Dissolution Behavior of Highly Isotactic Polyacrylonitrile in *N,N*-Dimethylformamide at an Elevated Temperature

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ABSTRACT: The dissolution behavior of highly isotactic poly(acrylonitrile) (PAN) prepared by canal polymerization into *N,N*-dimethylformamide was studied by laser-optical instruments. The principle and experimental apparatus for measuring this dissolution behavior of PAN at an elevated temperature were briefly discussed. The dissolution temperature (T_{sol}) was defined as a critical temperature, where the turbidity of polymer–solvent mixture disappears and a transparent solution is obtained. The T_{sol} of various kinds of PAN was studied, and the results were summarized as a function of the stereoregularity of the sample. It was shown that the value of T_{sol} is mainly defined by the stereoregularity of the sample and that there exists a valid quantitative relationship between them. A simple thermodynamic consideration on the dissolution phenomenon of PAN at an elevated temperature was tentatively made.

Introduction

It is well-known that highly stereoregular poly(acrylonitrile) (PAN) can be prepared by the canal polymerization of AN with urea through γ-ray irradiation.[1] The stereochemical structure of PAN prepared by such a method has been proved to be essentially isotactic in its configuration.[2,3] There have already been several studies on isotactic PAN.[4-7] For example, Kubasova and co-workers studied the effect of stereoregularity on the formation of conjugated $(-C{=}N)_n-$ sequences of PAN in a solution state.[4] Grobelny et al. reported the X-ray wide-angle diffraction pattern of isotactic PAN in comparison with an atactic sample.[5] Kamide et al. studied solution properties and tactic sequences of isotactic and atactic PAN.[6,7] However, the physical and chemical properties of isotactic PAN in the solid state have not been studied very much.

In a previous article,[8] we made a detailed infrared (IR) spectroscopic study about stereoregular PAN. The presence of IR characteristic absorption bands and their possible assignments were briefly discussed. In this connection, the dissolution behavior of stereoregular PAN into *N,N*-dimethylformamide (DMF) is described. It is necessary to mention briefly the specific dissolution behavior of highly isotactic PAN. That is, ordinary semicrystalline polymers swell on contact with good solvents at a moderately low temperature. This is because they consist of both crystalline and amorphous regions, and the penetration of organic solvents occurs preferentially in the latter region. In the case of isotactic PAN, however, such a swelling was not observed within our experimental range. That is, even when the sample was immersed in DMF for more than 1 year, no evidence of swelling was observed. The dissolution occurred only when the temperature was increased above 100 °C. This unique dissolution behavior is probably closely related to the specific molecular characteristics of isotactic PAN, as described in the text. To study such a specific dissolution behavior of isotactic PAN, a simple laser-optical instrument that enables the detection of the dissolution temperature (T_{sol}) of PAN at an elevated temperature was constructed, and some measurements were made. It was shown that this laser-optical instrument is quite useful for the investigation of dissolution behavior of PAN and for the characterization of solvent properties of various kinds of dipolar aprotic solvents, etc. Although one of us has already observed that canal-polymerized PAN is insoluble in DMF unless heated to a temperature above 100 °C,[9] little significant information on the dissolution behavior of stereoregular PAN has been obtained. In this article, the trial construction of a laser-optical instrument, some experimental results, related thermodynamic consideration, and the potential utility of this characterization method are described.

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Table I
Characterization of Samples

sample[a]			triad tacticity,[c] %			
polymerization	code	$[\eta]$,[b] dL/g	*I*	*H*	*S*	$4IS/H^2$
canal[d]	C-1	1.45	76	19	5	4.00
canal	C-2	1.61	72	22	6	3.47
canal	C-3	1.34	66	25	9	3.60
canal	C-4	4.96	48	36	16	2.41
canal	C-5	4.58	48	35	17	2.60
anion[e]	A-1	2.17	30	43	27	1.82
radical	R-1[f]	2.14	25	51	24	0.94
radical	R-2[g]	1.97	28	46	26	1.35
radical	R-3[h]	6.03	29	49	22	1.07
radical	R-4[i]	6.87	26	47	27	1.31

