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Dynamic nuclear magnetic resonance and Raman spectroscopic measurements of five kinds of *N,N*-dimethylformamide derivatives in relation to the dissolution mechanism of polyacrylonitrile

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The internal rotation of five kinds of *N,N*-dimethylformamide (DMF) derivatives was studied by dynamic nuclear magnetic resonance (n.m.r.) and Raman spectroscopic measurements in relation to the dissolution mechanism of polyacrylonitrile (PAN). The dissolution temperature (T_{sol}) of PAN was determined by the steric effect of the solvent molecules, i.e. the higher the bulkiness of a substituent, then the higher was the T_{sol} of PAN. The intermolecular interaction between the nitrile group and the solvents was evaluated by Raman spectra in terms of the large carbonyl shift ($\nu_{c=o}$). Dynamic ^{1}H n.m.r. spectroscopy measurements revealed that the value of the coalescence temperature (T_c) was not proportional to the steric factor, suggesting that the solvent properties are not determined solely by the latter and that internal rotation of the solvent molecules is defined by the extent of looseness in the packing of the solvent molecules in the liquid state. The significance of both intra- and intermolecular factors of the solvent molecules in the dissolution of PAN was also discussed. Copyright © 1996 Elsevier Science Ltd.

(Keywords: dynamic ^{1}H n.m.r. spectra; *N,N*-dimethylformamide derivatives; Raman spectra)

INTRODUCTION

The dissolution of polyacrylonitrile (PAN) is a quite interesting but also difficult problem. How to approach this complicated situation has not been clarified experimentally. This is particularly true for the stereoregular isotactic material prepared by urea-clathrate polymerization in the solid state. The sample is totally insoluble in such typical dipolar aprotic solvents as *N,N*-dimethylformamide (DMF) at room temperature[1]. The dissolution occurs only when the temperature is increased to above 100°C, when a transparent homogeneous solution is obtained. Since the dissolution occurs only at high temperatures, information on the kinetic data of both the solvent and the polymer at high temperatures is quite important from this point of view.

In this article, proton (^{1}H) dynamic n.m.r. spectroscopic measurements for five different kinds of DMF derivative were carried out, and the molecular motion of the solvent molecules at elevated temperatures was studied. Although the dynamic n.m.r. spectroscopic measurement itself is not a new technique and the results for DMF and related compounds have already been partly cited in some n.m.r. spectroscopy textbooks[2–4], this basic approach is quite important here. This is because we have succeeded in the preparation of not only highly isotactic (~ 80%) PAN[5] but also a syndiotactic material by the use of radiochemical methods[6,7]. In order to apply these polymers in industrial processes, it is vitally important to clarify the dissolution mechanism of PAN at elevated temperatures. With this in mind the results obtained from dynamic n.m.r. spectroscopic measurements and related discussions are presented in this paper.

EXPERIMENTAL

Solvents

Five different kinds of organic dipolar aprotic solvents were used in this way. In addition to DMF, these were *N,N*-dimethylacetamide (DMAc), *N,N*-diethylformamide (DEF), *N,N*-dimethylcarbamylchloride (DMCC), and *N,N*-dimethyltrichloroacetamide (DMTCAc). Careful distillation under reduced pressure was carried out twice for each solvent, with the results of their characterization given in *Table 1*.

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Table 1 Characterization of the solvents used in this study

Solvent	Substituent	Density[a] $(g\,cm^{-3})$	Raman band $\nu_{C=O}$[b] (cm^{-1})	$\nu_{C=O}$[c] (cm^{-1})	$\nu_{C=O}$[d] (cm^{-1})
DMF	H	0.9501	1661	1689	1671
DMAc	CH_3	0.9418	1637	1658 1670	1644
DEF	C_2H_5	0.9057	1660	1660	1667
DMCC	Cl	1.1724	1731	1747 1756	1736
DMTCAc	CCl_3	1.4396	1674	1688 1700	1675

[a] Average value of three measurements
[b] The carbonyl frequency of the pure solvents
[c] The carbonyl band of the solvent after the addition of a small amount of n-hexane (5 wt %), which was partially miscible. The appearance of two peaks may be due to the extent of dipole–dipole interaction, i.e. partial or complete destruction of solvent–solvent interaction
[d] The carbonyl band after addition of adiponitrile (5 wt %); this component was completely soluble and a homogeneous solution was obtained

Density measurements

A Lipkin-type of micropicnometer (volume = 3 ml) was used according to the manner described in ref. 8. The packing density (or bulkiness) of each solvent in the liquid state (at 20°C) was calculated.

