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The steric effect of solvent molecules in the dissolution of polyacrylonitrile from five different *N,N*-dimethylformamide derivatives as studied using Raman spectroscopy

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The steric effect of solvent molecules in the dissolution of polyacrylonitrile (PAN) from five different kinds of *N,N*-dimethylformamide (DMF) derivatives was studied using Raman spectroscopy and a laboratory constructed laser optical instrument. The dissolution behavior of PAN from solvents such as DMF, *N,N*-dimethylacetamide, *N,N*-diethylformamide, *N,N*-dimethylcarbamylchloride, and *N,N*-dimethyltrichloroacetamide was studied with the laser optical method. Raman spectra of the solvents and solutions provided significant information on the intermolecular interaction between nitrile and the solvents (i.e., dipole–dipole interaction). The carbonyl band in each solvent shifted from a lower to a higher frequency when nitriles were added, and the extent of the shift was directly related to the structure and geometry of a subtituent in each solvent molecule. An inverse linear relationship between the value of the dissolution temperature (T_{sol}) and the extent of the Raman carbonyl shift is demonstrated. It seems reasonable to explain this in terms of the steric effect of solvent molecules in the dissolution of PAN.

(Keywords: polyacrylonitrile; dissolution temperature; *N,N*-dimethylformamide derivatives)

INTRODUCTION

The dissolution of atactic polyacrylonitrile (PAN) from dipolar aprotic solvents including *N,N*-dimethylformamide (DMF) is quite interesting but difficult to study from both a scientific and an industrial point of view[1–4]. PAN is widely commercialized as acrylic fiber, and it is also used as the starting material for high-performance carbon fiber[1–5]. In these fiber applications, PAN is dissolved in a suitable polar solvent and spun to give fibers from solution by a wet or dry spinning process.

In the case of stereoregular samples prepared by urea clathrate polymerization in the solid state, however, the sample is quite insoluble in an ordinary dipolar aprotic solvent such as DMF and the like at room temperature[6]. Even when the powder sample is immersed in DMF for more than a year, any change such as swelling does not take place. Dissolution occurs only when the temperature is increased above 100°C. Once dissolution occurs, the solution is relatively stable and precipitation including gelation does not take place even when the temperature is lowered to the ambient temperature. Although there have already been several studies on the solvent properties of organic dipolar aprotic solvents toward PAN[7–11], experimental data and information on the dissolution phenomenon of PAN have not been obtained.

In this article, as a preliminary study on the structure and properties of PAN, the solvent properties of five different kinds of DMF derivatives toward PAN were studied using Raman spectroscopy. These solvents can be regarded as having part of the DMF molecular structure replaced by a suitable substituent (see *Figure 1*). Therefore, one can study the solvent properties as a function of such a substitution. It is clear that (1) the dissolution temperature (T_{sol}) is a useful measure of the dissolution power of the solvents, (2) the extent the interaction between nitrile and the solvents can be evaluated effectively with Raman spectra, and (3) the steric factors involving solvent molecules play an essential role in the above relationship between T_{sol} and Raman carbonyl shift. These results are comprehensively discussed.

EXPERIMENTAL

Sample

The sample was prepared by free-radical polymerization in an aqueous medium by use of ammonium

