Local Structure of Polyethylene Glycol–NaI Solid Polyelectrolyte as Studied by ^{13}C and ^{23}Na NMR

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^{13}C CP/MAS NMR, ^{23}Na powder NMR, and ^{23}Na two dimensional nutation NMR were applied to complexes of NaI with polyethylene glycol (PEG) and tetraethylene glycol (TEG) to study the conformation of the polyethers and local structure around the Na$^+$. ^{13}C chemical shift data suggest strongly that the polyether chains assume the gauche conformation in the complexes. ^{23}Na NMR spectrum of TEG–NaI complex gave a broad asymmetric line; simulation of the line shape led to e^2Qq/h=590 kHz and η=0.7. No significant temperature dependence of the line shape was observed between 200 K and room temperature. For PEG–NaI complex e^2Qq/h and η were estimated to be about 320 kHz and 0.7, respectively, from the nutation spectrum. On the basis of the above results, new model structures of PEG–NaI complex were presented.

Complexes of polyethylene glycol (PEG) with inorganic salts such as NaI, NaSCN, and KSCN[1,2] exhibit ionic conductivitiy of the order of 10^{-4}—10^{-3} S cm^{-1} and are classified to solid polyelectrolytes. Among them, the complex of PEG with NaI has been extensively studied by conductivity measurements, X-ray diffraction, and various other experimental methods.[3–7] Thus, Fauteux et al.[7] have reported that the ionic conductivity exhibits an Arrhenius behavior, and that the apparent activation energy above 60 °C depends on the salt concentration of the solid electrolyte. As to the structure of PEG–NaI complex, Himba[5] performed an X-ray fiber diffraction experiment and proposed a monoclinic unit cell with cell constants of a=1.701, b=0.8, c=1.688 nm, and β=115.1° in which PEG chains were oriented along the b-axis, but the detailed molecular arrangement was not determined. Also, Chatani and Okamura[6] reported results of their X-ray experiment on the PEG–NaI complex and proposed a model structure that Na$^+$ and I$^-$ ions alternate with each other to form a zigzag chain around which a helical PEG chain which possesses *tg* conformation forms an envelope.

^{13}C CP/MAS (cross polarization/magic angle sample spinning) NMR is one of the most powerful experimental tools for conformational analysis of polymer molecules in solid state and has been successfully applied to various kinds of polymers.[8–12] In the present work we applied this method to PEG–NaI and its model oligomer complex, tetraethylene glycol (TEG)–NaI, in order to study the conformation of the chain in these complexes. We also measured the ^{23}Na NMR lineshapes[13,14] to deduce some information on the coordination of ethylene oxide units to the sodium ion. This paper describes the results of these experiments and presents possible model structures for PEG and TEG complexes based on the analysis of the experimental data. We also present the results of ^{1}H and ^{23}Na spin-lattice relaxation time (T_1) measurements and show that, although the sodium ion transport has been believed to govern the high conductivity in PEG–NaI complex, the diffusion rate of Na$^+$ is very slow in the crystalline state.

Experimental

Polyethylene glycol #4000 (reagent grade: M_w=3000—3700), tetraethylene glycol and NaI (extra pure reagent grade) were purchased from Nakarai Tesque Inc. As PEG and NaI are both sensitive to the atmospheric moisture, they were dried and stored in a desiccator over P_2O_5 and $CaCl_2$. The polymer-salt complex with the molar ratio 4:1 (O:Na) was prepared by the standard method.[3] The stoichiometric mixture of NaI and the ethylene oxide unit of polymer (1:4) was dissolved in dry methanol and stirred for 24 h at room temperature. The solvent was then slowly evaporated at room temperature to dryness and the complex thus deposited as thin-film was stored in a desiccator over P_2O_5 and $CaCl_2$.

The tetraethylene glycol (TEG)–NaI complex was prepared by dissolving the mixture of TEG and NaI with the molar composition of 1:1 in tetrahydrofuran (THF), concentrated to about one-third of its original volume and then being kept at 4 °C; the deposited white polycrystals were collected and recrystallized twice from THF. The complex was dried and stored in a desiccator over P_2O_5 and $CaCl_2$.

