl and NaBr in the polyester is very low. Although the solubility of $NaClO_4$ is higher than that of NaI, the conductivity of the electrolyte with $NaClO_4$ is lower than that of NaI at a lower temperature, but the conductivity of the PTS-4,4-$NaClO_4$ complex is higher than that of the PTS-4,4-NaI complex at a higher temperature. This again indicates that the solubility of a salt is an important factor in conduction. This is further confirmed by the temperature dependence of conductivity for complexes formed by PTS-4,4 and potassium salts, as shown in Fig. 11. Their conductivity is

$KSCN > KI > KClO_4$

This again demonstrates that the smaller the radius of an anion, the higher is its conductivity. The conductivity gap between PTS-4,4-KSCN and PTS-4,4-KI or PTS-4,4-$KClO_4$ complexes reaches two orders of magnitude. The reason is mainly that the dissolution of KI and $KClO_4$ is lower than that of KSCN. From the above examples we can even conclude that anions also participate in conduction, which has precedent in the literature [23].

The Conductive Behavior and Transport Mechanism

The conductive behavior for some polymeric electrolytes can be described by the Arrhenius equation:

$$\sigma = \sigma_0 e^{-E/kT} \tag{3}$$

where σ_0 is the preexponential constant, E is the apparent activation energy for ion transport and k is the Boltzmann constant. Only an ion with a certain energy can transport by an activation-jump process. However, the conductivity for other polymeric electrolytes can be expressed by the WLF equation:

$$\log \frac{\sigma(T)}{\sigma(T_g)} = \frac{C_1(T - T_g)}{C_2 + (T - T_g)} \tag{4}$$

where $\sigma(T)$ and $\sigma(T_g)$ are the conductivities for an electrolyte at temperatures T and T_g, respectively; and C_1 and C_2 are the WLF equation parameters. Part of the incorporated salt dissociates in the polyester via the interaction of the polar groups in the polymer chains. The carrier ions in the complexes exist as ions solvated by the polar groups. The polymer segments constantly fluctuate and rearrange in the amorphous regions of the polymer. The associated ions also continuously follow the segmental motion. Meanwhile, ions can dissociate from and associate with the polar groups in the polymer chains at different locations. The rearrangement of polymer segments may change the local position of carrier ions. The complexation of ions by other polymer segments dominates some time after the change in local positions of ions, and then the segmental motion again causes ion migration. The repetition of the association of the ions with the polymer segments, the segmental motion with the associated ions, the dissociation from the polymer segments, and the

TABLE 7. WLF Equation Parameters for the Complexes Formed by PTS-4,4 and Alkali Metal Salts ([salt]/[unit] = 1/10)

Salt	T_g °C	$\sigma(T_g)$, s/cm	C_1	C_2 °C	Estimated error
$LiCLO_4$	−23.4	2.93×10^{-12}	10.1	88.6	2.83×10^{-3}
$NaClO_4$	−17.3	1.75×10^{-12}	8.84	63.6	3.62×10^{-3}
KSCN	−30.6	1.69×10^{-11}	7.91	99.0	3.75×10^{-3}
NaSCN	−16.5	1.61×10^{-10}	6.10	71.0	8.11×10^{-3}
NH_4SCN	−25.0	4.02×10^{-11}	7.35	89.6	5.83×10^{-3}
NaI	−18.0	2.97×10^{-10}	6.19	79.5	4.04×10^{-3}
KI	−18.7	1.09×10^{-12}	6.92	83.3	1.83×10^{-3}

association of the ions with other segments might bring about ion transport in the electrolytes.

The temperature dependence of the conductivity for PTS-4,4-salt complexes evidently doesn't correspond with Arrhenius behavior (see Figs. 8–11). As mentioned above, the alkali metal salts mainly dissolve in the amorphous regions of polyester. Therefore, the conductive behavior should follow the WLF equation. Multiple linear regression of $\left(\log \frac{\sigma(T)}{\sigma(T_g)}\right)^{-1}$ vs $\left(\frac{1}{T - T_g}\right)$ has been conducted. The results are tabulated in Table 7. C_1 and C_2 both deviate from the universal values ($C_1 = 17.4$, $C_2 = 51.6$). The conductivity distribution for various electrolytes is obtained by plotting $\log \left(\frac{\sigma(T)}{\sigma(T_g)}\right)$ vs $(T - T_g)$. As shown in Fig. 12, the distribution of $\log (\sigma(T)/\sigma(T_g))$ has a range which is about half an order of magnitude. This is much less than the distribution of $\log \sigma(T)$ vs $1/T$ whose range is as high as two orders of magnitude, e.g., PTS-4,4-KI and PTS-4,4-NaI complexes. If ion migration absolutely depends on polymer segmental motion, ionic conductivity should be independent of salt species. There is a master curve on the plot of $\log (\sigma(T)/\sigma(T_g))$ vs $(T - T_g)$ because the free volume for segmental motion is much larger than that for naked ion transport [24]. Therefore, ion transport relates to the motion of polymer segments to some extent, but the salt species still affect the conductivity of electrolytes.

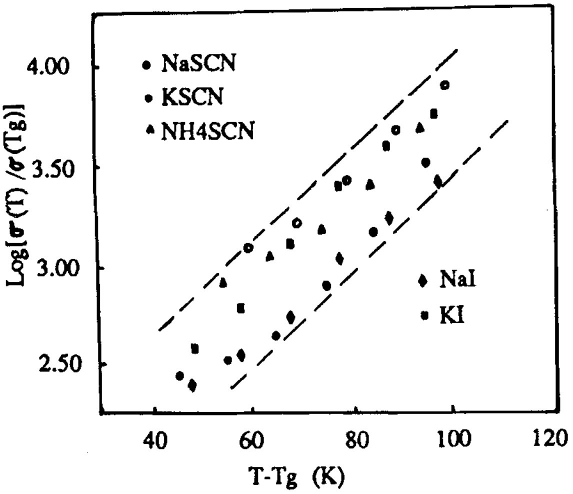


FIG. 12. Conductivity of PTS-4,4-salt complexes with molar ratio [salt]/[unit] = 1/10 as a function of the temperature $T - T_g$.

CONCLUSION

The polyester PTS-4,4 is capable of forming complexes with a majority of alkali metal salts. PTS-4,4-salt complexes are semicrystalline materials with crystallites similar to PTS-4,4. Inorganic salts mainly dissolve in the amorphous regions of the polyester, and their solubility depends on their lattice energy and melting point. The addition of salts decreases the melting temperature and crystallinity of the polymer, but it increases the glass transition temperature. The relationship between melting temperature of the polymer and salt content agrees with the Flory-Huggins theory in the lower content range. The conductivity of PTS-4,4-salt complexes varies with the concentration, solubility, and species of a salt. There is a maximum of conductivity in a plot of log σ vs salt concentration. Especially, the conductivity σ changes linearly with concentration in the lower concentration range at the same temperature, $T - T_g$. The smaller the radius of an ion, the higher the conductivity of its polyelectrolytes. The temperature dependence of conductivity deviates from the Arrhenius and WLF equations. However, the conduction of polyelectrolytes is related to the motion of polymer segments.

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