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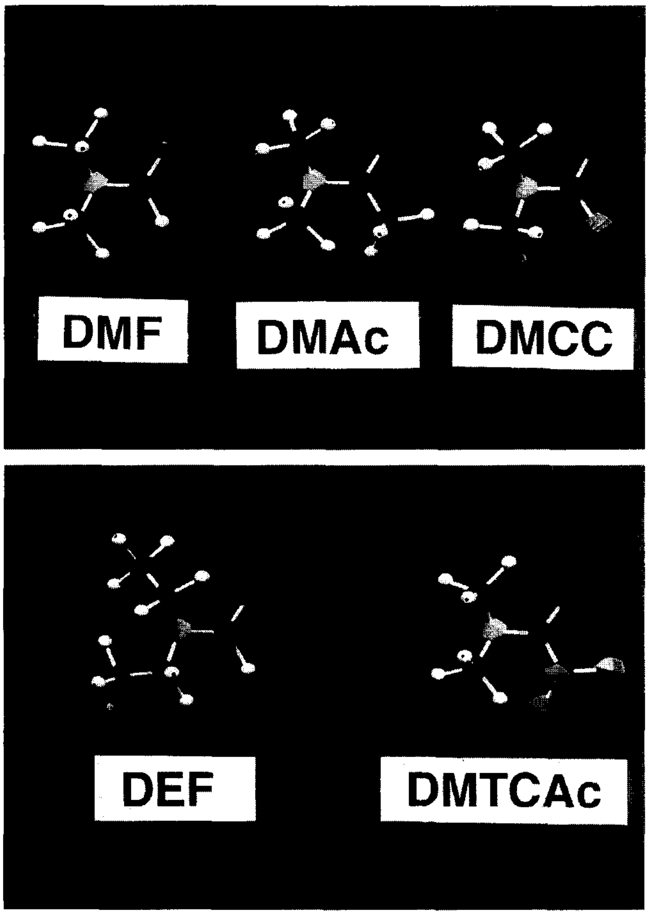

Figure 1 Molecular model of DMF derivatives. Note that these DMF derivatives can be regarded as a model, where a part of the DMF molecule is replaced by a suitable substituent

persulfate as initiator[12]. The polymerization conditions were as follows: $(M) = 7$ wt%; $(I) = 0.1$ wt%; temperature, 55°C; and polymerization time, 6 h. The value of the intrinsic viscosity (η) in DMF at 25°C was 6.79, and the molecular weight (M_v) from the Cleland–Stockmayer equation[13] was about 85 000. The sample was essentially atactic in its configuration ((mm) = 28%, (mr) = 50%, and (rr) = 22%) as confirmed by ^{13}C n.m.r. spectra. The particle size of the powder was controlled at less than 100 mesh.

Determination of microtacticity

A ^{13}C n.m.r. spectrometer (JEOL JNM EX-90) was used under the following conditions: solvent, deuterated dimethyl sulfoxide (DMSO-d_6); concentration, 2 wt%; and temperature, 60°C. Pulse conditions were PW1 6.0 μs (45° pulse), PD1.511 s (repetition time), and Point 16 K (data points).

Solvents

Five different kinds of organic solvents (Aldrich and Frington Chemical Company, Inc.) were used; in addition to DMF, these were *N,N*-dimethylacetamide (DMAc), *N,N*-diethylformamide (DEF), *N,N*-dimethylcarbamylchloride (DMCC), and *N,N*-dimethyltrichloroacetamide (DMTCAc). These are typical organic dipolar aprotic solvents. The molecular structure is shown in *Figure 1*. The solvents were twice distilled under reduced pressure immediately prior to use. Particular attention was paid to protection against moisture.

Raman spectroscopy

The JASCO Raman spectrometer (NR-1100 type, Ar$^+$ laser (514.5 nm)) equipped with a photon counter was used under the following conditions: laser power, 100 mW, slit width, 500 μm, and resolution, 4 cm^{-1}. Each solvent was sealed in a capillary tube and measured in a similar manner to that described in ref. 14 (*Figure 2*).

Determination of dissolution temperature (T_{sol})

A laboratory-constructed laser optical instrument reported in ref. 6. was used. The T_{sol} is obtained as a thermodynamic critical temperature, where dissolution takes place and homogeneous transparent solution is obtained.

