

Molecular Interpretation for the Solvation of Poly(acrylamide)s. I. Solvent-Dependent Changes in the C=O Stretching Band Region of Poly(*N,N*-dialkylacrylamide)s

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The solvation of poly(*N,N*-dimethylacrylamide) (PNdMA) and poly(*N,N*-diethylacrylamide) (PNdEA) in various protic and aprotic solvents has been studied by using infrared (IR) spectroscopy. Because PNdMA and PNdEA have the same polar functional group, their IR spectra show quite similar solvent effects. Unexpectedly, the solvent-dependent changes of the C=O stretching vibration ($\nu_{\text{C=O}}$) bands of the two polymers cannot be explained only by dielectric constants of the solvents. Then, infrared spectra of *N,N*-dimethylacetamide (NdMA) and *N,N*-diethylacetamide (NdEA), monomer models for PNdMA and PNdEA, respectively, in the same solvents as the polymer solutions have also been examined. Interestingly, the solvent-dependent spectra in the $\nu_{\text{C=O}}$ band region of NdMA and NdEA are correlated with those of PNdMA and PNdEA, respectively, except for slight deviations, which may be ascribed to molecular mobility and/or exclusive volume. These correlations permit one to regard the solvation of the polymers as that of the corresponding monomers. As a result, we have proposed the assignments of $\nu_{\text{C=O}}$ bands for the PNdMA and PNdEA solutions regarding the interactions between solvents and NdMA and NdEA as hydrogen bondings. In the IR spectra of PNdMA and PNdEA in the protic solvents, two C=O bands are mainly observed; one appears at a similar frequency to that of a C=O band observed for the monomer solution, and the other is characteristic of the polymer systems. The former band is likely to reflect the solvation behavior of PNdMA and PNdEA. The results clearly show that the solvation of a polymer can be interpreted at the molecular level using infrared spectroscopy sensitive to solvent effects.

Introduction

To investigate the solubility of polymers is very important for fundamental polymer science because basic properties of polymers are generally characterized for a dilute solution. Especially, the universality of polymer solutions in the vicinity of θ temperature, at which a polymer is assumed to behave as an unperturbed chain, has been widely studied.¹ A change in the solubility of polymers is thermally induced, and then the expansion of polymer chains dramatically varies near the θ temperature.² This phenomenon has been known as a coil–globule transition and a matter of extensive investigations.^{3–7}

Conventional theories for the coil–globule transition based on the lattice model or the exclusive volume effect insist that the attractive and repulsive interactions among segments and solvents are the major factors for the expansion of polymer chains in solutions.¹ While these theories have qualitatively explained the fundamental features of the coil–globule transition phenomenon, it has also been considered that a realistic polymer system always shows deviations from the theoretical prediction. As such a system, *N*-substituted acrylamide polymers, which have the stimuli sensitivity in aqueous solutions, have received

keen interest.^{8–21} Some of them, such as poly(*N*-isopropylacrylamide) (PNiPA) and poly(*N,N*-diethylacrylamide) (PNdEA), show a phase separation at around 305 K (32 °C).^{8,9} PNiPA has a swollen coil conformation below the θ temperature and becomes a globule as temperature is elevated above ca. 305 K. The coil–globule transition of PNiPA in an aqueous solution has been explored extensively^{9–20} because one finds this characteristic thermal behavior somewhat counterintuitive. Numerous researchers have suggested that strong and specific solvation behavior of water plays important roles in the transition phenomena of PNiPA in an aqueous solution and causes a shrinkage of the polymer at a higher temperature.^{10,14,15,17–20} For other acrylamide polymers that have a similar thermally induced phase separation, the specific solvation of water has also been enhanced.²¹ As a consequence, several research groups have tried to find the evidence for the specific solvation behavior of water molecules to polymer segments of acrylamide polymers.^{18–21}

On the basis of vibrational spectroscopy studies, several pictures have been proposed for the solvation of acrylamide polymers in aqueous solutions.^{18–21} Infrared (IR) bands are very sensitive to changes in the environment surrounding a target functional group. The variations in the amide I bands, which

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are mainly due to the C=O stretching vibration ($\nu_{\text{C=O}}$) modes during the phase separation of acrylamide polymers, have been studied.^{19–21} Below the θ temperature, an aqueous solution of PNiPA shows a unimodal peak at ca. 1625 cm^{-1} in the amide I region, while above the θ temperature, a new band appears around 1650 cm^{-1} . It has been generally considered that the appearance of a higher-frequency band in the amide I region is associated with the dehydration of the polymer side chains. However, the dehydration may not only be one reason for the appearance of the band at ca. 1650 cm^{-1} . It has been shown that the transition dipole coupling causes a frequency shift of the $\nu_{\text{C=O}}$ (or amide) bands. For example, Torii and Tasumi²² demonstrated that the peak position of an amide I band of proteins is strongly influenced by the transition dipole coupling among the neighboring amide groups incorporated in the main chains. Recently, we have studied IR spectral changes in the amide band regions of PNiPA observed during the coil–globule transition.^{23,24} In our studies,^{23,24} IR spectroscopic studies were combined with quantum chemistry calculations in order to examine the assignments for IR bands of PNiPA. As a result, it has been suggested that the spectral variations in the amide I and II regions are mainly associated with the changes in the C=O...H–N hydrogen bond between the neighboring amide groups along the polymer chain. However, the mechanism of changes in the solubility of PNiPA was not revealed in the previous works because the assignment for the $\nu_{\text{C=O}}$ band or the amide I band of acrylamide polymers in solutions was not solid enough. To reveal the solvation effects on the vibration bands of PNiPA and PNdEA, systematic and detailed investigations are required.

We have thought that vibrational spectroscopy is a powerful tool to explore molecular interactions between a solvent molecule and a target functional group incorporated into a polymer chain. Because the band assignments are very complicated for a polymer solution, a combined use of conventional analysis with quantum chemistry calculations is very effective.^{23–25} The purpose of the series of our studies is to establish the assignments for vibrational bands of acrylamide polymers in solutions and to propose a realistic picture of solvation of the polymers based on molecular interpretation. This approach is very important to reveal the solubility of acrylamide polymers.

