

# STUDY ON SOLUBILIZATION MECHANISM IN THE SYNTHESIS OF HIGH MOLECULAR WEIGHT POLY(p-PHENYLENE TEREPHTHALAMIDE)

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## ABSTRACT

The salts dissolved in the amide solvent play an important role in the synthesis of high molecular weight poly(p-phenylene terephthalamide) (PPTA). The solubilization of salts was investigated in this paper. The effects of association-dissociation equilibrium of salts and the solvation of their ions as well as hydrogen-bond on solubilization were discussed in some detail. The effects were attributed to cations and anions of salts respectively. Finally, the equation of solubilization was established according to the experimental results and some thermodynamic laws. The relations between molecular weight of PPTA and the solubilization were discussed.

## INTRODUCTION

Fiber of poly(p-phenylene terephthalamide) (PPTA) is one of the most distinguished high modulus and high strength fibers<sup>[1-3]</sup>. In general, the PPTA is prepared from p-phenylene diamine and terephthaloyl chloride in solvent mixture containing salts<sup>[4-9]</sup>, which (alkali metal or alkali earth metal halides) have a remarkable solubilization effect on polycondensation intermediates. Therefore, adding salts in solvent mixture can greatly increase the molecular weight of PPTA<sup>[8-10]</sup>.

The solubilization mechanism has been studied by Sokolov<sup>[11]</sup> and Panar et al.<sup>[12]</sup> However, the association-dissociation equilibrium of salts in amide solvent, the solvation of ions of salts, and the relations between these factors and the solubilization have not been mentioned. Thus the explanations about solubilization are unsatisfactory and leave much to be desired.

In the preceding paper, we reported the study on the above-mentioned factors<sup>[13]</sup>. The present paper attempts to deal with the effect of the factors and hydrogen bond interaction between anions of salts and polycondensation intermediates on solubilization, which is expressed as an equation. The relationship between solubilization and molecular weight of PPTA are discussed simultaneously.

## EXPERIMENTAL

### 1. Materials

N-methylpyrrolidinone (NMP): (Commercial compound from Japan), dehydrated by co-

boiling with benzene and distilled in vacuum. The water content is lower than 100 ppm.

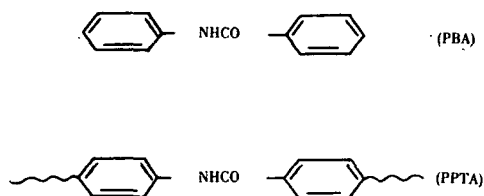
Anhydrous lithium chloride and calcium chloride: commercial chemically pure compounds dried before use.

Phenyl benzoylamide (PBA): commercial chemically pure compound.

## 2. NMR spectroscopy measurement

The proton NMR spectra were recorded on FX-90 Q NMR spectrometer equipped with a NMR Fourier transform accessory at 90 MHz and 30°C. The solutions were approximately 10%(w/v) model compounds in NMP solvent and in 5mm sample tube with TMS-acetone as capillary references.

The phenyl benzoylamide (PBA) was used as model compound for PPTA in NMR studies.

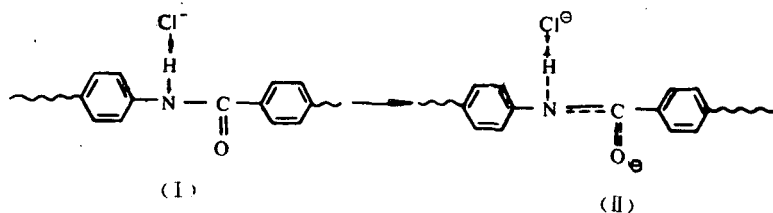


## RESULTS AND DISCUSSION

### Results of NMR Measurement

Fig.1 and Fig.2 show the proton NMR spectra of PBA in NMP-salt solutions with different salt concentrations. The resonance of proton of amide group in PBA shifts to lower magnetic field in salt solution. The chemical shifts  $\delta_H$  varies with the change of the salt concentrations (Fig.3). The lower field migration was attributed to the hydrogen-bond between the proton of amide group in PBA and anions of salts<sup>[12,14,15]</sup>.

It was also reported that aromatic polyamide showed electronegativity in amide-salt solution<sup>[12]</sup>. Furthermore, the NMR spectra of PBA showed that the resonance of proton on phenyl group also shifted to lower magnetic field when salts were added (Fig.1, Fig.2). It is supposed that when forming the hydrogen-bond the electric charge distribution of PPTA may change as follows.



