

Studies on the Semirigid Chain Polyamide— Poly(1,4-Phenylene terephthalamide)

BAO JINGSHENG,* YOU ANJI, ZHANG SHENGQING, ZHANG SHUFAN, HU CHANG, *Institute of Chemistry, Academia Sinica, Beijing, Peoples Republic of China*

Synopsis

In this article, the polycondensation of terephthaloyl chloride and *p*-phenylenediamine was systematically studied, including the liquid-crystalline state of the solution and the spinning of poly(1,4-phenylene terephthalamide) (PPTA). High-molecular-weight PPTA with $\eta_{inh} = 5-7$ was prepared and the main factors influencing the solution polycondensation of 1,4-phenylenediamine with terephthaloyl chloride were studied in detail. Experimental results showed that the water content of the reaction system, reactant concentration, and volume ratio of mix solvents have a great influence on the inherent viscosity of the poly(1,4-phenylene terephthalamide) obtained. The highest η_{inh} was obtained at 0.3M/liter reactant concentration in a mixed solvent ratio HMPA/DMAC of 4/1 (by volume), at 0.35M/liter reactant concentration in a mixed solvent of HMPA/NMP = 7/3, and at 0.5M/liter of reactant concentration in a mixed solvent of HMPA/THF = 9/1. The water content must be controlled to less than 100 ppm in the polymerization system. In the early stage of the polycondensation process, the η_{inh} of the polymer obtained increased rapidly with time. The system gelled within 2 or 3 min, while the monomer conversion reached about 100%. However, the reaction of polycondensation continued after gelation and the η_{inh} of the polymer increased appreciably. We have studied the viscosity behavior at 20–155°C for the anisotropic solution of PPTA in 100% sulfuric acid (η_{inh} of PPTA 2.5–4.9). Experimental results showed that, at low concentrations the viscosity of isotropic solution increases with the increase of polymer concentration to reach a maximum near the critical polymer concentration, beyond which the solution changes to an anisotropic liquid-crystalline solution. The appropriate spinning region was obtained as shown in the phase diagram determined by viscosity, degree of depolarization anisotropy, and region of thermal depolymerization. Fibers of PPTA with high modulus and high tenacity were obtained by dry-jet wet spinning. The fibers obtained have a tenacity of ~ 22 g/denier, a modulus of ~ 600 g/denier, and elongation at break $\sim 3.5\%$.

INTRODUCTION

In recent years, the study of para-aromatic polyamide has become a very attractive subject due to the semirigid chain in polymers like poly(1,4-phenylene terephthalamide), which can form anisotropic liquid-crystalline solutions.^{1,2} Fibers with high tenacity and high modulus can be obtained by spinning this kind of polymer solution.

Poly(1,4-phenylene terephthalamide) (PPTA) was first prepared from solution polymerization by Kwolek, Morgan, and Gorenson³ several years ago. Recently, Bair, Morgan, and Killian published the influence of reactant concentration on the inherent viscosity of PPTA.⁴

In this paper, the polycondensation of terephthaloyl chloride and *p*-phenyl-

* Other co-workers in this work are Lu Daohui, Xu Chaochou, Lou Yinxiang, Zhang Jiyu, Xie Ping, Zhai Fengyun, Zheng Shuhong, Han Baozhen. Other part-time co-workers are Ni Zhende, Hu Hanjie, Xi Fu, Li Xuefen, Liu Yunqi, Huang Changkai, Yue Zhenjie, Xi Shuyu, Wang Youhuai, Huang Meiyu.

enediamine was systematically studied, including the liquid-crystalline state of the solution and the spinning of PPTA.

EXPERIMENTAL

Poly(1,4-Phenyleneterephthalamide) Synthesis

1,4-phenylenediamine (*p*-phenylenediamine: commercially obtained 1,4-phenylenediamine was purified by vacuum distillation to white solids; melting point 140–141°C) (10.381 g, 0.096 mole) was dissolved in 160 ml of hexamethylphosphoramide (HMPA) and 80 ml of dimethylacetamide (DMAC) contained in a reaction kettle equipped with a stirrer and a N₂ inlet tube. The mixture was cooled at about 3°C with an ice/water bath and powdered terephthaloyl chloride* (19.489 g, 0.096 mole) was added with rapid stirring. The reaction mixture became a thick pastelike coagulant, so that stirring could not be continued. The reaction mixture was allowed to stand overnight and then worked up by agitating the contents with water in a blender to remove the solvent and the polymer was collected by filtration. This washing procedure was repeated several times. The collected polymer was dried to constant weight. The dried polymer had an inherent viscosity of 5.8 and the yield was nearly theoretical.

