

Influence of "Historical Effects" on the Rheological Properties of a Polyacrylonitrile Copolymer Solution

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Article Info

Received 27 August 2012

Accepted 31 November 2012

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Open Access

DOI: <http://dx.doi.org/10.5714/CL.2012.14.1.045>

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<http://carbonlett.org>

pISSN: 1976-4251

eISSN: 2233-4998

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Abstract

Polyacrylonitrile (PAN) copolymers of different molecular weights were synthesized by a suspension polymerization and precipitation polymerization method. The rheology behaviors of the synthesized PAN copolymers were investigated in relation to their molecular weight, solid content and melting temperature. The influence of "historical effects" on the spinning solution of PAN was studied by analyzing the laws of viscosity considering the diversification time and temperature. The viscosity disciplines of each spinning solution conformed well to the rheological universal laws in a comparison of the suspension polymerization product with that of precipitation polymerization. Viscosity changes in the swelling process of dissolution were gentler in the suspension polymerization product; a small amount of water will quickly debase the solution viscosity, and high-speed mixing can greatly shorten the time required by the spinning solution to reach the final viscosity.

Key words: historical effect, suspension polymerization, rheological property, apparent viscosity, precipitation polymerization, polyacrylonitrile

1. Introduction

High-quality precursor fiber is the basis for the preparation of high-performance carbon fiber [1]. The quality of spun fiber directly determines the quality of the final fiber to a large extent, and the quality of the spun fiber depends on the rheology of the spinning solution [2]. The "historical effects" represent a process or an influence related to the spinning solution when creating spun fiber. The solution goes through many different stages during the process of swelling and dissolving. Different polymerization methods and dissolution processes (including the heating rate conditions, stirring speed and time, as well as the type of solvent used and the dissolution time) will have a deep influence on the viscosity of a spinning solution, and this will directly determine the spinnability. These factors (the polymerization method and dissolution process) which affect the spinnability of spinning solution will have many different effects on the final performance of the spinning solution. Therefore, in this study, the spinning solution is put through a variety of historical processes and the rheology of the spinning solution is analyzed in an effort to determine the history effects. The most common methods for the synthesis of PAN are solution polymerization, suspension polymerization, and precipitation polymerization [3,4].

Currently, testing the rheology of a spinning solution mainly can be done using one of three methods: a dynamic rheological test [2], the 'viscosity of a falling ball' method [3], and the rotation viscosity method [5]. In this study, to simplify the experiment, the rotation viscosity method was used to analyze the rheology of the spinning solution.

The purpose of this study is to investigate how the "historical effects" influence the rheo-

logical properties of a polyacrylonitrile (PAN) copolymer solution. To do this, 1) PAN copolymers with different molecular weights were synthesized from PAN and comonomers, 2) the rheological properties of the viscosities and molecular weight distributions of the synthesized PAN copolymer solution were analyzed during agitation to obtain high-quality PAN precursor fiber, and 3) the historical effects on the rheological properties of the PAN copolymer solution were investigated.

2. Materials

Acrylonitrile (AN, Beijing Chemical Reagents Co.) was freed from an inhibitor by atmospheric distillation. Methyl acrylate and itaconic acid (MA, IA, Beijing Second Chemical Co.) were used as the second and the third monomer, respectively. The initiator, α, α' -azobisisobutyronitrile (AIBN, Shandong Xueyin Chemical Co.), was purified by recrystallization. Dimethyl sulfoxide (DMSO, Liaoning Panjin Chemical General Co.) was distilled under reduced pressure at 68°C for use as a solvent and dimethyl formamide (DMF, Beijing Second Chemical Co.) was used as a polymer solvent to measure the intrinsic viscosity of the PAN (Ubbelohde viscosity meter using DMF as a solvent).

2.1. Synthesis of the PAN copolymer solution

PAN copolymer powders with different molecular weights were prepared by precipitation polymerization and suspension polymerization from terpolymer (AN—methacrylate—itaconic acid) with a mass ratio of 96:3:1 at 65°C for 2 h, after which they were dried at 100°C for 24 h. For the precipitation polymerization solutions (first and second), 30 wt% (480 g) of monomers were dissolved in 1089 mL of solvent (DMSO:H₂O = 30:70). One wt% of AIBN initiator was then added to the solvent. For suspension polymerization solutions (third and fourth), 30 wt% (480 g) of monomers were dissolved in 1129 mL of solvent (DMF:H₂O = 15:85). One wt% AIBN initiator and 1 wt% polyvinyl alcohol dispersant were then added to the solvent. Then, a set amount (23.93 g) of polymer was dissolved into 1) pure DMSO and 2) 0.7% H₂O containing DMSO to obtain a 9% solid containing spinning solution.