^{1}H dynamic n.m.r. spectroscopic measurements

JEOL JNM EX-270 and EX-90 spectrometers were used. Typical n.m.r. measurement conditions for the former were as follows: PW1, 4.3 μs (45° pulse); PD 3.03 s (acquisition time); point 32 K (data points).

Raman spectroscopic measurements

A Jasco NR-1100 type of spectrometer was used under the same conditions as those given in ref. 9.

Measurement of dissolution temperature (T_{sol})

The laboratory-constructed laser optical instrument described in ref. 1 was used in these determinations.

RESULTS AND DISCUSSION

Dynamic ^{1}H n.m.r. spectra of DMF and DMTCAc

Figure 1 shows typical ^{1}H n.m.r. spectra of DMF measured at different temperatures. DMF has two methyl groups (CH_3) and these are detected as two signals in the n.m.r. spectra. This is due to the magnetic difference in the molecular environment, i.e. the existence of an electronegative carbonyl group. The methyl group (1) is more strongly affected than methyl group (2) by the electron-withdrawing effect of the nearby carbonyl group. Therefore, the former methyl group appears at a lower magnetic field than the latter. In the series of DMF derivatives, the amide group has some characteristics of a double bond (rather than a single bond), and there exists a rotational barrier in the potential energy curve[10–12]. When the temperature is low, internal rotation is inhibited and the two methyl groups remain separate, whereas when the temperature is increased, internal rotation is permitted and the methyl groups begin to rotate around the bonding axis. When the temperature is sufficiently high, the rotation is greatly accelerated and the differentiation of the two methyl groups becomes virtually impossible, i.e. the signals from the two methyl groups merge into a single peak (see *Figure 2*). The temperature at which this occurs is defined as a kind of critical temperature, namely the coalescence temperature $(T_c)^{2-4}$. From *Figure 2*, the T_c of DMF was determined to be 147°C.

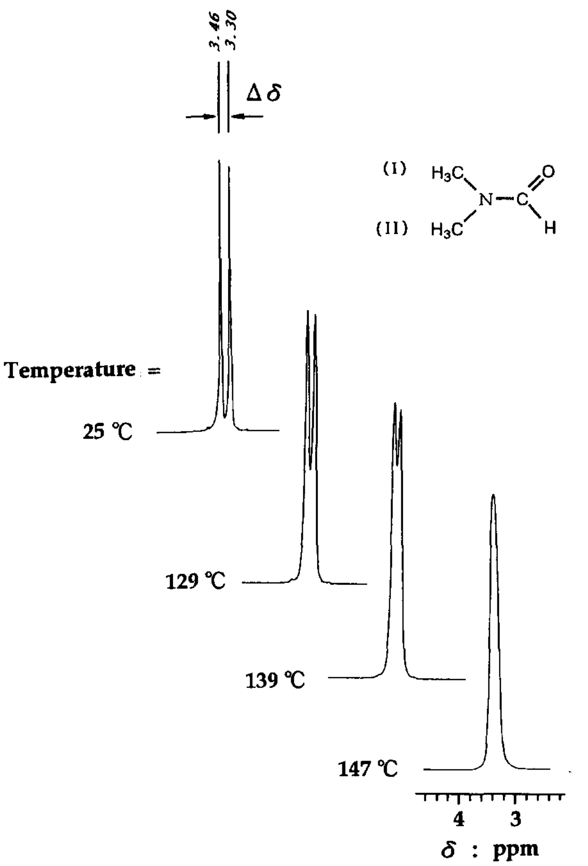

Figure 1 Typical ^{1}H dynamic n.m.r. (270 MHz) spectra of DMF measured at different temperatures