In the present paper, effects of the solvation on the $\nu_{\text{C=O}}$ bands of PNdEA and poly(*N,N*-dimethylacrylamide) (PNdMA) are investigated for the water, alcohols, tetrahydrofuran (THF), acetone, and chloroform solutions. These solvents are common good solvents for acrylamide polymers and expected to interact with the amide groups of PNdMA and PNdEA in various ways; water and alcohols act as proton donors to the C=O group, while acetone and THF are polar and aprotic solvents. Using several alcohols (methanol, ethanol, and propanol), we can examine the effect of dielectric property of protic solvents on the $\nu_{\text{C=O}}$ bands. The results for the polymers are compared with those for *N,N*-dimethylacetamide (NdMA) and *N,N*-diethylacetamide (NdEA) used as monomer model compounds. These kind of systematic studies on the solvation of the acrylamide polymers, which have never been reported, lead us to more reliable assignments for the $\nu_{\text{C=O}}$ bands of PNdMA and PNdEA in the solutions. The goal of this work is to make a clear guideline to the molecular interpretation of the solvation of acrylamide polymers for the next step of our studies, in which the quantum chemistry calculations will be employed, aiming to establish a simulation method of an IR spectrum for the acrylamide polymers in solutions.

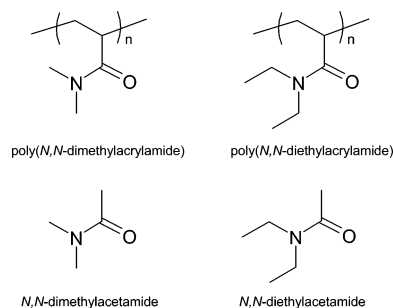


Figure 1. Chemical structures of poly(*N,N*-dimethylacrylamide), poly(*N,N*-diethylacrylamide), *N,N*-dimethylacetamide, and *N,N*-diethylacetamide.

Experimental

Sample Preparation. Poly(*N,N*-dimethylacrylamide) (PNdMA) and poly(*N,N*-diethylacrylamide) (PNdEA) were synthesized by radical polymerization of *N,N*-dimethylacrylamide and *N,N*-diethylacrylamide in benzene by using 2,2'-azobis(isobutyronitrile) as an initiator, respectively. *N,N*-Dimethylacrylamide was purchased from Wako (Osaka, Japan), and *N,N*-diethylacrylamide was kindly donated by Kohjin (Tokyo, Japan). The monomers and initiator were used without further purification. The synthesized polymers were purified by reprecipitation from *n*-hexane, and the precipitate was dried under vacuum for 24 h. *N,N*-Dimethylacetamide (NdMA), *N,N*-diethylacetamide (NdEA), the infinity pure grade of methanol, ethanol, 1-propanol, tetrahydrofuran (THF), acetone, chloroform (CHCl_3), benzene, carbon tetrachloride (CCl_4), *n*-hexane, and cyclohexane, the special grade of 1-propanol, 1-butanol, 1-pentanol, and 1-hexanol were purchased from Wako and used as received. The resistance of the finally prepared water used was greater than 18.1 M Ω . Figure 1 shows the chemical structure of PNdMA, PNdEA, NdMA, and NdEA.

IR Measurement. PNdMA, PNdEA, NdMA, and NdEA were dissolved in solvent (ca. 20 g/L). A sample solution was placed onto an attenuated total reflection (ATR) cell. The ATR cell was made of a horizontal ZnSe crystal (the refractive index is 2.403) with an incidence angle of 45° (Thermal A.R.K., Spectra-Tech, Inc.). Infrared spectra were measured with a 4 cm^{-1} resolution by using a Nicolet Magna 760 Fourier transform IR spectrometer with a liquid-nitrogen-cooled mercury–cadmium–telluride detector. A total of 512 scans were co-added for each spectrum. Throughout the whole experiment, the temperature of the ATR cell was kept at 297 K (23.8 °C) by use of a thermoelectric device (CN4400, OMEGA) with an accuracy of ± 0.1 K. A toggle-clamp-type sealing cover was placed on the ATR cell to prevent the evaporation of solvent. Transmission IR spectra were measured by using a CaF_2 transmission cell (2 mm).

Data processing, such as the subtraction of a solvent spectrum and the calculation of a second derivative spectrum, was performed by software composed by one of the authors (Y.K.). The programs were written in C++ language (Visual C++ 6.0, Microsoft). The pretreatment procedure for the ATR/IR spectra of polymers in solutions, including the subtraction of a solvent spectrum from a spectrum of sample solution, was described in the previous paper.²⁴ Second derivatives were calculated by using the Savitzky–Golay method,²⁶ with the number of smoothing points being equal to 7.

Results and Discussion

Solvent-Dependent Changes in the C=O Stretching Band Region of PNdMA and PNdEA. Figures 2 and 3 show IR

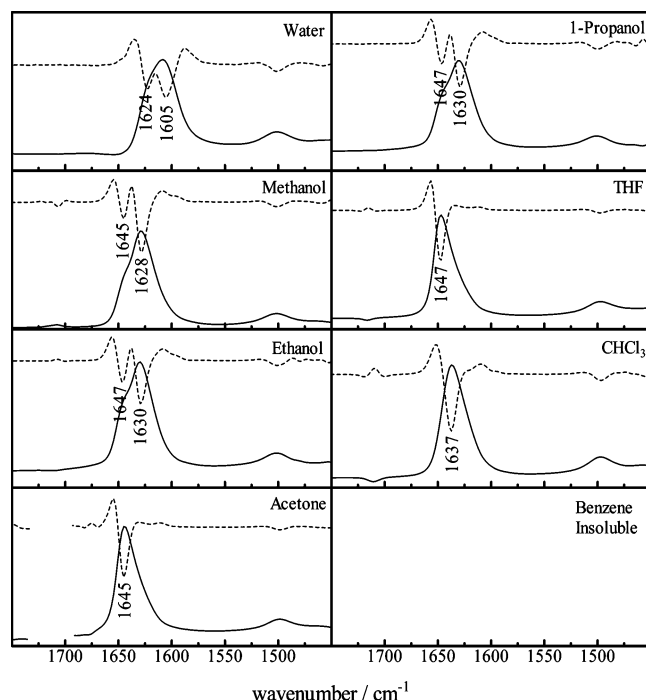


Figure 2. IR spectra of PNdMA in the 1750–1450 cm^{-1} region observed for the various solutions (solid line) and their second derivatives (dotted line). For each sample, an IR spectrum of a pure solvent is subtracted from that of the solution.

