ORIGINAL CONTRIBUTION

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A segment concept in the dissolution of stereoregular isotactic polyacrylonitrile into three dinitrile solvents, CN-(CH$_2$)$_n$-CN (n = 1, 2, and 3), at elevated temperatures

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Abstract The dependence of the dissolution temperature (T_{sol}) of isotactic polyacrylonitrile (PAN) on tacticity was studied for three dinitrile solvents. A linear relationship was obtained in the inverse plots of the tacticity dependence of the T_{sol} of PAN. A phenomenological analogy between the tacticity dependence of the T_{sol} of isotactic PAN and the molecular-weight dependence of the glass-transition temperature of amorphous polystyrene is discussed from a thermodynamic point of view.

The linear relationships in both phenomena are explained in terms of a common mechanism: a breakdown of thermodynamic competition, enthalpy, and entropy through the segment mobility. The significance of segment concept and molecular mobility at elevated temperatures are discussed.

Key words Isotactic polyacrylonitrile · High-temperature dissolution · Dinitrile solvents · Segment mobility

Introduction

The dissolution behavior of stereoregular isotactic polyacrylonitrile (PAN) prepared by urea clathrate polymerization in the solid state was described in a previous article [1]. The dissolution behavior of this polymer is quite specific:

1. Dissolution does not take place at room temperature; even after immersion in N,N-dimethylformamide (DMF) for more than 1 year, no swelling was observed.
2. Dissolution occurs only at elevated temperature; it occurs suddenly at some critical temperature (T_{sol}) like an equilibrium phase transition such as melting.
3. Once a homogeneous solution is obtained, the polymer does not precipitate, even when then temperature is lowered to an ambient temperature.

In the characterization of the dissolution power of organic solvents toward isotactic PAN, quite interesting results have been obtained: plots of T_{sol} against the inverse value of isotacticity provide a linear relationship for many dipolar aprotic solvents, such as dimethyl sulfoxide (DMSO), dimethyl acetamide (DMAc), DMF, and the like [2]. The reason why such a linear relationship holds good universally for many solvents has not been clarified either theoretically or experimentally.

In this article, this problem is discussed in detail. For this purpose, a phenomenological analogy between the dissolution of PAN and the glass-transition temperature (T_g) of amorphous polystyrene (PSt) is described from a thermodynamic point of view. Of course, these are two quite different physical phenomena, but similar linear relationships in both phenomena suggest that these are defined by a common or the same mechanism. Here, a simple theoretical consideration is tentatively presented.

Experimental

Materials

The isotactic PAN samples were the same materials (23 in number) used previously [2]. The sample preparation conditions are given in

Refs. [3, 4] and the characterization is given in Table 1. Monodisperse atactic PSt was supplied by Polymer Laboratories (UK) and is characterized in Table 2.

^{13}C NMR measurements

A JEOL JNM GX-270 NMR spectrometer was used under the same conditions as described in Ref. [5]. The tacticity was determined from the intensity of the methine carbon (CH) signals in the ^{13}C NMR spectra. The isotacticity is defined by the following equation.

$$\text{Isotacticity } (\%) = (mm)/[(mm) + (mr) + (rr)] \times 100 , \qquad (1)$$

where (m) and (r) are meso and recemo placements in the polymer chain, respectively.

Solvents

Three kinds of dinitriles were used: malononitrile (MaN), succinonitrile (SuN), and glutaronitrile (GuN); $CN-(CH_2)_n-CN$, where, n is

Table 1 Characterization of polyacrylonitrile samples. The particle size of the samples was controlled to be less than 100 mesh. The viscosity was measured in *N,N*-dimethylformamide (*DMF*) at 25 °C. The dissolution temperature was measured in DMF. The temperature variation was within ±2 °C

