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Study on conductivity of two kinds of cross-linked polyether solid electrolytes and electrorheological properties of anhydrous suspensions based on them

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Two kinds of cross-linked polyether solid electrolytes (CPESE) with high ionic conductivity (σ) of 8.0×10^{-5} S cm^{-1} (25°C, for double ionic conducting CPESE2) or 4.0×10^{-6} S cm^{-1} (30°C, for single ionic conducting CPESE1) were obtained by polymerizing α,ω-bismethacryloyl capped poly(ethylene glycol) (BMAPEG) after complexing with LiClO$_4$ or copolymerizing BMAPEG with salt of methacrylic acid (MAAM), respectively. In the mean time, the CPESE based anhydrous electrorheological (ER) fluids with relatively high activity were directly synthesized by inverse suspension polymerization of BMAPEG after complexing with LiClO$_4$ or of BMAPEG with MAAM. The influences of structure of CPESE on their conductivity and properties for ER fluids based on them were studied. The results showed that maximum σ occurred at an optimum molecular weight of poly(ethylene glycol) segment (M_{PEG}) as well as a certain value of [Li$^+$]/[EO] or [MAAM]/[EO], while σ decreased with increasing functionality of BMAPEG (f). For ER fluids containing CPESE2, yield stress (τ_s) increased with f while τ_s showed a maximum value at a certain [Li$^+$]/[EO]. Leak current density (J) increased with increasing [Li$^+$]/[EO] or with decreasing f. A maximum J occurred with change of M_{PEG}. For ER fluids containing CPESE1, both τ_s and J showed a maximum value with increasing M_{PEG} or [MAAM]/[EO], while τ_s and J decreased with increasing f. τ_s hardly depended on the type of its counterion, while J decreased in the following counterion order: K$^+$ $\approx$ Li$^+$ > Na$^+$. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: cross-linked polyether; polymeric solid electrolyte; electrorheological fluid)

INTRODUCTION

Since the discovery of electrorheological (ER) fluids by Winslow[1] in the 1940s, the ER fluids, which have superior features of rapid, reversible and controllable changes from liquid into solid upon application of electric field, have attracted great interest owing to the potential of improving the electronic control of mechanical devices[2,3]. ER fluids may be classified into hydrous ER fluids and anhydrous ER fluids. The former, for example, suspensions of salt of poly(methacrylic acid) in chlorinated hydrocarbon, fluoroluble FS, dipolar halogenated aromatics, or pentachlorophenyl phenyl ether, which were first discovered by Stangroom and Harness[4,5] and recently synthesized directly by us using inverse emulsion polymerization to overcome the crippling problems of poor stability and complicate post-treatment[6], still have several problems about operating temperature, leak current density, reproducibility and durability because of the essential requirement of water or other low molecular weight polar liquids, so far hydrous ER fluids are not applicable to engineering. The anhydrous ER fluid, first developed in the late 1980s[7–9], offer a possibility to overwhelm the exhausting problems of hydrous ER fluids. Anhydrous ER fluids most contain electronic

semiconducting particles such as polyaniline (PAn)[10–13], polyphenylene[14], poly(phenyl diacetylene)[15] and poly(pyridinium) salt[16]. PAn was widely used as dispersed particles to design high performance ER fluids owing to its low density, low temperature coefficient of conductivity, non-melting, insolubility as well as its adjustable dielectric constant and conductivity in a large range. Recently, we have modified PAn particles used in anhydrous ER fluids by three different methods of blending, graft copolymerization or non-equilibrium deprotonation, as a result, we have greatly both improved the ER effect and decreased the leak current density for the ER fluids based on PAn[17].

Following Wright's discovery of high ionic conductivity from several crystalline complexes of poly(ethylene oxide) (PEO) with various alkali metal salts[18,19] and Armand's suggestion of the use of these materials as ionic conductors for lightweight rechargeable batteries using alkali metal electrodes[20], polymer solid electrolytes, to which a great deal of scientists groups worldwide have devoted considerable research effort, have already been developed to be a kind of advanced functional materials and identified to have many important potential applications in electrochromic devices, capacitors and sensors etc.[21], apart from in the high energy density solid-state secondary lithium battery. These have mainly been owing to their high plasticity, good viscoelastic property as well as chemical and

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electrochemical stability. Since PEO has strong solvating power for alkali metal salts and forms complexes with good redox stability as well as acceptable ionic conductivity (σ) at temperatures in excess of 100°C, researches on polymer solid electrolytes have mainly focused on the systems consisting of PEO and inorganic alkali salts, i.e. $LiClO_4$ or $LiCF_3SO_3$[22]. It is well accepted that whatever the mechanism of ion transport in the PEO matrix, the amorphous phase only is involved[23]. However, suffering from the disadvantage of forming partially crystalline polymer–salt complex, the PEO–salt polymer solid electrolytes at ambient temperature have poor conductivity, therefore much effort since the 1980s has been concentrated on modification of PEO aimed at optimizing the ionic conductivity and mechanical properties of these PEO–salt polymer solid electrolytes[24–27]. These include synthesis of blending, block, graft, cross-linked or interpenetrating networks polymers, which incorporate PEO segments in such a way as to eliminate or even restrain the crystallization both of PEO and of the PEO–salt complex, thus increasing the amorphous phase and improving ionic conductivity. For example, polymer solid electrolytes with both good mechanical properties and ambient ionic conductivity as high as 10^{-3}–10^{-4} S cm^{-1} were reported to be available by introducing such organic liquids as propylene carbonate into the amorphous cross-linked PEO systems[28] or the systems prepared by complexing PEO with flexible polymers by means of intermolecular hydrogen bonding[29]. Using polymer containing PEO and low-melting inorganic mixture to design a new kind of 'polymer-in-salt', polymer solid electrolytes[30] have also recently begun to attract scientists' interests. In addition, owing to the bi-ionic conductive behaviour of complexes between PEO-containing polymers and inorganic alkali salts, which suffers from the inconvenience of decreasing ionic conductivity with time under DC conditions, Tsuchida *et al.*[31] first synthesized poly[oligo(oxyethylene) methacrylate-*co*-alkali metal methacrylate], which allows only cationic single-ion conduction.

