polymer

Ionic conductivity of alkali-metal carboxylated dendritic poly(amidoamine) electrolytes and their lithium perchlorate salt complex

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Abstract

The ionic conductive dendrimer electrolytes, prepared by the terminal alkali-metal (Li^+, Na^+, K^+) carboxylation of poly(amidoamine) (PAMAM) of generation 2.5 and 3.5, exhibit a conductivity of 10^{-5}–10^{-6} S cm^{-1} at 30°C. The temperature and frequency dependence of ion conductivity are investigated. It is found that the temperature dependence fits neither the WLF mechanism nor the Arrhenius equation; this is attributed to the unique molecular structure of the dendrimer. Blending of lithium carboxylated PAMAM with lithium perchlorate is carried out and results in improved conductivity. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Dendritic electrolyte; Ionic conductivity; Alkali-metal carboxylated dendritic poly(amidoamine)

1. Introduction

Since the first polymer–salt electrolyte complexes of polyethers with alkali-metal salts were reported in 1970s by Wright [1] and Armand [2], great attention has been paid to these polymer electrolytic systems. In the last 20 years a great number of polyelectrolytes based on linear-chain matrices, with high ionic conductivity, the highest value reached being 10^{-3} S cm^{-1}, such as polyethers, poly(ethylene oxide) or poly(propylene oxide) have been prepared by hybridizing [3], adding plasticizers or small molecular salts [4–7], co-blending or grafting modification [8–10].

However, since these matrices are bi-ion conductors, if such a material is used in an electrochemical device involving direct current the motion of the anions will offset the property of the device by forming a polarized potential opposing the applied voltage. An efficient solution to this problem is to design single-ionic conductors with the opposite anions fixed covalently in the macromolecules [11–22]. The study of single-ionic conductors has been reviewed in detail [11]. These materials can be divided into blends [12,13], copolymers [14–16], networks [17–19] and homopolymer systems [20–22].

Recently dendrimers, a relatively new class of macromolecules, have been attracting great attention. Their highly branched, monodisperse structures and globular, void-containing shapes make them interesting and important building blocks in synthesis. Tomalia et al. [23] reported the preparation of the carboxylate-terminated PAMAM dendrimers with Group I metals (e.g. Na^+, K^+, Cs^+ or Rb^+) for the direct observation and measurement of single dendrimer molecules by electromicrography. They reported in another paper [24] the complex formation between poly(dimethyldiallylammonium chloride) and carboxylated starburst dendrimer, and described the host–guest interaction at the external surfaces of carboxylate-terminated PAMAM dendrimers. These host–guest complexes were also considered by Tomolia et al. as models of polyelectrolytes. In fact, the alkali-metal carboxylate-terminated PAMAM dendrimer is a fascinating structural homopolymer electrolyte which shows some interesting features such as the nanoscopic sizes of the dendrimer molecules, cavernous interiors and the terminal carboxylate functional groups concentrated on the spherical surfaces. In the present paper, we report the single-ionic conductivity of alkali-metal (Li^+, Na^+, K^+) carboxylated poly(amidoamine) (CPAMAM) prepared by hydrolysis of PAMAM (generation 2.5 or 3.5) with alkali-metal hydroxide. The carboxylate-terminated PAMAM homopolymers obtained are briefly expressed here as CPAMAM-*X*M (*X*: generation 2.5 or

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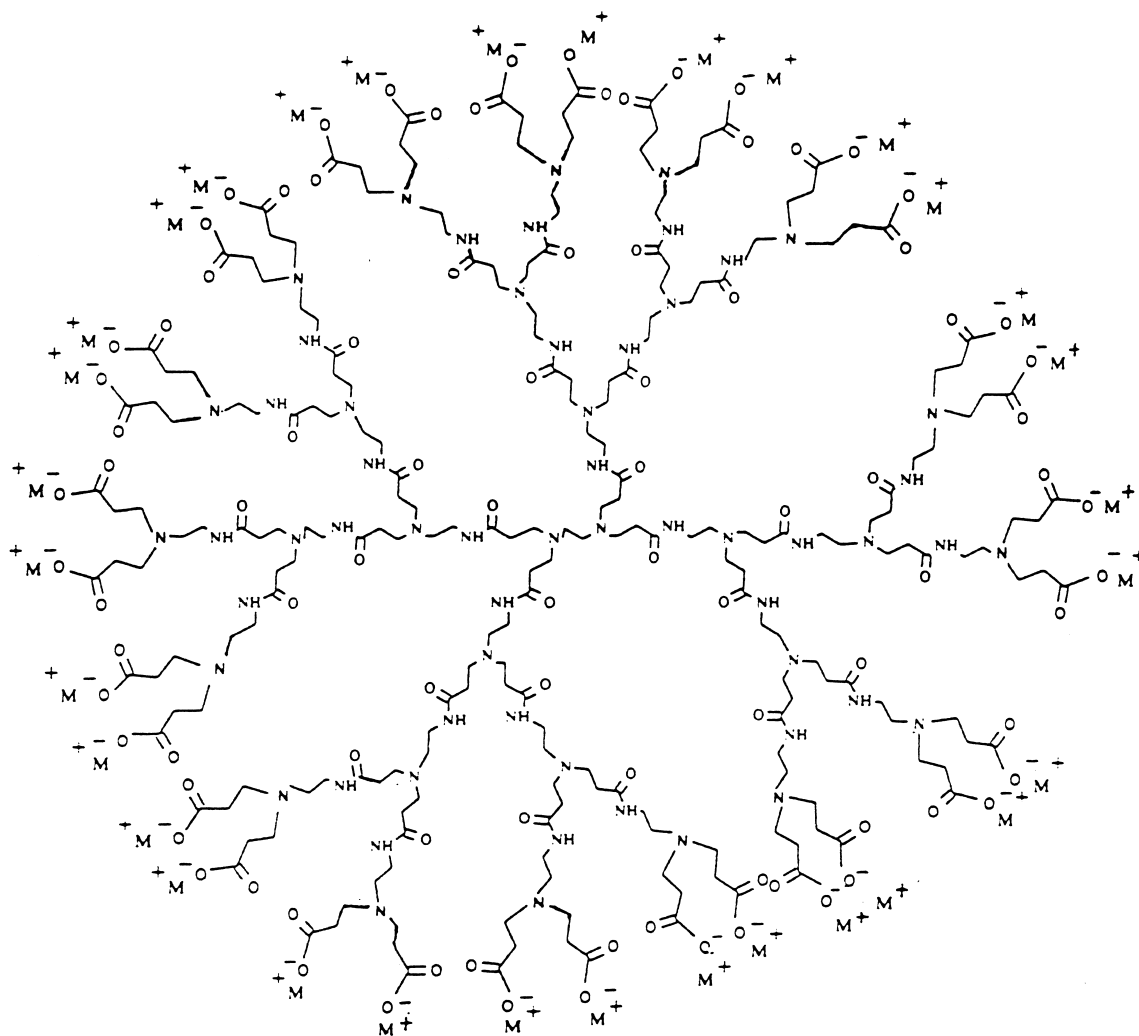
CPAMAM-2.5*M*