Determination of Inherent Viscosity

The inherent viscosity number [$\eta_{inh} = 2.3 \log (\eta_{rel})/c$] was determined at 30°C on solutions containing 0.5 g of polymer per 100 ml of concentrated (~98%) H₂SO₄ with Ubbelodhe viscometer.

Degree of Depolarization Anisotropy (DDA)

The degree of depolarization anisotropy⁵ was determined by the method described in ref. 5. The quantity is a measure of the depolarization of the plane polarized light passing through a sample, and is defined by the following equation:

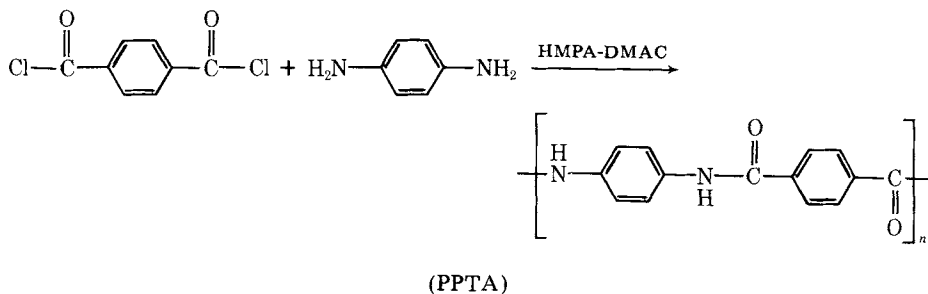
$$DDA = \frac{I_{\sigma}^{\perp}/I_{\sigma}^{\parallel} - I^{\perp}/I^{\parallel}}{I_{\sigma}^{\perp}/I_{\sigma}^{\parallel} - 1} \times 100$$

where I_{σ}^{\perp} , I_{σ}^{\parallel} and I^{\perp} , I^{\parallel} denote the values of photoelectric current of the blank (completely isotropic) and sample measurements made with polarizer and analyzer parallel and perpendicular, respectively.

* Terephthaloyl chloride was prepared by refluxing the mixture of terephthalic acid, thionyl chloride, and a small amount of dimethylformamide, and then distilled off the excess thionylchloride. The white solids with a melting point 83–84°C terephthaloyl chloride were obtained by twice vacuum distillation.

RESULTS AND DISCUSSION

Polycondensation of Poly(1,4-Phenyleneterephthalamide)



The polycondensation of terephthaloyl chloride and *p*-phenylenediamine was studied, various factors influencing on the molecular weight of polymer formed, such as reactant concentration, water content, composition of the mixed solvent system, reaction time, and temperature of polycondensation were systematically examined. The polycondensation product PPTA of high molecular weight with η_{inh} in the range of 5–7 was prepared for the spinning from liquid crystalline solution.

Effect of Reactant Concentrations

By using three different kinds of mixed solvents system, the effect of reactant concentration on the inherent viscosity of polymer is shown in Figure 1. In the HMPA–DMAC, HMPA–NMP, and HMPA–THF solvent systems, the best reactant concentration to give the highest inherent viscosities of polymer was 0.3, 0.35, and 0.5 mole/liter, respectively.

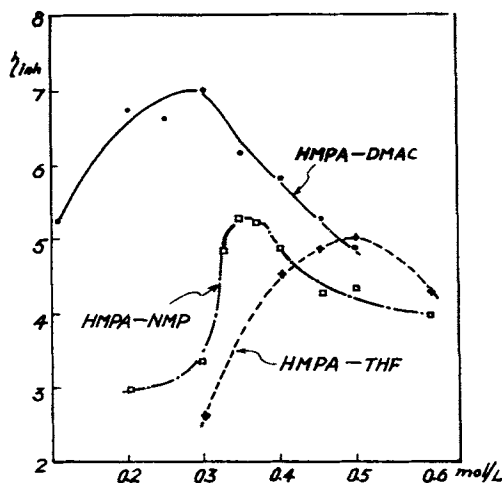


Fig. 1. Effect of molar concentration of monomer on η_{inh} of polymer. (●—) HMPA-DMAC; (□- - -) HMPA-NMP; (○ · · ·) HMPA-THF.