Using polymer solid electrolytes to design ER fluids may not only avoid the problems of low ambient ionic conductivity and poor mechanical property, occurring in most PEO-containing systems, but also have the advantages of lightweight and allowing us to tailor the properties of ER fluids by adjusting the structure and ionic conductive properties of polymer solid electrolytes. Further, it is expected that ER fluids based on them may have an ER effect even without a low molecular 'activator' such as water because polymer solid electrolytes contain movable ions themselves, thus, they seem to have the potential to be a new kind of anhydrous ER fluids to overcome the disadvantages of hydrous ER fluids, which were mentioned before. However, polymer solid electrolytes such as amorphous PEO are usually difficult to make into particles and disperse in insulating oil because of their viscoelastic state at ambient temperature and easy agglomeration of PEO particles in insulating oil. To overcome these obstacles, Bloodworth *et al.*[32,33] synthesized the anhydrous polyurethane based ER fluid by reacting trifunctional EO–polyether with toluene diisocyanate in insulating oil containing stabilizer in the condition of high temperature and high-speed stirring.
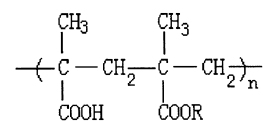
Since α,ω-bismethacryloyl capped poly(ethylene glycol) (BMAPEG) has hydrophilic and easily polymerizable properties, we first synthesized two kinds of the cross-linked polyether solid electrolytes (CPESE), respectively,

with bi-ionic, or single ionic conductive properties, then directly synthesized these two kinds of CPESE based anhydrous electrorheological (ER) fluids with somewhat high activity by inverse suspension polymerization of BMAPEG after complexing with $LiClO_4$ or copolymerization of BMAPEG with MAAM, followed by azeotropic distillation, overcoming the obstacles as mentioned earlier. This paper deals with the synthesis and some factors influencing ionic conductivity (σ) of CPESE as well as properties for ER fluids based on them.

EXPERIMENTAL

Materials

α,ω-bismethacryloyl capped poly(ethylene glycol)s (BMAPEG) with different functionality (f) from 1.1 to 2.0 were prepared by reacting poly(ethylene glycol)s (PEG) samples with different molecular weight of 400, 600, 1000, 2000 and 8000 with different amount of methacryloyl chloride in the presence of pyridine as catalyst in toluene to different extent. f of BMAPEG was calculated as $f = 2-N_{OH}$, where the number of hydroxyls of BMAPEG N_{OH} was determined by the isocyanate method. The synthesis and characterization were described in detail in our previous paper[34]. Methacrylic acid (MAA), C.P., was purified by distillation under reduced pressure; lithium, sodium and potassium salts of MAA were obtained by reacting MAA with corresponding alkalis. Polymeric stabilizer (PSR) was self-made with the following structure:

$$-\left(C\!-\!CH_2\!-\!C\!-\!CH_2 \right)_{\!n}$$

(structure: two repeating units each with CH$_3$ group on top; left carbon bears COOH, right carbon bears COOR)

where $R = C_mH_{2m+1}$. Azobisisobutyronitrile (AIBN), C.P., was recrystallized with 95% ethanol. $(NH_4)_2S_2O_8$, C.P., was recrystallized by distilled water. Poly(diethyl siloxane) (PDES), supplied by Wuhan Institute of Chemical Technology, was used as dispersing media. Other reagents such as xylene, $LiClO_4$ and P_2O_5 etc. were chemically pure and used without treatment.

Synthesis and characterization of cross-linked polyether solid electrolytes

To an aqueous solution in which BMAPEG and $LiClO_4$, or MAAM were dissolved, aqueous $(NH_4)_2S_2O_8$ solution was added. Polymerization was carried out by heating in an N_2 atmosphere for several hours. Then, the samples were completely dried under vacuum at 70°C, and were finally put in a desiccator with P_2O_5 in it to cool to room temperature. Thus, two kinds of the cross-linked polyether solid electrolytes (CPESE) were obtained. They are symbolized as CPESE1, synthesized from BMAPEG and MAAM, and CPESE2, from BMAPEG in the presence of $LiClO_4$, respectively.

The soluble parts of the specimens were available by Soxhlet extracting the specimens in water for 48 h. The IR spectra of CPESE1 or the water Soxhlet extracts solutions were recorded on a Shimadzu IR-408 spectrophotometer directly or using NaCl plate cells. Differential scanning calorimetry (d.s.c.) was carried out using a TAS-100 Thermal Analyzer with a standard technique described by

Ballard *et al.*[28]. Some specimens were also observed using a Leitz large polarizing microscope.

Measurements of ionic conductive properties of CPESE

The specimens were cut into circular plates with diameter of 13 mm and thickness of 1–2 mm. Conductivity measurements were carried out using two polished copper disks electrodes for all specimens by means of a DDS-11A conductometer at 1100 Hz after the specimens were completely dried under vacuum at 70°C, and dried in a desiccator with phosphorus pentoxide in it for at least 48 h. All measurements were conducted between ambient temperature and 100°C in the presence of P_2O_5. The rate of raising temperature was about 1–2°C/min unless cooling was labelled, in this case, the cooling rate was about 15°C/min. To calculate ionic conductivity (σ), sample area and thickness were taken into consideration to calibrate the electrode constant. The method of measurement was proved to be effective by the fact that the data obtained in the present condition is almost the same as that calculated by depicting the Cole–Cole plot measured with Hewlett-Packard 4275A Multi-frequency LCR Meter in the frequency range from 20 Hz to 10 MHz.