[a] All the samples were obtained in powder form, and the particle size was controlled at less than 100 mesh. [b] Viscosity; DMF, at 25 °C. A solution was prepared at 140 (canal sample) and at 100 °C (anionic and radical samples). [c] NMR results; peak intensity was calculated based on methine carbon. [d] All the canal samples were prepared by in-source method. [e] Prepared in THF by sodium naphthalene, at −78 °C. [f] Homogeneous solution (DMSO/AIBN, at 55 °C). [g] Aqueous redox slurry (H_2O/APS–$NaHSO_3$, at 40 °C). [h] Aqueous solution (H_2O/APS, at 50 °C). [i] Bulk (photoinitiated, at 14 °C). THF, tetrahydrofuran; DMSO, dimethyl sulfoxide; AIBN, azobisisobutyronitrile; APS, ammonium peroxodisulfate.

Experimental Section

Sample. The samples were prepared by canal polymerization.[1,10] For comparison, several different types of radical and anionic samples were used.[11] These are listed in Table I. All the samples except for C-1 polymer were employed previously.[8] These samples (except for A-1 and R-1) had no contact with organic solvent such as DMF except for methanol and pure water in their preparation.

^{13}C NMR Measurements. Details of the NMR conditions are given in ref 8. Analysis was made according to the manner of Inoue and Nishioka.[3] The isotacticity discussed here is defined by three monomer units (i.e., triad tacticity).

Turbidity Measurements. The dissolution behavior of PAN at an elevated temperature was studied by use of laboratory-

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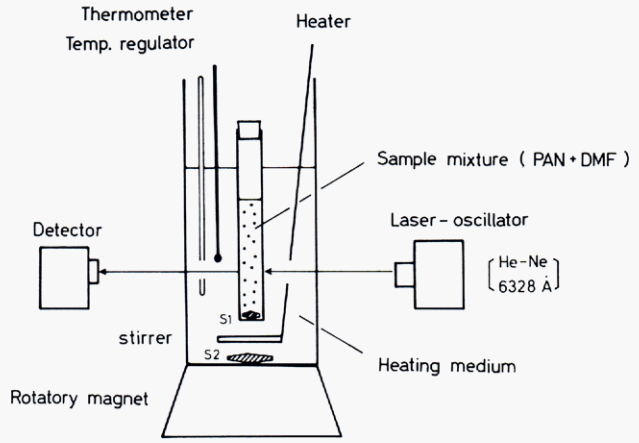

Figure 1. Schematic view of laser-optical instruments. The laser beam emitted from an oscillator is passed through a Pyrex glass tube, which contains a mixture of polymer (i.e., powder) and cooled DMF under magnetic agitation, before reaching a detector. Two stirrers (S1 and S2) rotate simultaneously by a rotatory magnet.

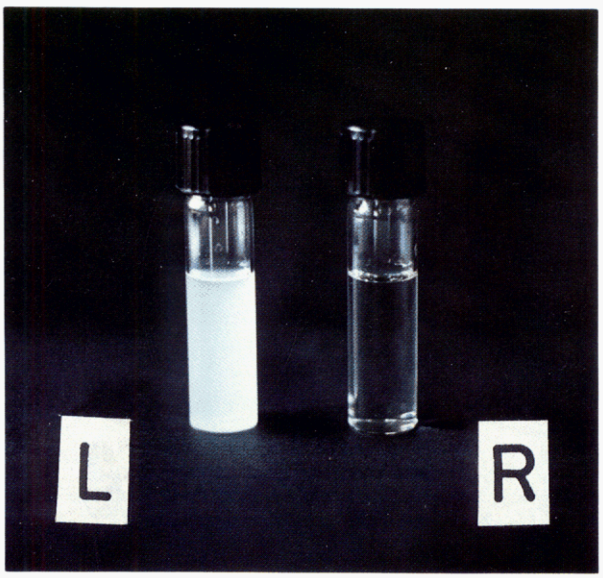

Figure 2. Photograph of the system before and after dissolution: L, a milky suspension; R, a transparent solution. Polymer neither precipitated nor gelled when the temperature was lowered to an ambient temperature (see ref 12).

constructed laser-optical instruments (see Figure 1). The experimental conditions were determined on the basis of preliminary experiments as follows: sample (15 mg) is mixed with cooled DMF (40 mL). The system is heated in steps at intervals of 5 °C, and the temperature is kept isothermally at each temperature for 20 min, during which five measurements are taken. The recorded results from the laser light is the average value of these five measurements. Figure 2 shows a turbidity change of the system before and after dissolution.