2.2. Molecular weight determination of the PAN copolymers

PAN copolymer powder (0.01-0.1 g) was dissolved in 10 mL DMF for 48 h at a fixed volume in a 25 mL volumetric flask. This was then maintained at a constant temperature (35 ± 0.1°C).

The intrinsic viscosity $[\eta]$ of the high PAN sample was determined by a three-tube Ubbelohde viscometer, and the average molecular weight M_{η} was determined from the following equation [4]:

$$[\eta] = 2.78 \times 10^{-4} M_{\eta}^{0.76} \quad (1)$$

The apparent viscosities $[\eta_a]$ of the spinning solution were measured using an LEDVE230 rotary rheometer under different conditions (different rotor speeds).

2.3. Rheology of the PAN copolymer solution

The PAN copolymer was dissolved in DMSO at 35°C for 24 h under ordinary mixing conditions at 100 r/min, after which the solution was heated slowly to 75°C at a rate of 10°C/3 h so that it would expand. The apparent viscosities were then measured. To compare the effect of mixing, the PAN copolymer was dissolved in DMSO at 35°C for 20 h under ordinary mixing conditions at 100 r/min and then emulsified for 15 min with a homogenizer (at a shear rate of 5000 s⁻¹). The apparent viscosity was then determined by the rotary rheometer, and the solution was finally heated to 75°C in 2 h.

3. Results and Discussion

The rheological properties of the PAN solution in terms of the viscosity were used as a key index [6]. A solution with high viscosity possesses poor liquidity, and it is difficult to remove air bubbles from it. Therefore, during the spinning process, it is easy to produce hairy silk strands at the ends, and they will influence the spinnability of the solution. It is difficult to mold fiber if the solution is less viscous. Also, it is difficult to obtain a precursor fiber from a highly viscous PAN copolymer solution. The influences of other factors, such as the relative molecular mass of the polymer solution when swelling and dissolving, and other factors, should be considered for the successful spinning of a PAN copolymer solution. The viscosity of the spinning solution can be the key factor; therefore, this study seeks to determine the properties of the viscosity of a spinning solution by means of a compare and contrast method.

The average molecular weights of the first and second precipitation polymerization solutions (Fig. 1) were 477,689.4 and 678,534.8, and those of the third and fourth suspension polymerization solutions (Fig. 2) were 403,913.07 and 603,884.7, respectively. From the average molecular weights, the apparent viscosities of the solution at different temperatures were obtained. These are listed in Tables 1-4.

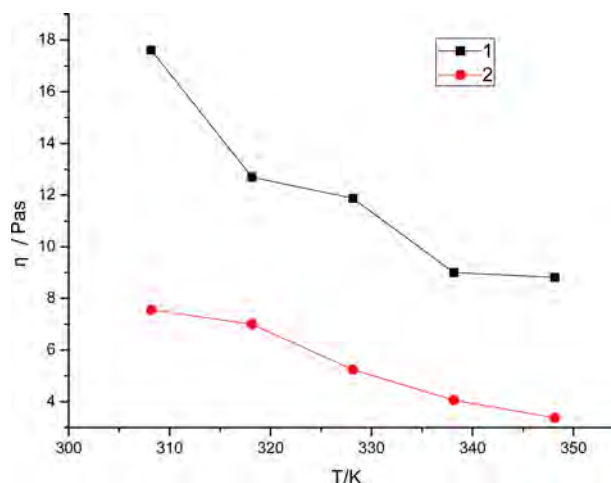


Fig. 1. Relationships between the temperature and apparent viscosity of the first and second suspension polymerization results.

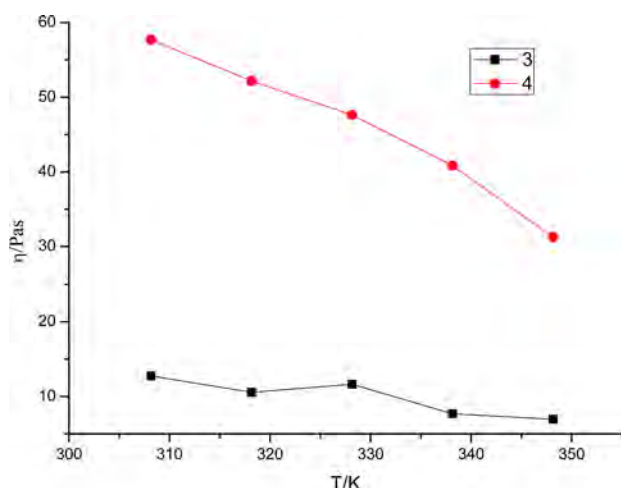


Fig. 2. Relationships between the temperature and apparent viscosity of the third and fourth suspension polymerization results.