Scheme 1.

3.5; M: alkali-metal cations, Li$^+$, Na$^+$, K$^+$). The perfect structure of CPAMAM-2.5M is shown in Scheme 1.

2. Experimental

2.1. Materials

Poly(amidoamine) generation 2.5 (molecular weight = 6004) and 3.5 (molecular weight = 12 404) were synthesized according to the literature [23]. All reagents were anhydrous and kept in a 4 Å molecular sieve. Alkali-metal hydroxides were dried in a vacuum oven before use.

2.2. Synthesis

A typical preparation is as follows. A 25 ml flask, equipped with a magnetic stirring bar, was charged with PAMAM generation 3.5 (8.06×10^{-5} mol) solution in 5 ml methanol and a stoichiometric amount of lithium hydroxide (5.16×10^{-3} mol). The reaction mixture was stirred under nitrogen at room temperature for 28 h, and then distilled under reduced pressure to dryness. The crude product was purified by dissolving in a small amount of methanol and precipitating in ethyl ether three times. After the Li-salt of CPAMAM (CPAMAM-3.5Li) was collected by filtration and dried in vacuum for 48 h, a white solid powder (0.95 g) was obtained.

2.3. Characterization

Fourier transformed-IR spectra reveal that the characteristic carbonyl absorption peaks around 1730 cm^{-1} in the terminal methyl ester groups of CPAMAM-2.5 or CPAMAM-3.5 have completely disappeared (see Fig. 1). The absorption of new formed carbonyl groups in terminal carboxylates are shown at 1571 (–COOLi), 1567

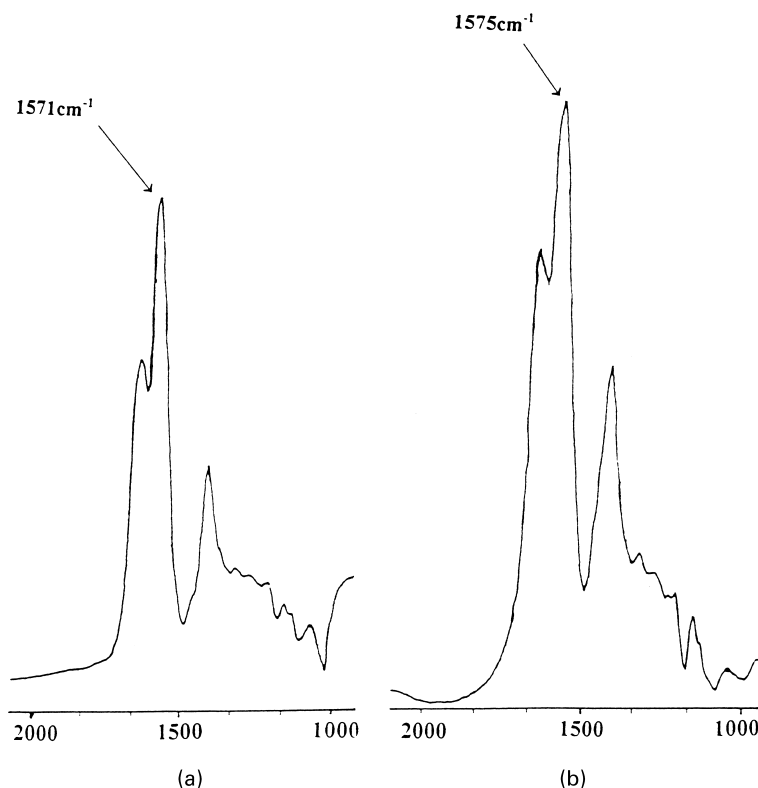Fig. 1. FT-IR spectra of carbonyl regions of: (a) CPAMAM-2.5Li; and (b) CPAMAM-3.5Li.