Polymerization	Code	Viscosity (η)	T_{sol} (°C)	NMR results triad tacticity (%)			$4IS/H^2$
				I	H	S	
Canal[a]	C-1	1.28	127	82	14	4	6.69
Canal[a]	C-2	1.19	115	74	20	6	4.44
Canal[a]	C-4	1.44	105	67	26	7	2.78
Canal[a]	C-17	2.85	94	60	35	15	2.94
Canal[b]	C-9	4.96	100	50	37	13	1.90
Anion[c]	A-3	2.17	42	30	43	27	1.75
Radical[d]	R-2	1.97	5	28	46	26	1.38
Radical[e]	W-3	6.03	22	29	49	22	1.06
Radical[f]	B-4	6.87	11	26	47	27	1.27

[a] γ irradiation post polymerization
[b] γ irradiation insource polymerization
[c] Prepared in tetrahydrofuran using sodium naphthalene, at −78 °C
[d] Aqueous redox slurry ($H_2O/(NH_4)_2S_2O_8$-$NaHSO_3$, at 40 °C)
[e] Aqueous solution ($H_2O/(NH_4)_2S_2O_8$, at 50 °C)
[f] Bulk (UV-initiated, at 14 °C)

Table 2 Characterization of low-molecular-weight monodisperse polystyrene showing the molecular weight determined by gel permeation chromatography (M_p), the degree of polymerization (*DP*), and the polydispersity index (M_w/M_n)

Notation	M_p^a	DP	M_w/M_n
S1	480	4.6	1.15
S2	860	8.3	1.10
S3	1050	10.1	1.16
S4	1350	13.0	1.08
S5	1770	17.0	1.06
S6	2550	24.5	1.06
S7	3650	35.1	1.01
S8	5100	49.0	1.04

[a] $M_p = (M_w M_n)^{1/2}$, This is a nominal value given by a producer

1, 2, and 3. These were superior grade reagents from Wako Chem. Co (Japan) and were carefully distilled twice under reduced pressure.

Determination of dissolution temperature

A laboratory-constructed laser-optical instrument described in Ref. [1] was used. The dissolution temperature (T_{sol}) was determined from the turbidity–temperature curve according to the method given in Ref. [1].

Differential scanning calorimetry measurements

A Seiko DSC 10 (Seiko Instruments & Electronics) was used under the following conditions: sample weight, 5 mg; heating rate, 10 °C/min; atmosphere, under N_2 stream (50 ml/min).

Results and discussion

Dissolution temperature of isotactic PAN in dinitrile solvents

A typical turbidity–temperature curve of PAN for MaN is shown in Fig. 1. When the temperature is low, the polymer is suspended in the solvent; however, when the temperature is increased and exceeds some critical threshold, dissolution takes place and a transparent solution is obtained. The value of T_{sol} was 43 °C (28%), 85 °C (60%) and 125 °C (82%). The dissolution temperature increased with stereoregularity.

All the PAN samples were measured in this way. The results are summarized in Fig. 2. A typical saturation curve was obtained. The temperature range of T_{sol} was from −30 °C to 120 °C. (Note that similar saturation curves have already been observed in DMF with fewer
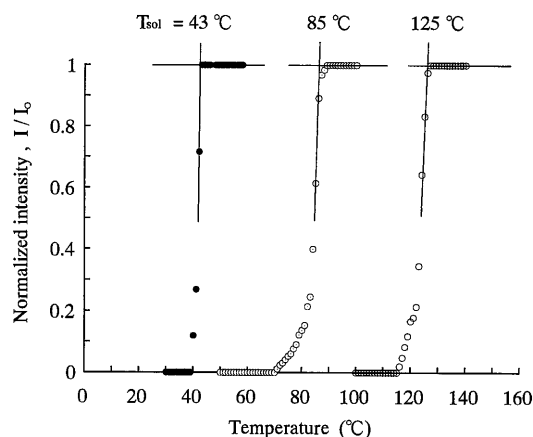