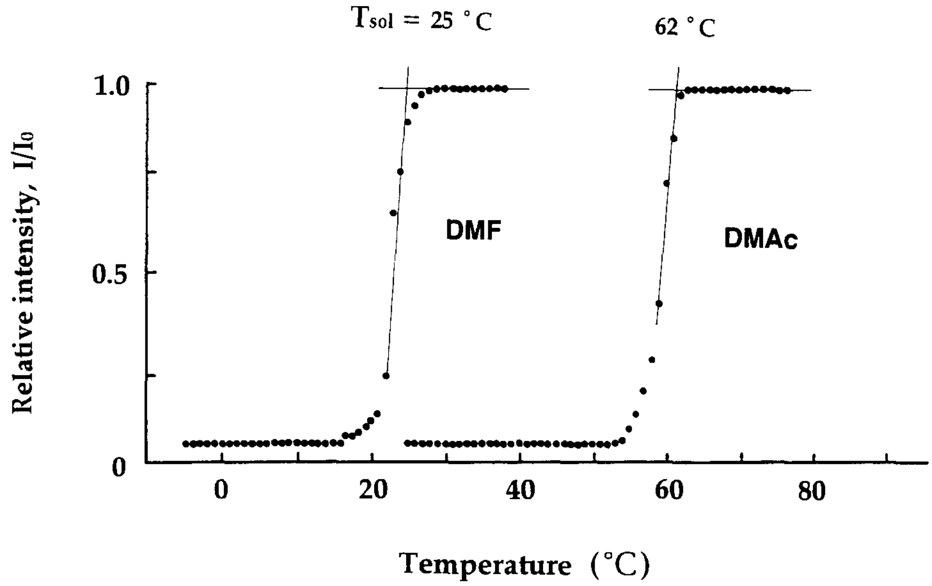

Figure 2 Turbidity–temperature curves of PAN in several DMF derivatives. The value of T_{sol} can be determined uniquely as shown in this figure. Conditions: PAN, 40 mg; solvent, 10 ml

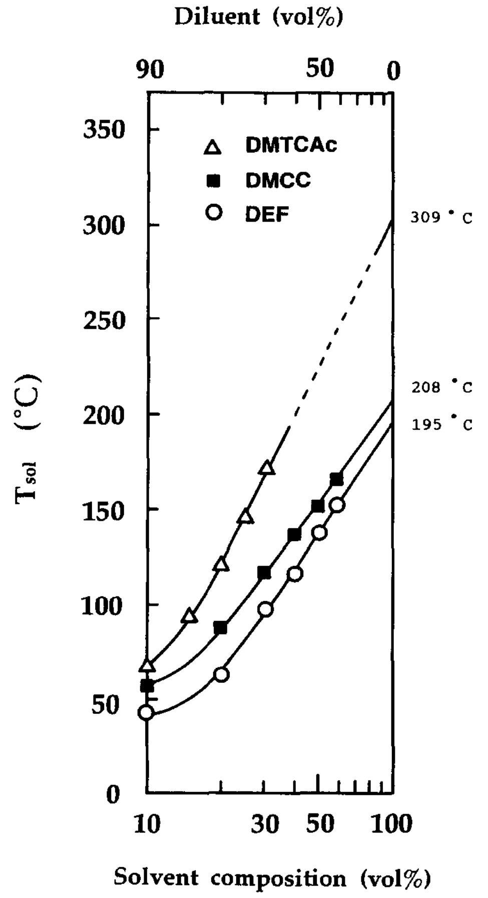

Figure 3 Determination of T_{sol} by extrapolation method. The value of T_{sol} for DEF was determined by dilution with DMF, whereas T_{sol} for DMCC and DMTCAc were determined by the use of DMAc. In the case of DMTCAc particularly, some unknown crystalline needles (white addition products (?)) precipitated at higher DMAc content (> 40 wt%) indicated by a broken line. Reproducibility was quite good