Direct synthesis and characterization of anhydrous ER fluids based on CPESE

ER fluids were directly synthesized by inverse suspension polymerization, i.e. to an oil phase involving PSR, AIBN, xylene and PDES, aqueous BMAPEG solution containing $LiClO_4$ or MAAM was added slowly with stirring. After stirring for 30 min, polymerization was initiated by heating in an N_2 atmosphere with stirring. Polymerization lasted for several hours at 70°C. Then, water and xylene were completely removed by azeotropic distillation under reduced pressure. The sample was finally dried in vacuum at 80°C for at least 24 h, and was put in a desiccator with P_2O_5 in it to cool to ambient temperature. Thus, the anhydrous ER fluid was obtained.

The method of measurements for content of particles is the same as that in our previous paper[6]. The weight percents of particles were fixed at 45.0 wt% in ER fluids in this paper. The particles in ER fluids were examined to be perfect sphere with diameter of 2.5–15.0 μm by using a JEOL.JMS-35C scanning electronic microscope.

### *Measurements of static yield stress (τ_s) and current density (J) of anhydrous ER fluids*

Static yield stress was determined by the static yield stress apparatus made by ourselves according to the literature[7,8] and calculated as $\tau_s = (mg - m_0 g)/S$, where mg is the load needed to cause the ER fluid to flow under electric field, $m_0 g$ the load needed to cause the ER fluid to flow without electric field, and S the electrode area ($1.5 \times 10^{-3} m^2$). The distance between the two electrodes is 1.0 mm. High DC voltage was supplied by a high voltage test transformer. Electric current (I) was monitored by a microamperemeter. Current density $J = I/S$.

RESULTS AND DISCUSSION

Conductivity of bi-ionic conductive cross-linked polyether solid electrolytes

The cross-linked polyether solid electrolytes synthesized by polymerization of BMAPEG in the presence of lithium perchlorate, consisting of cross-linked polyethers and $LiClO_4$, with conductive properties bi-ionic in character, are named the bi-ionic conductive cross-linked polyether solid electrolytes, and symbolized as CPESE2. The structure of CPESE2 is described in the following:
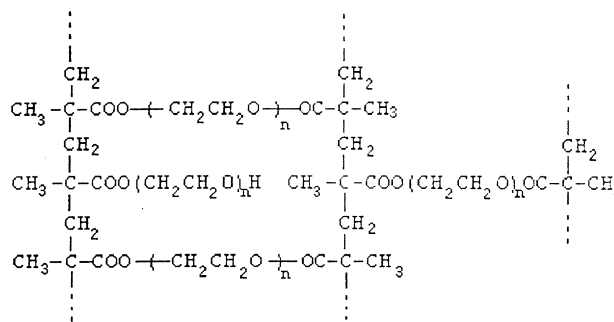
CPESE2 with molecular weight of PEG segments (M_{PEG}) not more than 1000 are fully amorphous because they only show a glass transition temperature (T_g), which decreases from -50°C to -56°C as M_{PEG} increases from 400 to 1000. However, CPESE2 with M_{PEG} of 2000 or 8000 shows both a melting endothermic peak at about 60°C and T_g. Together with polarized micrographs, which indicate clear spherulites, these d.s.c. results support that CPESE2 with M_{PEG} of 2000 and 8000 are semicrystalline polymeric solid electrolytes. *Figure 1* shows the dependence of conductivity of CPESE2 with different M_{PEG} on temperature. It is shown that the conductivity (σ) at 25°C goes through a maximum with increasing M_{PEG}. At $M_{PEG} \leq 1000$, the sequence of the increase of σ is in accordance with that of the decrease of T_g, thus the increase of σ with increasing M_{PEG} may be reasonable to result from the increase of the mobility of PEG segments, represented by T_g, and enhancement of migration of Li^+ complexed by O atoms in PEG chains.
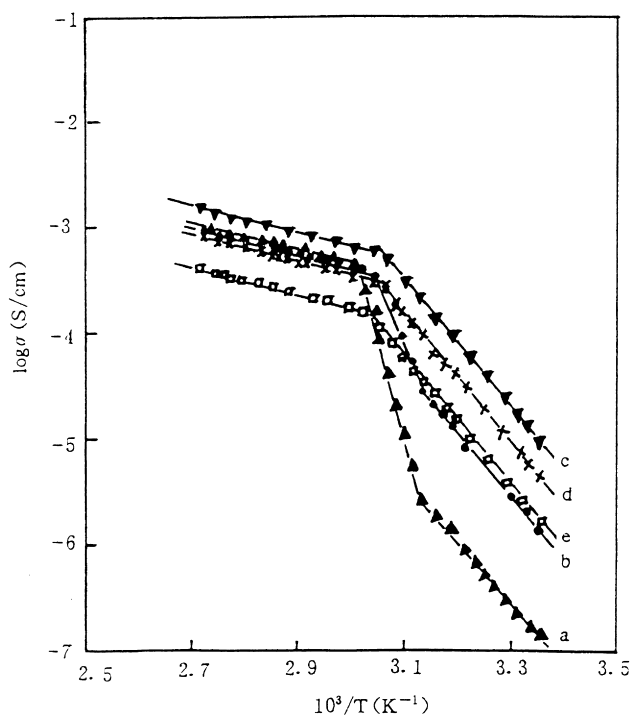