For the ^{13}C NMR measurements each specimen was packed into the MAS sample rotor (ZrO_2) under the N_2 atmosphere and dried under vacuum at room temperature for several hours. The specimen for the ^{23}Na and ^{1}H measurements were sealed into an ampoule with the He heat exchange gas.

^{13}C CP/MAS and ^{23}Na spectra, and ^{23}Na spin-lattice relaxation times, T_1, were measured with the Bruker MSL-200 spectrometer. A home-built pulse NMR spectrometer operating at 17 MHz was used for ^{1}H relaxation time measurements. The experimental errors in the ^{1}H and ^{23}Na relaxation measurements were estimated to be within 5% and 10%, respectively. The temperature was controlled within ±1 K with the Bruker VT-1000 unit for the ^{23}Na relaxation measurements. It was measured to within ±0.5 K by Chromel-*p*-Constantan thermocouples for ^{1}H relaxation measurements.

^{13}C CP/MAS NMR experiments were done at 50 MHz with the sample spinning rate of ca. 3 kHz at room temperature.

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^{13}C chemical shifts were determined with the external standard tetramethylsilane.

^{23}Na NMR lineshapes, the spin-lattice relaxation times and 2D nutation spectra[15] for the two complexes were measured at the resonance frequency of 53 MHz. In order to derive the quadrupole coupling constant, e^2Qq/h, and the asymmetry parameter of the electric field gradient tensor, η, we prepared computer program[16] to describe the evolution of the spin system using the Liouville operator formalism[17] and used it to simulate the ^{23}Na nutation spectral data.

Results and Discussion

^{13}C CP/MAS NMR Spectra. Figure 1 shows the ^{13}C CP/MAS NMR spectrum of PEG–NaI complex and the ^{13}C dipolar decouple(DD)/MAS NMR spectrum of PEG at room temperature. The spectrum of PEG sample consists of two sharp peaks due to carbons in the crystalline part and of a broad component which comes from the noncrystalline part.[18] The fact that the intensity of the broad component is rather high indicates that the crystallinity of our PEG specimen is relatively poor.

On the other hand, the spectrum of the PEG–NaI complex gives only a single sharp peak, which shows strongly that the complexation gives rise to almost perfect crystalline material. Moreover, all the carbon atoms in the complex are equivalent and only one kind of conformation can exist with respect to the carbon bonds.

In order to examine the effect of the complexation on the conformation of the –O–CH$_2$CH$_2$– chain in more detail we measured the ^{13}C CP/MAS spectrum in the TEG–NaI complex which can be regarded as a model compound for the PEG–NaI complex. The ^{13}C CP/MAS-NMR spectrum of the TEG–NaI complex together with ^{13}C high resolution NMR spectrum of the neat liquid of TEG are shown in Fig. 2.

In the case of liquid TEG the spectrum consists of three peaks with the intensity ratio of 1 : 2 : 1 in the order of decreasing field. These peaks are easily assigned as follows: The terminal carbon bonded to the hydroxyl group gives the peak at the highest field, the one next to the terminal carbon appears at the lowest field and the other four carbons give the central peak.

In contrast to pure TEG, the TEG–NaI complex gave two peaks with the intensity ratio of 1 : 3. The magnitude of the chemical shift at the highest field is the same as that of the terminal carbon in the pure TEG, suggesting strongly that the terminal OH groups of TEG do not participate in the complexation. The strong signal due to inner carbons shows an upfield shift due obviously to the complexation. The fact that the inner carbons give