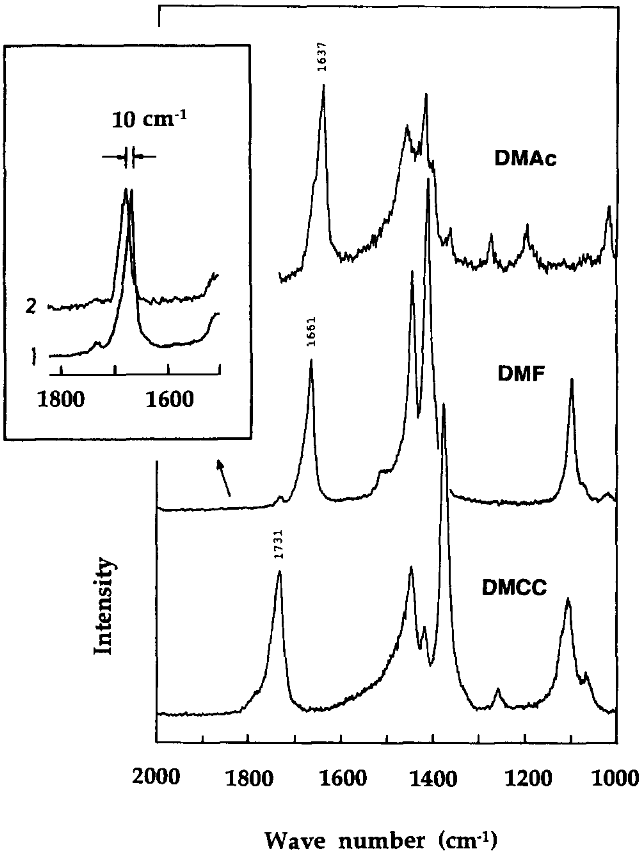

Figure 4 Raman spectra of typical DMF derivatives. Enlarged spectra (left-hand side) indicate a typical shift of the carbonyl band due to the addition of equimolar nitriles (see text)

RESULTS AND DISCUSSION

Characterization of dissolution power of DMF derivatives toward PAN

At first, it is necessary to evaluate the dissolution power of the DMF derivatives toward PAN. *Figure 2* shows typical turbidity–temperature curves for PAN obtained by the laser optical method. This procedure is based on the fact that when the temperature is low, polymers (fine powder) are insoluble in DMF and suspended, whereas when the temperature is increased dissolution takes place and homogeneous transparent solution is obtained. It is possible to determine the dissolution temperature (T_{sol}) uniquely as the cross-point between a tangential line and the asymptote in the turbidity–temperature curve. The dissolution temperature of PAN into DMF was 25°C, while T_{sol} into DMAc was 62°C.

Three other solvents did not show good solubility, and therefore the T_{sol} was determined by an extrapolation method, i.e., these solvents were diluted with an appropriate good solvent (DMF or DMAc), and the T_{sol} was measured at various solvent compositions (*Figure 3*). The T_{sol} was determined as an extrapolated point, where the concentration of the diluent was zero. From *Figure 3*, T_{sol} was determined to be 195°C (in DEF), 208°C (in DMCC), and 304°C (in DMTCAc), respectively. Although the values of T_{sol} obtained in this way contain several degrees of ambiguity, this does not affect the conclusions obtained here.

According to the thermodynamic theory of polymer solutions[4], the dissolution of a given polymer occurs when the polymer–solvent interaction overwhelms the polymer–polymer and solvent–solvent interactions. Therefore, the value of T_{sol} can be regarded as a useful measure of the dissolution power of the solvents. A lower T_{sol} indicates that the dissolution power of the solvent is high, whereas a higher value indicates the power is low. It is possible to list the dissolution power of the solvents on this basis as follows: DMF > DMAc > DEF > DMCC > DMTCAc. It is also interesting to note that the above ordering seems to be closely related to the bulkiness of substituent; hydrogen (H), methyl (CH_3), ethyl (C_2H_5), chlorine (Cl), and trichloromethyl (CCl_3) groups. The larger the substituent size, the higher the dissolution temperature. Thus, although the solubility judgement based on simple observation has been carried out[1–4], one can define it (T_{sol}) uniquely with the laser optical method employed here.

Raman spectra of five kinds of DMF derivatives

The solvent properties of the DMF derivatives were studied by Raman spectroscopy. *Figure 4* shows typical Raman spectra. Several Raman bands exist which are inherently characteristic of all the solvent molecules, the most interesting of which is the carbonyl band (C = O). In DMF, the carbonyl band appears at 1661 cm^{-1}, while

Table 1 Summary of Raman carbonyl band of the DMF derivatives

Solvent	Substituent	$\nu_{c=o}$[a] (cm^{-1})	Effect[b] (cm^{-1})	$\nu_{c=o}$[c] (cm^{-1})	Shift[d] (cm^{-1})
DMAc	CH_3	1637	−24	1644	+7
DEF	C_2H_5	1660	−1	1666	+6
DMF	H	1661	0	1671	+10
DMTCAc	CCl_3	1674	+13	1675	+1
DMCC	Cl	1731	+70	1737	+6