Table 1. Apparent viscosities of PAN copolymer solution obtained from the first precipitation polymerization results

Temperature (°C)	Apparent viscosity (mPa·s)	Probe speed (rpm)	Torque (%)	Time (h)
35	17 620	0.3	28.2	24
45	12 690	0.3	20.3	27
55	11 880	0.3	19.0	30
65	9000	0.3	14.4	33
75	9250	0.3	14.8	45
75	9190	0.3	14.7	48
75	8810	0.3	14.1	51
75	8060	0.3	12.9	54
75	8000	0.3	12.8	70

PAN: polyacrylonitrile.

Table 2. Apparent viscosities of PAN copolymer solution obtained from the second precipitation polymerization results

Temperature (°C)	Apparent viscosity (mPa·s)	Probe speed (rpm)	Torque (%)	Time (h)
35	7560	0.3	12.1	24
45	7000	0.3	11.2	27
55	5250	0.3	8.4	30
65	4060	0.3	6.5	33
75	3380	0.3	5.4	48
75	3380	0.3	5.4	51
75	4620	0.3	7.4	54
75	3130	0.3	5.0	57

PAN: polyacrylonitrile.

Table 3. Apparent viscosities of PAN copolymer solution obtained from the third suspension polymerization results

Temperature (°C)	Apparent viscosity (mPa·s)	Probe speed (rpm)	Torque (%)	Time (h)
35	12 750	0.3	20.4	24
45	10 560	0.3	16.9	27
55	11 630	0.3	18.6	30
65	7690	0.3	12.3	33
75	6940	0.3	11.1	36
75	6810	0.3	10.9	56
75	6190	0.5	16.5	59
75	6080	0.5	16.2	74
75	6040	0.5	16.1	77

PAN: polyacrylonitrile.

Table 4. Apparent viscosities of PAN copolymer solution obtained from the fourth suspension polymerization results

Temperature (°C)	Apparent viscosity (mPa·s)	Probe speed (rpm)	Torque (%)	Time (h)
35	57 690	0.3	92.3	24
45	52 190	0.3	83.5	27
55	47 630	0.3	76.2	30
65	40 810	0.3	65.3	46
75	31 250	0.3	50.0	49
75	41 380	0.3	66.2	52
75	41 380	0.3	66.2	52
75	29 000	0.3	46.4	55
75	28 560	0.3	45.7	70
75	28 190	0.3	45.1	73

PAN: polyacrylonitrile.

3.1. Apparent viscosity under ordinary mixing

From Tables 1 and 2, the apparent viscosity decreases with an increase in the temperature, and the trend clearly shows that the molecular weight distribution of the precipitation polymerization product is quite wide. Therefore, the micro-molecules account for a greater proportion, while with the progress of swelling and dissolving, the apparent viscosity drops quickly. Although the molecular weight of the second sample is higher than that of first, the apparent viscosity shows an opposite trend due to the addition of water. This occurs because water can lower the intermolecular forces of the PAN by hydrogen bonding.

According to Tables 3 and 4, the apparent viscosity decreases with an increase in the temperature; the trend is moderate, showing that the molecular weight distribution of suspension polymerization product is quite narrow and that the intermediate

molecular weight accounts for the majority. As a result, the apparent viscosity does not change significantly with the progress of swelling and dissolving.

3.1.1. Viscous flow activation energy of PAN solutions of different molecular weights

The apparent viscosity of PAN polymer solution with the temperature was obtained from the following Arrhenius equation:

$$\eta_a = A \exp(E\eta/RT) \quad (2)$$

Here, A represents the physical constant. $E\eta$ is the flow activation energy, R is the molar gas constant, 8.314 J/(mol·K), and T is the thermodynamic temperature.

According to the changed viscosity data of PAN/DMSO solutions with different relative molecular masses with the temperature, as shown in the table, linear fitting to the $\ln\eta_a$ -T⁻¹ curve under a fixed shear rate was carried out. As a result, the viscous flow activation energy can be obtained by the linear slope, and the four linear slopes showed a sequence of 1751.37, 2275.49, 1623.75, and 1553.14 from the calculations, corresponding to the viscous flow activation energies of the four samples, at 14.56 KJ/mol, 18.92 KJ/mol and 13.50 KJ/mol, and 12.91 KJ/mol.