Figure 1 Logσ *versus* $1/T$ for CPESE2 containing different M_{PEG} of 400 (e); 600 (d); 1000 (c); 2000 (b); and 8000 (a)
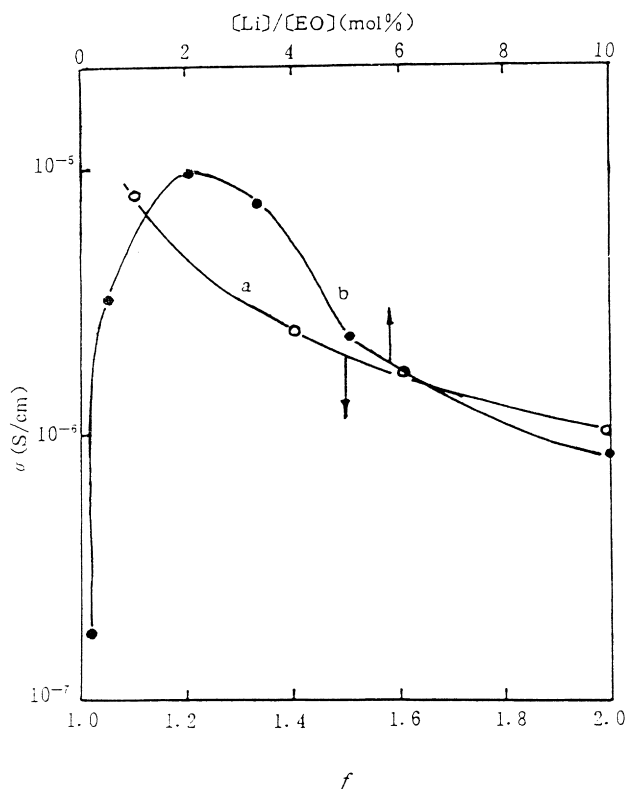
Figure 2 Influence of f (a) and [Li]/[EO] (b) on σ of CPESE2. $T = 25°C$

However, at $M_{PEG} > 1000$, with increasing M_{PEG}, σ decreases. This is owing to the crystallization of PEG, which hinders the motion of PEG segments. This interpretation, on the other hand, may be verified, at least to some extent, by the observation that CPESE2 with an M_{PEG} of 2000 or 8000 exhibits a conductivity as high as that of CPESE2 with M_{PEG} of 1000 when the temperature is raised over the melting point of the PEG crystals in the CPESE (about 60°C measured by d.s.c.). *Figure 1* also shows that σ increases with temperature, and that the relationship between $\log\sigma$ and $1/T$ is a broken line, and at $M_{PEG} \leq 1000$, with a knee indicating a transition to a lower activation energy for conduction at higher temperature. This knee may be attributed to the disintegration of locally organized complexed aggregates[35]. At $M_{PEG} > 1000$, with increasing T, the occurrence of phase transition from crystalline phase into amorphous phase makes $\log\sigma$ *versus* $1/T$ to go through two knees. Between these two knees, σ changes significantly. This phenomenon is owing to the rapid decrease of microviscosity as well as enhancement of the mobility of PEG segments and conductive pathways as a result of melting from crystalline phase into amorphous phase, which contributes to ionic conductivity.

Curve (a) in *Figure 2* shows the effect of functionality (f) of BMAPEG used in polymerization on σ of CPESE2. It can be seen that σ decreases with increasing f. It is well known that increasing f would decrease the number of graft PEG chains and increase the degree of crosslinking of CPESE2. However, the d.s.c. results show that T_g of CPESE2 is independent on f, thus, increasing the degree of crosslinking of CPESE2 by increasing f does not prevent the motion of PEG segments. This is different from that case of increasing the degree of crosslinking of CPESE2 by decreasing M_{PEG}, where T_g of CPESE2 increases with decreasing M_{PEG} at $M_{PEG} \leq 1000$. So, the decrease of σ is reasonable to result

from the decrease of the number of graft PEG chains, which could act as 'bridges' to connect the ionic conductive pathways separated by the chains containing methacrylol groups. In this case, it is reasonable to suppose that the graft PEG chains in CPESE2 would be helpful to promote the migration of Li^+ complexed by O atoms in PEG side-chains, hence increase σ. Together with the effect of M_{PEG} on σ, the contributions of graft PEG chain to ionic conductivity suggest that σ of CPESE2 does not mainly depend on the motion of PEG segments between two crosslinks, but also depends on graft PEG chains. This similar conclusion was also drawn by Hu *et al.* in research on graft polyether networks[36]. σ of CPESE2 with an f of 1.1 and M_{PEG} of 1000 reaches 8.0×10^{-5} S cm^{-1} at 25°C. This indicates that slightly cross-linked CPESE2 have relatively high ionic conductivity.

From curve (b) of *Figure 2*, for CPESE2 with M_{PEG} of 1000 and f of 1.1, with increasing complexing ratio [Li]/[EO], a maximum σ occurs at [Li]/[EO] = 2 mol%. That is to say, σ reaches a maximum not at [EO]/[Li] = 20, but at [EO]/[Li] = 50. The same results were observed in graft polyether networks[36] and some systems of branched 'comb' polymer containing PEO[37]. It is well accepted that σ depends on both the number and the immigration of charge carriers. Increasing [Li]/[EO], the number of charge carriers increases, so does σ at low value of [Li]/[EO]. On the other hand, when [Li]/[EO] is increased, it also increases the degree of aggregation of inorganic alkali salts[36] and microviscosity[31] owing to ion–dipole interaction between O atoms in PEG chains and alkali metal ions, thus decreasing the number of carrier ions and suppressing the mobility of carrier ions. Therefore, at [Li]/[EO] more than a critical value, i.e. 2 mol% for CPESE2, σ decreases with increasing [Li]/[EO].