[a] Carbonyl band of pure solvent
[b] Electronegative effect by substituent
[c] Carbonyl band after addition of equimolar nitriles
[d] Extent of carbonyl shift before and after addition of nitriles

in DMAc, it is found at 1637 cm^{-1}, i.e., the carbonyl frequency is lowered by 24 cm^{-1}. The results for other solvents are summarized in *Table 1*. In the case of DEF, the carbonyl band appeared near 1660 cm^{-1}, i.e., with a smaller frequency shift relative to DMF of 1 cm^{-1}. Although the DEF sample shows only a small shift due formally to the substituent being in a remote position from the carbonyl group, it is certain that replacement by an electropositive substituent should show a lower frequency shift of the carbonyl band. In the case of DMCC and DMTCAc, however, the carbonyl band appears near 1731 and 1674 cm^{-1}. The rises in frequency of 70 cm^{-1} and 13 cm^{-1} above that of DMF must arise from the chlorine and trichloromethyl groups, respectively. From these results, it is possible to conclude that (1) the electronic nature of the substituent basically determines the frequency of the carbonyl band of the DMF derivatives, (2) an electropositive substituent causes a lower frequency shift, whereas an electronegative substituent causes a higher one from 1661 cm^{-1}, and (3) the extent of the shift was as large as 94 cm^{-1} in the above two extremes.

Raman shifts of carbonyl bands due to interaction with nitriles

When lower nitriles such as adiponitrile (AdN) were added to DMF, homogeneous mixing occurs immediately. The resulting DMF/nitrile mixture gives some remarkable changes in the Raman spectra. One such change is the carbonyl shift of the solvent to a higher frequency. In the case of the DMF/nitrile mixture, the carbonyl band appeared at 1671 cm^{-1}, the extent of the shift from 1661 cm^{-1} being 10 cm^{-1} (see expanded spectra (left) in *Figure 4*). The shift of 10 cm^{-1} is very important. It is caused by simple mixing with nitriles, and the origin of the shift can be ascribed to secondary factors (solvent–nitrile interaction), probably due to dipole–dipole interactions between the nitriles and the carbonyl group, i.e. according to the molecular theory of organic solvents[15,16], dipolar aprotic solvents such as DMF generally associate with each other through strong dipole–dipole interaction (self-association of solvent molecules). When such an association is destroyed by added nitriles, a shift of the carbonyl band is expected. The shift toward higher frequency indicates that new interaction (between carbonyl and nitrile groups) is weaker than that of the former. In fact, such a high frequency shift can be convincingly explained in terms of the enhancement of the C = O force constant in Raman scattering theory[17,18].