It was observed in HMPA-DMAC and HMPA-NMP systems that, in low reactant concentration forming solutions of low polymer concentration, coagulation did not appear in the later stage of polycondensation. This mixed reaction solution had better fluidity, and could be stirred continuously. However, in fact, the lower reactant concentration gave polymers with lower inherent viscosities. Besides the reason of lower reaction concentration inducing the lower rate of polymerization, it seems that the main factor was the side-reaction induced by the impurities (such as water, etc.) in the solvent system.

The HMPA-THF solvent system was different than the HMPA-DMAC and HMPA-NMP systems. At the lower reactant concentration (such as 0.3 mole/liter), the polymer precipitated as powders when the polycondensation proceeded, and became pastelike, then finally coagulated. It seems that the solubility of produced polymer was poor, and the inherent viscosity was low ($\eta_{inh} = 2.57$). However in the higher reactant concentration (such as 0.5 mole/liter) the reaction solutions became viscous and pastelike, when the polycondensation proceeded. It seems that in the higher molar concentration of reactants, the polymer had better solubility in solvents, and higher inherent viscosity of polymer was obtained ($\eta_{inh} = 4.95$). The reason for this phenomenon is now under investigation.

Effect of Water Content of Solvents in the Reaction System

The effect of water content of solvent system on the viscosity of polymer is important. The η_{inh} of polymer decreased with increasing water content of solvent system is shown in Figure 2. In the presence of water as impurity in the reaction system, the hydrolysis of terephthaloyl chloride or of acid chloride end group of the polymer should occur, thus leads to the chain termination. Therefore, when water is present in the reaction system it is very disadvantageous for obtaining the polymer of high molecular weight. This is shown by the results in Figure 2. We suggest that the water content in the polymerization system must be carefully controlled below 100 ppm.

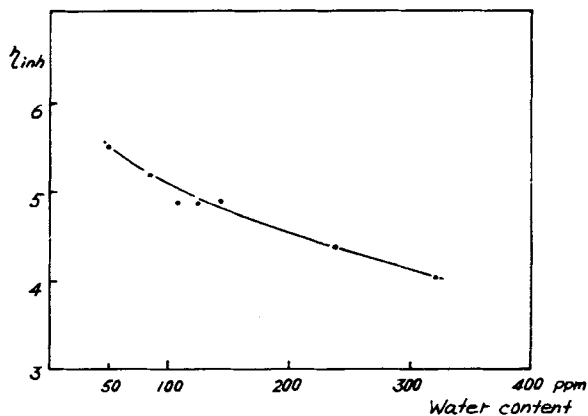


Fig. 2. Effect of water content of solvent system on η_{inh} of polymer.

Effect of Volume Ratio of Mixed Solvents on the η_{inh} of Polymer

Three systems of mixed solvents were selected (such as HMPA-DMAC, HMPA-NMP, and HMPA-THF) and a variety of volume ratios of the solvent components in each group were investigated. The experimental results were shown in Figure 3. Polymers with highest η_{inh} were obtained at a mixed solvent ratio of HMPA/DMAC = 4/1 (by volume), HMPA/NMP = 7/3, and HMPA/THF = 9/1. It was noted that when the solvent of HMPA was used alone, the polymer precipitated as powders. The solubility of the polymer in HMPA was very low, hence much lower η_{inh} of the polymer was obtained. On the contrary, if the second component of solvent was added, it could greatly improve the solubility of polymers. In the system of HMPA-DMAC, the highest η_{inh} of polymer was obtained within the range of volume ratio of HMPA/DMAC from 9/1 to 1/1. In HMPA/NMP the allowable range of variation was smaller and in HMPA-THF system a narrow peak appeared, showing that when the THF content (by volume) changes from 10 to 8% or 12%, the inherent viscosity of polymer decreased abruptly.

Effect of Time and Temperature on the Polycondensation Process

The effect of time on the polycondensation process is shown in Figure 4. (in curve I, HMPA/DMAC = 3/1, reactant concentration 0.4 mole/liter; in curve II, HMPA/THF = 9/1, reactant concentration 0.5 mole/liter).

In the early stage of the polycondensation process, the η_{inh} of polymer increased rapidly, the η_{inh} of polymer at different reaction time for curve I is shown in Table I.