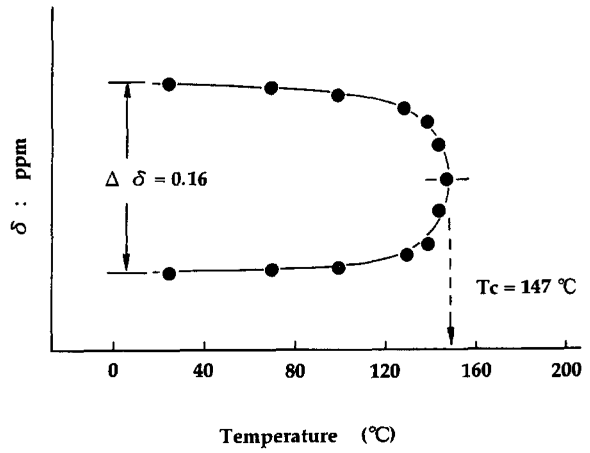

Figure 2 Determination of the T_c of DMF; note that the value of T_c was slightly lowered (to 140°C) when the 90 MHz spectrometer was used

Figure 3 shows similar dynamic ^{1}H n.m.r. spectra of DMTCAc. The spectral characteristics of this solvent are essentially identical to those of DMF, except that the rotation is initiated at a far lower temperature. From *Figure 4*, the T_c value of this solvent was determined to

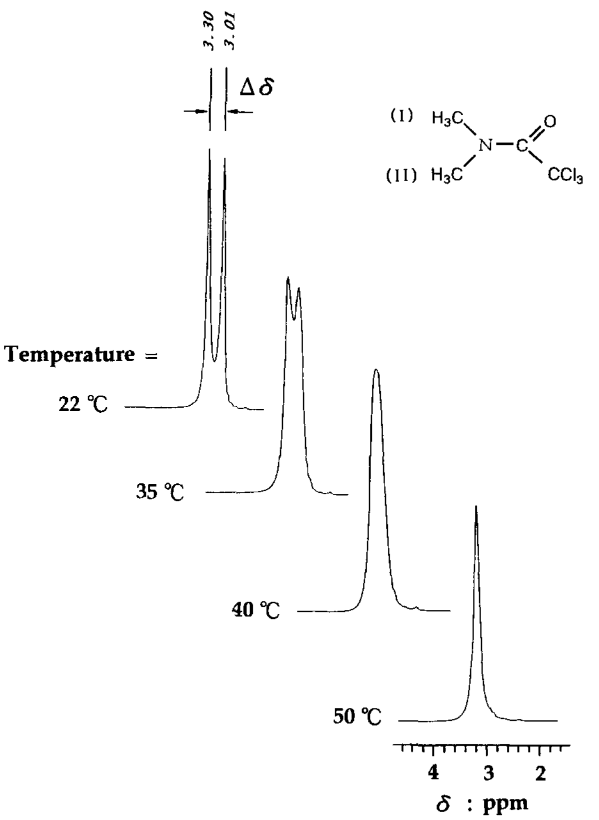

Figure 3 Dynamic ^{1}H n.m.r. (270 MHz) spectra of DMTCAc measured at different temperatures

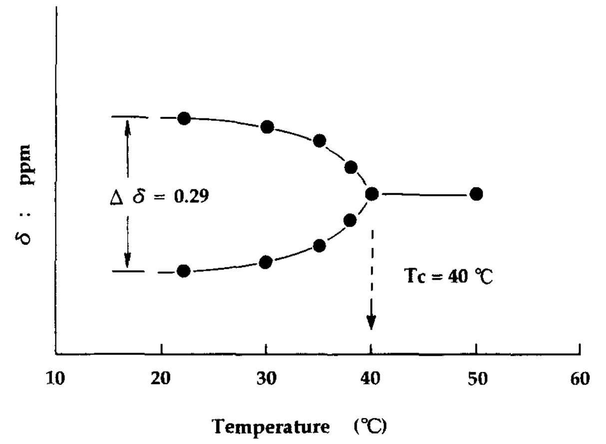

Figure 4 Determination of the T_c of DMTCAc; note that the value of T_c was slightly lowered (to 35°C) when the 90 MHz spectrometer was used

be 40°C. The value of T_c is not a constant of the material as it depends on the magnetic intensity, but under the given n.m.r. conditions it has a clear meaning, namely the extent of internal rotation of the solvent molecules. The difference in T_c due to the use of different spectrometers (270 and 90 MHz) was relatively small, i.e. 5–7°C.