(–COONa) and 1569 cm^{-1} (–COOK) for CPAMAM-2.5M; and at 1575 (–COOLi), 1571 (–COONa), 1573 cm^{-1} (–COOK) for CPAMAM-3.5M.

^{1}H NMR spectra (see Fig. 2) give characteristic patterns that show –CONH– at δ 2.22–2.33 ppm (120H), –NCH$_2$– at δ 2.51–2.67 ppm (180H) and –CONCH– at δ 3.19–3.21 ppm (56H) for CPAMAM-2.5Li, and –CONH$_2$ at δ 2.20–2.39 ppm (248H), –NCH$_2$ at δ 2.47–2.68 ppm (372H) and –CONCH– at δ 3.16–3.20 ppm (120H) for CPAMAM-3.5Li. The absorption peak for –OCH$_3$ disappears, and the integral area ratio of hydrogen protons at different circumstances coincides with its theoretical value.

2.4. Complex electrolytes preparation

The blends of CPAMAM-XLi (X = 2.5 or 3.5) with lithium perchlorate (treated in a vacuum oven at 80, 100 and 150°C for 24 h before use) were prepared by dissolving them in anhydrous methanol with the desired composition. After a clear solution was formed, the solvent was removed by distillation and the product was dried in vacuum for at least 48 h in order to obtain a white solid mixture.

2.5. Measurement

Fourier transformed-IR spectra were recorded on a Perkin–Elmer 2000 spectrometer. ^{1}H NMR spectra were carried out on a Varian 300 MHz spectrometer in CDCl$_3$ at room temperature. A DSC scan was conducted under a nitrogen atmosphere using a Perkin–Elmer DSC-7 differential scanning calorimeter at a heating rate of 20°C min^{-1}. X-ray diffraction patterns were obtained on a Rigaku D/max-3B diffractometer with 0.154 nm wavelength of CuK$_\alpha$ radiation.

Ionic conductivity was determined in parallel-connection measurement mode using a HIOKI 3520 LCR Hi tester over the frequency of 1–100 kHz. The disc sample (13 mm in diameter and 0.6 mm thick) was sandwiched between two stainless steel electrodes. Impedance spectra were obtained using an HP 4192A LF impedance analyser over the frequency of 5 Hz–13 MHz. The output voltage was 10 mV. All the operation was in a drying box filled with argon gas. The temperature dependence of conductivity was determined over the temperature range 30–80°C. Before each measurement, the sample was kept at the constant temperature for at least 30 min.

3. Results and discussion

3.1. Frequency response of CPAMAM-XM (X: 2.5 or 3.5; M: Li$^+$, Na$^+$ or K$^+$)

Ionic conductivity values of CPAMAM-XM were measured under an alternating current. The plots of ionic

(a)

-CONCH$_2$

-NCH$_2$

-CONH$_2$

ppm 5 4 3 2 1 0
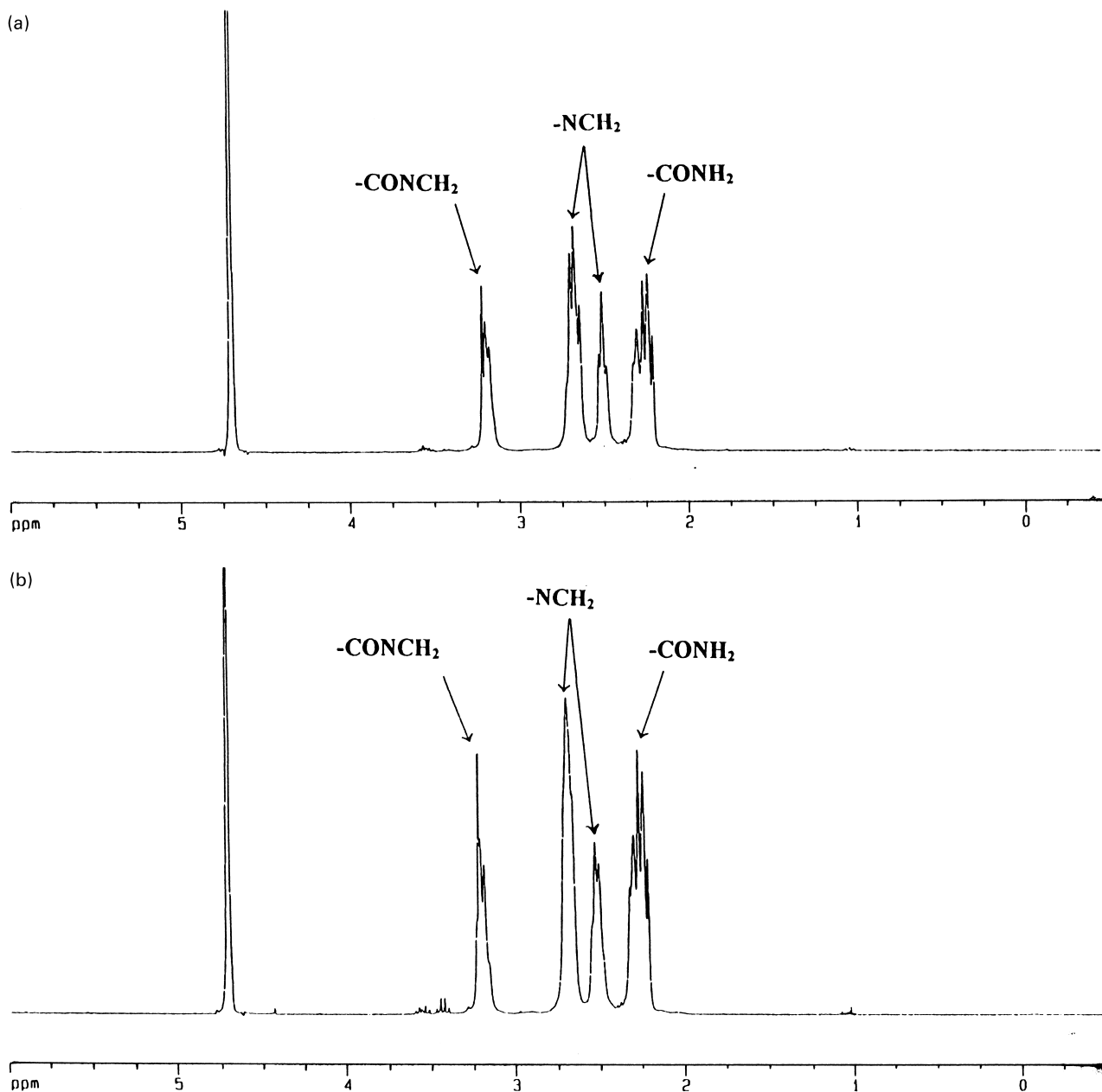
(b)