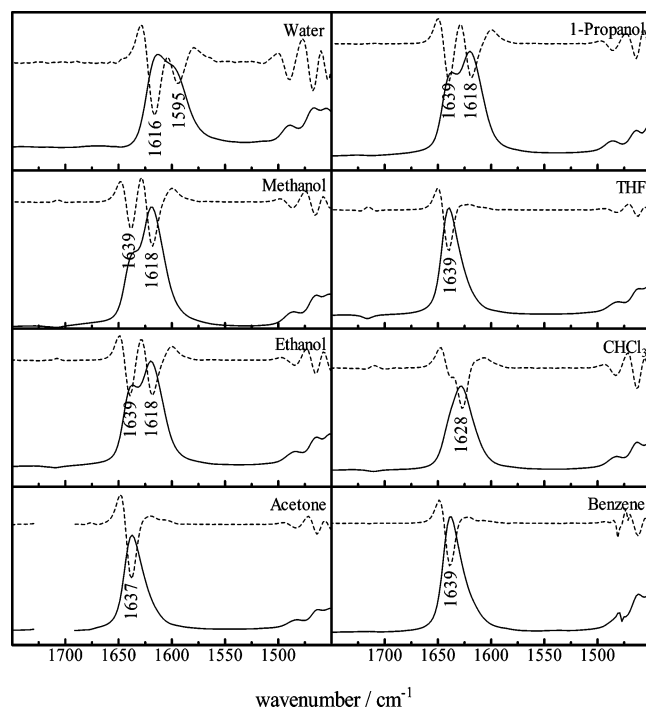


Figure 3. IR spectra of PNdEA in the 1750–1450 cm^{-1} region observed for the various solutions (solid line) and their second derivatives (dotted line).

spectra in the 1750–1450 cm^{-1} region of PNdMA and PNdEA in various solvents and their second derivatives, respectively. Note that PNdMA does not dissolve into benzene. All prominent bands in the IR spectra in Figures 2 and 3 originate from the $\nu_{\text{C=O}}$ modes. It is obvious that the peak positions and band shapes of the $\nu_{\text{C=O}}$ bands strongly depend on the solvents used. The number of peak components involved in the $\nu_{\text{C=O}}$ band envelopes is also varied from solvent to solvent. For the aqueous and alcohol solutions, at least two bands exist in the $\nu_{\text{C=O}}$ region,

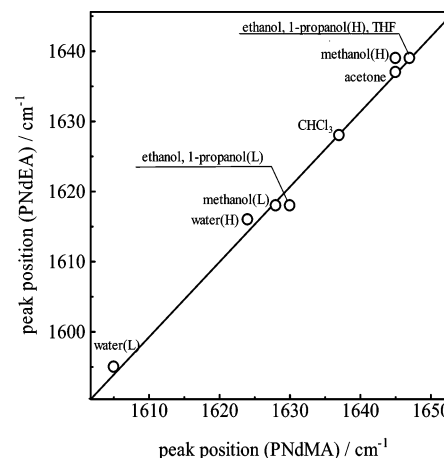


Figure 4. Correlation plot of the peak position(s) of the C=O stretching band for PNdEA versus that (those) for PNdMA in each solution. The symbols (L) and (H) indicate the peak position of the lower and the higher frequency bands detected in the C=O stretching region for aqueous and alcohol solutions, respectively.

whereas a unimodal peak is found for the acetone, THF, and CHCl_3 solutions. The $\nu_{\text{C=O}}$ band of PNdEA in benzene is also unimodal. For PNdMA, a band with the lowest frequency is observed at 1605 cm^{-1} for the aqueous solution, while that with the highest frequency appears at 1645–7 cm^{-1} for the alcohol, acetone, and THF solutions. Although the frequencies of $\nu_{\text{C=O}}$ bands for PNdEA in the solutions are lower by ca. 10 cm^{-1} than those for PNdMA, the shapes of the $\nu_{\text{C=O}}$ bands of PNdMA and PNdEA are similar to each other except in the aqueous solutions. It is worth noting that the relative intensity of the two bands observed for the aqueous solutions of PNdMA and PNdEA is different from each other.

Figure 4 plots the peak positions of the $\nu_{\text{C=O}}$ bands of PNdEA versus those of PNdMA for each solvent. All of the points are diagonally aligned on the graph. The correlation plot obtained here clearly indicates that the solvent effects on the $\nu_{\text{C=O}}$ band of the polymers are independent from the alkyl groups attached to the nitrogen atom. As a result, we classify the frequencies of the $\nu_{\text{C=O}}$ bands for PNdMA and PNdEA solutions into four groups: 1605 (1595), 1624–30 (1616–18), 1637 (1628), and 1645–7 (1637–9) cm^{-1} . The frequencies of the $\nu_{\text{C=O}}$ bands for PNdEA are indicated in parentheses. To assign these bands, several possibilities must be examined: (1) the solvation of the C=O groups, (2) the accessibility of solvent to the polymer chain (the effect of a steric hindrance on the solvation of the C=O groups incorporated in the polymer chain), and (3) the transition dipole coupling between the neighboring amide groups.²² By comparing the solvent-dependent changes in the $\nu_{\text{C=O}}$ bands of the polymers with those of NdMA and NdEA as the monomer model compounds, two former possibilities (1) and (2) can be discussed in more detail.

Solvent-Dependent Changes in the C=O Stretching Bands of the Monomer Model Compounds. Figure 5 shows the solvent-dependent changes in the $\nu_{\text{C=O}}$ band region of NdMA. The peak positions and band shapes of the $\nu_{\text{C=O}}$ bands strongly depend on the solvents used as in the case of the polymer solutions. For the alcohol solutions, at least three bands exist in the $\nu_{\text{C=O}}$ region, whereas a unimodal peak is found for the aqueous, acetone, THF, CHCl_3 , CCl_4 , benzene, cyclohexane, and *n*-hexane solutions. A band with the lowest frequency is observed at 1603 cm^{-1} for the aqueous solutions, while that with the highest frequency appears at 1675 cm^{-1} for the *n*-hexane solution. Note that the $\nu_{\text{C=O}}$ bands of NdMA in several apolar solvents seem to have an asymmetry shape arising