From the geometrical consideration outlined in ref. 9, however, the above results seem to be quite unreasonable. The highly bulky trichloromethyl group (CCl_3) should inhibit rotation about the molecular axis due to its steric effect. However, experimental results indicate that far from being restricted, rotation is, in fact, rather promoted.

Relationship between T_c *and the Raman carbonyl band*

The above points are more clearly indicated in *Figure 5*. In this figure, the value of T_c of several DMF derivatives was plotted against the Raman carbonyl shift. The latter is a measure of the intensity of the interaction between the solvent and the nitrile group, the extent of which is directly proportional to the value of T_{sol}[9]. The stronger interactions produced the larger carbonyl shifts. *Figure 5* shows that the increase in carbonyl shift is in agreement with the increase of T_c, or that when the bulkiness is increased, internal rotation is no longer inhibited, but rather accelerated.

The only possible explanation for the above results is that the bulkiness of a substituent in a solvent molecule permits rotation through a loosening of the packing of the solvent molecules in the liquid state. In other words, solvent molecules are strongly associated with each other (through dipole–dipole interactions) in the liquid state and this strong self-association may be weakened by the steric effect of the substituent. The bulky substituent may promote this loosening effect. If this explanation is true, then the higher the bulkiness, the lower the coalescence temperature (T_c).

Relationship between T_c *and bulkiness of solvents*

Figure 6 shows plots of T_c against the bulkiness of the various solvents. The quantity in the abscissa has the following meaning, namely the available volume occupied by one mole of solvent. The results indicate that the value of T_c is directly proportional to the bulkiness of the solvents. The T_c is defined by a value which represent how loose the solvent molecules are packed in a given unit volume. The looser the molecular packing of the DMF derivative, then the easier will be the molecular rotation (as indicated by the lower T_c).

This is more clearly indicated by *Figure 7*. When the

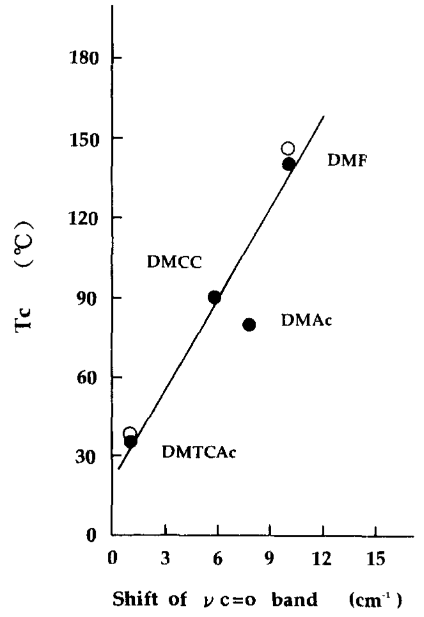

Figure 5 Relationship between T_c and the Raman carbonyl shift of the various solvents. DEF showed no coalescence behaviour, and therefore the results for this derivative are omitted here. Solid and open circles indicate the results obtained by using different n.m.r. spectrometers; although there is a difference in these values (5–7°C), this difference does not affect the conclusion obtained in this work

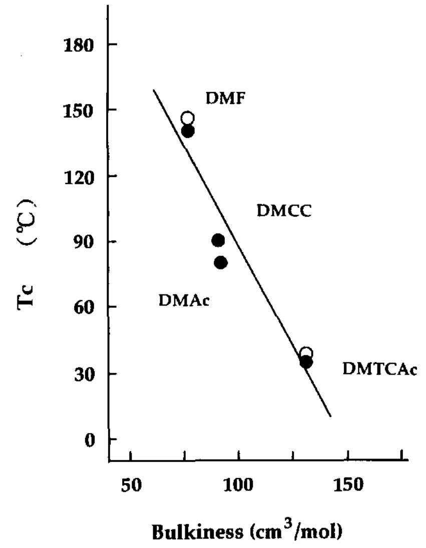

Figure 6 Relationships between T_c and the bulkiness of the various solvents, where the physical meaning of each symbol is the same as that used in *Figure 5*