Conductivity of single-ionic conductive cross-linked polyether solid electrolytes

Because of localization of ion pairs in the bi-ionic conductive solid electrolyte, its σ decreases under long-time subjection to DC current even when alkali metal nonblocking electrodes are used. This prevents the bi-ionic conductive solid electrolyte from being employed in high-performance devices for DC current in spite of its high ionic conductivity. On the other hand, the DC ionic conductivity of single-ionic conductive solid electrolytes shows excellent stability[31]. So, in this paper, in an attempt to overcome the disadvantage of the bi-ionic conductive polymer solid electrolytes mentioned above, we are also encouraged to synthesize another kind of cross-linked polyether solid electrolytes by copolymerization of BMAPEG and MAAM. The fact of the absence of feature peak at 1717 cm^{-1} for unsaturated C = C in the IR spectra of this kind of cross-linked polyether solid electrolytes films indicates that MAAM and BMAPEG were completely polymerized. Further, the absence of homopolymers of MAAM in this kind of cross-linked polyether solid electrolytes films was also confirmed by the IR spectra of water Soxhlet extract solutions with the absence of the characteristic peak of 1560 cm^{-1} for $\nu_{C=O}$ in the -COO$^-$M$^+$ group. On the other hand, at $M_{PEG} \leq 1000$, this kind of cross-linked polyether solid electrolyte shows only one glass transition temperature in the range from $-100°C$ to $+150°C$ in the d.s.c. profiles, and the polarizing micrographs, independent of counterions M$^+$ in MAAM, indicate no phase separation. Therefore, it is reasonable to suggest that this kind of cross-linked polyether solid electrolytes are single ionic-conductive polymer solid

electrolytes with only the desired cationic species as charge carriers owing to the fixation of the opposite charges -COO- on the polymeric matrix. Here, we called them single-ionic conductive cross-linked polyether solid electrolytes and symbolized them as CPESE1, where 1 represents single-ionic conductive, possibly with the following structure:
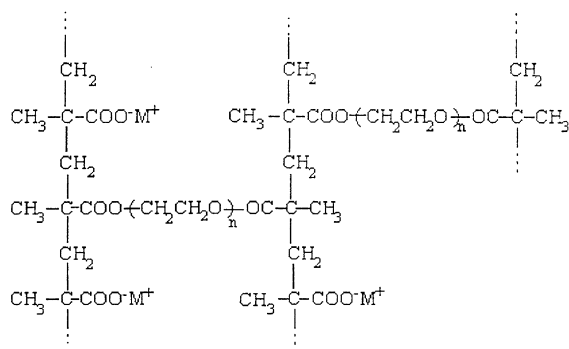
where $M^+ = Li^+$, Na^+ or K^+.

Figure 3 shows the relationship between $\log\sigma$ and $1/T$ for CPESE1 with different M_{PEG}. It can be seen that at 30°C, σ of CPESE1 with various M_{PEG} decreases in the following order: $PEG_{1000} > PEG_{600} > PEG_{400} > PEG_{2000}$. This observation is consistent with that for CPESE2 and can be explained by the same reasons for CPESE2, as discussed before. σ of CPESE1 containing PEG_{2000} is the minimum owing to the existence of strong crystallizing power. However, as temperature rises, σ increases rapidly, and at $T = 54°C$ or more, σ is higher than that of any others because the crystallites become amorphous. To clearly elucidate the effect of crystallite of PEG segments on σ, the changes of σ of CPESE1 containing PEG_{2000} during cooling (at cooling rate of about 15°C/min) from a high temperature are described as plot (e) in *Figure 3*. In a comparison of (a) and (e), it can be seen that at $T \geq 54°C$, σ measured during heating is almost the same as that measured during cooling. But, below 54°C, σ measured during cooling is obviously higher than that measured during heating. This may be explained by that at $T < 54°C$, although the polymeric solid electrolyte may have a tendency to crystallize, CPESE1 containing PEG_{2000} are cooled too quickly to crystallize. Thus, σ measured during cooling is higher.

Figure 4 shows that for CPESE1 synthesized by copolymerization of MAAM and BMAPEG, σ is affected by both the amount of comonomer MAAM and the type of counterions. A maximum σ (σ_{max}) occurs in each system with increasing [MAAM]/[EO]. This is similar to CPESE2, and the reasons have already been discussed. The σ_{max} of CPESE1 with different counterions fits the following order: $Li^+ \approx K^+ > Na^+$; while the value of [MAAM]/[EO] corresponding to σ_{max} decreases in the following order: $Li^+ > Na^+ > K^+$. The former phenomenon may possibly be connected with the compensation of two factors, namely, the migrating resistance and dissociation energy of counterions, because with increasing counterion radius (r_{M^+}), on one hand, the migrating resistance of M^+ increases thus decreasing σ, on the other hand, the dissociation energy of M^+ decreases thus increasing σ. The latter phenomenon is in agreement with the increasing order of r_{M^+} because the number of EO units needed to complex M^+ increases with increasing r_{M^+}.

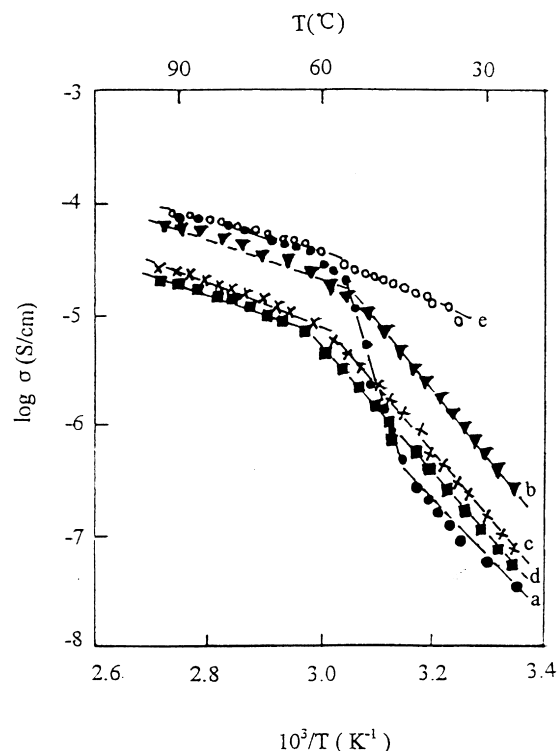Similar to σ of CPESE2, σ of CPESE1 also decreases with

Figure 3 $\log\sigma$ *versus* $1/T$ for CPESE1 with M_{PEG} of 2000 (a); 1000 (b); 600 (c); 400 (d); 2000 (e, cooling). [EO]/[MAAM] = 50, $f = 2.0$