Fig. 1 Turbidity–temperature curve of isotactic PAN. The value of T_{sol} was defined as a crossover point between two tangential lines. This figure was obtained from the heating process, where temperature elevation was carried out stepwise as described in Ref. [1]. Conditions: polymer, 40 mg; solvent, 10 ml. Sample: S-1 (isotacticity, 28%); C-5 (60%); C-1 (82%). Solvent: malononitrile
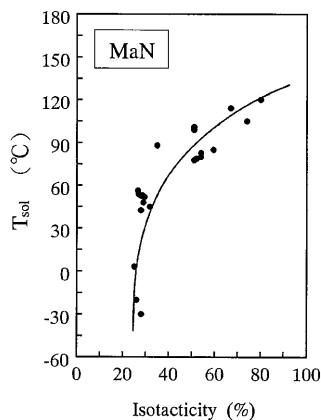
Fig. 2 T_{sol} of polyacrylonitrile (*PAN*) in malononitrile (*MaN*) as a function of stereoregularity

Fig. 3 T_{sol} of PAN in succinonitrile (*SuN*) as a function of stereoregularity

samples (10) [1] and that little dependence of T_{sol} on the molecular weight of PAN was confirmed [1].)

The results for other nitriles are summarized in Figs. 3 and 4. Similar saturation curves were obtained, but the extent of saturation decreased and the experimental data points were concentrated in the higher temperature region. The temperature range T_{sol} was from 70 °C to 150 °C for SuN and from 110 °C to 180 °C for GuN.

Fig. 4 T_{sol} of PAN in glutaronitrile (*GuN*) as a function of stereoregularity

Inverse plots of the T_{sol} of PAN against isotacticity

When these T_{sol} values were plotted against the inverse value of isotacticity, a straight line was obtained (Fig. 5); the slope and intersepts were different. It must be noted that such a linear relationship is obtained not only with the dinitriles used here but also with other dipolar aprotic solvents such as DMSO, DMF, DMAc, ethylene carbonate, tetramethylene sulfone, and the like [2].

In the comparison of the disparity of experimental data, a relatively large scattering around a straight line was observed for MaN. For SuN and GuN, however, the scattering decreased. This is closely related to the dissolution mechanism of isotactic PAN as described later.

In a good solvent, such as MaN, the effect of both stereoregularity and molecular weight (molecular-weight distribution) appears in the results, whereas in a poor solvent, as SuN and GuN, only the effect of the former is prevalent. More specifically

1. Dissolution of isotactic PAN is quite difficult without increasing the temperature.
2. When the temperature is increased, the intermolecular interaction between polymer and solvent is enhanced.
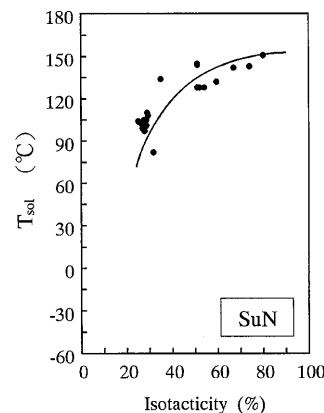3. At some critical temperature dissolution finally occurs.

4. The isotactic PAN molecular chain is probably quite stiff and its segment mobility would be enhanced only at elevated temperature. At the final stage, near T_{sol}, the incorporation of solvent molecules into the PAN molecular chain must happen for dissolution to occur.

Parameters derived from the inverse plots of the T_{sol} of PAN

One can obtain two significant empirical parameters from the linear data: the point of intersection and the slope (Fig. 6). The former is the dissolution temperature (T_{sol}^*) of a perfectly stereoregular sample (isotacticity being 100%). From these values, the dissolution power of the solvents was in the following order: MaN > SuN > GuN. The increase in methylenic length, $(CH_2)_n$-, brought about the decrease in the dissolution power. This is quite natural from a molecular viewpoint, since nitrile groups in solvent molecules interact strongly