X-ray Measurements. Wide-angle X-ray diffraction (WAXD) measurements were carried out by use of the Rigaku Rotaflex RAD-rA diffractometer (Rigaku Denki Co. Ltd.) with Cu Kα radiation at 50 kV and 200 mA.

Differential Scanning Calorimetry Measurements. A Seiko DSC 200 calorimeter (Seiko Instruments & Electronics Co. Ltd.) was used. The DSC conditions are described in the text.

Results and Discussion

Turbidity–Temperature Curves of PAN. Typical turbidity–temperature curves are shown in Figure 3. The dissolution process can be detected as a sharp step in the turbidity–temperature curve. That is, when the temperature is low, the sample is insoluble in DMF. However, when the temperature is increased, the dissolution takes

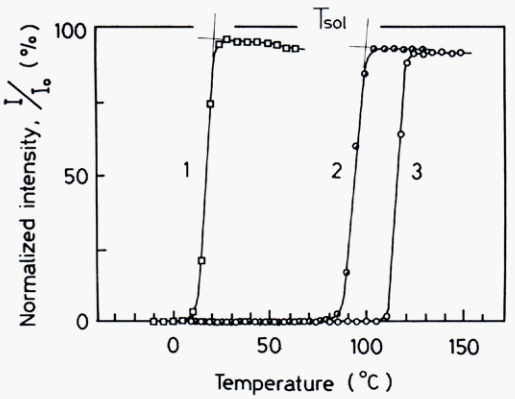

Figure 3. Turbidity–temperature curves of different kinds of PAN: 1, radical sample (R-3; Isotacticity, 29%); 2, canal sample (C-5; 48%); 3, canal sample (C-1; 76%).

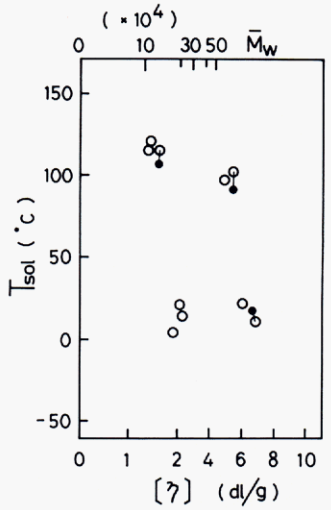

Figure 4. T_{sol} as a function of intrinsic viscosity. Molecular weight M_w was derived from the Cleland–Stockmayer equation[14] without regard to the difference of tacticity. The effect of solvent is shown by a solid circle. That is, the contact with DMF produced a noticeable effect on T_{sol} with little change in molecular weight (see Table II).

place, and a transparent solution is obtained. It is apparent that the dissolution occurs in quite a narrow temperature range over several degrees centigrade. One can define the dissolution temperature (T_{sol}) uniquely as being at the cross-point between the tangential line and level-off line as shown typically in Figure 3. This means that at the T_{sol} the dissolution is almost completely over and a true solution is obtained. According to this definition, the value of T_{sol} for radical and canal samples in Figure 3 is 22, 97, and 118 °C, respectively. It is worthwhile noting that there is a distinct difference in the value of T_{sol} for the canal samples.

T_{sol} as a Function of Molecular Parameters. At first, the T_{sol} was plotted against the intrinsic viscosity, but no significant relationship was obtained (Figure 4). Although it is well-known empirically that the dissolution behavior of a polymer is generally strongly dependent on molecular weight, the T_{sol} of PAN obtained under increased temperature is not as strongly affected by molecular weight as expected.

