Effect of additive salts on ion conductivity characteristics in solid polymer electrolytes

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Effects of lattice energy of the additive salt on ionic species and ion conductivity characteristics were studied in the solid polymer electrolyte. Poly[oligo(oxyethylene) methacrylate] and several lithium salts were used as matrix and additive salt for solid polymer electrolytes, respectively. Salt and salt content deeply affected the ion conductivity characteristics as well as morphology even for amorphous type solid polymer electrolytes. The relationship between ion conductivity at constant reduced temperature ($T - T_g = 90°C$) and lattice energy of the additive salt was evaluated at each salt content. A different relationship was found for each salt content. Multiple ion aggregate formation was considerably affected by the salt, and was revealed to be effective to increase the ion conductivity.

(Keywords: polymer electrolyte; ion conductivity; lithium salt; lattice energy; ionic species)

INTRODUCTION

Solid polymer electrolytes have received much attention mainly due to possible applications as electrolytes in electrochemical devices such as solid state batteries, electrochromic devices, sensory systems, etc.[1,2]. We have already described a solid state electrochromic device with a cell composed of WO_3/solid polymer electrolyte/ Prussian blue. It was revealed that the electrochromic device showed good colouring and bleaching behaviour and that the electrochromic characteristics are considerably affected not only by the cation but also by the anion[3–6]. In an electrochromic device with a colouring layer of inorganic material, such as WO_3 and Prussian blue, the electrochromic characteristics are believed to be mainly controlled by the cation transport reaction at the colouring layer or at the interface of the colouring layer and electrolyte. Therefore, the size of the conducting cations is one of the important factors in the electrochemical reaction in such an inorganic electrochromic material.

The matrix polymer of the solid polymer electrolyte has a relatively lower dielectric constant than that of the organic low molecular weight solvent. Ions in the solid polymer electrolyte with high salt concentration are likely to present as ion pairs and multiple ion aggregates such as triple ions. There are many papers pointing out that multiple ion aggregates exist in solid polymer electrolytes as the conducting carrier[7–11]. In order to produce novel solid state electrochemical devices, it is essential to quantitatively evaluate the nature of the conducting ionic species in the solid polymer electrolyte. These ionic species affect the electrochromic behaviour when the solid polymer electrolytes are employed as the electrolyte layer in all solid state electrochemical devices. Actually, the ion transport at the interface of the solid polymer electrolyte and the intercalation electrode particularly plays an important role in solid state electrochemical devices. Analyses of ion transport properties at the interface have been carried out by some d.c. electrochemical and a.c. impedance methods[12–14].

The aim of this study is to analyse the effects of salt content and lattice energy of the salt on the ion conducting characteristics and to evaluate their relationship with the form of salt and conducting carrier species in the solid polymer electrolyte. These analyses were carried out with a.c. conductivity measurements and glass transition temperature (T_g) measurements.

EXPERIMENTAL

Materials

Oligo(oxyethylene) methacrylate with nine oxyethylene units (MEO_9) was donated by Nippon Oil & Fats Co. Ltd. This monomer was homogeneously polymerized in dry tetrahydrofuran solution with azobisisobutyronitrile as a radical initiator under nitrogen at 333 K for 24 h. The polymer [$P(MEO_9)$] was purified by precipitating twice from ether. The polymer thus obtained was dissolved in chloroform, stored over molecular sieves (4 Å) for 2 days, and subsequently dried at 343 K for 24 h. The absence of water contamination was confirmed by the disappearance of the peaks around 1640 and 3500–3600 cm^{-1} in the Fourier transform i.r. spectra. As pointed out earlier, however, it is extremely difficult to prepare lithium ion systems that are completely free from water. The average molecular weight of polymer obtained was estimated to be >7000 (by g.p.c.). The polymer was stored in a dry argon-filled dry box prior to use.

$LiClO_4$, LiI, LiBr and LiCl were used as the additive salts in the solid polymer electrolyte. These salts were purified according to conventional methods, and were

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dried under suitable conditions. LiI, LiBr and LiCl were dried in the absence of light to prevent photochemical reactions of the halogen ions. The lattice energies of LiCl, LiBr, LiI and $LiClO_4$ are 834, 788, 730 and 709 kJ mol^{-1}, respectively. The anionic radii of LiCl, LiBr, LiI and $LiClO_4$ are 1.67, 1.82, 2.06 and 2.36 Å, respectively.