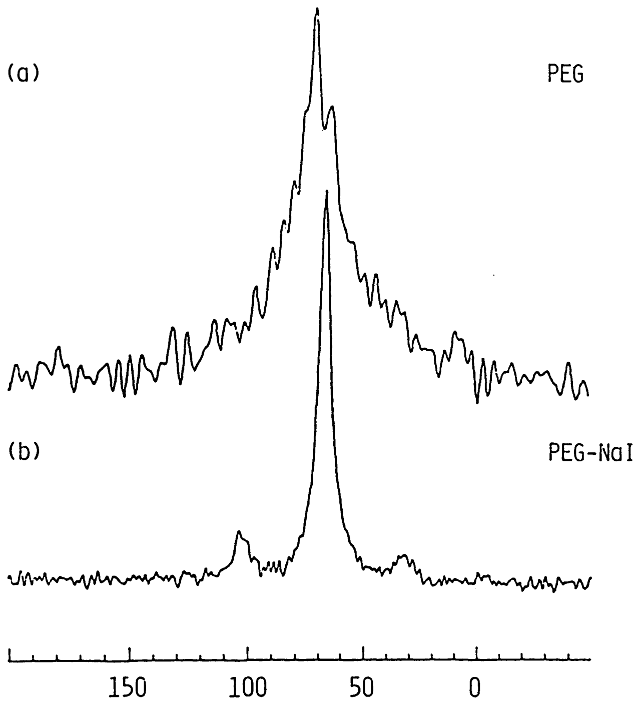

Fig. 1. ^{13}C dipolar decouple (DD)/MAS NMR spectrum of PEG (a) and ^{13}C CP/MAS NMR spectrum of PEG–NaI complex (b) at room temperature. The spinning rates for samples: (a) 3 kHz; (b) 2 kHz. The small peaks in the spectrum (b) are the spinning side bands.

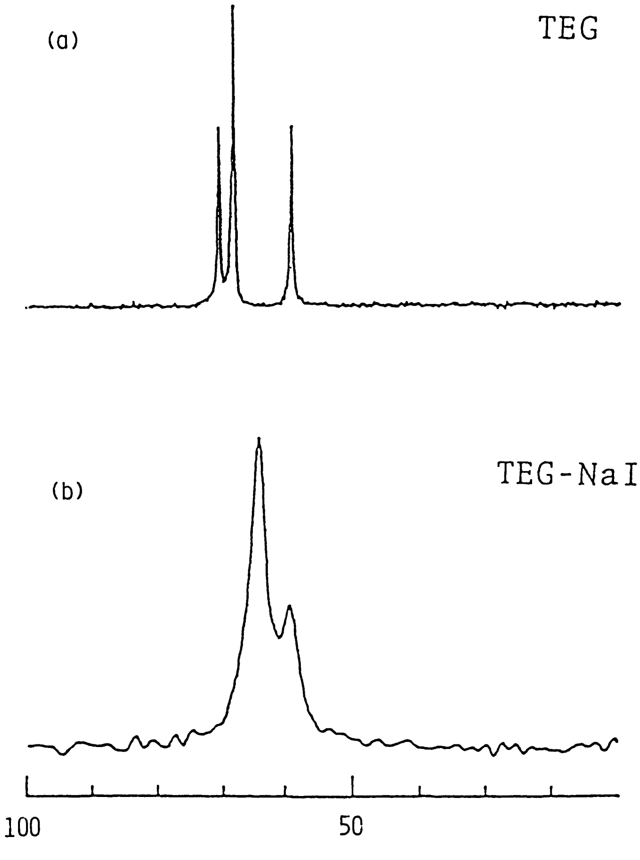

Fig. 2. ^{13}C NMR spectrum of pure TEG (neat liquid) (a) and ^{13}C CP/MAS NMR spectrum of TEG–NaI complex (b) at room temperature. The spinning rate for the TEG–NaI complex is 3.5 kHz.

Table 1. ^{13}C Chemical Shifts of TEG and PEG, and their Complexes with NaI (ppm from TMS)

Sample	I	II	III
PEG (solid)	70.6 64.0	—	—
PEG–NaI	67.2	—	—
PEG (soln)	69.6	72.0	60.6
TEG–NaI	63.7	—	58.8
TEG (liq.)	66.0	70.3	58.8

$-O-\underset{I}{\underline{CH_2CH_2}}-O-\underset{II}{\underline{CH_2}}-\underset{III}{\underline{CH_2}}-OH$

altogether only a single peak indicates that all the inner carbon atoms assume the same conformation. The values of the chemical shifts determined in the present ^{13}C CP/MAS-NMR experiments are listed in Table 1. A systematic work on the ^{13}C CP/MAS-NMR spectra of crown ether complexes by Saito et al.[11] showed that the *tg* conformer($-O^g-C^t-C-$) gives the ^{13}C signal at about 71 ppm whereas the *gg* conformer($-O^g-C^g-C-$) at about 67 ppm. Although the value of the chemical shift, 67.2 ppm, in the present NaI complex does not coincide with these values, it is lower than 69.6 ppm in the pure PEG solution which is the weighted average of the chemical shifts of the *tg* and *gg* conformations. Thus, the peak at 67.2 ppm in the NaI–PEG complex is assigned to the *gg* conformer.