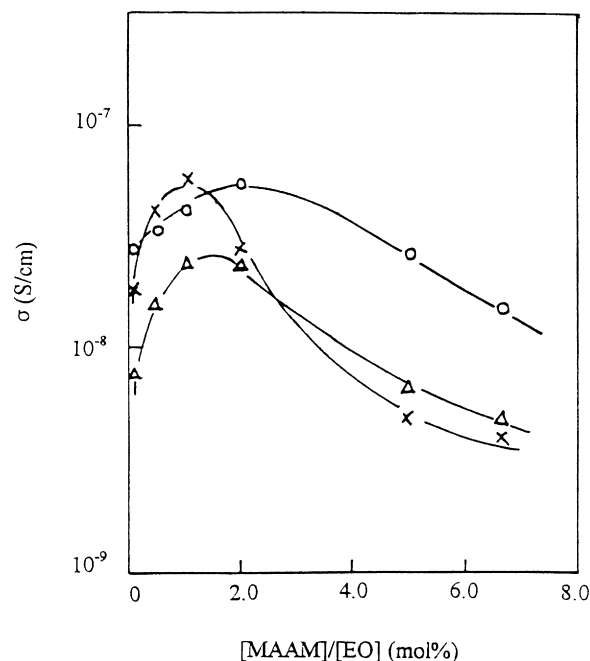**Figure 4** Influence of [MAAM]/[EO] on σ of CPESE1 containing M^+: Li^+ (O); Na^+ (△); K^+ (×). $T = 30°C$, $f = 2.0$, $M_{PEG} = 2000$

increasing f for BMAPEG used. At f of 1.1 and $M_{PEG} = 1000$, σ of CPESE1 with counterion of Li^+ reaches 4.0×10^{-6} S cm^{-1} at 30°C, which is not the half of the σ for CPESE2, but less than that of CPESE2 by more than one order. This can be explained by considering two aspects. First, there are only one kind of ion, M^+, used as charge carriers in CPESE1, but two in CPESE2. Second, counter anions of alkali metal ions strongly influence the
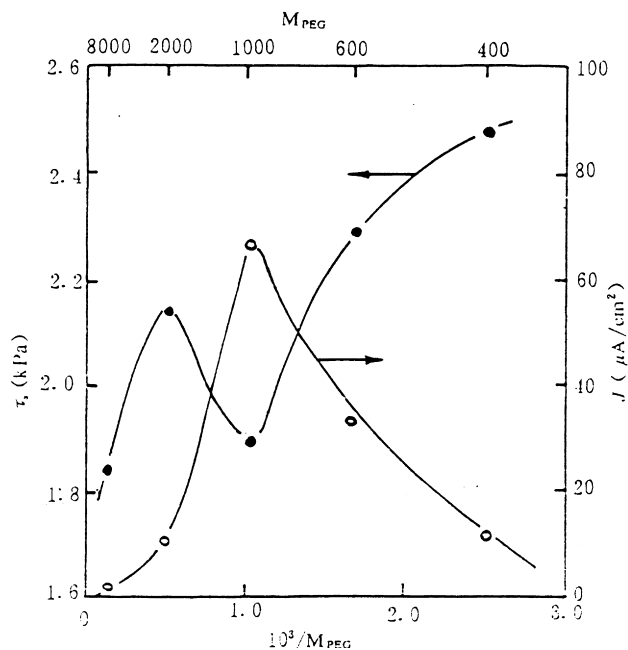
Figure 5 Influence of M_{PEG} on τ_s and J for ER fluids of CPESE2 in PDES at E of 2.8 kV mm^{-1}. [Li]/[EO] = 1 mmol mol^{-1}, $f = 2.0$
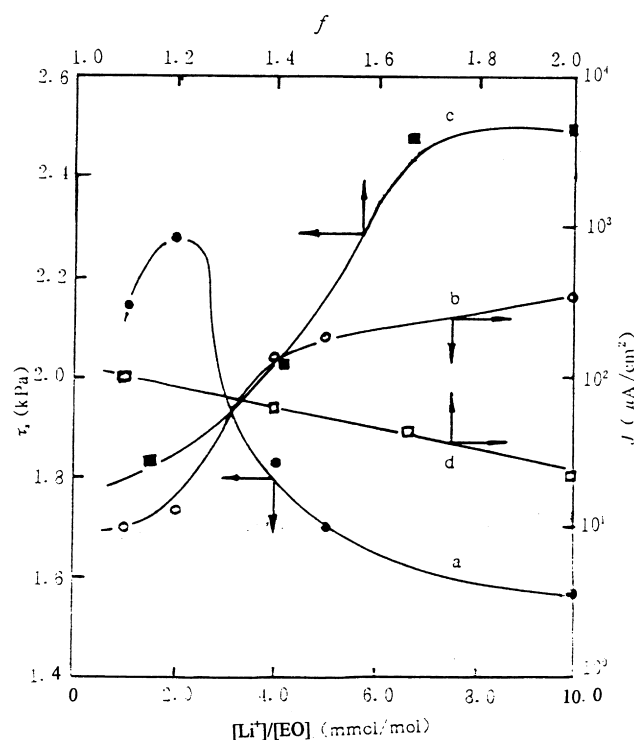

Figure 6 Influence of [Li]/[EO] (a and b) and f (c and d) on τ_s and J for ER fluids of CPESE2 in PDES at E of 2.8 kV mm^{-1}. $M_{PEG} = 2000$, $f = 2.0$ (a and b); $M_{PEG} = 400$, [Li]/[EO] = 1 mmol mol^{-1} (c and d)

conductivity of the polymer solid electrolytes with the formation of ion-pairs resulting in a decrease of σ[38], and counter anions in CPESE1 have a strong tendency to form ion-pairs owing to the simple electrostatic repulsive effect of –COO$^-$ of polymer chain rather than ClO$_4^-$ in CPESE2.