-CONCH$_2$

-NCH$_2$

-CONH$_2$

ppm 5 4 3 2 1 0

Fig. 2. ^{1}H NMR of: (a) CPAMAM-2.5Li; and (b) CPAMAM-3.5.

conductivity vs. frequency (1–100 kHz) of CPAMAM-XM at different temperatures are shown in Fig. 3.

With increasing frequency, the ionic conductivity of all the samples increased in the range of 1–100 kHz. Among them the CPAMAM-3.5Li, CPAMAM-3.5Na, CPAMAM-3.5K and CPAMAM-2.5Li appear at a peak value of around 60–80 kHz, in which the peak value of CPAMAM-3.5Li at 80 kHz had even surpassed its conductivity value at 100 kHz, while the samples CPAMAM-2.5Na and CPAMAM-2.5K did not show any obvious peak value in their plots. In order to compare all samples against the same standard, the measurements of conductivity vs. other factors were carried out at 100 kHz.

3.2. Ionic conduction of CPAMAM-XM (X: 2.5 or 3.5; M: Li$^+$, Na$^+$ or K$^+$)

The dependence of ionic conductivity of CPAMAM-XM on temperature is shown in Fig. 4. The results for all the homopolymers do not comply with a simple relationship of conductivity vs. temperature. As temperature increased, their ionic conductivity at first kept a relatively constant value, then, usually after 50°C, the ionic conductivity values decreased. This phenomenon is quite different from that reported for linear or comb-like polyelectrolytes, where their conductivity increased while the temperature increased. As a result, it seems that the relationship of
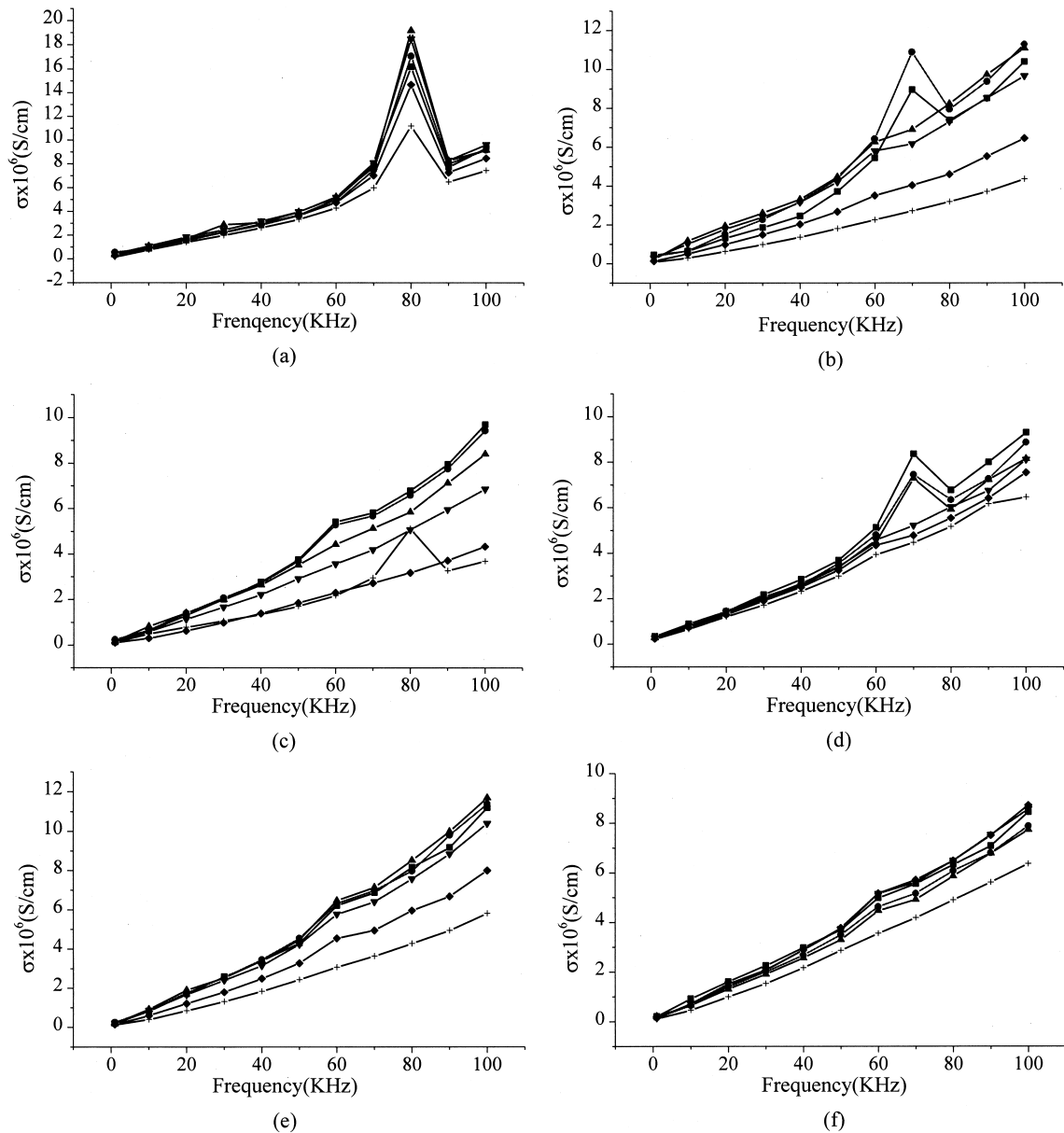
Fig. 3. The dependence of ionic conductivity ($\sigma \times 10^6$ S cm^{-1}) vs. frequency (kHz) for CPAMAM-*X*M at the temperature of 30°C (■), 40°C (●), 50°C (▲), 60°C (▼), 70°C (◆) and 80°C (+): (a) CPAMAM-3.5Li; (b) CPAMAM-3.5Na; (c) CPAMAM-3.5K; (d) CPAMAM-2.5Li; (e) CPAMAM-2.5Na; and (f) CPAMAM-2.5K.