The T_{sol} was plotted against the stereoregularity of PAN (Figure 5). A simple saturation type of curve was obtained. It is apparent that when the stereoregularity of PAN is increased, the T_{sol} increases rapidly and becomes saturated. This indicates that a small increase in stereoregularity causes a remarkable decrease in the solubility of PAN into DMF. That is, the introduction of a stere-

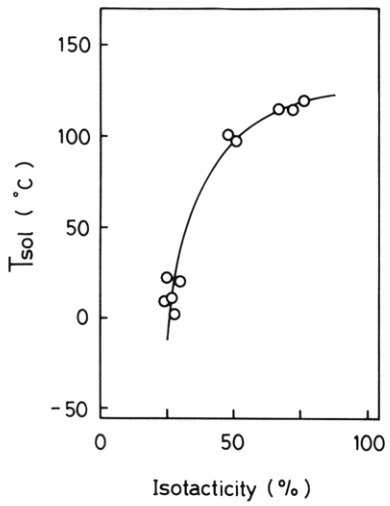

Figure 5. T_{sol} as a function of isotacticity of PAN.

oregular sequence in the polymer backbone causes a remarkable decrease in the solubility of PAN molecules into the solvent. In other words, a higher value of T_{sol} indicates that a higher temperature is necessary for the occurrence of the dissolution, which suggests that the solubility of PAN molecules into the solvent is decreased.

From the geometrical shape of the curve in Figure 5, one can express the dependence of T_{sol} on the stereoregularity of PAN in the following numerical form:

$$T_{sol}(°C) = a - (b/X) \quad (1)$$

where a and b are constants and X is the content of isotactic triad units (percent). It is important to notice that eq 1 has a functional form similar to that of the dependence of the transition temperature (T_g) of glassy polymers on molecular weight.[15]

Analogy between T_{sol} and T_g and Segment Concept. The above fact indicates that (i) in the dissolution phenomenon of PAN at an elevated temperature, the extent of isotacticity plays the same degree of importance as the degree of polymerization in the glass transition phenomenon and (ii) the dissolution temperature of PAN at an elevated temperature is defined by the same or a common thermodynamic principle as in T_g. More specifically, this means that a segmentlike concept plays an important role in the dissolution phenomenon of isotactic PAN at an elevated temperature. Namely, the stiff and rodlike chain characteristics of an isotactic sequence will play the role of segment in this case. Such structural characteristics of isotactic PAN can be confirmed by the comparison of not only solution properties[6,7] but also WAXD results of powder sample (see Figure 6). In the WAXD results, sharp diffraction characteristics with a reduced half-width value of isotactic PAN have already been reported by Turska and co-workers.[5] Further, careful observation revealed that the diffraction angle of the main peak at 17° varies slightly according to the difference of isotacticity of PAN.[16] Infrared characteristic absorption bands (1250 and 1230 cm^{-1}) of PAN also showed similar corresponding results (see Figure 6, right).[17] These results can be reasonably explained in terms of the stiff and extended chain characteristics of isotactic PAN in the powder state.

The segmentlike concept is also supported by a linear relationship in the inverse plot (see next section). That is, when the value of T_{sol} was plotted against the inverse value of isotacticity, a linear relationship was obtained (see Figure 7). Such a linear relationship appears to be observed invariably for the phenomena defined by the concept of segment. One of the examples, which verifies this estimation, is the molecular weight dependence of T_g for amorphous polystyrene (PSt). That is, as has been demonstrated by Fox and Flory,[19] a simple saturation type of curve expressing the molecular weight dependence of T_g for PSt is easily transformed into a straight line in the inverse plot.