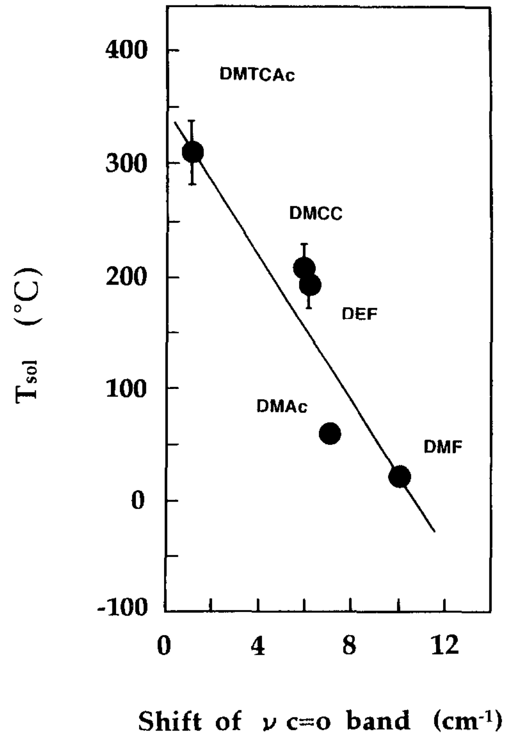

Figure 5 Relationship between T_{sol} and Raman shift of the carbonyl band

Even in other DMF derivatives, a similar high-frequency Raman shift is invariably observed, although the extent of this shift depends on the derivatives (see *Table 1*). Generally speaking, the extent of this shift is smaller when the substituent is geometrically large. This is more clearly indicated in *Figure 5*. In this figure the Raman carbonyl shift is plotted vs the value of T_{sol}. It is apparent that an inverse linear relationship exists between them. Since the dissolution temperature is closely related to the bulkiness of the substituent, *Figure 5* clearly indicates that the extent of the shift of the carbonyl band is directly determined by the bulkiness of the substituent in the DMF derivatives through the intensity of the interaction between them.

Solvent properties of DMF derivatives and the dissolution mechanism

It is interesting to consider the dissolution mechanism in relation to the solvent properties of DMF derivatives (i.e., the dynamic nature in solvent action). The structural features in these DMF derivatives are the polar carbonyl group (C = O) connecting directly with an electropositive dimethyl amino group of the structural unit (R-N-R′). The carbonyl group acts as an interaction site during solvation, whereas the dimethyl amino structural unit does so as an electron storage site. Since DMF is a typical soft solvent (in Lewis's definition)[19], the electronic charge distribution in the solvent molecule varies significantly according to the extent of polarity of the solute molecules. When the solute molecules are highly polar, the charge distribution of electrons in the DMF molecule becomes highly localized (through supply from the dimethyl amino structural unit) and a strong interaction can be expected (see *Figure 6*). When the solute molecules are not so polar, the localization of electron density is proportionally reduced and a weaker

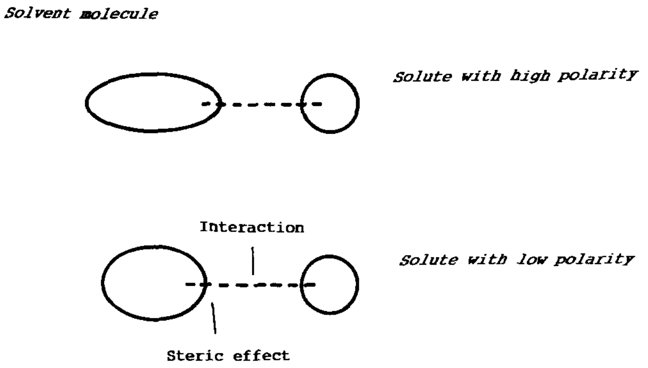

Figure 6 Schematic representation of solvent nature of DMF derivatives. Deformation of a single solvent molecule indicates the enhancement of polarity due to the concentration variation of electron density in DMF derivatives

interaction will be realized. In this way, the intensity of interaction between the solvent and the solute molecules varies spontaneously according to the nature of the solute molecules (i.e., the dynamic nature in solvent action of typical dipolar aprotic solvents). In the case of the DMF derivatives discussed here, the steric effect of the subtituent is most remarkably developed. That is, when the substituent is geometrically small, a strong interaction is exerted, whereas when the substituent is bulky a weaker interaction can be expected. An inverse linear relationship in *Figure 5* clearly indicates that the bulkiness of the substituent in the DMF derivatives directly determines both the dissolution temperature (T_{sol}) and the Raman carbonyl shift of the solvents.

CONCLUSIONS

(1) The T_{sol} of PAN in five different kinds of DMF derivatives was studied using the laser optical method. In several solvents, T_{sol} was obtained by an extrapolation method. The values of T_{sol} is a useful measure of the dissolution power of the DMF derivatives. (2) Intermolecular interaction between solvent and nitriles was studied by the use of Raman spectroscopy. The Raman carbonyl band clearly indicates the extent of interaction between the carbonyl groups of the DMF derivatives and nitriles (dipole–dipole interaction). (3) There exists an inverse linear relationship between T_{sol} and the Raman carbonyl shift. These results can be explained in terms of the steric effect of the solvent molecules in the dissolution of PAN in these solvents.

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