The resonance of proton of phenyl group shifts to lower magnetic field because of the stronger magnetic anisotropic effect in (II).

### Expression of solubilization

1. Anions of salts: The salts' anions can form hydrogen-bond with protons of amide groups in polycondensation intermediates, restraining the hydrogen-bonds between the intermediates. Therefore, the resulted effect is the increase in solubility of polycondensation intermediates in amide-salt solution.

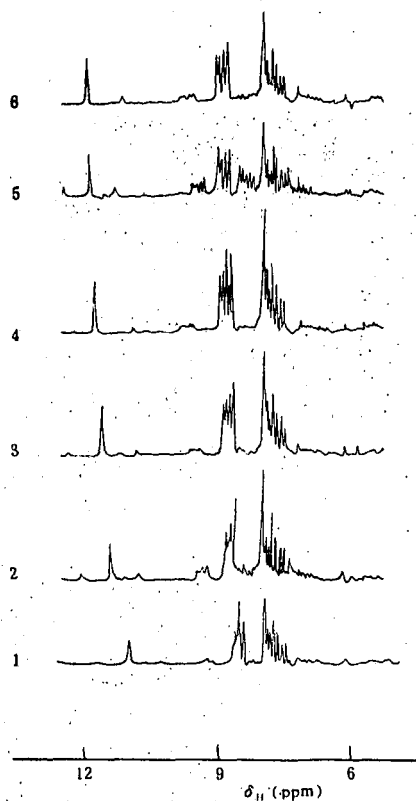


Fig. 1 The proton NMR spectra of phenyl benzoylamide in NMP-LiCl solutions with different LiCl concentrations.

1) 0.5 2) 1.0 3) 1.5 4) 2.0 5) 2.5 6) 3.0 (%)

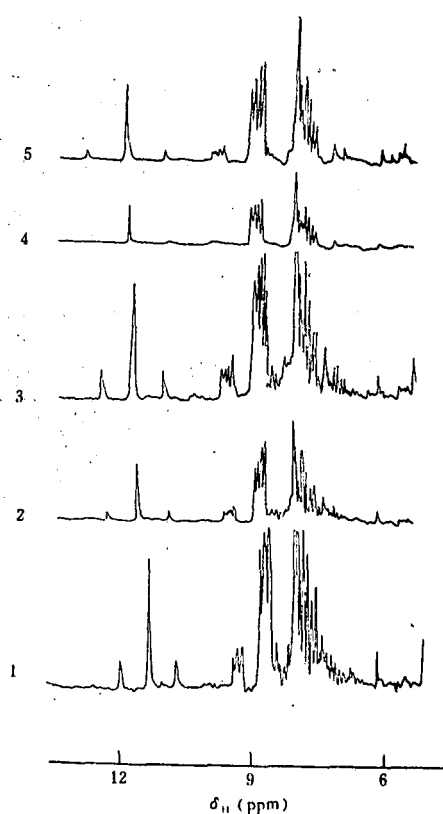


Fig. 2 The proton NMR spectra of phenyl benzoylamide in NMP-CaCl<sub>2</sub> solutions with different CaCl<sub>2</sub> concentrations.

1) 1.0 2) 2.0 3) 3.0 4) 4.0 5) 5.0 (%)

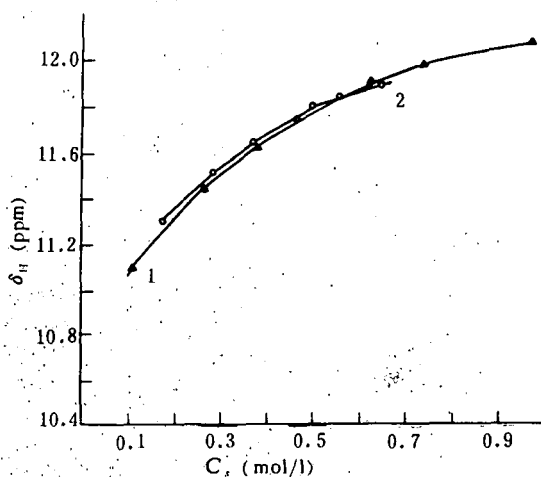
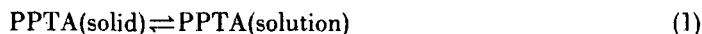