Inverse Plot of Isotacticity against T_{sol}. Let us now consider the physical meaning of Figure 7. The junction of the extrapolated line and the ordinate axis is a critical point. From the definition of T_{sol}, this point indicates the value of T_{sol} of a 100% isotactic sample. That is, if a

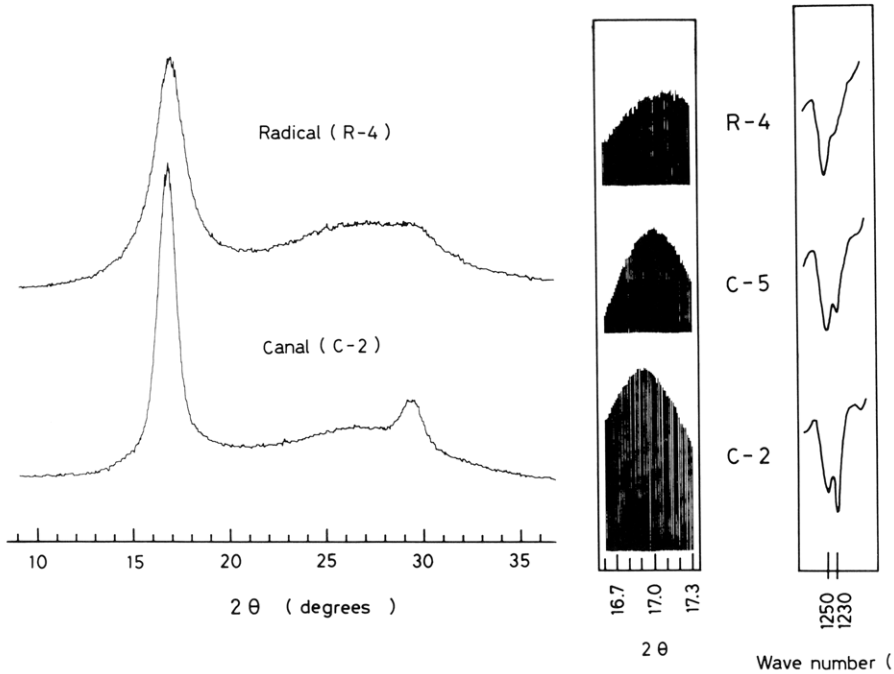

Figure 6. Comparison of WAXD results and IR characteristic bands of powder samples. The WAXD pattern (left) was recorded by continuous scanning. The area of the peak at 17° was almost equal for both samples. The WAXD pattern (middle) was recorded by step interval scanning. The IR spectra were measured by KBr disk method. Isotacticity of these samples was 26% (R-4), 48% (C-5), and 72% (C-2), respectively.

Table II
Redissolution Experiments of Recovered Products

sample (code)	isotacticity, %	original PAN			recovered PAN[a]		
		T_{sol}, °C	[η], dL/g	D_{1230}/D_{1250}[b]	T_{sol}, °C	[η], dL/g	D_{1230}/D_{1250}
canal (C-2)	72	115	1.61	1.44	105	1.54	1.14
canal (C-4)	48	101	4.96	0.85	93	4.85	0.71
radical (R-4)	26	11	6.87	0.51	16	6.73	0.47

[a] The samples were recovered by pouring DMF solution into methanol. [b] Ratio of absorbance in the IR characteristic bands of powder samples.

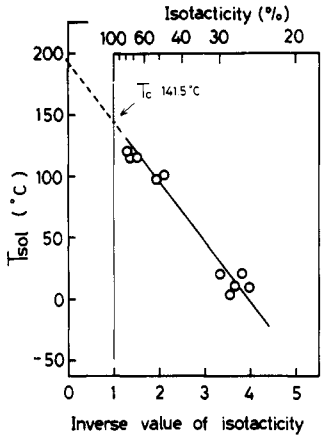

Figure 7. T_{sol} against the inverse value of percentage isotacticity.

completely isotactic sample (the isotactic percentage being 100%) is prepared in the future, the dissolution temperature into DMF will be 141.5 °C, although such an ideal sample has not yet been obtained in our own experiments. The value of T_{sol} can be expressed quantitatively as a function of inverse value of percentage isotacticity (X, percent) in the following way:

$$T_{sol}(°C) = 190 - 48.5X^{-1} \quad (2)$$

One may argue that in such a linear relationship the differences of crystallinity rather than configuration contributes to the results. This leads to the above-mentioned segmentlike concept and is worth investigation. Thermobalance in the dissolution process of PAN was measured by DSC. Typical DSC curves are shown in Figure 8. It is apparent that a clear endothermic peak appears in the temperature region corresponding to the dissolution process of PAN. The correspondence between them is extremely good. Of course, there were several cases in which such good agreement was not obtained. It is important to notice that the dissolution process of stereoregular PAN is a distinct endothermic process, since the dissolution phenomenon of polar macromolecules into a highly polar solvent is generally exothermic, due to the strong intermolecular interaction between them. The results suggest that the crystallinity is closely related to the dissolution phenomenon of stereoregular PAN.