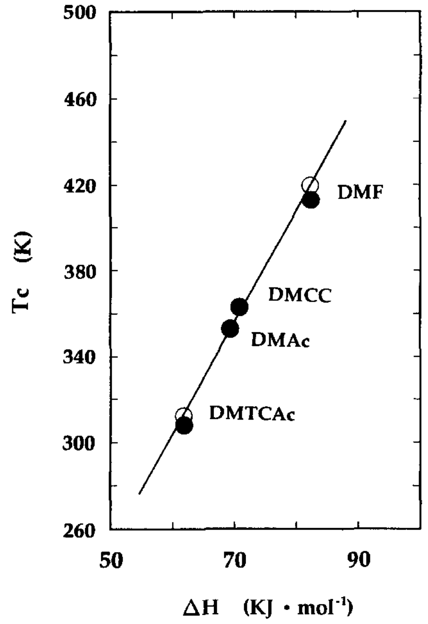

Figure 7 Relationship between the value of T_c and the enthalpy term (based on kinetic analysis)

experimental data were analysed kinetically[3,13], the enthalpy and entropy terms were calculated. When the T_c value was plotted against the enthalpy term, a linear relationship was obtained (*Figure 7*). The results indicate that the T_c value is directly determined by the enthalpy, i.e. the intermolecular interaction term.

We can summarize the experimental results in the following way:

(1) The bulkiness of the solvent is of primary importance for the dissolution of PAN. The higher the bulkiness, then the higher will be the dissolution temperature (T_{sol}), due to the restriction of the intermolecular interactions between solvent and polymer (i.e. the steric effect of the solvent molecules).

(2) On the other hand, the bulkiness exerts an opposite effect. The higher the bulkiness, then the smaller will be the packing density of the solvent molecules in the liquid state, and therefore the easier the internal rotation, as shown by the lower coalescence temperature (T_c). The important point to mention here is that the bulkiness of a substituent acts as a loosener (or as a filler) in the packing of solvent molecules under the given conditions, and thus the rotation is permitted at a lower temperature.

Raman spectra and molecular association of DMF derivatives

By considering the Raman spectra, the relatively complex solvent properties of the DMF derivatives were clarified to a certain extent under limited conditions. This can be expressed as shown in *Figure 8*; the dynamic n.m.r. spectroscopic results of the DMF derivatives provide information on the pure solvent in the self-associated state (one can designate this as a *free solvent* (A), which has not yet participated in the solvation), whereas the Raman carbonyl shift provides information on the solvent that has associated with the secondary component (B). This leads to the key feature of the interpretation of the dissolution mechanism of PAN, namely *solvated (solvent) molecules* (C). The important factor here is, of course, the state (C), with information on this being obtained from measurements of various binary mixtures (nitrile–solvent mixtures). This problem will be discussed in detail in a future publication[14]. Before starting the discussion at this point, we will briefly note the specific nature of the *free solvent*, based on the Raman spectroscopic results.