conductivity vs. temperature for CPAMAM-*X*M systems coincides with neither the WLF formula nor the Arrhenius equation. On the other hand, the decline of conductivity was not so rapid as that in PEO systems. In the range of experimental temperatures, 30–80°C, the highest value for CPAMAM-*X*M was 10^{-5} S cm^{-1} and the lowest value was 10^{-6} S cm^{-1}, both of which are higher values than that reported so far for a polyelectrolyte "homopolymer" without any additives.

By contrast, the disparity in ionic conductivity of CPAMAM-3.5M and CPAMAM-2.5M, which contain the same alkali-metal ions, is not very distinct, but there is still a slight difference in conductivity between them and even

between the same system with different ions as shown in Fig. 4(a) and (b). Both CPAMAM-3.5Na and CPAMAM-2.5Na have a peak value (1.11×10^{-5} S cm^{-1} for PAMAM-3.5Na and 1.17×10^{-5} S cm^{-1} for PAMAM-2.5Na) appearing at 40 and 50°C, respectively. In other homopolymers, only CPAMAM-3.5Li and CPAMAM-2.5K present the peak values (9.36×10^{-6} S cm^{-1} for CPAMAM-3.5Li and 8.73×10^{-6} S cm^{-1} for CPAMAM-2.5K) at 50 and 70°C, respectively, while CPAMAM-3.5K and PAMAM-2.5Li do not appear at the peak value of 30–80°C, and their highest conductivity values (9.72×10^{-6} S cm^{-1} for CPAMAM-3.5K and $9.32 \times 10 - 6$ S cm^{-1} for CPAMAM-2.5Li) are detected at 30°C. Though all samples have a
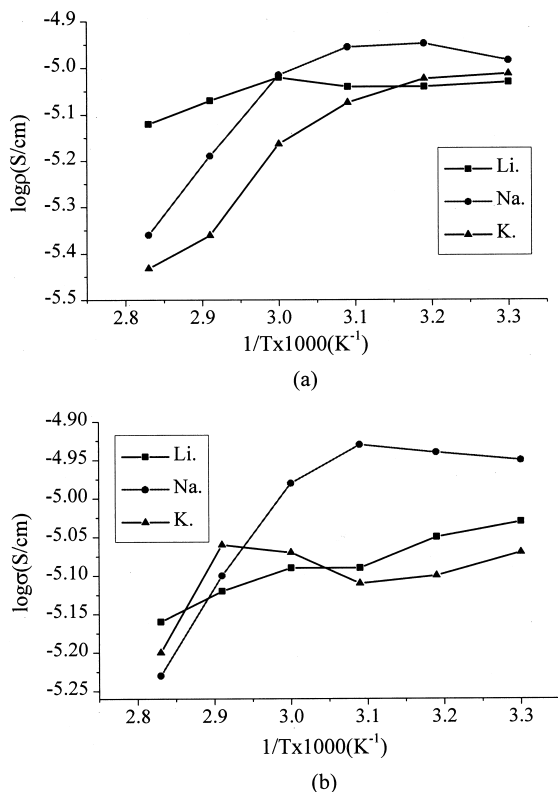
Fig. 4. The dependence of conductivity (log σ) vs. temperature (1/T × 1000) for CPAMAM-XM: (a) CPAMAM-3.5M; and (b) CPAMAM-2.5M.