^{23}Na NMR Spectra. The ^{23}Na-NMR spectrum of the TEG–NaI complex is shown in Fig. 3. This spectrum corresponds to the central transition broadened by the second order quadrupolar perturbation. We carried out the simulation for the lineshape by the usual procedure[13,14] and estimated, from comparison with the observed spectrum, the quadrupole coupling constant, e^2Qq/h, and the asymmetry parameter, η, of the electric field gradient tensor, to be 590±10 kHz and 0.7±0.1, respectively. The simulated spectrum with these parameters is given in Fig. 3 by the broken line. Fig. 4(a) shows the projection onto the F_1 axis of the ^{23}Na two dimensional nutation NMR spectrum. The spectrum indicates that all the Na$^+$ occupy crystallographically equivalent sites. The simulated spectrum with the above values of e^2Qq/h and η is shown by the broken line, reproducing fairly well the experimental result. The large e^2Qq/h and η suggest that the Na$^+$ is coordinated by the oxygens asymmetrically.

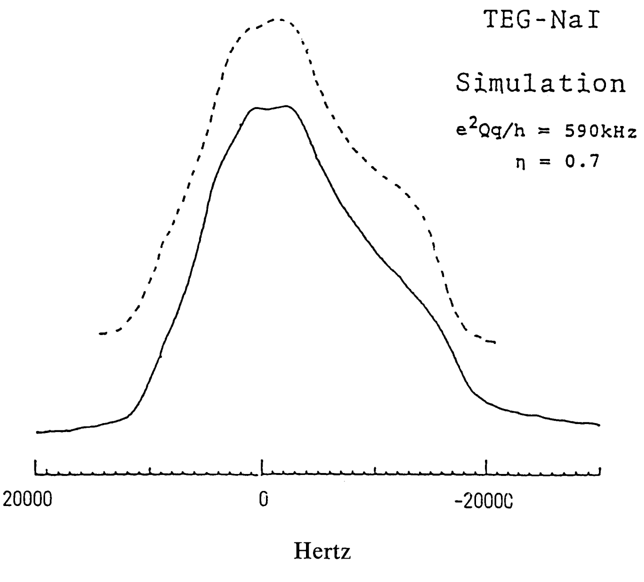

Fig. 3. ^{23}Na NMR spectrum of TEG–NaI complex (solid line) at room temperature and the simulated spectrum (broken line) with e^2Qq/h=590 kHz and η=0.7.