$P(MEO_9)$ and each salt were dissolved in dry methanol, and the resulting solution was cast on ITO glass electrodes or gold vacuum-evaporated polymer film electrodes (Daicel Chem. Ind. Ltd, Celec®). All the preparation procedures were carried out under red lamp conditions to prevent chemical reactions of the anions, such as the iodide ion. Methanol was slowly evaporated under nitrogen flow over P_2O_5 for 24 h, and the resulting hybrid was dried *in vacuo* at 60°C for 24 h. Electrodes coated with hybrid were brought into contact with each other by light pressure in a dry argon atmosphere. The samples were completely sealed with silicone resin to prevent the absorption of moisture. The samples were handled in the dry argon-filled dry box. Undoped $P(MEO_9)$ resembled a stickly melt, but it became a self-supporting film with a salt content of >3 or 5 mol%. The film quality of the hybrids differed due to the variety of salts and salt contents used. However, the area and thickness of the hybrids in the cell even at low salt content did not change during the experimental procedure. The film thickness was ~50–80 μm. The residual conductivity for the undoped $P(MEO_9)$ was $<10^{-9}$ S cm^{-1} at 25°C.

Measurements

The impedance and phase angle at each frequency were measured with an LCR meter (Hioki 3520 LCR Hi tester or Sorlartron 1260 frequency analyser), and ion conductivity was calculated by complex impedance plane plotting with computer curve fitting. Temperatures were controlled to within ±0.5°C by a thermal test chamber (Yashima Works, BX-10W).

The thermal history of the hybrid film was analysed with a differential scanning calorimeter (MAC Science, DSC-3100, TAPS 1000). The scanning speed used was 10°C min^{-1}. The T_g was taken as the lowest intersection point of the base line with the extrapolated slope of the thermogram.

RESULTS AND DISCUSSION

The temperature dependence of the ion conductivity in $P(MEO_9)$/Li salt hybrids is shown in *Figure 1*. The relationship between $\log \sigma_i$ *versus* $1/T$ for hybrids containing LiBr, LiI or $LiClO_4$ was estimated to be curved, suggesting that the ion conduction obeyed Williams–Landel–Ferry (WLF) behaviour. The ion conduction behaviour in these hybrids is characterized as that in the amorphous polymer electrolyte. This supports the argument that ion conduction in these hybrids is greatly affected by the segmental motion of the polymer matrix. Ion conduction in LiCl hybrids was also estimated to fit WLF behaviour. The knee was, however, found at ~65°C in a study of the temperature dependence of ion conductivity for hybrids containing LiCl (particularly >10 mol%). In the d.s.c. thermogram of these hybrids, LiBr, LiI and $LiClO_4$ hybrids showed no phase transition except the T_g. On the other hand, an endothermal phase transition was observed around 70°C in LiCl hybrids, indicating that this endothermal phase transition was related to the knee in the temperature dependence of ion conductivity in LiCl hybrids. Furthermore, wrinkles were found on the surface of the hybrid films containing LiCl but not LiBr, LiI and $LiClO_4$. The morphology of the hybrid is also affected by the additive salt in the amorphous polymer.

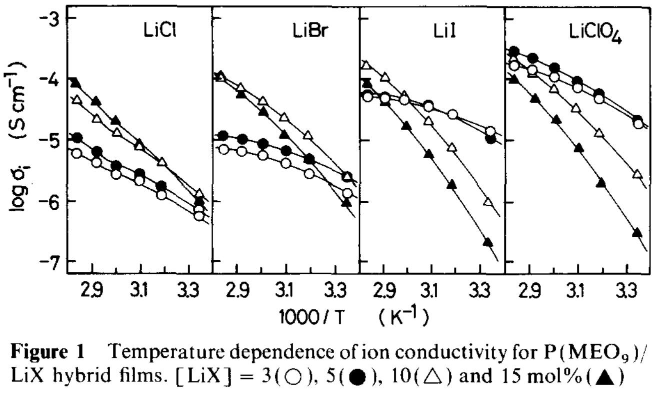

Figure 1 Temperature dependence of ion conductivity for $P(MEO_9)$/LiX hybrid films. [LiX] = 3(○), 5(●), 10(△) and 15 mol%(▲)