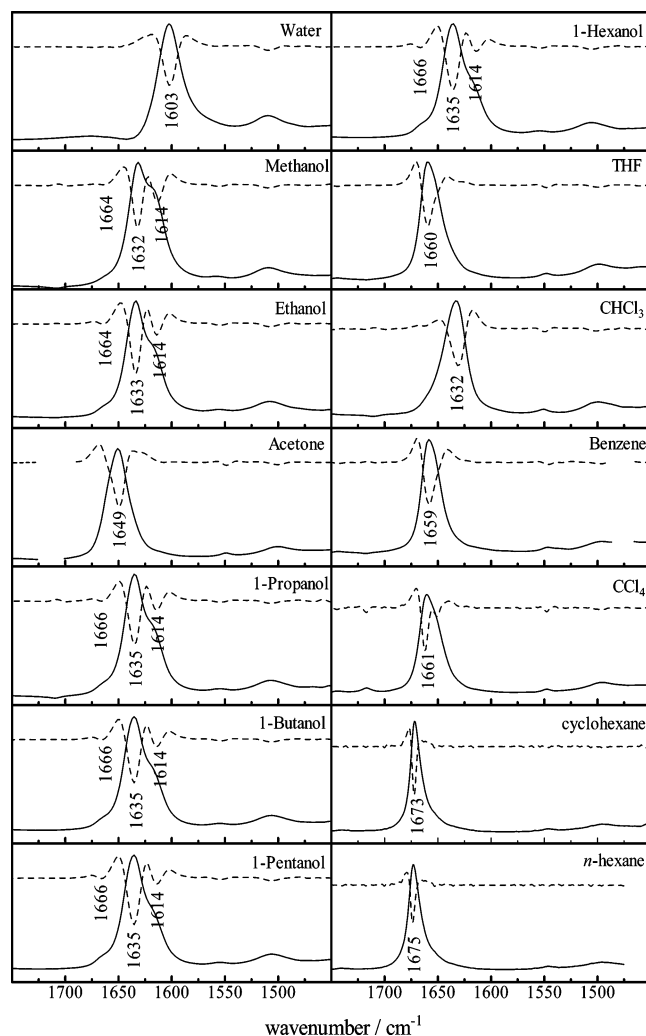


Figure 5. IR spectra of NdMA in various solutions (solid line) at the concentration of 0.2 M and their second derivatives (dotted line). All the spectra were measured with the ATR method except the spectra for CCl₄, cyclohexane, and *n*-hexane solutions, which were obtained by the transmission method.

from a weak intermolecular interaction. This will be discussed in a future paper. The frequencies of the $\nu_{\text{C=O}}$ bands of NdMA in the various solutions are estimated by second derivatives and compiled in Table 1.

As the first step, the relationship between the solvent-dependent changes in the $\nu_{C=O}$ bands of NdMA and the dielectric property of the solvents must be discussed, assuming that NdMA is embedded in a dielectric continuum medium. The dielectric constants of the solvents reported in the literature are listed in Table 1. The present IR results reveal that the dielectric constant of a continuum medium plays a minor role in the solvent-dependent changes in the $\nu_{C=O}$ band of NdMA. To support this conclusion, three typical examples are given below. First, the three $\nu_{C=O}$ bands of the alcohol solutions show only slight shifts despite large differences in the dielectric constant from 13.3 to 32.66. The second example can be seen in the IR spectra of NdMA in acetone and 1-propanol. Though the dielectric constants of these two solvents are similar to each other (20.7 for acetone and 20.1 for 1-propanol), the IR spectra of NdMA in acetone and 1-propanol are totally different; a unimodal peak is observed at 1649 cm^{-1} for the $\nu_{C=O}$ envelope of the acetone solution, while three peaks appear at 1666, 1635, and 1614 cm^{-1} in the spectrum of the 1-propanol solution. Third, in the CHCl_3 solution spectrum, the $\nu_{C=O}$ band appears at a

TABLE 1: Frequencies of the C=O Stretching Vibration Bands of NdMA in Various Solvents at 0.2 M

solvent	ϵ^a (298 K)	number of peaks ^b	the band due to C=O stretching vibration mode			
			wavenumber/cm ⁻¹ ^b			
<i>n</i> -hexane	1.89	1				1675
cyclohexane	2.22	1				1673
CCl ₄	2.228	1				1661
benzene	2.27	1				1659
CHCl ₃	4.81 ^c	1		1632		
THF	7.6 ^c	1				1660
1-hexanol	13.3	3	1614	1635		1666
1-pentanol	13.9	3	1614	1635		1666
1-butanol	17.1	3	1614	1635		1666
1-propanol	20.1	3	1614	1635		1666
acetone	20.7	1			1649	
ethanol	24.3	3	1614	1633		1664
methanol	32.7	3	1614	1633		1664
water	78.4	1	1603			

^a Lide, D. R., Ed. Handbook of Chemistry and Physics, 74th ed.; CRC Press: Boca Raton, 1993. ^b Estimated by the second derivatives. ^c Value at 293 K (20 °C).

lower frequency compared with those in the THF and benzene solution spectra. The dielectric constant of 4.81 for CHCl_3 is lower than that of 7.6 for THF, but higher than that of 2.27 for benzene. Therefore, the experimental results obtained here show that the shape and wavenumber of the $\nu_{\text{C=O}}$ band are concerned with an interaction between the functional group of solvent and the C=O group of NdMA. That is to say, we have to consider a solvent as a “real” molecule in order to investigate the solvent effects on the $\nu_{\text{C=O}}$ band.

Eaton and Symons²⁷ suggested that the frequencies for the $\nu_{\text{C=O}}$ bands of NdMA in protic solutions can be interpreted in terms of the strength of the hydrogen bonding between the C=O group of NdMA and the OH or NH group of the solvent. They proposed that the bands at around 1625 and 1610 cm^{-1} are assignable to the mono- and dihydrogen-bonded C=O groups, respectively. When Nyquist and Luoma²⁸ investigated the frequency shift of the $\nu_{\text{C=O}}$ band of NdMA in $\text{CHCl}_3/\text{CCl}_4$ mixed solvent, they suggested the existence of hydrogen-bonded complexes between NdMA and CHCl_3 . The effects of the hydrogen-bonded complex formation between amide compounds on IR bands have also been investigated by using quantum chemical calculations.²⁹ Although these microscopic approaches are limited to the explanation for the solvation of NdMA by a proton-donor-type solvent such as water, alcohols, and CHCl_3 , they are suitable for interpreting the experimental results obtained here. The multiple components in the $\nu_{\text{C=O}}$ envelope observed for the alcohol solutions may be due to the variations of the hydrogen-bonded complexes. To confirm this, we have been carrying out theoretical calculations on the formation of the solvent-solute complex.