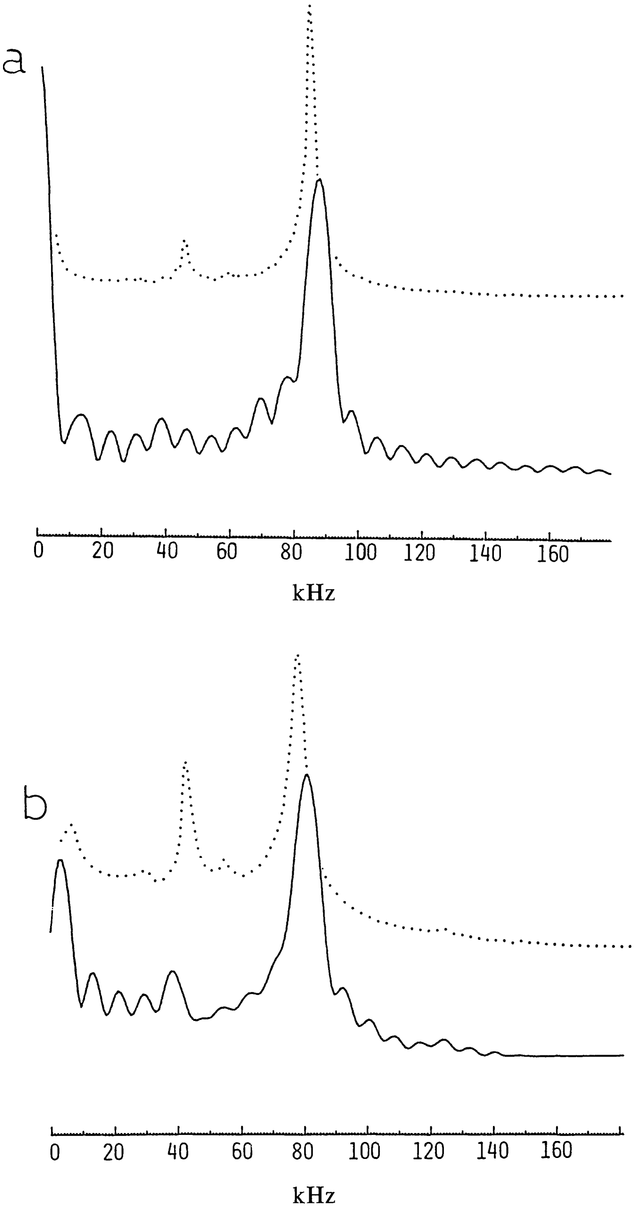

Fig. 4. ^{23}Na 2D nutation NMR spectrum of the TEG–NaI complex (a) and of the PEG–NaI complex (b), and the simulated spectrum (broken line) with e^2Qq/h =590 kHz, η=0.8 and ω_{rf}=39.3 kHz for the TEG–NaI complex and e^2Qq/h=320 kHz, η=0.7 and ω_{rf}=37.5 kHz for the PEG–NaI complex.

In the case of the PEG–NaI complex, the ^{23}Na NMR gives a relatively narrow, symmetric spectrum at room temperature as shown in Fig. 4. A similar spectrum was reported for the PEO–NaClO$_4$ (EO : Na$^+$=4.5 : 1) by Greenbaum.19) These results predict a fairly small quadrupole interaction. In order to confirm this point we conducted a 2-dimensional nutation NMR experiment for ^{23}Na in the PEG–NaI complex. The information for quadrupole interaction are involved in the projection of the 2D spectrum onto the F_1 axis as is shown in Fig. 4. From the computer simulation of the nutation spectrum we estimated the quadrupole coupling constant and the asymmetry parameter of ^{23}Na to be about 320 ± 10 kHz and about 0.7 ± 0.1, respectively, for the PEG–NaI complex. As in the TEG–NaI complex all Na$^+$ occupy crystallographically equivalent sites.

Conductometric studies20) of PEO–KSCN complex in methanol and experiments21) on ^{23}Na NMR chemical shift in Na-containing complexes in solutions give some evidence that the cations are probably coordinated tetrahedrally by four ether oxygens. The value of the asymmetry parameter, η, which reflects the site symmetry of the Na$^+$ ion site, is also similar to the values for the NaBr$\cdot$2(D$_2$O) and NaCl$\cdot$2(D$_2$O) (0.7962 and 0.77, respectively).23) In these compounds, the Na$^+$ ions are coordinated by four oxygens of water. Therefore, it is reasonable to consider that each Na$^+$ in the PEG–NaI complex is also coordinated tetrahedrally in the solid state. But the coordinated tetrahedron is appreciably distorted so as to produce a finite and highly asymmetric electric field gradient at the cation site. Assumption of the distorted tetrahedral coordination under the conditions that the *gg* conformation applies to each carbon–carbon bond and that a unit cell contains two monomer units as shown by a previous X-ray diffraction experiment5) allows us to build some probable model structures for PEG–NaI complex. Among a few model structures which satisfy the above conditions, two of the most probable models are presented in Fig. 5. In these two model structures each EO segment assumes the *gg* conformation and all ether oxygens coordinate favorably to the cation. The model(a) looks, however, less stable than model(b) because in the former structure the distance between the protons in the –CH$_2$–O–CH$_2$– segments is unreasonably short (ca. 1.4 Å) as the van der Waals distance. Therefore we adopt only the model structure(b). The characteristics of our model structure(b) for the PEG–NaI complex is compared with the previous model by Chatani and Okamura (C–O model)5) as follows:

(1) The molar ratio (EO : Na) is 4 : 1 for our model, whereas the previous one (C–O model) is 3 : 1.