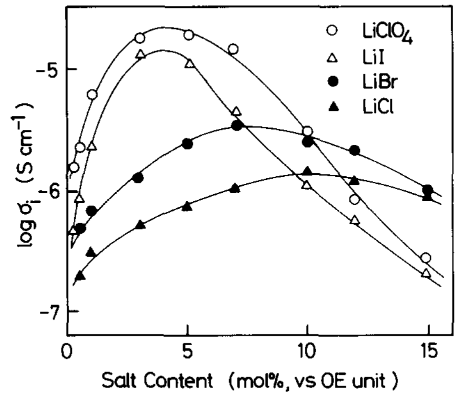

Figure 2 Salt content dependence of ion conductivity for $P(MEO_9)$/LiX hybrid films at 25°C

Figure 2 shows the salt content dependence of ion conductivity for each hybrid. The maximum ion conductivity for each hybrid was similar to that observed in the solutions of oligo(oxyethylene) dissolving each salt. The maximum ion conductivity ($>10^{-5}$ S cm^{-1}) was particularly observed in the hybrids containing $LiClO_4$ or LiI at 25°C. This conductivity is comparable to that reported for the hybrid prepared by cast polymerization[15]. The maximum ion conductivity appeared for a $LiClO_4$ content around 10–20 mol% for the $P(MEO_7)/LiClO_4$ hybrid film prepared by cast polymerization[15]. Although the present polymer has longer side chain length (OE units = 9) than the earlier reported matrix polymer (OE units = 7), the ion conductivity maximum lies at a $LiClO_4$ content around 3–5 mol%. Generally, the degree of polymerization is limited in homogeneous polymerization such as the present system, but the cast polymerized polymer is believed to have a broader molecular weight distribution. Low molecular weight polymer fractions in the cast polymerized hybrid may affect the salt dissociation as well as mobility in the hybrid. The salt content corresponding to the ion conductivity maximum shifted to lower values with decreasing lattice energy of the additive salt (LiCl > LiBr > LiI > $LiClO_4$). Further, the maximum ion conductivity increased in this sequence. This suggests that ion dissociation is facilitated in hybrids containing lower lattice energy salts especially in low salt content regions. Generally, when ion dissociation

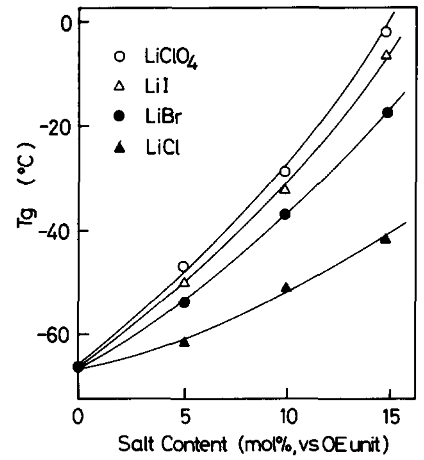

Figure 3 Salt content dependence of T_g for P(MEO$_9$)/LiX hybrid films

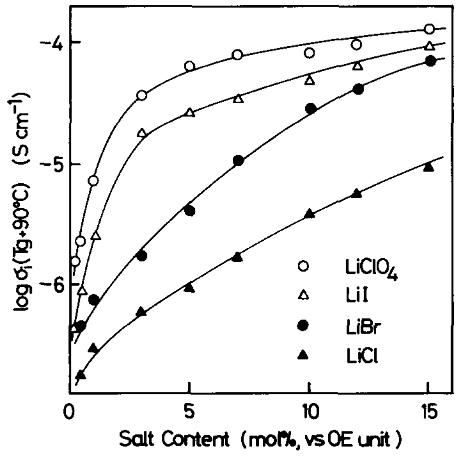

Figure 4 Salt content dependence of ion conductivity for P(MEO$_9$)/LiX hybrid films at the constant reduced temperature ($T - T_g = 90$°C)