ER properties of suspensions based on CPESE2

Figure 5 shows the effect of molecular weight of PEG segments on the static yield stress (τ_s) and current density

(J) for the anhydrous ER fluids containing CPESE2 with different M_{PEG}. It can be seen that with increasing M_{PEG}, the changes of τ_s is intricate; τ_s exhibits a maximum as well as a minimum. In contrast, J only goes through a maximum with increasing M_{PEG}, this is in agreement with the relationship between σ of CPESE2 and M_{PEG}. So, it is reasonable to suggest that J is predominantly determined by σ. At $M_{PEG} \leq 1000$, the mobility of PEG segments increases with increasing M_{PEG}, thus increasing long-range mobility of ions or migration of ions between particles, and decreasing the 'local field' as well as effective polarization of particles. Consequently, τ_s for ER fluids decreases and J increases. However, at $M_{PEG} > 1000$, CPESE2 can have strong power to crystallize, eliminating the amorphous phase, thus with increasing M_{PEG} long-range migration of ions to neighbouring particles is initially hindered and increases the local field, then even short-range migration of ions and effective polarization of particles are also deeply prevented. As a result, a maximum τ_s occurs, following initial increase of τ_s, and J decreases. Thus, it is reasonable to suppose that the complicated relationship between τ_s and M_{PEG} is related with polarization caused by migration of charge carriers, which strongly depends on a number of factors such as crosslinking degrees of polymer, mobility of PEG segments, crystallization phases and local field etc. The maximum J corresponding to the minimum τ_s at the same M_{PEG}, to some extent, gives support to the suggestion that J in ER fluids may possibly lead to a decrease in local field and τ_s.

It is known that at [Li$^+$]/[EO] < 1 mol%, the increase of [Li$^+$]/[EO] mainly causes an increase in the number of charge carriers, thus improving σ (*Figure 2*). From curves (a) and (b) of *Figure 6*, it can be seen that with increasing [Li$^+$]/[EO], τ_s for ER fluids exhibits a maximum value, while J increases monotonically. It is reasonable to suppose that a maximum τ_s occurs with increasing σ of particles. The same results were demonstrated in ER fluids based on electronic semiconductors[11,39], for example polyaniline, about which we discussed the relationships between τ_s for ER fluids and σ of particles in detail in terms of the 'conductivity effect'[11]. However, to explain the occurrence of maximum τ_s with increasing σ, Block et al.[39] have assumed that ER effect depends on not only polarization strength, but also polarization rate of particles.

From curves (c) and (d) of *Figure 6*, it is shown that with increasing f of BMAPEG used, τ_s increases and J decreases owing to the reduction of the number of graft PEG chain, which act as 'bridges' to connect the ionic conductive pathways and would be helpful to promote long-range migration of ions or migration of ions between particles rather than short-range mobility ions or ionic migrating polarization. In this case, we may consider that the number as well as the length of graft PEG chain play an important role in destroying ER effect and increasing J of ER fluids. This once more supports the idea that the growth of crosslinking degrees of particles, either by decreasing M_{PEG}, where the length of bridges is shortened, or by increasing f of BMAPEG used, where the number of bridges is reduced, primarily prevents migration of ions between particles, and enlarges the local field, and has little effect on short-range mobility of ions or ionic migrating polarization.

ER properties of suspensions based on CPESE1

As in the case of ER fluids containing CPESE2, properties for ER fluids containing CPESE1 depend on both molecular weight of PEG segments and functionality (f) of BMAPEG used. *Figure 7* demonstrates that both τ_s
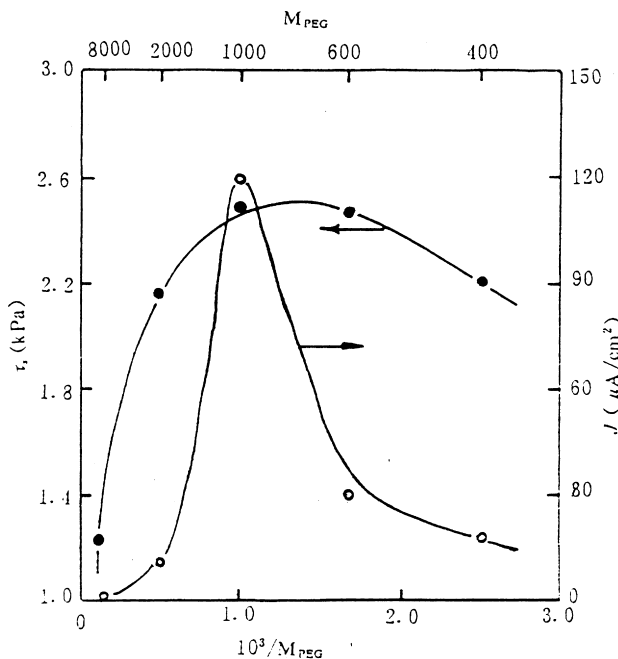
Figure 7 Influence of MPEG on τ_s and J for ER fluids of CPESE1 in PDES. [MAAM]/[EO] = 5.0 mol%, f = 2.0, E = 2.8 kV mm^{-1}
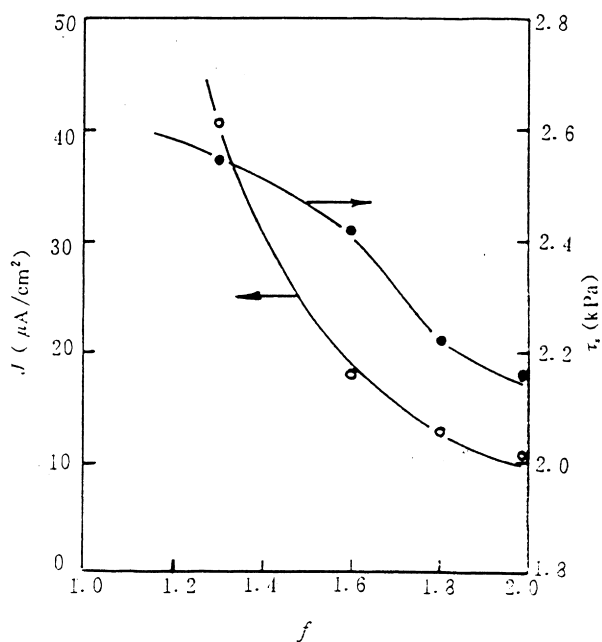