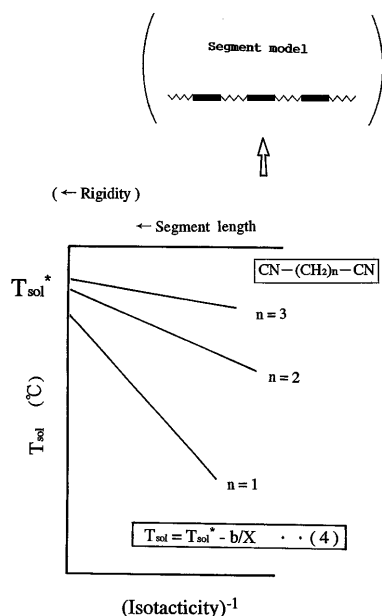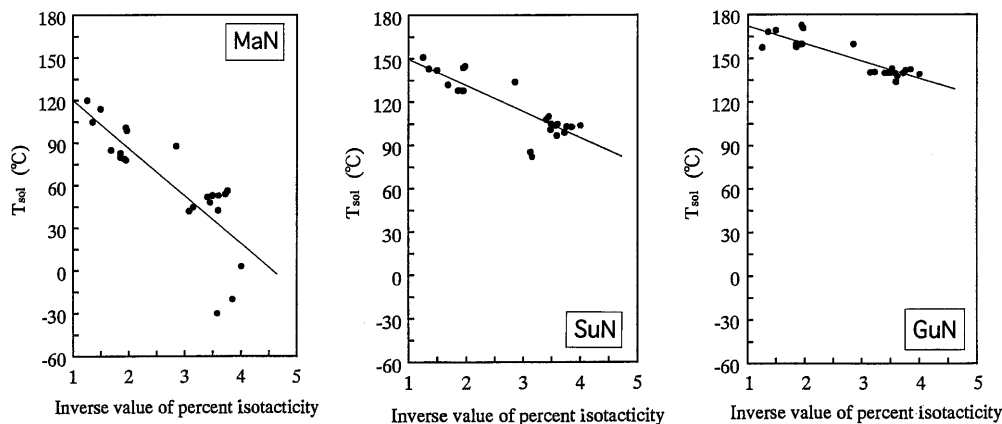**Fig. 5** Inverse plots of T_{sol} versus isotacticity

Fig. 6 Relationship between T_{sol}^* and the slope. The stronger the solvent power, the steeper the slope and the lower the T_{sol}^*. The segment model of a single PAN molecular chain is given at the *top* of this figure. The significance of the segment length can be clearly understood by this model, which duplicates the segment model of semiflexible liquid-crystalline polymers given in Ref. [5]

Table 3 Summary of inverse plots in dinitrile solvents giving the number of methylenic groups (n), the extrapolated value of the dissolution temperature (T_{sol}), the slope, and the dipole moment from Ref. [13]

Solvent	n	T_{sol}^* (°C)	Slope	Dipole moment (D)
Malononitrile	1	120	−33	3.74[a]
Succinonitrile	2	150	−18	3.68[b]
Glutaronitrile	3	172	−12	3.91[c]

[a] Microwave spectroscopy
[b] Solution, toluene, 30 °C
[c] Solution, benzene, 25 °C

the unit length (entropy effect)". The stiff isotactic PAN molecular chain has been reported by us [1, 6] from wide-angle X-ray diffraction studies and the solution properties have been reported by Kamide et al. [7].

Formal analogy between the T_{sol} of PAN and the T_g of PSt

Let us now consider the physical meaning of the straight lines in the inverse plots in Figs. 5 and 6. We consider that such a linear relationship has some scientific significance that has not been clarified sufficiently. In fact, we can find many linear relationships in various types of transition phenomena. Miyata and Inoue [8] reported a similar negative straight line in the inverse plots of melting temperature (T_m) against lamellar thickness of polyethylene (PE) based on Ref. [9]. Fox and Flory [10] reported that the ideal molecular-weight dependence of the T_g of fractionated amorphous PSt is converted into a linear line in the inverse plots. We have confirmed this for monodisperse PSt (Fig. 7).