is facilitated in poly(ether)-type solid polymer electrolytes, the number of quasi-crosslinking points caused by the interaction between ether oxygens and ions increases, resulting in the decrease in segmental motion of the polymer chain. Actually, at low salt contents, the slope of T_g *versus* salt content increased in the sequence shown for hybrids containing LiClO$_4$ > LiI > LiBr > LiCl (*Figure 3*). The T_g of undoped polymer is ~ −65°C. This T_g value is higher than that reported earlier[15]. The difference in the T_g was also attributed to the low molecular weight fraction in the hybrid prepared by cast polymerization as described above. On the other hand, T_g rises even with high salt contents in the present solid polymer electrolytes. This tendency, especially for hybrids containing low lattice energy salts, is not considered to arise from the increase in the quasi-crosslinking points caused by ion–dipole interactions. This is because the dielectric constant of the polymer matrix is too low (~5.4 at 25°C by dielectric relaxation measurements) to dissociate the salt into ions effectively at high salt contents. In order to analyse this point, the effect of segmental motion on ion conductivity, especially ion mobility, was normalized for the salt content dependence of the ion conductivity. Namely, the dependence of salt content on ion conductivity was evaluated at a constant reduced temperature [$T = (T_g$ of the hybrid) + 90°C] for each hybrid (*Figure 4*). The ion conductivity was saturated at higher salt contents, and this tendency was more clearly observed in the hybrid containing a lower lattice energy salt. This relationship is considered to include information on the effect of salt content on the carrier number in solid polymer electrolytes, because carrier mobility is greatly affected by segmental motion of the polymer matrix. Taking these results into account, ion dissociation is probably suppressed at high salt content in the hybrid containing the lower lattice energy salt. This suggests that the ion–dipole interaction is not a dominant factor to increase the T_g at high salt contents. The increase of the T_g at high salt contents, particularly seen in lower lattice energy salt hybrids, may be affected not only by ion–dipole interactions but also by the size of the salt in solid polymer electrolytes. Namely, the undissociated salt may exist as a suitable size in the free volume, which effects the decrease in segmental motion. These factors bring about the increase in T_g up to higher salt contents particularly in the hybrid containing the lower lattice energy salt, as shown in *Figure 3*. Consequently, in *Figure 2*, the larger conductivity decrease was found at the high salt content in the hybrid films containing the lower lattice energy salt.

The lattice energy of the added salt affects the ion conductivity and morphology of the solid polymer electrolyte, as has already been pointed out[16,17]. In order to analyse the effect of salt content on the salt dissociation in solid polymer electrolytes, the relationship between the lattice energy of the salt and the ion conductivity at constant reduced temperature ($T - T_g = 90$°C) was evaluated for each salt content. These relationships are shown in *Figure 5*. In the electrolyte solution with low salt concentration, the logarithm of conductivity is well known to have a linear relationship with the lattice energy of the salt. However, three tendencies were apparently found in the relationships as shown in *Figure 5*. For a salt content of 0.5 or 1.0 mol%, the conductivity non-linearly increased with decrease in lattice energy. At 3 or 5 mol%, the relationship was estimated to be linear. For salt content of >7 mol%, there was no large ion conductivity

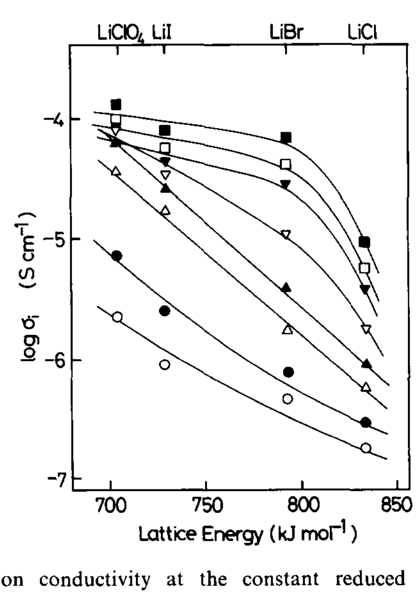

Figure 5 Ion conductivity at the constant reduced temperature ($T - T_g = 90$°C) as a function of the lattice energy of the hybridized salts. [LiX] = 0.5(○), 1(●), 3(△), 5(▲), 7(▽), 10(▼), 12(□) and 15 mol%(■)