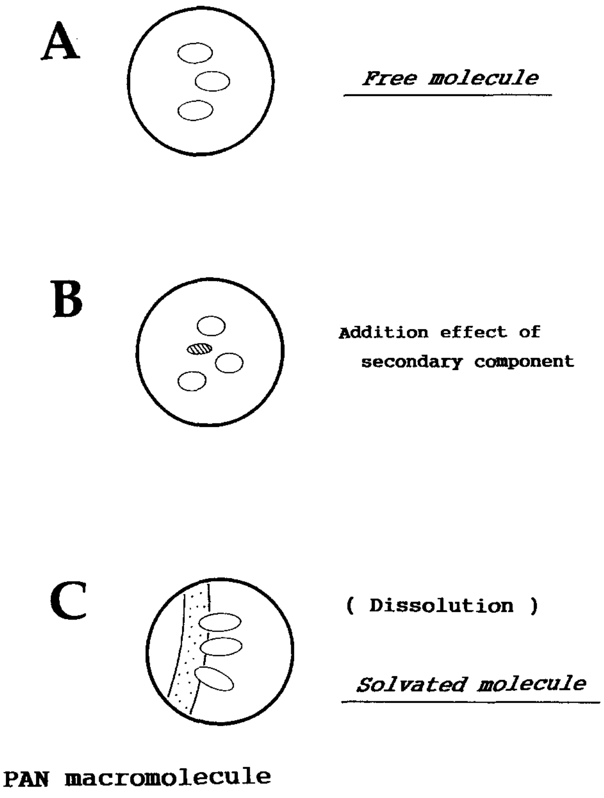

Figure 8 Differentiation between the two different states of the solvent molecules in the dissolution of PAN

Figure 9 shows stick diagrams of the Raman spectra of several solvents. For comparison purposes, in addition to the DMF derivatives being considered here, other types of solvents are presented. Acetic anhydride is shown as an example of an anhydride compound; this solvent does not form hydrogen bonds, and the carbonyl band appears in the standard region of 1750 cm^{-1}. If hydrogen bonding is permitted, e.g. acetic acid, the carbonyl band shifts to a lower frequency (i.e. the 1650 cm^{-1} region). The observation of such a comparatively large value for the carbonyl shift (100 cm^{-1}) is a good measure for the identification of the type of intermolecular interaction and the evaluation of the extent of its effect. In pure DMF, where solvent molecules are strongly associated with each other through dipole–dipole interactions (self-association), the carbonyl band appears in the 1661 cm^{-1} region. We would like to emphasize here, however, that this value of 1661 cm^{-1} is unusually low among carbonyl compounds, i.e. the dipole–dipole interaction is strong enough to lead to a relatively large lower frequency shift, although the extent of this is not so strong as would be caused by hydrogen bonding. When secondary components such as n-hexane were added and the dipole–dipole interaction is destroyed, a shift of the carbonyl band to a higher frequency easily occurs (1689 cm^{-1}). A similar high frequency shift is, of course, observed when such a polar compound as adiponitrile was added, but the extent of the shift was relatively smaller (~ 10 cm^{-1}; see *Table 1*). The difference in the extent of these shifts (30 and 10 cm^{-1}) will be related to what extent the dipole–dipole interactions are destroyed by the diluent. We can at least say that its effect was stronger in non-polar substances than in polar substances (see *Table 1*).

It is of importance to note that (1) the unusually low frequency of the carbonyl band in the DMF derivatives is caused by the enhanced polarity of the DMF molecules in the self-associated state, and (2) the corresponding high frequency shift is caused by the destruction of the self-association brought about by the secondary component.

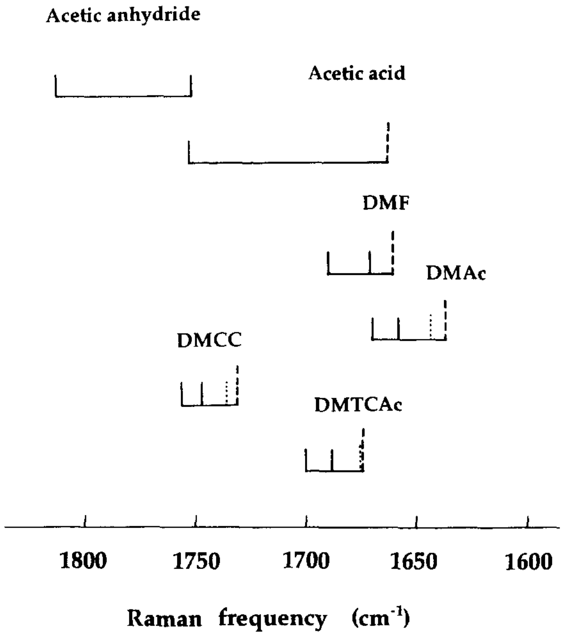

Figure 9 Stick diagrams of the Raman carbonyl bands of several solvents: the broken lines for the DMF derivatives represent the carbonyl bands in situations where dipole–dipole interactions are present; dotted lines indicate these bands after the addition of a secondary component

CONCLUSIONS

(1) Dynamic ^{1}H n.m.r. spectroscopic measurements for five kinds of DMF derivatives were carried out, and the ^{1}H methyl signals provided significant information on the internal rotation of the solvent molecules at elevated temperatures. The value of T_c for each solvent was determined.