Fig. 3 The chemical shift of amide proton of phenyl benzoylamide varies with the change of the salt concentration 1, NMP-LiCl; 2, NMP-CaCl<sub>2</sub>

Assuming that the polycondensation intermediates with degree of polymerization  $n$  reach the dissolution-precipitation equilibrium in the solution.



the chemical potentials of the intermediates in two phase should be equal. Thus

$$u_{\text{solid}} = u_{\text{soln.}} = u^\circ(P, T) + RT \ln(rL_n) \quad (2)$$

Here,  $L_n$  is the saturated solubility of the intermediates. Since the chemical potential of pure solid equals its molar free energy  $\tilde{G}$ . Thus, Eq.2 is the relation between saturated solubility  $L_n$  and molar free energy  $\tilde{G}$ .

Furthermore, assuming that there are two kinds of polycondensation intermediates of PPTA whose inner hydrogen-bonding numbers have a difference  $m$  in molar unit. From Eq.2, both saturated solubilities of the intermediates have a relation as follows:

$$u_{\text{solid}_2} - u_{\text{solid}_1} = -m\Delta\tilde{G}_H = RT \ln(L_{n2}/L_{n1}) \quad (3)$$

$\Delta\tilde{G}_H$  is the increment of the free energy when forming one mole of hydrogen-bond in the intermediates of PPTA. From Eq.3

$$L_{n2}/L_{n1} = \exp(-m\Delta\tilde{G}_H/RT) \quad (4)$$

According to the above-mentioned solubilization mechanism,  $m$  is equal to the molar number of the hydrogen-bonds between salt anions and the intermediates with degree of polymerization  $n$ .

2. Cations of Salts: After forming hydrogen-bond, the polycondensation intermediates exhibit partial negative charges. Because of Coulomb interaction with salt cations, the concentration of intermediates around the cations will increase.

It can be assumed that average inter-attracting potential between a cation and a negative amide group of condensation intermediate is  $U_a$ . According to Boltzmann distribution law, the molar number of negative amide groups in a spherical shell  $4\pi r^2 dr$  at a distance  $r$  from the cation is

$$dN_j = (2n - 1) L_{n0} \cdot \exp(-U_a/RT) \cdot 4\pi r^2 dr \quad (5)$$

if the radius of the cation is  $r_a$  and the radius of solvation sphere is  $r_b$ , the molar number of negative amide groups in the solvation sphere is

$$N_j = \int_{r_a}^{r_b} (2n - 1) L_{n0} \cdot \exp(-U_a/RT) \cdot 4\pi r^2 dr \quad (6)$$

Multiplying  $N_j$  by cation numbers in per-unit volume  $A_0 C_i$  ( $A_0$  is the Avogadro Number,  $C_i$  is cation concentration), and dividing by the ratio of the solvation region of cations to total volume  $a_v$ , it can deduce the concentration of negative amide groups of the intermediates in all cation solvation region.

$$N = C_i A_0 / a_v \int_{r_a}^{r_b} (2n - 1) L_{n0} \cdot \exp(-U_a/RT) \cdot 4\pi r^2 dr \quad (7)$$

Dividing both sides of Eq.7 by  $(2n - 1)$ ,  $N/(2n - 1)$  is the concentration of the intermediates in cation solvation region

$$\begin{aligned} L'_{n0} &= N/(2n - 1) \\ &= C_i A_0 / a_v \int_{r_a}^{r_b} L_{n0} \cdot \exp(-U_a/RT) \cdot 4\pi r^2 dr = C_i L_{n0} \rho \end{aligned} \quad (8)$$

Here

$$\rho = A_0/a_v \int_{r_a}^{r_b} \exp(-U_a/RT) 4\pi r^2 dr \quad (9)$$

3. Equation of solubilization: It can be assumed that the saturated solubilities of polycondensation intermediates with degree of polymerization  $n$  are  $L_n$  and  $L_n^0$  in amide-salt solution and pure amide solvent respectively. Furthermore, the  $L_n$  can be divided into saturated solubility in cation solvation region  $L'_n$  and solubility in free solvation region  $L''_n$ . Thus

$$L'_n \cdot a_v + L''_n (1 - a_v) = L_n \quad (10)$$

From Eq.4 and Eq.8, there are relations among  $L'_n, L''_n$  and  $L_n^0$ .