Figure 6 shows the $\nu_{C=O}$ bands of NdEA in water, methanol, ethanol, 1-propanol, acetone, THF, chloroform, and benzene. The solvent-dependent changes in the $\nu_{C=O}$ bands of NdEA are very similar to those of NdMA (Figure 5). When compared with the $\nu_{C=O}$ bands observed for NdMA, all of the bands for NdEA appear at a lower frequency by 5–12 cm^{-1} . This will be discussed in the next paper, reporting the result of quantum chemical calculation. The shapes of the $\nu_{C=O}$ bands of NdMA and NdEA in a same solvent are very similar to each other. The peak position(s) of the $\nu_{C=O}$ band of NdMA and NdEA for each solution shows a good correlation, as shown in Figure 7. Thus, we conclude that the solvent effects on the $\nu_{C=O}$ bands are almost identical for both NdMA and NdEA.

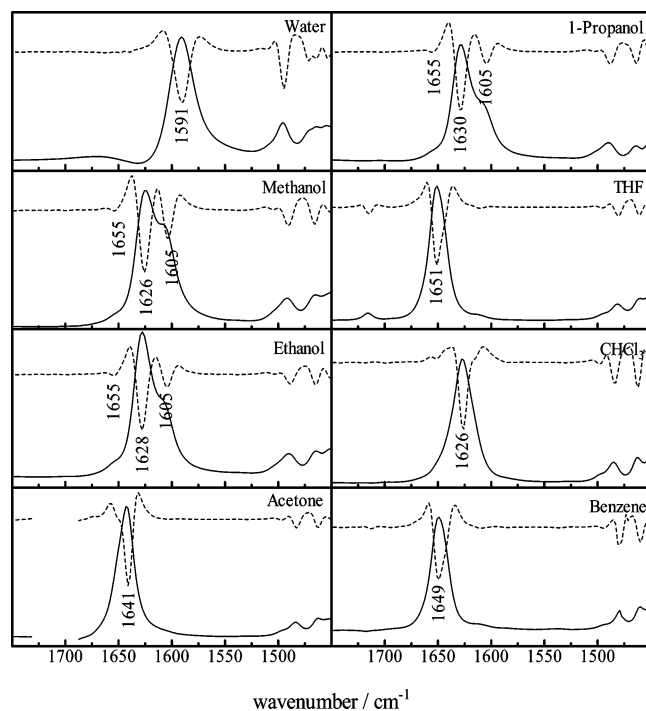


Figure 6. IR spectra of NdEA in various solutions (solid line) and their second derivatives (dotted line).

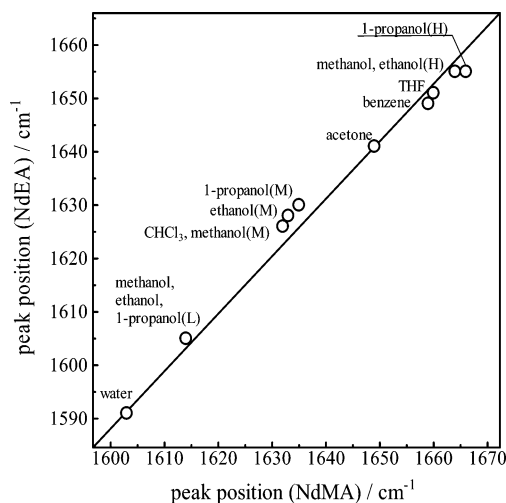


Figure 7. Correlation plot of the peak position(s) of the C=O stretching band for NdEA versus that (those) for NdMA in each solution. The symbols in the parenthesis indicate the peak position of (L) the lowest, (M) the middle, and (H) the highest frequency bands detected in the C=O stretching region for alcohol solutions.

Correlation Between the Frequencies of the $\nu_{\text{C=O}}$ Bands of the Monomer Model Compounds and the Polymers in Solutions. Is it possible to assign the $\nu_{\text{C=O}}$ bands of PNdMA and PNdEA in solutions, referring to the frequencies and intensities of the corresponding $\nu_{\text{C=O}}$ bands of NdMA and NdEA measured under the same conditions? To examine this point, we developed a correlation plot of the $\nu_{\text{C=O}}$ bands between NdMA and PNdMA, as shown in Figure 8. The same plot was also made for NdEA and PNdEA (see Figure 9). In the correlation plots, it is assumed that the lowest-frequency $\nu_{\text{C=O}}$ bands of NdMA and NdEA for the alcohol solutions are not observed for the polymer solutions. That is, the bands at around 1628–30 cm^{-1} of PNdMA in the alcohol solutions are assumed to correspond to the band at 1632–5 cm^{-1} of NdMA. For PNdEA and NdEA, the corresponding bands are observed at 1616–8 and 1626–28 cm^{-1} , respectively. In Figures 8 and 9,

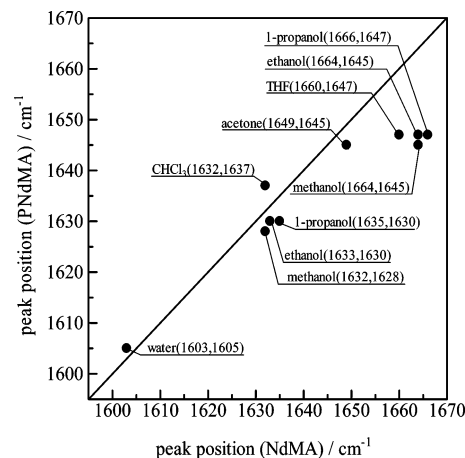


Figure 8. A correlation plot of the peak position(s) of the C=O stretching band for NdMA versus that (those) for PNdMA in each solution. In the parenthesis, the frequency of the bands for NdMA is represented at the left-hand side and that for PNdMA is at the right-hand side.