When polycondensation proceeded to 50 sec, nearly theoretical yield was obtained, i.e., all the monomers had taken part in the reaction; the reaction mass coagulated at 330 sec, and the reaction mixture was allowed to stand at coagulated

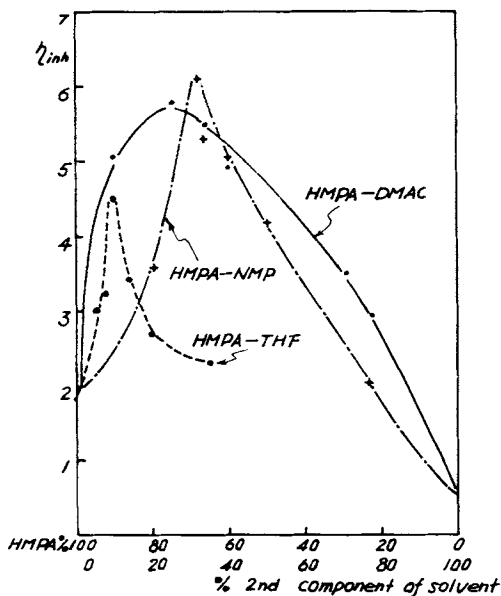


Fig. 3. Effect of volume ratio of mixed solvents on η_{inh} of polymer. Symbols as in Figure 1.

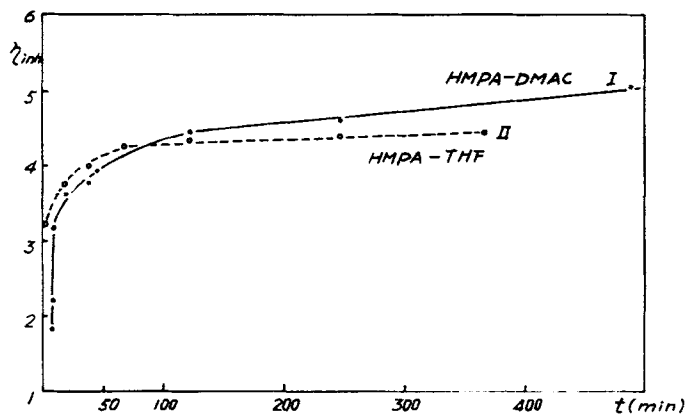


Fig. 4. Effect of time on the polycondensation process.

state, the value η_{inh} increased steadily although slowly, until the final equilibrium state was reached about 8 hr). This shows that, the polycondensation reaction continues after coagulation, so, the total time of polycondensation reaction should not be less than 6 hr. Elevation of temperature after coagulation would favor the further condensation of the polymers. Figure 5 shows the effect of temperature on the polycondensation process. A solvent mixture of HMPA/DMAC = 3/1 (by volume) and reactant concentration = 0.3 mole/liter was cooled in an ice/water bath. After the reaction proceeded for 30 min, two parts of the reaction product were rapidly taken out and then one was heated at 70°C , and the other cooled at -50°C ; then, the inherent viscosities of the coagulated products in three different reaction temperatures were successively determined at different intervals

TABLE I
Effect of Time on the Polycondensation Process^a

Reaction time (t)	50 sec	75 sec	270 sec	15 min	30 min	60 min	120 min	240 min	480 min	1240 min	1800 min
η_{inh}	1.81	2.21	3.20	3.66	3.81	4.24	4.40	4.62	5.00	4.99	5.01

^a Solvent system HMPA/DMAC = 3/1; reaction concentration 0.4 mole/liter.

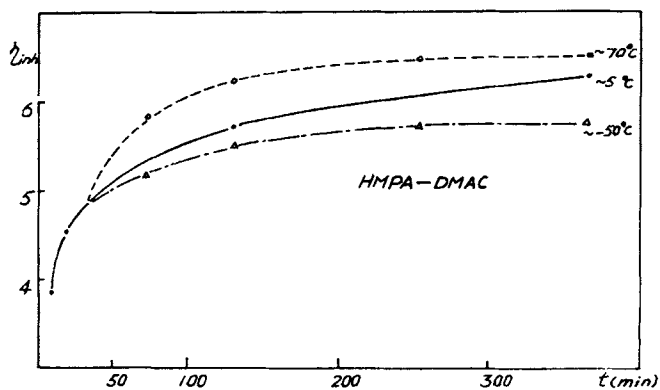


Fig. 5. Effect of temperature on the polycondensation process.