$$L''_n = L_n^0 \exp(-m\Delta\tilde{G}_H/RT) \quad (11)$$

$$L'_n = L''_n C_i \rho = L_n^0 C_i \rho \exp(-m\Delta\tilde{G}_H/RT) \quad (12)$$

Substitute Eq.11 and Eq.12 into Eq.10,

$$C_i \rho L_n^0 \exp(-m\Delta\tilde{G}_H/RT) \cdot a_v + L_n^0 \exp(-m\Delta\tilde{G}_H/RT) (1 - a_v) = L_n \quad (13)$$

Finally, Eq.13 can be expressed as

$$L_n/L_n^0 = \{1 + (C_i \rho - 1)a_v\} \cdot \exp(-m\Delta\tilde{G}_H/RT) \quad (14)$$

*Meaning and utility of solubilization equation*

1. Meaning: In Eq.14,  $L_n$  and  $L_n^0$  are the saturated solubilities of condensation intermediates with degree of polymerization  $n$  in amide-salt solution and pure amide solvent respectively.  $L_n/L_n^0$  is the increasing times of saturated solubility when salts are added.

When the temperature and pressure are kept constant, hydrogen forming-bond in polycondensation intermediates is a spontaneous process ( $\Delta\tilde{G}_H < 0$ ). Therefore,  $\exp(-m\Delta\tilde{G}_H/RT)$  should be larger than unit and will increase as  $m$  increase. This part can be attributed to anions of salt. From Eq. 9

$$\begin{aligned} C_i \rho &= C_i A_0/a_v \int_{r_a}^{r_b} \exp(-U_a/RT) \cdot 4\pi r^2 dr \\ &= C_i A_0/a_v \int_{r_a}^{r_b} \left\{ 1 + (-U_a/RT) + \frac{1}{2}(-U_a/RT)^2 + \dots \right\} 4\pi r^2 dr \\ &= 1 + C_i A_0/a_v \int_{r_a}^{r_b} \left\{ (-U_a/RT) + \frac{1}{2}(-U_a/RT)^2 + \dots \right\} 4\pi r^2 dr \end{aligned} \quad (15)$$

When there is an inter-attraction between salt cations and negative amide groups of condensation intermediates,  $U_a < 0$ , the integration in last equation of Eq.15 is obviously larger than 0. Therefore,  $(C_i \rho - 1)$  is larger than 0 and will increase as  $|U_a|$  increase. Thus, the term preceding exponent function in Eq.14 will increase as  $|U_a|$  and  $a_v$  increase. The tendency agrees with the solubilization of cations of salt.

2. Utility: It can be seen from Eq.14 that  $L_n/L_n^0$  will increase when  $m$ ,  $|U_a|$  and  $a_v$  increase. In other words, salt improves the solubility of the condensation intermediates. When concentration of salt reaches a certain amount,  $a_v$ ,  $|U_a|$  decrease gradually and the hydrogen-bond with associated

ions may reduce the solubility of polycondensation intermediates<sup>[13]</sup>. Thus, when salt's concentration is too high, solubility of the intermediates decrease. Eq.14 manifests the relation between solubilization and concentration of salt through  $m$ ,  $U_a$  and  $a_v$  terms.

3. Relationship between solubilization and molecular weight of PPTA: We define  $L_n/L_n^0$  as solubilization parameter  $I$ . In solution polycondensation, the molecular weight of synthesized PPTA also depends on the monomer concentration. If the concentration of polycondensation intermediates  $C_M/n$  less than  $L_n$ , the polycondensation reaction will continue in homogeneous phase. If  $C_M/n$  is larger than  $L_n$ , the intermediates will precipitate out and the propagation will stop. Therefore, maximum degree of polymerization of PPTA ( $n_{\max}$ ) can be expressed as

$$G(n_{\max}) = C_M / IL_1^0$$

$G(n_{\max})$  is a decreasing function of  $n_{\max}$  and  $L_1^0$  is the saturated solubility of polycondensation intermediates with degree of polymerization 1 in pure amide solvent. Thus,  $n_{\max}$  will increase as  $I$  and  $L_1^0$  increase or  $C_M$  decreases.

The quantitative calculation by the solubilization equation will be reported later,

#### Keywords:

Poly (p-phenylene terephthalamide); Solubilization mechanism

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