This is also confirmed by redissolution experiments of recovered products. That is, the dissolved samples were recovered, and the T_{sol} of these samples were measured. The results are summarized in Table II. The T_{sol} of the recovered samples was generally lower than those of original samples. The extent of the decrease in T_{sol} was on the order of 10 °C. This reduction in T_{sol} can be ascribed to the loss of crystallinity, although the effect of a trace amount of residual solvent, the difference of molecular weight distribution, etc., can be considered. At any rate, it is possible to conclude that there is some contribution of crystallinity on T_{sol} (~10 °C). However, its effect is relatively small, and the value of T_{sol} is mainly defined by the configuration of PAN.

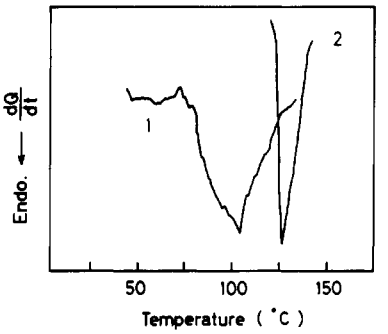

Figure 8. Typical DSC curves of canal samples: 1, C-4 (isotacticity 48%); 2, C-1 (76%). DSC conditions: sample weight, 1 mg; heating rate, 5 °C/min; atmosphere, in N_2. Peak characteristics in the DSC curves may be correlated with the difference of molecular weight distribution or tactic sequence distribution. This is because the dissolution interval of these samples obtained from turbidity–temperature curve was considerably different; C-4 (17 °C, 84–101 °C), and C-1 (8 °C, 110–118 °C).

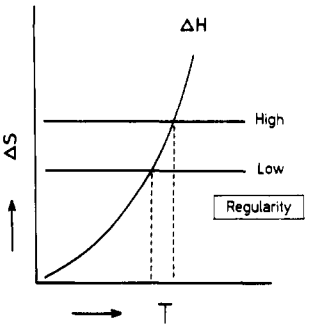

Figure 9. Thermodynamic interpretation of T_{sol}.

Thermodynamic Consideration on the Dissolution of PAN. Let us now consider the dissolution process of PAN theoretically. Although any theory explaining such a dissolution phenomenon of PAN at an elevated temperature has not yet been presented, a simple thermodynamic consideration is quite useful in this case. One can formulate the dissolution process as follows:

$$\Delta G = \Delta H - T\Delta S \quad (3)$$

where ΔG is the Gibbs' free energy, ΔH is the enthalpy term, ΔS is the entropy term, and T is the absolute temperature. The dissolution condition is given by $\Delta G = 0$:

$$T_{sol} = \Delta H/\Delta S \quad (4)$$

where ΔH is the enthalpy term relating to the intermolecular forces and ΔS is the entropy term relating to intramolecular structural factors.

This is shown in Figure 9. The dissolution occurs at the junction between the rising curve and the horizontal line. The rising curve indicates that (1) the polymer–solvent interaction is enhanced under an elevated temperature and (2) it is a nonlinear type of increasing function with regard to the temperature. The horizontal line indicates the extent of stereoregularity of PAN. Namely, when the temperature is increased, the interaction between the polymer and solvent is highly enhanced, and

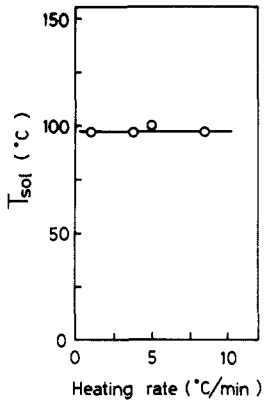

Figure 10. Independence of T_{sol} on the heating rate. Sample: canal PAN (C-5; isotacticity, 48%).