(2) Na$^+$ ions are arranged so as to make the EO molecule to form a zigzag chain in our model, while Na$^+$ and I$^-$ ions are arranged alternately to realize a 2/1 helix in the C–O model. Although at present we cannot locate the large anions(I$^-$), we may presume that the coordination number with respect to the Na$^+$–I$^-$ coordination is 2.

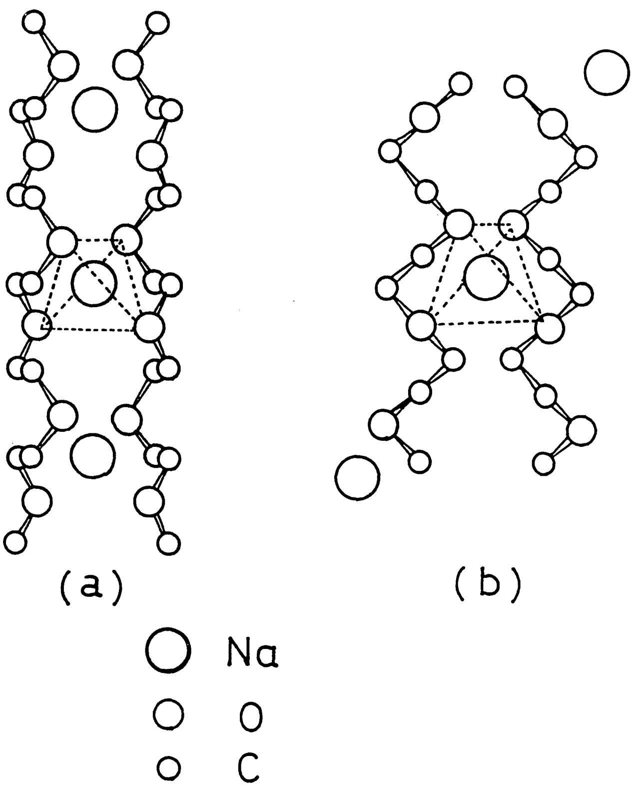

Fig. 5. The model structures of PEG–NaI complex. The conformation of the PEG chain is *gg*. The PEG chain has S-shape in the model (a) and forms helix in the model (b).

(3) The Na$^+$ and I$^-$ are incorporated into a helical PEG chain that makes a fiber period of 7.98 Å with six EO units in the case of the X-ray experiment, while in our model structure Na$^+$ are interposed by two helical PEG chains that make the fiber period of 13.8 Å with four EO units. The polymer chain assumes a 4/3 helix and the conformation is *gg* $(-\mathrm{O}^{g}-\mathrm{C}^{g}-\mathrm{C}-)$ conformer.

(4) Each Na$^+$ ion is coordinated by four ether oxygens and the Na$^+$–O distance in our model structure is 2.15 Å. In the C–O model the Na$^+$ is coordinated by three oxygens and two I$^-$ ions with the Na$^+$–O distances of 2.28, 2.48, and 2.70 Å which are longer than 2.15 Å in our model.

(5) The *gg* conformation in our model structure can interpret the ^{13}C NMR results but the C–O model which is based on the *tg* conformation predicts the ^{13}C chemical shift of about 71 ppm, conflicting with our experimental results.

A point to be interpreted is why the polymer assumes the *gg* conformation in the complex in spite of reduced stability of this conformation22) which is obviously less stable than the *tg* or the *tt* conformation observed in other polymers. Energy consideration upon the stability of the whole system will be required.