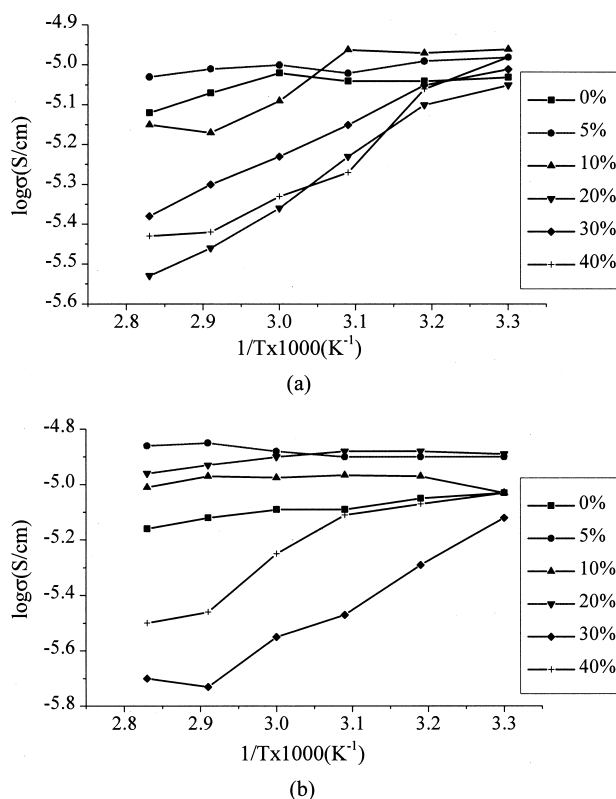

Fig. 5. The dependence of ionic conductivity vs. temperature for: (a) PAMAM-3.5Li; and (b) PAMAM-2.5Li blends with different concentrations of LiClO$_4$ (0, 5, 10, 20, 30 and 40%).

tendency of conductivity reduction as temperature increases, an interval still exists when their conductivity does not decline until the temperature at which their peak values appear is reached. Then above this temperature, their conductivities decrease to their lowest values (3.70–7.46 × 10^{-6} S cm^{-1}) at 80°C.

From the description above, it might be concluded that CPAMAM-XM homopolymers show three distinct conductivity properties: firstly, their conductivity values are relatively high at room temperature; secondly, their dependence of conductivity on temperature complies with the different laws before and after the peak temperature value; and finally, they are a kind of fast ionic conductor and their highest conductivity values appear at high frequency.

3.3. Correlation between thermal behaviour and ionic conductivity of CPAMAM-XLi

Analysis of two typical homopolymers, CPAMAM-2.5Li and CPAMAM-3.5Li using DSC, shows that only the glass translation is observed over the temperature range of 0–200°C, with a characteristic typical of completely amorphous polymers. The T_g is shown at 104 and 159°C for CPAMAM-3.5Li and CPAMAM-2.5Li, respectively. Although the T_g of CPAMAM-3.5Li is 55°C lower than that of CPAMAM-2.5Li, its ionic conductivity (see Fig. 4(a) and (b)) is just a little higher than that of the latter.

This phenomenon is quite different from that of linear and comb-like polyelectrolytes, where with the decline of glass transition temperature there is a notable increase in their ionic conductivity [20–22].

3.4. Ionic conduction of CPAMAM-XM with varying amounts of LiClO$_4$

In order to investigate the effect of small molecular inorganic salt additives on the ionic conductivity of PAMAM-XM systems, CPAMAM-XLi (X = 2.5 or 3.5) was chosen as a matrix polymer and was blended with varying amounts of lithium perchlorate (LiClO$_4$/PAMAM-XLi wt% = 5, 10, 20, 30, 40). The dependencies of ionic conductivity on the temperature for the different LiClO$_4$ contents are shown in Fig. 5. All plots have similar regularity to their homopolymers in that the ionic conductivity decreases as the temperature increases. The decline of conductivity vs. temperature for higher concentrations of lithium perchlorate is more rapid than for lower concentrations. The influence of LiClO$_4$ content on the ionic conductivity is shown in Fig. 6.