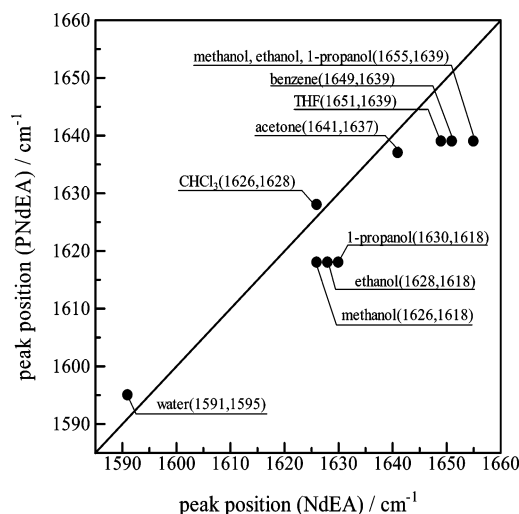


Figure 9. A correlation plot of the peak position(s) of the C=O stretching band for NdEA versus that (those) for PNdEA in each solution. In the parenthesis, the frequency of the bands for NdEA is represented at the left-hand side and that for PNdEA is at the right-hand side.

the abscissa and ordinate have the same range. Therefore, if a frequency of the $\nu_{\text{C=O}}$ band of a polymer is in good agreement with that of a corresponding monomer, then the points should appear along the diagonal line. Figures 8 and 9 clearly suggest that several $\nu_{\text{C=O}}$ bands for PNdMA and PNdEA in solutions are assignable by the analogy of the corresponding bands for the monomers. In those cases, it is very likely that the solvation of the C=O group in PNdMA and PNdEA is similar to that in NdMA and NdEA, respectively. If a plot shows deviations from the diagonal line, we can identify a difference in the solvation behavior between the polymer and the monomer solutions.

As mentioned above, we have proposed the classification of the $\nu_{\text{C=O}}$ bands observed for the polymer solutions into four groups: 1605 (1595), 1624–30 (1616–18), 1637 (1628), and 1645–7 (1637–9) cm^{-1} . As inferred from the result shown in Figure 7, the bands of PNdMA at 1605 cm^{-1} (water), 1628–30 cm^{-1} (alcohols), 1637 cm^{-1} (CHCl_3), and 1645 cm^{-1} (acetone) may have the same origin as the $\nu_{\text{C=O}}$ bands of NdMA observed for each solvent. On the other hand, it seems impossible to assign the bands at 1624 cm^{-1} in (water), 1647 cm^{-1} (THF), and 1645–1647 cm^{-1} (alcohols) by analogy with

the frequencies of the $\nu_{\text{C=O}}$ bands for NdMA solutions. Note that the band at 1614 cm^{-1} for NdMA in the alcohol solutions is not observed for the alcohol solutions of PNdMA. For PNdEA, the bands at 1595 cm^{-1} (water), 1628 cm^{-1} (CHCl_3), and 1637 cm^{-1} (acetone) may be assignable by analogy with those of NdEA. The frequency of a $\nu_{\text{C=O}}$ band for the alcohol solutions of PNdEA observed at 1618 cm^{-1} seems to be lower by $8\text{--}10\text{ cm}^{-1}$ than that of the corresponding band for alcohol solutions of NdEA observed at $1626\text{--}30\text{ cm}^{-1}$. The bands at 1616 (water) and 1639 cm^{-1} (alcohols, THF, and benzene) are characteristic of the polymer solutions.

As seen in the correlation plots (Figures 4 and 7), the frequencies of the $\nu_{\text{C=O}}$ bands for PNdEA and NdEA in solutions are in good agreement with those for PNdMA and NdMA, respectively. Thus, we use the frequencies of the $\nu_{\text{C=O}}$ bands of PNdMA and NdMA for discussion, and those of PNdEA and NdEA are indicated in the parenthesis hereafter.

Assignments for the $\nu_{\text{C=O}}$ Bands for the Polymers in Protic Solvents. For small molecules, solvent-induced vibrational frequency shifts of the $\nu_{\text{C=O}}$ band have been studied.^{27–30} In particular, the frequency shifts in a dilute solution with protic solvents have been analyzed in terms of donor–acceptor interactions.^{31,32} By referring to these reports, assignments for the $\nu_{\text{C=O}}$ bands of the polymers in protic solvents can be discussed. For the polymers, the band at 1605 (1595) cm^{-1} is characteristic of the aqueous solution. The corresponding bands of the monomers are observed at 1603 (1591) cm^{-1} . Eaton and Symons²⁷ indicated that the $\nu_{\text{C=O}}$ band at around 1608 cm^{-1} is assignable to dihydrogen-bonded NdMA in protic solutions. Note that dihydrogen bonding occurs, not only in an aqueous solution, but also in the alcohols. It has been considered that the band at 1614 (1605) cm^{-1} is associated with the dihydrogen-bonded NdMA in the alcohol solutions.²⁷ To establish the assignments for the $\nu_{\text{C=O}}$ bands in alcohol solutions, a simulation study on the IR spectrum is being currently performed in our group by using quantum chemistry calculations. The IR results obtained here suggest that the band at 1605 (1595) cm^{-1} for the polymers arises from the dihydrogen-bonded C=O groups by water molecules. In the same manner, we can conclude from the present IR results that the $\nu_{\text{C=O}}$ band at 1637 (1628) cm^{-1} for the polymers in CHCl_3 arises from a $\text{C=O}\cdots\text{H-C}$ hydrogen bonding.²⁸ The assignments for the band at $1624\text{--}30$ ($1616\text{--}18$) cm^{-1} are very important to investigate the solvation of the polymers in an aqueous solution. For example, the changes in the relative intensity of the band at $1624\text{--}30$ ($1616\text{--}18$) cm^{-1} to that at 1605 (1595) cm^{-1} have been reported for a phase separation process of PNdEA in an aqueous solution.²¹ In addition, the relative intensity of the two $\nu_{\text{C=O}}$ bands for PNdEA in the aqueous solution is different from that of PNdMA, as shown in Figures 2 and 3. This is certainly concerned with the fact that the aqueous solution of PNdMA does not undergo a thermally induced phase separation. Despite its importance, the assignment for the band at $1624\text{--}30$ ($1616\text{--}18$) cm^{-1} is still controversial.