Figure 8 Influence of f on τ_s and J for ER fluids of CPESE1 in PDES. M_{PEG} = 2000, other conditions are the same as in *Figure 7*

Figure 9 Influence of [MAAM]/[EO] on τ_s and J for ER fluids of CPESE1 with M$^+$ of Li$^+$ ($\bullet$, $\circ$); Na$^+$ ($\blacktriangle$, $\triangle$); K$^+$ ($\blacksquare$, $\square$). M_{PEG} = 2000, other conditions are same as in *Figure 7*

and J for ER fluids containing CPESE1 go through a maximum value with increasing M_{PEG}. As mentioned before, CPESE1 produces more easily crystallites with increasing M_{PEG}. Thus, these phenomena may be explained by the decrease of σ of particles, with increasing crystallizing power for CPESE1, because τ_s shows a maximum value with decreasing σ of particles. From *Figure 7*, it can be further seen that J depends on M_{PEG} more strongly than τ_s, especially at M_{PEG} below 2000. It is reasonable to suggest that for ER fluids containing CPESE1, of which the conductive properties are single-ionic in character, M_{PEG} has little effect on τ_s as well as the local field in ER fluids.
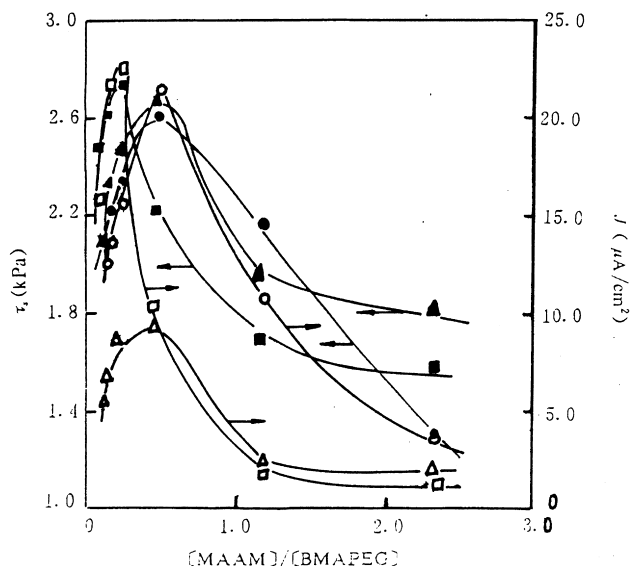
Figure 8 indicates that both τ_s and J for ER fluids containing CPESE1 decreases monotonously with increasing f, whereas the amplitudes that τ_s decreases is by far less than that J decreases. It is reasonable to suggest that with increasing f of BMAPEG used in polymerization or crosslinking degrees of CPESE1, the mobility of both Li$^+$ and the PEG segments, which determines ionic migrating polarization of particles and migration of ions to the neighbouring particles, is impeded, resulting in a decrease of both τ_s and J, because τ_s is proportional to ionic migrating polarization of particles, and J is related with migration of ions to the neighbouring particles. The latter result implies that by adjusting f, the loss energy that ER fluids consume to get ER effect or τ_s can be decreased a lot in the condition that τ_s decreases a little. That is to say, with increasing f of BMAPEG used, the efficiency of ER fluids, which is proportional to τ_s/J, will be improved.

Figure 9 shows the effects of the amount of comonomer MAAM used in polymerization on τ_s and on J for the ER fluids containing CPESE1 in PDES, respectively. It is evident that τ_s and J both reach a maximum value with increasing [MAAM]/[EO] in each ER fluid, just as a maximum σ of CPESE1 occurs with increasing [MAAM]/[EO]. For ER fluids of CPESE1 with its counterions of K$^+$, the maximum values of both τ_s and J occur at a lower [MAAM]/[EO] than that for those of CPESE1 with its counterions of Li$^+$ or Na$^+$ owing to its largest radius of K$^+$. The type of its counterions has almost no effect on the maximum τ_s, but shows strong effect on the maximum J (J_{max}). J_{max} decreases in the following order: K$^+$ $\approx$ Li$^+$ > Na$^+$. This can be attributed to the compensation of such factors as the dissociation energy and migrating resistance of counterions. It is reasonable to conclude that from the efficiency of ER fluids, which is proportional to τ_s/J, the ER fluid synthesized by copolymerization of BMAPEG with the optimum amount of Na-MAA has superior comprehensive ER properties than those synthesized by copolymerization of BMAPEG with Li-MAA or K-MAA.

CONCLUSION

Both the bi-ionic conductive cross-linked polyether solid electrolyte with conductivity (at 25°C) of 8.0×10^{-5} S cm^{-1} and the single-ionic conductive CPESE with σ (at 30°C) of 4.0×10^{-6} S cm^{-1} can be obtained by polymerizing BMAPEG in the presence of LiClO$_4$ or MAAM, respectively. σ decreased with increasing functionality of BMAPEG while σ increases with T, and the relationship between log σ and $1/T$ was a broken line. The maximum σ occurred at an optimum value of both molecular weight of PEG segments and the [Li$^+$]/[EO] or [MAAM]/[EO].

The CPESE1 or CPESE2 based anhydrous electrorheological (ER) fluids with somewhat high ER activity can be synthesized directly by inverse suspension polymerization followed by azeotropic distillation. ER properties can be improved by increasing crosslinking degree of CPESE particles, and the influence of molecular structure of particles on ER properties can be explained in terms of the dependence of ER properties on conductivity of particles. ER fluids containing CPESE1 with its counterions of Na$^+$ have superior comprehensive ER properties than those of Li$^+$ or K$^+$.

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