It is generally believed that a higher relative molecular mass leads to greater intermolecular force. Thus, more steric hindrance is required to overcome the solution flow, and the viscous flow activation energy should be higher as a result [7,8]. However, in this study, the viscous flow activation energy of the suspension polymerization sample is relatively low. This may be related to the molecular weight distribution of the two polymerization products. The molecular weight distribution of the suspension polymerization product is quite narrow, and the polymerization of the intermediate molecular weight is relatively large in proportion to the product overall. During the swelling and dissolution process, the spinning viscosity does not change with the dissolution process to a great extent. Therefore, the straight line of $\ln\eta_a$ -T⁻¹ is relatively flat and the line slope is relatively small, leading to a low level of viscous flow activation energy (Fig. 3). For suspension polymerization products 3 and 4, a higher molecular weight leads to lower viscous slightly flow activation energy. This is very important that the polymer chain structure, especially the chain flexibility when selecting and controlling the polymer molding process. According to the mobile mechanism of the polymer section, a smaller cavity is required for a flexible chain, and lower viscous flow activation energy is required for flowing. The chain flexibility is greatly affected by the relative molecular mass. The greater the relative molecular mass is, the longer the molecular chain, Hence, a greater number of molecules may arise, leading to greater flexible. Therefore, it can be considered that an increase in the relative molecular mass improves the flexibility of the molecular chain, reduces the chain rotation barrier, shortens the mobile unit chain segment, and lowers the viscous flow activation energy [9].

3.1.2. Impact of the temperature on the apparent viscosity of PAN dope

The viscosity of the PAN solution determines the spinning quality of the fibers during the forming process, and the temperature of the solution is very sensitive to the effect of the

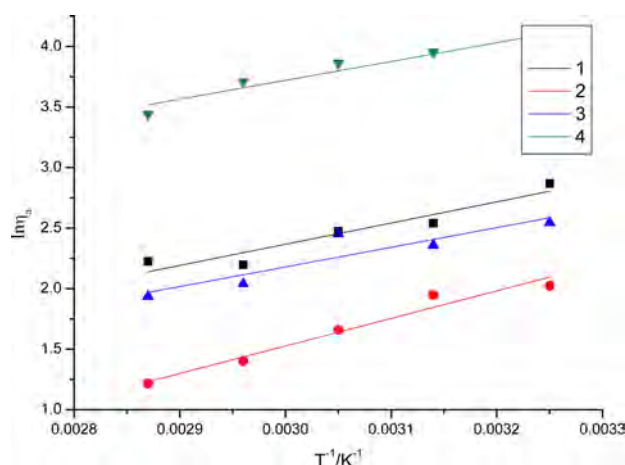


Fig. 3. Relationships between the temperature (T⁻¹) and apparent viscosity (lnη_a) in the polyacrylonitrile polymer solutions.

viscosity. Therefore, examining the viscosity changes with the temperature has important guiding significance for selecting the appropriate spinning temperature.

From the four tables above, it can be seen, for the same PAN solution, that the apparent viscosity of the PAN solution drops as the experimental temperature rises and as the dissolution time is prolonged. For the first sample as an example, the viscosity is reduced from 17.62 Pa·s to 9.25 Pa·s with an increase in the temperature and the dissolution time, resulting in a reduced amplitude of about 47.5%. For the third sample, the viscosity is reduced from 12.75 Pa·s to 6.94 Pa·s with an increase in the temperature and dissolution time, reducing the amplitude by about 45.6%. In terms of molecular motion theory, if conceiving the polymer molecular chain as a freely jointed chain segment, the relative displacement of a large molecular chain segment can be regarded as representing the overall results of a segment to the hole transition. That is to say, the polymer solution flow is mainly caused by the displacement produced by the molecular chain of the gravity flow direction and the mutual slip among the chains. Determining the chain motion requires a certain amount of energy, and when the temperature rises, it can provide more energy for the sliding of a large molecular chain segment. At the same time, the free volume in the solution increases, the activity of the chains increases, and the interaction force between the molecules is reduced; that is to say, the flexibility of the polymer chains increases, allowing for the easy formation of the molecular chain orientation along the shear direction and for segment to hole transition diffusion, an increase in the solution fluidity, and a decrease in the viscosity.