A C=O band with the lowest frequency of NdMA in the alcohol solutions is located at 1614 (1605) cm^{-1} and that with the second lowest is observed at $1632\text{--}5$ ($1626\text{--}30$). For NdMA in methanol, it has been proposed that the bands at 1614 and 1632 cm^{-1} are due to di- and monohydrogen-bonded C=O groups, respectively.²⁷ However, in the alcohol solutions of the polymers, a $\nu_{\text{C=O}}$ band with the lowest frequency is observed at $1628\text{--}30$ (1618) cm^{-1} , and the corresponding band is not found in the alcohol solutions of NdMA (NdEA). On the other hand, in the aqueous solutions of the monomers, the $\nu_{\text{C=O}}$ band

is unimodal and no band exists around 1624 (1616) cm^{-1} , while two bands exist in the $\nu_{\text{C=O}}$ vibration region for the polymer solutions. Thus, we conclude that the band at $1624\text{--}30$ ($1616\text{--}18$) cm^{-1} is characteristic for the aqueous and alcohol solutions of the polymers. No band with the frequency of $1624\text{--}30$ ($1616\text{--}18$) cm^{-1} was observed for the $\nu_{\text{C=O}}$ band of polymers in an aprotic solvent. This implies that the band is concerned with a $\text{C=O}\cdots\text{H-O}$ hydrogen bonding. As a result, we suppose that the interaction between the C=O groups in the polymer side chain and the OH group of alcohol molecules is partially inhibited. In other words, the band at $1624\text{--}30$ ($1616\text{--}18$) cm^{-1} may result from both the hydrogen bonding of solvent molecules to a C=O group and the steric hindrance of polymer chains to the solvation.

The band at $1645\text{--}7$ ($1637\text{--}9$) cm^{-1} of the polymers is observed not only for the alcohol solutions, but also acetone and THF solutions. We discuss it in the next section.

Assignments for the $\nu_{\text{C=O}}$ Bands for the Polymers in Aprotic Solvents. The frequency of $1645\text{--}7$ ($1637\text{--}9$) cm^{-1} is the highest among those of the $\nu_{\text{C=O}}$ bands for the polymers in solutions. The results indicate that the highest frequency of the $\nu_{\text{C=O}}$ band for the polymers in solutions is not dependent upon the solvent used. For the monomers, the highest-frequency $\nu_{\text{C=O}}$ band exists at 1649 (1641) cm^{-1} in the acetone solution spectra and at 1660 (1651) cm^{-1} in the THF solution spectra. The corresponding $\nu_{\text{C=O}}$ bands of NdEA and PNdEA in benzene are observed at 1649 and 1639 cm^{-1} , respectively. Note that the highest-frequency $\nu_{\text{C=O}}$ bands for the monomers in the alcohol solutions are located at $1664\text{--}6$ (1655) cm^{-1} . For the aprotic solutions, the IR results clearly reveal that the solvent-dependence of the $\nu_{\text{C=O}}$ band of the monomers are different from those of the polymers. For PNdEA, Maeda et al.²¹ reported that the band at 1638 cm^{-1} is assignable to the free C=O group. This band corresponds to the band at $1645\text{--}7\text{ cm}^{-1}$ of PNdMA. However, the frequency of $1645\text{--}7$ ($1637\text{--}9$) cm^{-1} is too low to be assigned to the free C=O group. For example, the $\nu_{\text{C=O}}$ bands of NdMA in the cyclohexane and *n*-hexane solutions are observed at 1673 and 1675 cm^{-1} , as shown in Figure 5.

For the THF solutions, it is evident that the frequency of the $\nu_{\text{C=O}}$ band of the polymers is significantly lower than those of the monomers. Because those solvents are not a proton donor, the lower-frequency shift of the $\nu_{\text{C=O}}$ band in THF and acetone is not owed to the changes in the hydrogen bonding. Therefore, it is very likely that the lower-frequency shift is concerned with the interaction between the neighboring amide groups, such as a transition dipole coupling.²² On the other hand, the frequency of 1645 (1637) cm^{-1} observed for the polymers in the acetone solution is comparable to that of 1649 (1641) cm^{-1} for the monomers. This suggests that the $\nu_{\text{C=O}}$ band attributed to the solvated C=O groups by acetone also appears at around 1645 (1637) cm^{-1} . Thus, two possible interactions should be considered in order to assign the band at $1645\text{--}7$ ($1637\text{--}9$) cm^{-1} for the polymer solutions: (1) the interaction between the C=O group and aprotic solvent, and (2) the interaction between the neighboring amide groups.

Conclusions

The solvent-dependent changes in the $\nu_{\text{C=O}}$ bands of PNdMA and PNdEA have been studied in detail by using various good solvents for the polymers. Both protic and aprotic solvents that have various dielectric properties have been examined in the present study. Comparative studies using the monomer model compounds under the same conditions have also been carried out. The IR results for the monomers have led us to conclude

TABLE 2: Frequencies of the C=O Stretching Vibration Bands of PNdMA (PNdEA) in Various Solvents and their Assignments

	frequency of the C=O stretching vibration bands ^{a,b} /cm ⁻¹			
	hydrogen-bonded C=O by water molecule(s)	weakly hydrogen-bonded C=O and/or intramolecular interaction ^d	C=O...H-C interaction with CHCl ₃	intramolecular interaction ^d and/or solvated C=O by aprotic solvent ^c
benzene				--- (1639)
chloroform			1637 (1628)	
THF				1647 (1639)
1-propanol		1630 (1618)		1647 (1639)
acetone				1645 (1637) ^b
ethanol		1630 (1618)		1647 (1639)
methanol		1628 (1618)		1647 (1639)
water	1605 (1595)	1624 (1616)		

^a The frequency of the $\nu_{\text{C=O}}$ bands for PNdEA is indicated in parentheses. ^b Estimated by the second derivatives. ^c The frequency of the $\nu_{\text{C=O}}$ band of NdMA and NdEA for acetone solution is higher by 2–4 cm⁻¹ than that of the polymers. ^d Including steric hindrance of polymer chains to the solvation and an interaction between the amide groups such as the dipole interaction between neighboring amide groups.

that the shapes and frequencies of the $\nu_{\text{C=O}}$ bands in solutions are not strongly dependent on the dielectric property of the solvent, but concerned with molecular interactions between a functional group of solvent molecules and the C=O group of NdMA and NdEA. It has also been revealed that the solvent effects on the $\nu_{\text{C=O}}$ band of the polymers and the monomer model compounds are almost independent from the alkyl groups attached to the nitrogen atom. Thus, we have concluded that molecular interpretation for the solvation of PNdEA and PNdMA is necessary to understand the solvent-dependent changes in their IR bands.