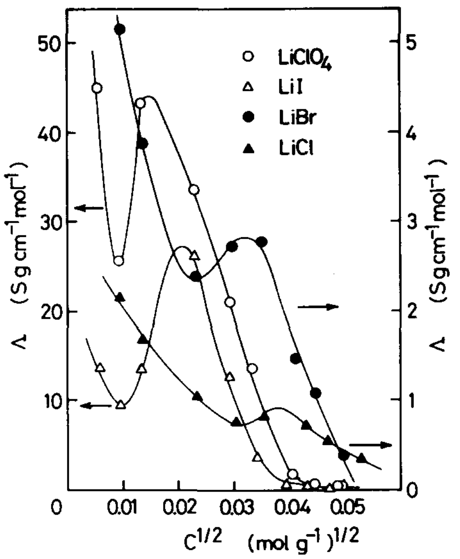

Figure 6 Equivalent conductance at each salt concentration in P(MEO$_9$)/LiX hybrid films at 25°C

difference found in the hybrids containing the lower lattice energy salt. Some considerations have been reported elsewhere on ionic species in solid polymer electrolytes[7–11]. At low salt content, it may be understood that the added salts exist as neutral ion pairs and free ions. The undissociated salts are, of course, present even at low salt contents in the solid polymer electrolyte. In order to analyse the effect of ionic species on the ion conductivity, the ion conductivity at a salt content of 0.5 mol% at the constant reduced temperature was compared with that at 1.0 mol%. For LiBr and LiCl hybrids, the conductivity at 1.0 mol% was ~1.7 times larger than that at 0.5 mol%. The increase of conductivity with salt content is somewhat smaller than the theoretical value predicted by the quantitative dissociation of added salt. This deviation can be explained by neutral ion pair formation with increasing salt content as seen in the electrolyte solution. On the other hand, for LiClO$_4$ and LiI hybrids, the conductivity at 1 mol% was about three times larger than that at 0.5 mol%. This behaviour cannot be explained only by an increase in number of mobile carrier ions with increasing salt content. Other factors, such as increase in carrier mobility, may contribute to the ion conductivity. For electrolyte solutions, the expression of molar conductance is useful to analyse the relationship between salt dissociation and conductivity. The analyses of molar conductance have also been applied to solid polymer electrolytes to obtain information about conducting ionic species[7,8,10]. *Figure 6* shows the relationship between molar conductance at 25°C and salt concentration for each hybrid film. The density of the polymer was ~1.2 g cm^{-3}, similar to the value reported earlier[10]. However, as it was difficult to measure the density of all the hybrid films accurately, the concentration is given in mol g^{-1} and this unit is used to calculate the molar conductance. In *Figure 6*, the maximum of the molar conductance appeared for each hybrid. This maximum point shifted to the lower salt concentration side with decreasing lattice energy of the salt. Further, the maximum in molar conductance increased in this sequence. The appearance of the maximum for the molar conductance is attributed to multiple ion aggregate formation by the interaction between free ions and neutral ion pairs[7,8,10]. The shift of the maximum in molar conductance indicates that the multiple ion aggregate formation is likely to take place on the lower salt concentration side with decreasing lattice energy of added salt. If the multiple ion aggregate had a monovalent charge and the electron moved freely in the multiple ion aggregate, the charge density of the aggregate would be smaller than that of the free cation and anion. This decreases the interaction between the ion and ether oxygen, resulting in an increase in carrier ion mobility, and a consequent increase in the ion conductivity. We do not have experimental results for this consideration. However, it is hard to speculate that the degree of dissociation increases at the concentration range in which the molar conductance maximum appears. Work is under way to analyse better the effect of variety of salts and salt concentrations on the mobility of the ionic species.

The relationships shown in *Figure 5* were analysed taking the results in *Figure 6* into account. In the electrolyte solution with low salt concentration, the logarithm of conductivity has a linear relationship with the lattice energy of the salt. This is because the molar conductance of the solution decreases monotonously in the lower salt concentration range, and the effect of ion mobility and viscosity on ion conductivity is almost normalized in each solution. In *Figure 5*, the effect of segmental motion on ion conductivity was normalized because the ion conductivity in each hybrid was measured at constant reduced temperature. On the other hand, in the hybrid films at a salt content up to 1 mol% (salt concentration 0.015 mol g^{-1}), the molar conductance for the LiCl and LiBr hybrids decreased monotonously, but that for the LiClO$_4$ and LiI hybrids gradually increased via a minimum point. This indicates that the multiple ion aggregate affects the ion conductivity at lower salt content in hybrids containing a lower lattice energy salt, such as LiClO$_4$ and LiI, as shown in *Figure 6*. Multiple ion aggregate formation may cause the increase in ion mobility as described above. Multiple ion aggregate formation is one of the reasons why the ion conductivity is about three times larger for a salt content of 1.0 mol% than for 0.5 mol% in LiClO$_4$ and LiI hybrids. As a result, upward deviation from the linear relationship at 0.5 and 1.0 mol% in *Figure 5* is probably obtained. With increasing salt content, multiple ion aggregate formation takes place in the LiBr hybrid system. This also affects the ion conductivity in the LiBr hybrid, resulting in a linear relationship between ion conductivity at constant reduced temperature and the lattice energy of the salt (*Figure 5*). On the higher salt content side, carrier generation is restricted in the LiClO$_4$ or LiI hybrid. On the other hand, phase transition takes place in the LiCl hybrid. These factors affect the ion conductivity in each hybrid, and the downward deviation from the linear relationship at higher salt content was consequently observed (*Figure 5*). This suggests that ion conductivity is greatly affected by the form of ionic species, and that the lattice energy of the salt affects the salt content in which the muliple ion aggregate formation is observed.