When the temperature increases to 75°C and the dissolution time of the spinning solution continues to extend, we find that the viscosity of the spinning solution will stabilize, indicating that the process of dissolution with a swelling time of 24 h plus 12 h for the gradient heating process is a valuable reference when seeking to determine the final balance of the spinning solution viscosity.

3.1.3. Relative molecular mass and water content of the apparent viscosity of PAN dope

For the molecular weight of the suspension polymerization of the third sample at a molecular weight of 403,913.07 in contrast

to the fourth, at a molecular weight of 603,884.7, clearly shown in the table, with an increase in the molecular weight, the viscosity of the PAN solution increases. Moreover, the range of the increase is particularly large. With the spinning solution at 35°C, the viscosity of the samples of the third case was 12.75 Pa·s; for the fourth sample the viscosity was 57.69 Pa·s, with a final temperature of 75°C. For the third sample, the viscosity was 6.94 Pa·s, while for the fourth sample, it was 31.25 Pa·s. This occurred because the molecular chain length becomes longer with an increase in the relative molecular mass, the molecular entanglement between the chains becomes larger, and the flow resistance increases, leading to an increase in the viscosity. In other words, the intermolecular force of the PAN solution with a high molecular weight is strong, macromolecular chain entanglement occurs between the chains, physical entanglement points appear according to the molecular Van der Waals force, the intermolecular entanglement becomes serious (leading to a decrease in the hydrodynamic volume), and the activities of the chain segments make it more difficult to accelerate the increase of the viscosity of the system.

However, comparing the first and second samples, the molecular weight of the second (678,534.8) is far greater than the molecular weight of first (477,689.4), but the viscosity is far less than the first, which is clearly due to the moisture content of 0.7% of sample 2. The addition of a small amount of water in the spinning solution will change the nature of the solvent; a very small amount of water not only reduces the force between the solvent molecules and PAN molecules but also forms hydrogen bonds between the water molecules and PAN molecules, thereby reducing the PAN intermolecular force and promoting curling into a group of macromolecules, after which the apparent viscosity of the spinning solution becomes low [10].

3.2. Apparent viscosity of the solution with high speed mixing

For the high-speed mixing of the dissolution process, we used the same samples with ordinary mixing with different dissolution processes. As shown in the four tables above (Tables 5–8), the high-speed stirring swelling time was only 20 h, and the ordinary mixing time is 24 h. However, for the same sample in each group, for example the first sample, the viscosity after general mixing at the initial temperature of 35°C is 17.62 Pa·s, while the viscosity of the initial 35°C case under high speed stirring is 13.06 Pa·s. For the fourth sample, the viscosity upon ordinary mixing at the initial 35°C is 57.69 Pa·s, while the initial viscosity at 35°C under high-speed agitation is 43.50 Pa·s. The other two samples follow this as well. The high-speed stirring experiment occurred later than the ordinary mixing experiment; it is likely that the samples absorbed moisture from the air, in addition to DMSO, which also contains a small amount of water, likely affecting the swelling and dissolution process during the placement and the moisture absorption of the sample. This case is similar to the case of ordinary mixing of the second sample, which contains water and where the solvent water causes a drop in the spinning liquid viscosity.

Comparing the four tables of high-speed mixing and ordinary stirring, for example the first, after 20 h of swelling and just 15 min of high-speed mixing, the spinning solution viscosity

Table 5. Apparent viscosities of a PAN copolymer solution obtained from the first precipitation polymerization process

Temperature (°C)	Apparent viscosity (mPa·s)	Probe speed (rpm)	Torque (%)	Time (h)
35	13,060	0.3	20.9	20
35	4,090	0.6	13.1	20.25
35	2,440	1.0	13.0	20.50
75	1,910	1.0	10.2	22.50

PAN: polyacrylonitrile.

Table 6. Apparent viscosities of PAN copolymer solution obtained from the second precipitation polymerization process

Temperature (°C)	Apparent viscosity (mPa·s)	Probe speed (rpm)	Torque (%)	Time (h)
35	7,560	0.3	12.1	20
35	7,060	0.3	11.3	20.25
35	4,990	0.3	13.3	20.50
75	3,810	1.0	20.3	22.50

PAN: polyacrylonitrile.

Table 7. Apparent viscosities of a PAN copolymer solution obtained from the third suspension polymerization process

Temperature (°C)	Apparent viscosity (mPa·s)	Probe speed (rpm)	Torque (%)	Time (h)
35	11,440	0.3	18.3	20
35	3,690	0.3	11.8	20.25
35	2,340	1.0	12.5	20.50
75	3,660	1.0	19.5	22.50

PAN: polyacrylonitrile.