Compared with CPAMAM-2.5Li or CPAMAM-3.5Li, the conductivity of the blended system has been slightly improved from 10^{-6}–10^{-5} S cm^{-1}, over all experimental temperatures, at lower contents of LiClO$_4$. At higher
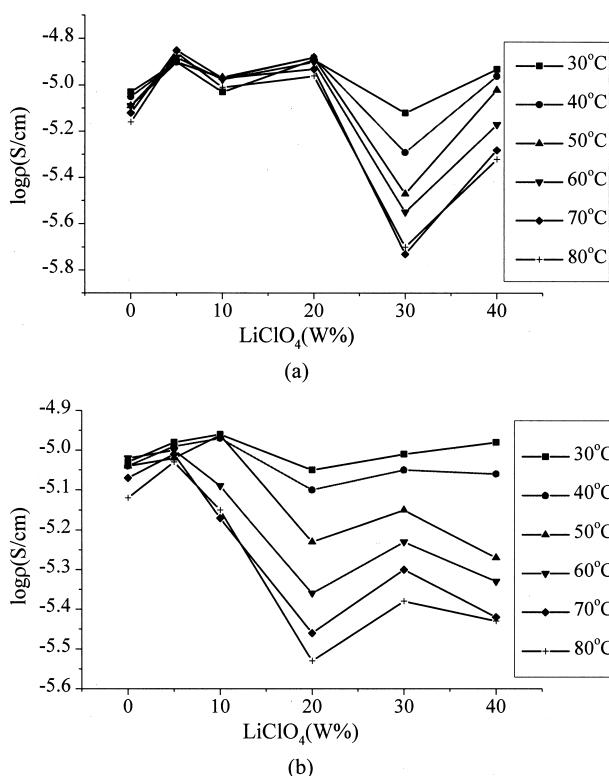
Fig. 6. The dependence of conductivity vs. LiClO$_4$ content in: (a) CPAMAM-3.5Li; and (b) CPAMAM-2.5Li from 30–80°C.

contents of LiClO$_4$, the conductivity behaviour becomes more complicated.

The typical impedance spectra obtained are depicted in Fig. 7.

3.5. X-ray diffraction analysis of CPAMAM-XM

In order to explore the influence caused by a crystal state that might exist in the samples, the CPAMAM-3.5Li and its blends are taken for X-ray diffraction analysis. The results show that all samples detected are in an amorphous state even at higher contents of LiClO$_4$ (Fig. 8).

3.6. Conduction mechanism of dendritic electrolytes

In general, the conductivity of the single-ionic conducting polymer electrolytes is influenced by several factors, including the number of charge carriers and the morphological structure of polymer. A low glass transition temperature is also especially important, i.e. the flexible main chain backbone of polymer would be favourable to the ion transport. A typical phenomenon for ordinary ion conductive electrolytes, such as linear comb-like and cross-link electrolytes, is that with rising temperature, their ion conductivity is correspondingly increased [14–16]. However, in our present work, the dendritic polymer ionic conducting system exhibits more specific and more complicated conducting behaviour, which is estimated to be attributed to the unique molecular structure of the dendrimer that is
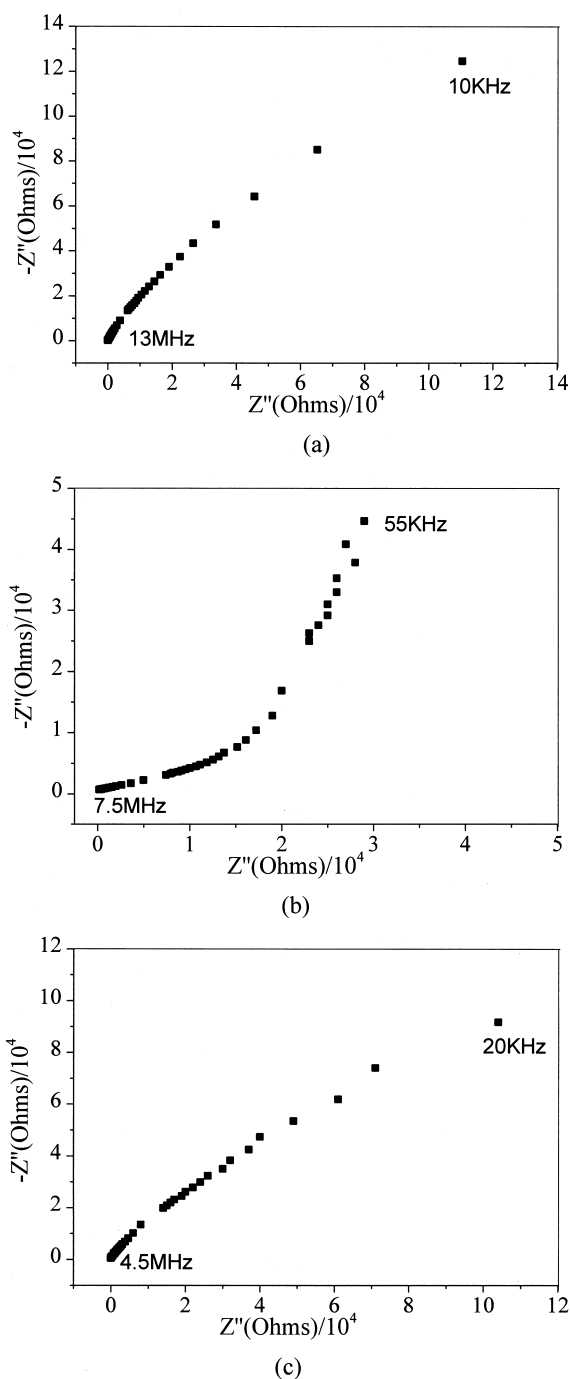

Fig. 7. Impedance spectra of: (a) CPAMAM-3.5Li; (b) CPAMAM-3.5Na; and (c) CPAMAM-3.5K.