In these results, one can find that these transition temperatures (T_m, T_g) are determined by a common mechanism: the breakdown of thermodynamic competition between enthalpy and entropy through chain
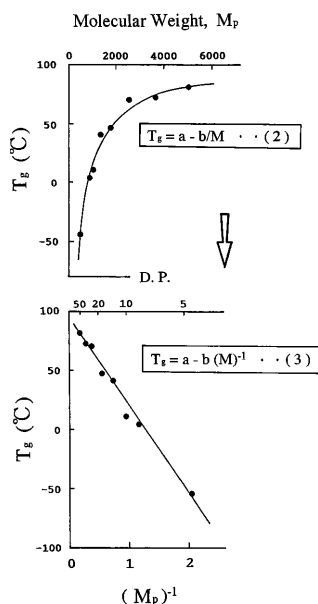
with the polar PAN molecule chain, whereas methylenic groups do not. A typical homologous behavior was observed in this way. These results are summarized in Table 3.

The slope of each line is also very important. Generally speaking, the stronger the dissolution power, the steeper the negative slope. This is clearly shown in Fig. 6. The slope means the variation of the dissolution temperature due to the improvement of isotacticity per unit length of the PAN molecular chain. Namely, it is a measure of "to what extent the dissolution temperature varies with the stiffening of the PAN molecular chain in

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Fig. 7 Molecular-weight dependence of the T_g of monodisperse polystyrene and its inverse plot

mobility (or segment mobility). In the case of the T_m of PE, partial melting will start from the amorphous region and the crystalline region will remain in the bulk sample. In the case of the T_g of PSt the onset of molecular motion will be initiated from the chain ends (or sequence ends) and the unit of chain motion is a "segment". In Fig. 7, in particular, the inverse value of the molecular weight can be replaced by the inverse value of the degree of polymerization and so this value is a useful measure of segment length. The longer the segment length, the higher the transition temperature (T_g).

Meaning of the linear relationship in the T_{sol} and segment concept

We consider that a similar situation would be realized for the T_{sol} of PAN. First, the isotacticity is the percentage of the (mm) component defined by Eq. (1) and so its inverse value is a good measure of the segment length (Fig. 6). Second, thermodynamic competition invariably occurs in the heating process: dissolution takes place only when the temperature is increased and the entropy (ΔS) overwhelms the enthalpy (ΔH). This can be expressed thermodynamically in the following way [11, 12].

$$T_{sol} = \Delta H / \Delta S , \qquad (2)$$

where ΔH is the enthalpy term due to the intermolecular interaction force and ΔS is the entropy term due to the

difference of stereoregularity through the configurational entropy.

This equation explains well the results for isotactic PAN. The higher the isotacticity, the higher the dissolution temperature due to its enhanced entropy term. The essential point is that the stiffness of the polymer chain can be correlated with the thermodynamic parameter through the entropy.

The criterion of dissolution of isotactic PAN into dinitrile solvents

The dissolution mechanism of isotactic PAN is quite complex; however, it may be possible to establish the dissolution theory in the near future. The complexity is because the dissolution temperature of isotactic PAN is defined by at least only three factors: stereoregularity (PAN), dissolution power (solvents), and conditions (temperature). (In fact, one of the bulk properties of the solvents, such as dipole moment, had little effect on the T_{sol}, Table 3. Quite local solvent structure and molecular mobility of polymers are outstandingly important in this case.) If one can connect the three factors at a molecular level with segment mobility at high temperatures, the dissolution criterion of stereoregular PAN will be obtained as a comprehensive result of these factors. To confirm this idea, many experiments are needed.

Conclusion

1. The T_{sol} of a series of PAN with different isotacticity was studied for three dinitrile solvents: simple saturation curves, i.e., three homologous curves, were obtained.
2. Plots of T_{sol} against the inverse value of the isotacticity provided straight lines, from which two parameters were derived. The dissolution power was in the following order: MaN > SuN > GuN.
3. A phenomenological analogy between the T_{sol} of PAN and the T_g of PSt was discussed from a thermodynamic point of view. The significance of segment length and segment mobility at high temperature in both phenomena was emphasized.

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