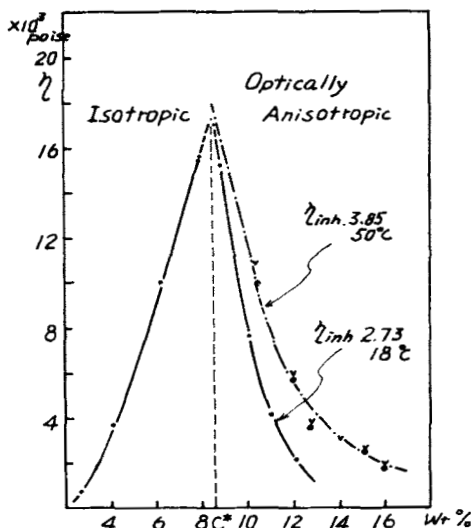


Fig. 6. Effect of solution concentration on viscosity of solution (1) η_{inh} 3.85 at 50°C, 100% H₂SO₄; (2) η_{inh} 2.73 at 18°C, 100% H₂SO₄.

as the reaction proceed. The results are shown in Figure 5. The rate of polycondensation increased at 70°C, and the η_{inh} of sample increased more rapidly than the sample in ice/water bath. The η_{inh} obtained from the -50°C sample was much slower.

From the results of these experiments, we found that in the early stage of polycondensation the reaction was favored by lower temperature, while the polycondensation proceeded smoothly to keep the system homogeneous. However after the reaction mixture gelled it was no longer necessary to keep a lower temperature. On the contrary, the rate of reaction and the η_{inh} of polymer could be increased by the elevation of temperature.

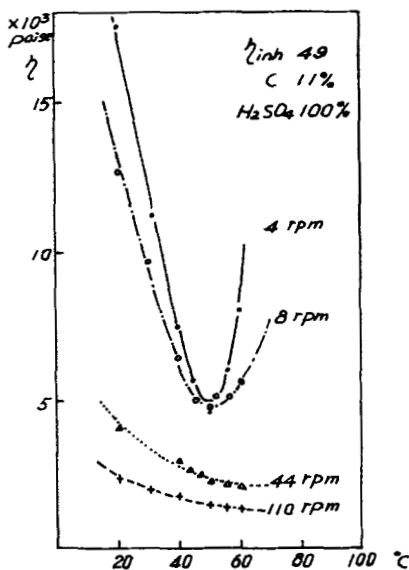


Fig. 7. Effect of shear rate on viscosity of solution at different temperature.

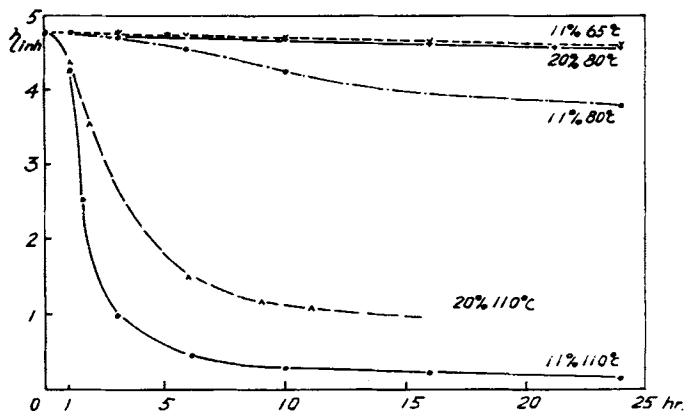


Fig. 8. Effect of temperature, concentration of solution and time on the η_{inh} of polymer. (1) 11% c at 65°C; (2) 20% c at 80°C; (3) 11% c at 80°C; (4) 20% c at 110°C; (5) 11% c at 110°C.

Liquid-Crystalline State of the Solution of Poly(1,4-Phenyleneterephthalamide) and Its Spinning

We have studied the effects of different factors on the viscosity of the anisotropic solution of poly(1,4-phenyleneterephthalamide) in 100% sulfuric acid (η_{inh} of polymer were 2.5–4.9).