The $\nu_{\text{C=O}}$ bands for the polymers in the solutions can be classified into four groups: (1) a band at 1605 (1595) cm⁻¹ for aqueous solutions, (2) a band in the 1624–30 (1616–18) cm⁻¹ region for aqueous and alcohol solutions, (3) a band at 1637 (1628) cm⁻¹ for CHCl₃ solutions, and (4) a band at 1645–7 (1637–9) cm⁻¹ for alcohol, acetone, and THF solutions (for PNdEA, the corresponding band is also observed for the benzene solution). We have proposed the assignments for the above four $\nu_{\text{C=O}}$ bands as compiled in Table 2. The band at 1605 (1595) cm⁻¹ is characteristic of the aqueous solution and assignable to dihydrogen-bonded C=O groups with water molecules. The band in the 1624–30 (1616–18) cm⁻¹ region is involved in a hydrogen bonded by a OH group of protic solvent molecules, which is weakened by the steric hindrance of the polymer chains. The band at 1637 (1628) cm⁻¹ may be due to a hydrogen-bonded C=O group by CHCl₃. Comparing with the frequencies of the $\nu_{\text{C=O}}$ bands of NdMA and NdEA in the aprotic solvents, the frequency of 1645–7 (1637–9) cm⁻¹ is markedly low. It is supposed that two possible mechanisms can be considered to discuss the origin of the band at 1645–7 (1637–9) cm⁻¹: a solvation of C=O group by aprotic solvents and an interaction between the neighboring amide groups.

In this paper, we have revealed that the frequency and shape of the $\nu_{\text{C=O}}$ band for PNdMA and PNdEA in solutions can be interpreted in terms of the molecular interactions, which originates not only from an interaction between a functional group of the solvents and the C=O group of the polymers, but also from an interaction such as a steric hindrance of the chains to the solvation and an interaction between neighboring amide groups. The latter may be very important to investigate the solvation of the polymers in solutions because, in all of the solutions, a characteristic $\nu_{\text{C=O}}$ band for the polymer systems is found. The IR results presented here are directly concerned with the molecular interpretation for the solvation of the polymers that may enable us to understand the solubility of a realistic polymer.

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References and Notes

- Ptitsyn, O. B.; Kron, A. K.; Eizner, Y. Y. *J. Polym. Sci., C* **1968**, 16, 3501.
- de Genne, P. G. *J. Phys. Lett.* **1975**, 36, L55.
- Nishio, I.; Sun, S. T.; Swislow, G.; Tanaka, T. *Nature* **1979**, 281, 208.
- Sun, S. T.; Nishio, I.; Swislow, G.; Tanaka, T. *J. Chem. Phys.* **1980**, 73, 5971.
- Chu, B.; Park, I. H.; Wang, Q.; Wu, C. *Macromolecules* **1987**, 20, 1965.
- Matsuyama, A.; Tanaka, F. *J. Chem. Phys.* **1991**, 94, 781.
- Nakata, M.; Nakagawa, T. *J. Chem. Phys.* **1999**, 110, 2703.
- Heskins, M.; Guillet, J. E. *J. Macromol. Sci., Chem.* **1968**, A2, 1441.
- Fujishige, S.; Kubota, K.; Ando, I. *J. Phys. Chem.* **1989**, 93, 3311.
- Tong, Z.; Zeng, F.; Zheng, X.; Sato, T. *Macromolecules* **1999**, 32, 4488.
- Kubota, K.; Fujishige, S.; Ando, I. *J. Phys. Chem.* **1990**, 94, 5154.
- Wan, X.; Qiu, X.; Wu, C. *Macromolecules* **1998**, 31, 2972.
- Schild, H. G.; Tirrell, D. A. *J. Phys. Chem.* **1990**, 94, 4352.
- Tiktupulo, E. I.; Bychkova, V. E.; Riëka, J.; Ptitsyn, O. B. *Macromolecules* **1994**, 27, 2879.
- Winnk, F. M. *Macromolecules* **1990**, 23, 233.
- Walter, R.; Riëka, J.; Quellet, C.; Nyffenegger, R.; Binkert, T. *Macromolecules* **1996**, 29, 4019.
- Ohta, H.; Ando, I.; Fujishige, S.; Kubota, K. *J. Polym. Sci., Polym. Phys. Ed.* **1991**, 29, 963.
- Platé, N. A.; Lebedeva, L.; Valuev, L. I.; *Polym. J.* **1999**, 31, 21.
- Percot, A.; Zhu, X. X.; Lafleur, M. *J. Polym. Sci., Polym. Phys. Ed.* **2000**, 38, 907.
- Maeda, Y.; Higuchi, T.; Ikeda, I. *Langmuir* **2000**, 16, 7503.
- Maeda, Y.; Nakamura, T.; Ikeda, I. *Macromolecules* **2002**, 35, 10172.
- Torii, H.; Tasumi, M. *J. Chem. Phys.* **1992**, 96, 3379.
- Katsumoto, Y.; Tanaka, T.; Sato, H.; Ozaki, Y. *J. Phys. Chem. A* **2002**, 106, 3429.
- Katsumoto, Y.; Tanaka, T.; Ozaki, Y. *Macromol. Symp.* **2004**, 205, 209.
- Katsumoto, Y.; Tanaka, T.; Ozaki, Y. *Kobunshi Ronbunshu* **2003**, 60, 256.
- Savitzky, A.; Golay, M. J. E. *Anal. Chem.* **1964**, 36, 1627.
- Eaton, G.; Symons, M. C. R.; Rastogi, P. P. *J. Chem. Soc., Faraday Trans. 1* **1989**, 85, 3257.
- Nyquist, R. A.; Luoma, D. A. *Appl. Spectrosc.* **1991**, 45, 1501.
- Kim, K.-Y.; Lee, H.-J.; Karpfen, A.; Park, J.; Yoon, C.-J.; Choi, Y.-S. *Phys. Chem. Chem. Phys.* **2001**, 3, 1973.
- Wang, B.; Yamaguchi, T.; Nakao, S. *J. Phys. Chem. B* **2001**, 105, 3143.
- Nyquist, R. A.; Streck, R.; Jeschek, G. *J. Mol. Struct.* **1996**, 377, 113.
- Liu, Q.; Sang, W.; Xu, X. *J. Mol. Struct.* **2002**, 608, 253.