(2) The value of T_c was critically evaluated. It is not a constant of the material, but has a clear physical meaning under the conditions used, representing the extent of internal rotation of the solvent molecules. The difference in the T_c values obtained when using different n.m.r. spectrometers (270 and 90 MHz) was within 5–7°C.

(3) The value of T_c was not proportional to the bulkiness of the substituent. The higher the bulkiness, then the lower the value of T_c. Thus, the bulkiness has an inverse effect on the internal rotation of a solvent molecule.

(4) There existed a linear relationship between the value T_c and the bulkiness of the solvent. The internal rotation is defined by the extent of looseness in the packing of the solvent molecules rather than the steric effect of a single molecule.

(5) Kinetic analysis also showed that the value of T_c can be directly determined by the enthalpy term (ΔH) relating to the intermolecular interaction. The significance of this enthalpy term was confirmed theoretically.

(6) Raman spectra showed the enhanced association of DMF molecules in the liquid state. The unusually low frequency of the carbonyl band, and its corresponding higher frequency shift by the addition of nitrile groups, were reasonably explained in terms of the relatively strong dipole–dipole interaction (in the self-associated state) and its subsequent destruction.

(7) The temperature exerts quite opposite effects on the dissolution of PAN, namely an increase in the internal rotation speed, and an enhancement of the intramolecular interaction between solvent and polymer. A discrimination between free solvent and solvated solvent is also necessary.

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REFERENCES

1 Minagawa, M., Miyano, K., Morita, T. and Yoshii, F. *Macromolecules* 1989, **22**, 2054
2 Jackman, L. M. and Cotton, F. A. 'Dynamic Nuclear Magnetic Resonance Spectroscopy', Academic Press, New York, 1975

3 Paudler, W. M. 'Nuclear Magnetic Resonance—General Concepts and Applications', Wiley, New York, 1987

4 Rahman, A. U. 'Nuclear Magnetic Resonance', Springer, New York, 1988

5 Minagawa, M., Yamada, H., Yamaguchi, K. and Yoshii, F. *Macromolecules* 1992, **25**, 503

6 Minagawa, M., Kita, S., Shibuya, T., Takasu, T., Chujo, R., Makuuchi, K. and Yoshii, F. *Polym. Prepr. Jpn* 1993, **42**, 174

7 Minagawa, M., Takasu, T., Kita, S., Chujo, R., Yatabe, J., Yoshii, F. and Makuuchi, K. *Polym. Prepr. Jpn* 1993, **42**, 1898

8 Shriner, R. L., Fuson, R. C., Curtin, D. Y. and Morrill, T. C. 'The Systematic Identification of Organic Compounds', 6th Edn, Wiley, New York, 1980, p. 54

9 Minagawa, M., Takasu, T., Morita, T., Shirai, H., Fujikura, Y. and Kameda, Y. *Polymer* 1995, **36**, 2243

10 Phillips, W. D. *J. Chem. Phys.* 1955, **23**, 1363

11 Gutowsky, H. S. and Holm, C. H. *J. Chem. Phys.* 1956, **25**, 1228

12 Dimitrov, V. S. and Ladd, J. A. *J. Mol. Struct.* 1987, **159**, 107

13 Friebolin, H. 'Basic One- and Two-Dimensional NMR Spectroscopy', 2nd Edn, VCH, Weinheim, 1993, p. 293

14 Minagawa, M., Shirai, A., Morita, T., Fujikura, Y. and Nishimoto, Y., unpublished results