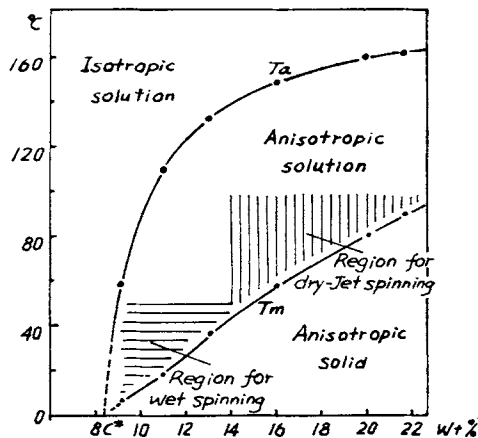


Fig. 9. Phase diagram of the anisotropic solution of PPTA in 100% H_2SO_4 (η_{inh} 4.9).

TABLE II
Properties of PPTA fibers

Properties	Wet spinning		Dry-jet wet spinning (as-spun)
	As-spun	heat-treated	
Tenacity (g/d)	7	14	~22
Elongation (%)	20	11	3.5
Modulus (g/d)	200	410	~600

Viscosity of Poly(1,4-phenyleneterephthalamide)

Effect of solution concentration on viscosity of solution. Poly(1,4-phenyleneterephthalamide) readily forms liquid-crystalline solutions, since it has an inherently semirigid chain structure desirable for forming such solutions. When a liquid-crystalline solution of poly(1,4-phenyleneterephthalamide) is formed by dissolving increments of polymer in a solvent or by preparing a series of solutions with increasing concentrations, there occurs a sudden drop in viscosity. Figure 6 shows the relationship of viscosity and polymer concentration for a solution of the polymer in 100% sulfuric acid. The viscosities were determined with Hoppler viscometer at low shear rates. As concentrations of the polymer increases, the viscosity also increases. The slope of the curve, however, changes abruptly when polymer concentration reaches about 8.8%, i.e., at the critical concentration point. The viscosity now begins to drop and the solution separates into two phases. As more polymer is added, viscosity drops further and the amount of anisotropic phase increases. Effect of shear rate on viscosity of solution. Figure 7 shows the effect of shear rate on the viscosity of 11% concentration of polymer with η_{inh} 4.9 in 100% sulfuric acid at different temperatures. Viscosities were determined with rotary viscosimeter at different shear rate. At lower shear rates, the viscosity of solution decreases rapidly with increasing temperature to a minimum point and then increases (change to isotropic state). Experimental results showed that the effect of temperature on viscosity became less important when the shear rate was increased and the viscosity of solution decreased with increasing shear rate at the same temperature.

Depolymerization of Polymer in 100% Sulfuric Acid Solution

The effects of temperature, concentration of solution, and time on the depolymerization of polymer are shown in Figure 8. Experiments were carried out at different concentrations (11% and 20% by weight) and different temperatures (65, 80, and 110°C). Results showed that polymer in the solution of lower concentration depolymerized more rapidly than that of higher concentration. However, it seems that temperature is a more predominating factor for depolymerization, since the polymer depolymerized rapidly at 110°C although the solution was at higher concentration, i.e., 20% (by weight).

The stability of PPTA in 100% H₂SO₄ with 13% concentration liquid-crystalline solution at 18°C for 10 days and then at 50–60°C for 20 hr, shows that the sample of PPTA was not depolymerized. But polymer depolymerization occurred rapidly when excess SO₃ was present in sulfuric acid (106–108%) at higher temperature. For example the polymer of η_{inh} 3.5–4.5, the η_{inh} changed to η_{inh} = 1.0 after 4 hr at 80°C.

Spinning of Liquid-Crystalline Solution of Poly(1,4-Phenyleneterephthalamide)

The appropriate spinning region was obtained as shown in the phase diagram (Fig. 9). It was determined by viscosity, the degree of depolarization anisotropy (DDA) and region of thermal depolymerization.

According to the appropriate spinning region, fibers of PPTA with high modulus and high tenacity were obtained. The properties of PPTA fibers are shown in Table II.

Other co-workers in this work are Liu Daohui, Xu Chaochou, Lou Yinxing, Zhang Jiyu, Xie Ping, Zhai Fengyun, Zheng Shuhong, Han Baozhen. Other (part-time) co-workers are Ni Zhende, Hu Hanjie, Xi Fu, Li Xuefen, Liu Yungi, Huang Changkai, Yue Zhenjie, Xi Shuyu, Wang Youhuai, Huang Meiyu.

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