Table 8. Apparent viscosities of PAN copolymer solution obtained from the fourth suspension polymerization process

Temperature (°C)	Apparent viscosity (mPa·s)	Probe speed (rpm)	Torque (%)	Time (h)
35	43,500	0.3	69.6	20
35	7,060	0.3	11.3	20.25
35	3,730	1.0	19.9	20.50
75	4,410	1.0	23.5	22.50

PAN: polyacrylonitrile.

was reduced rapidly from 13.06 Pa·s to 4.09 Pa·s, and the rate of reduction reaches 68.7%. For sample 3, the viscosity of the spinning solution dropped quickly from 11.44 Pa·s to 3.69 Pa·s,

and the lower margin reaches 67.7%. The other two groups of samples also follow this law. This shows that high-speed stirring conditions can greatly reduce the viscosity of the spinning solution. To determine the high-speed mixing time, we can control the viscosity of the spinning solution in an approximate range within a very short time, and the actual production process can be determined from this experience.

4. Conclusions

1) The “historical effects” of the polymerization method, swelling time, solution temperature, the process of heating and dissolving, the mixing method and the use of different solvents clearly influence the rheological properties of PAN polymer solutions. By comparing PAN solutions prepared by suspension polymerization to a PAN solution prepared by precipitation polymerization, the viscosity of the former changed somewhat more and the viscous flow activation energy was lower.

2) Temperature was a key factor to control the viscosity of the spinning solution. In a certain temperature range, the higher the temperature was, the lower the viscosity of the spinning solution was. Taking every factor into account, the temperature during the wet spinning of high-molecular-weight PAN should be in the range of 70°C to 80°C.

3) The molecular weight had an important effect on the viscosity of the spinning solution. The greater the molecular weight, the higher the viscosity of the spinning solution. A small amount of water would quickly reduce the viscosity of the spinning solution. Using a mixed solution of water and DMSO, we could not only control the viscosity of the spinning solution but also reduce the double diffusion rate of the spinning solution. Therefore, the process of solidified forming became gentler, and fiber with a more uniform structure could be obtained.

4) High-speed stirring as a means of dissolving can reduce the viscosity of the spinning solution in a great extent. It is useful

to control the viscosity of high-molecular-weight PAN spinning solutions in a short period of time. Consequently, the dissolution time should be reduced and the work efficiency should be improved for a practical process. Products of suspension polymerization have slick surfaces in a coagulation bath, while products of precipitation polymerization show poor performance.

References

- [1] Zhu KL, Mao PJ, Yang MY. Rheological behavior of polyacrylonitrile spinning solution for making carbon fiber. *Synth Technol Appl*, 4, 4 (2002).
- [2] Tan LJ, Ye W, Chen HF, Pan D. Rheology of the gelation behavior of PAN/DMSO solution. *Synth Technol Appl*, 4, 6 (2009).
- [3] Zhang L, Yang MY, Mao PJ. Preparation of high molecular quality of PAN by Suspension polymerization. *Synth Fiber Ind*, 29 (1998).
- [4] Zhou Y, Zhang J, Yi K, Zhang L, Li N, Jin RG. The molecular weight regulation of high molecular weight PAN polymer by precipitation polymerization, *New Chem Mater*, 3 (2012).
- [5] Jia CL, Qin QF, Dai YQ, Jin RG. Study on spinning solution of super-fine and high-strength PAN-based carbon fiber precursor, *New Chem Mater*, 106 (2011).
- [6] Hong ZC. Characteristics and influence of the rheological behavior of the spinning solution (PAN). *Anqing Petrochem*, 1 (1996).
- [7] Shen CY, Mao PJ, Zhang L, Yang MY. Rheological properties of high molecular weight PAN spinning solution. *Synth Fiber Ind*, 8 (2001).
- [8] Jia Z. Rheological Properties of high molecular weight PAN solution. *Zibo Inst Technol*, 67 (2001).
- [9] Zhang GP, Mao PJ, Zhang L, Yang MY. Rheological properties of high molecular weight PAN spinning solution. *J Text Univ*, 106 (2000).
- [10] Yang WP, Ma CX, Chen HF, Qin ZY, Pan D. The impact of water on PAN/DMSO/H₂O rheological behavior and strand performance. *Aerosp Mater Technol*, 56 (2009).