The relationship in *Figure 6* was not evaluated at constant reduced temperature. The decrease in molar conductance at higher salt concentration was, therefore, greatly affected by the decrease in segmental motion. When the molar conductance was evaluated at constant reduced temperature ($T - T_g = 90$°C), an incomprehensible increase in molar conductance was found at higher salt concentration. We have no clear explanation for this tendency. As the salt dissociation was probably restricted at higher salt content, the ion mobility may increase with increasing salt content especially on the higher salt content side. On the other hand, molar conductance maxima were also found for the relationship between molar conductance at constant reduced temperature and salt concentration. The maxima shifted to the lower salt concentration side with decreasing lattice energy of the salt, as in *Figure 6*. These results also support the theory that the relationships in *Figure 5* are considerably affected by multiple ion aggregate formation in each hybrid.

In conclusion, the ionic species in hybrid films is revealed to be greatly affected by the salt content and the lattice energy of the salt. The ion conduction behaviour depends on the form of ionic species and undissociated salt species in the solid polymer electrolytes.

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REFERENCES

1 Shriver, D. F. and Farrington, G. C. *Chem. Eng. News* 1985, 42

2 Scrosati, B. in 'Polymer Electrolyte Reviews-I' (Eds J. M. MacCallum and C. A. Vincent), Elsevier, London, 1987

3 Kobayashi, N., Ohno, H., Tsuchida, E. and Hirohashi, R. *Kobunshi Ronbunshu* 1987, **44**, 317

4 Kobayashi, N., Nishikawa, M., Ohno, H., Tsuchida, E. and Hirohashi, R. *J. Soc. Photo. Sci. Technol. Jpn* 1988, **51**, 184, 375

5 Kobayashi, N., Hirohashi, R., Ohno, H. and Tsuchida, E. *Denki Kagaku* 1989, **57**, 1186

6 Kobayashi, N., Hirohashi, R., Ohno, H. and Tsuchida, E. *Solid State Ionics* 1990, **40/41**, 491

7 Hall, P. G., Davies, G. R., Ward, I. M. and McIntyre, J. E. *Polym. Commun.* 1986, **27**, 100

8 Robitaille, C. D. and Fauteux, D. *J. Electrochem. Soc.* 1986, **133**, 315

9 Schantz, S., Sandahl, J., Borjesson, L. and Torrell, L. M. *Solid State Ionics* 1988, **28–30**, 1047

10 Gray, F. M. *Solid State Ionics* 1990, **40/41**, 637

11 Schantz, S., Kakihana, M. and Sandberg, M. *Solid State Ionics* 1990, **40/41**, 645

12 Fauteux, D. *J. Electrochem. Soc.* 1988, **135**, 2231

13 Scrosati, B. *J. Electrochem. Soc.* 1989, **136**, 2774

14 Bruce, P. G. and Vincent, C. A. *New Polym. Mater.* 1990, **2**, 19

15 Kobayashi, N., Uchiyama, M., Shigehara, K. and Tsuchida, E. *J. Phys. Chem.* 1985, **89**, 987

16 Kobayashi, N., Ohno, H. and Tsuchida, E. *Nippon Kagaku Kaishi* 1986, 441

17 Watanabe, M., Itoh, M., Sanui, K. and Ogata, N. *Macromolecules* 1987, **20**, 569