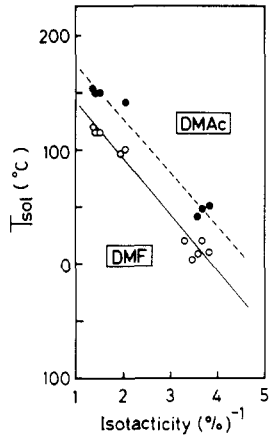

Figure 11. Comparison of solvent action of some solvents (DMAc = *N,N*-dimethylacetamide). Two straight lines were in parallel, and the value of T_{sol} was lower in DMF than in DMAc on all ranges. These facts indicate that solvent action is generally stronger in DMF than in DMAc (i.e., DMF > DMAc). This is because higher values of T_{sol} indicates that higher temperature is needed for dissolution, which suggests the solvent action is low. By applying this laser-optical method to other kinds of solvents, one can evaluate semiquantitatively the extent of solvent action of various dipolar aprotic solvents on PAN (see ref 20).

beyond some critical threshold the dissolution occurs drastically. This threshold value is defined by the entropy, i.e., the extent of stereoregularity, of each sample. The stereoregularity of PAN can thus be reasonably connected with the entropy through configurational entropy. One can explain with this figure how the dissolution occurs when the temperature is increased and how the T_{sol} varies when the stereoregularity of the sample is varied.

It is necessary to confirm that the above treatment is justifiable. It is sufficient to show that this dissolution process is a reversible or equilibrium process. Strictly speaking, the dissolution process of PAN is not a reversible one, since polymer does not precipitate immediately when the temperature is lowered to an ambient temperature (see Figure 2). However, this process is undoubtedly an equilibrium process. This is because, as shown in Figure 10, the dissolution temperature does not depend on the heating rate employed (i.e., 1–10 °C/min). That is to say, the dissolution occurs at some critical temperature region and does not depend on the heating path. The independence of the heating path is one of the most distinguishing features of the thermodynamic equilibrium process, and one can take this process as an object of theoretical considerations.

Finally, it is important to note the utility of the laser-optical method described here for various types of physicochemical measurements of isotactic PAN, such as crystallization and dissolution processes, gel formation process, and the evaluation of solvent action of different kinds of dipolar aprotic solvents (Figure 11), etc.

Conclusion

The dissolution behavior of highly isotactic PAN into DMF was studied in comparison with that of an atactic sample. That is, trial construction of a laser-optical instrument detecting T_{sol} was briefly described. The T_{sol} of various kinds of PAN was studied, and the results were summarized as a function of molecular parameters. Molecular weight had a minor effect, whereas stereoregularity had the predominant effect. The relationship between T_{sol} and stereoregularity of PAN was quantitatively obtained. A simple thermodynamic consideration of the dissolution phenomenon of PAN at an elevated temperature was tentatively presented.

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Registry No. PAN, 29436-44-0; DMF, 68-12-2.

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(12) The solution was stable when the temperature was lowered to an ambient temperature. However, in a few days, the transparent solution turned to a cloudy solution. Electron microscopic and electron diffraction results indicate that single crystals of isotactic PAN are formed in the solution (see ref 13).
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(16) A decrease in Bragg's angle (2θ) in Figure 6 suggests the increase of the mean distance between neighboring molecules due to the stiffness of molecular chain. It is under debate whether the concept of ordinary semicrystalline polymers (i.e., fringed micellar model or two-phase structure) can be applied directly to isotactic PAN in a powder state (see ref 13).
(17) The IR characteristic bands depend on not only configuration but also conformation. Generally, the 1230-cm^{-1} band is highly enhanced when the stereoregularity of PAN is increased. However, when the sample was dissolved in the solvent and then recovered, the IR characteristic bands varied in their intensities as shown typically in Table II. It is possible to show that under a given constant configuration, the 1230-cm^{-1} band is enhanced when molecular chain is extended along the chain axis (see ref 18).
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