different from the ordinary ion conductive electrolytes. For example, the influence of temperature on ionic conductivity is not as obvious as in ordinary ionic electrolytes, and their ionic conductivities have a tendency to increase with decreasing temperatures. Besides, the dendritic electrolytes exhibit higher ionic conductivities $(10^{-5}–10^{-6}\ \text{S cm}^{-1})$ than the corresponding linear electrolytes such as the alkali-metal salts of poly(methyl acrylic acid) $(<10^{-11}\ \text{S cm}^{-1})$ [15].
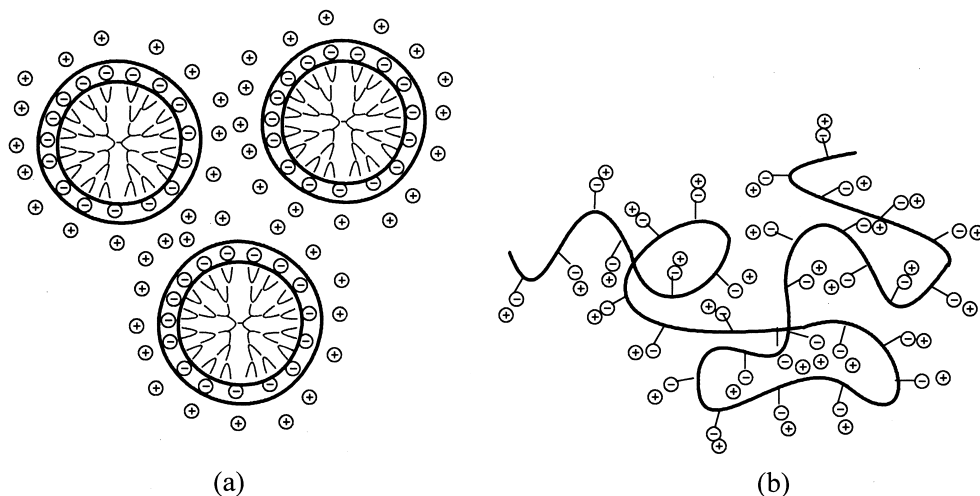
Scheme 2. Ionic conductive electrlytes: (a) dendrimer; (b) linear polymer.

Such differences might be considered to be because of the specific structure of the dendrimer, as can be seen from the schematic representations of the dendritic electrolytes and the ordinary linear polymer electrolyte (Scheme 2). The dendritic electrolytes consist of spheric macromolecules with a void inner and a dense outer, with the movable cations dispersed on the sphere's molecular surface. In the linear polymer electrolyte case, the cations are dispersed more uniformly along the flexible polymer chains. When the temperature is increased, the thermomovement of the segment in the linear polymer chain is accelerated, which could result in the ionic conductivity increasing. For the dendritic electrolytes, charge carriers are not dispersed uniformly in the electrolyte system, but concentrated on the surface of the nanometer size global dendrimers. It might be suggested that the transportation would take place mainly on the surface of the dendrimers rather than in the void inner. Meanwhile, the hyperbranched structure of the dendrimer inner might also be unfavourable for the segment thermomovement. As a result, the thermomovement of the branched chain in the inner of dendrimers will only have a little influence on the transportation of the cations at the global surfaces. The reason for the slight

increase of the ionic conductivity with decreasing temperatures is not yet clear.

In linear electrolyte systems, such as alkali-metal salts of (sulfoalkyl methacrylate) [25], the cation species influence the cationic conductivity, and the cationic conductivity increases in the order of $Li < Na < K$ in agreement with the order of metal ionic radius. In the system of dendritic electrolytes in this work, however, the influence of the cation species on the conductivity is not very distinct, and the conductivities are 9.3×10^{-6} (Li), 1.1×10^{-5} (Na), 8.4×10^{-6} S cm^{-1} (K) at 30°C, and 6.9×10^{-6} (Li), 5.9×10^{-6} (Na), 6.3×10^{-6} S cm^{-1} (K) at 80°C for CPAMAM-3.5M samples.

4. Conclusion

The single-ionic dendritic homopolymer electrolyte CPAMAM-XM (X: generation 2.5 or 3.5; M: Li$^+$, Na$^+$ or K$^+$) showed a unique dependence of ionic conductivity on temperature, which did not fit either the WLF mechanism or the Arrhenius equation. Unlike the linear and comb-like homopolymer electrolytes, its ionic conductivity increased slightly with decreasing temperatures, and reached 10^{-5}–10^{-6}S cm^{-1} at room temperature. During the detection range of frequency (1–100 kHz), the highest ionic conductivity appeared at the higher frequency. This is suggested to be a result of by the spherical molecular structure of dendrimer. When a small molecular additive, lithium perchlorate was added, the lithium carboxylated PAMAM showed improved conductivity at the lower content of LiClO$_4$.
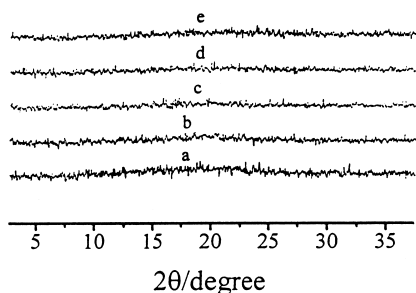

Fig. 8. The powder X-ray diffraction curve for: (a) CPAMAM-3.5Li and its complexes with LiClO$_4$. CPAMAM-3.5Li/LiClO$_4$: (b) 100/10, (c) 100/20, (d) 100/30; and (e) 100/40.

Acknowledgements

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