^{1}H and ^{23}Na Relaxation Times. We measured the ^{1}H and ^{23}Na spin-lattice relaxation times, T_1, at 17 MHz and 53 MHz, respectively, for PEG–NaI complex for the purpose of examining the possible relation between the ionic motion and the high conductivity in this material. The results are shown in Fig. 6. ^{23}Na relaxation time does not change appreciably below about 200 K; it means that lattice vibrations of only small amplitude govern the relaxation. The monotonous decrease in T_1 above about 200 K indicates that some motion which contributes to the relaxation is excited above 200 K. The slope in Fig. 6 gives the activation energy for that motion 12 kJ mol^{-1}. This value is much smaller than 81 kJ mol^{-1} obtained in the conductivity measurement.[7)]

The T_1 for the proton also decreases monotonously on heating, leading to the activation energy of ca. 13 kJ mol^{-1}, which is comparable with that for ^{23}Na. The T_1 for the proton changes discontinuously at the eutectic point (321 K) of the complex.[7)] Above this temperature the motion of the polymer chain is rapid compared with the Larmor frequency and its apparent activation energy is 25 kJ mol^{-1}; it is impossible to identify the motion at the present stage. These results show that in the crystalline state of the complex a motion or motions are responsible commonly for the relaxation of both ^{23}Na and ^{1}H and, because the dipolar relaxation of ^{1}H must be governed by some large amplitude motion of the CH$_2$ segments; this motion of CH$_2$ groups is ascribed to the result of motion of a polymer chain such as twisting of the ethylene groups. The relaxation of Na$^+$, on the other hand, is caused by small fluctuation of EFG associated with such chain motion: We could not therefore detect the diffusion nor the hopping of Na$^+$ by NMR at least up to the eutectic point of complex. The present relaxation measurements suggest that the rate of the Na$^+$ transport is very low in the crystalline state.

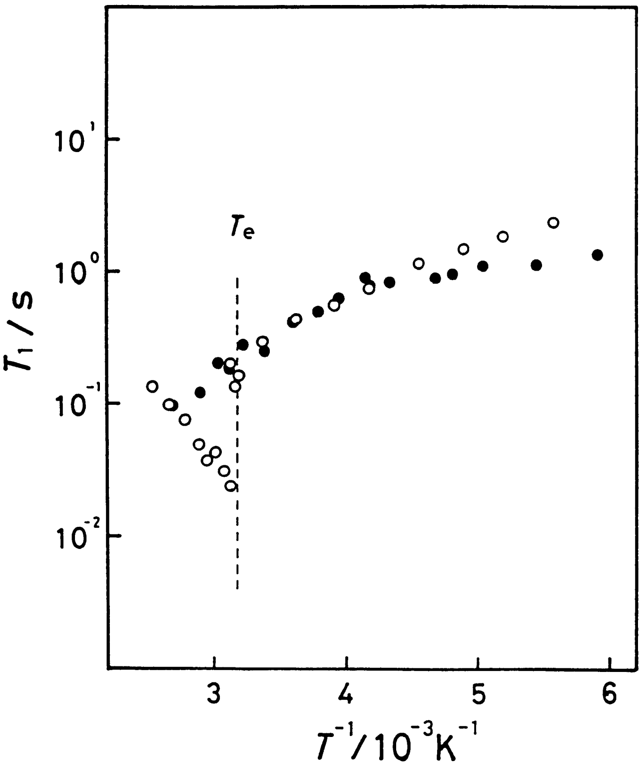

Fig. 6. Temperature dependence of ^{1}H (○) and ^{23}Na (●) spin-lattice relaxation times (T_1) in PEG–NaI complex at 17 MHz and 53 MHz, respectively. The eutectic point (T_e) is 321 K.

Conclusion

The ^{13}C CP/MAS NMR experiments on the PEG–NaI and the TEG–NaI complexes revealed that the bond conformation around each ethylene carbon atom is *gg*. This fact conflicts with model structure for the PEG–NaI complex presented recently on the basis of X-ray fiber diffraction. Quadrupole-perturbed ^{23}Na NMR spectrum together with 2D ^{23}Na nutation NMR showed that the quadrupole coupling constants and the asymmetry parameters are significantly large in both complexes, implying that distorted tetrahedral coordination of oxygens to the cation is realized. Based on the present ^{13}C and ^{23}Na NMR data we proposed a new model for the PEG complex. The results of ^{1}H and ^{23}Na relaxation time measurements indicated that the rate of transport of Na$^+$ is extremely low at ambient temperature.

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