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A new way of step-mass-thermal transferring to control phase inversion for polyacrylonitrile(PAN)/DMSO/water system

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Abstract: The step-mass-thermal transferring meant that for PAN/DMSO/water system, the kinetic of phase inversion and droplet ripening was controlled by employing several consecutive coagulation baths with different concentrations and temperatures. In this way, the morphology of fiber could be adjusted based on modelling. The phase diagram of PAN/DMSO/water was calculated based on Flory–Huggins theory. The mass and thermal transferring was calculated according to Fick's second law and Fourier heat equation respectively.

Introduction

Properties of carbon fiber based on polyacrylonitrile are dominated by protofilament quality. Condensed state of protofilament including pore size, even property, crystallization, and macromolecule orientation represents the quality of protofilament, which is controlled by thermodynamic, kinetic [1, 2], and stretching during solidification of polymer solution in coagulation bath. For spinning, due to the dynamic coupling [3, 4] between stress and phase inversion for PAN/DMSO/water system, stretching would cover some phenomena related to thermodynamic and kinetic behaviour during phase inversion, for example, the formed pores during phase inversion are deformed under strain force, in this case, whether the phase inversion is attributed to nucleation growth or spinodal decomposition is uncertain. Meanwhile, due to the coupling effects involved in either wet-spinning or dry-wet spinning, it's hard to identify which parameter is more important for protofilament quality. Maybe stretching is more important than the others for spinning since the strain force could deeply change the morphology of fiber, or contrary to this view, maybe phase inversion has great effect on protofilament, especially at the initial stage of phase separation in coagulation bath, whereas stretching as the exterior affecting morphology cannot produce decisive effects on microscopic structures of fiber.

In this paper, in order to reveal the influence of phase inversion on morphology of fiber, stretching hasn't been taken into consideration and consequently the research on fiber is equivalent to studying the forming mechanism for membrane. Most published papers on membranes [5, 6] emphasized the importance of kinetic process for phase inversion as well as needed morphology. So an explanation of the kinetic process based on modelling is necessary; maybe some useful information could be obtained from modelling. Though some mathematical models related to depicting the development of morphology [7] have been constructed, seldom they referred to step controlling phase inversion. In this study, under the assumed condition that the streamlet of polymer solution, without stretching, quickly travels through several consecutive coagulation baths, the kinetic of different layer of fiber at consecutive coagulation baths was discussed based on modelling and step-mass-thermal transferring was proposed to control the morphology of fiber for PAN/DMSO/water system.

Theory

Thermodynamics of ternary systems

Flory–Huggins theory is used to describe the thermodynamic behavior of PAN/DMSO /water system. Gibbs free energy of ternary polymer system [8, 9, 10] is formulated by the following Eq.(1).

$$\frac{\Delta Gm}{RT} = n_1 \ln \Phi_1 + n_2 \ln \Phi_2 + n_3 \ln \Phi_3 + g_{12} n_1 \Phi_2 + \chi_{13} n_1 \Phi_3 + \chi_{23} n_2 \Phi_3 \tag{1}$$

Here, n_i and Φ_j are the mole number and the volume fraction of component respectively. The subscripts refer to 1- water, 2-DMSO and 3-PAN respectively. g_{12} is the interaction parameter of water/DMSO calculated according to an empirical equation: $g_{12} = a + b(1 - c\Phi_2)$. x_{23} is the interaction parameter of DMSO/PAN calculated using Hildebrand's equation: $\chi_{23} = (V_2/RT)(\delta 2 - \delta 3)$. Here, δ_2 and δ_3 are solubility parameters. Due to little interaction between water and PAN, x_{13} is regarded as a constant value, no concentration and temperature dependency.

The binodal line of phase diagram is calculated according to equation:

$$\Delta\mu_i^{\alpha} = \Delta\mu_i^{\beta} . \quad i = 1, 2, 3$$

α and β represent polymer rich phase and polymer poor phase respectively. $\Delta\mu_i$ expresses the chemical potential of component of each phase.

The spinodal line of phase diagram is calculated according to Eq.(2).

$$|G| = \begin{vmatrix} \mathbf{G}_{22} & \mathbf{G}_{23} \\ \mathbf{G}_{32} & \mathbf{G}_{33} \end{vmatrix} = 0 \ , G_{ij} = \left(\partial^2 \overline{\Delta Gm} / \partial\phi_i \partial\phi_j \right)_{V_{ref}} \tag{2}$$

ΔGm is the mixed free energy of unit volume. v_{ref} is the mole volume referred component.

The critical point is on the spinodal line expressed as Eq.(3).

$$G_{222} G_{33} - 3 G_{223} G_{23} G_{33} + 3 G_{233} G_{23} - G_{22} G_{23} G_{333} = 0 \tag{3}$$

On the basis of equation operation, the phase diagram of PAN/DMSO/water system was obtained.

Calculation of mass and thermal transferring

Mass transferring for cylinder fiber without stretching can be written as following equation according to Fick's second law [11].

$$\frac{\partial c_i}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left[D_i(T) r \frac{\partial c_i}{\partial r} \right] \quad i = 1, 2 \tag{4}$$

Here, subscripts refer to 1-solvent and 2-nonsolvent respectively. The diffusion coefficient $Di(T)$, without regard to the effect of solidification of fiber on diffusion coefficient, varies with temperature depicted as following equations:

$$D_1(T) = 1\text{e-}10 \times (0.0468T\text{-}11.6519\,),\ D_2(T) = 1\text{e-}10 \times (0.0528T\text{-}13.3699)$$

Eq.(4) is converted to Eq.(5) employing molar concentration c_i multiplied by mole volume v_i of corresponding component. The converted variable ϕ_i expresses the volume fraction of component.

$$\frac{\partial \phi_i}{\partial t} = \frac{1}{r}\frac{\partial}{\partial r}\left[Di(T) r \frac{\partial \phi_i}{\partial r} \right] \tag{5}$$

Thermal transferring equation is written as following equation according to Fourier heat law:

$$\frac{\partial T}{\partial t} = \frac{1}{r}\frac{\partial}{\partial r}\left[a r \frac{\partial T}{\partial r} \right] \tag{6}$$

Boundary conditions:

$$\left.\frac{\partial \phi_1}{\partial r}\right|_{r=0} = 0\,,\ \phi_1(r,0) = \phi_{solution}\,, \phi_1(R,t) = \phi_{1x}\,; \qquad \left.\frac{\partial \phi_2}{\partial r}\right|_{r=R} = 0\,, \phi_2(r,0) = 0\,, \phi_2(R,t) = \phi_{2x}$$

R is the fiber radius. r is the distance to axes in the direction of radius of fiber. ϕ_{1x} and ϕ_{2x} are determined by the concentration gradient between coagulation bath and polymer solution at the boundary: $r = R$. Here, it should be also emphasized that the shifting of boundary between fiber and mixed precipitator at coagulation bath has not been taken into consideration.

$$T(R,t)\big|_{r=R} = T_{bath}\ ,\left.\frac{\partial T}{\partial r}\right|_{r=0} = 0\,, T(r,0) = T_{solution}$$

Basic parameters: Polymer solution temperature of 353 K, PAN volume fraction of 0.2, PAN molecular weight of 8.9e+4, thermal coefficient of 5e-8, and fiber radius of 5e-5 m. The mass and thermal transferring of fiber is obtained by calculation of Eq.(5) and Eq.(6) using finite difference and Runge-Kutta. In this study, the fiber was divided into 12 layers from axis of fiber to surface with every layer about 4.5 μm.

Results and discussion

Research on spinodal decomposition

The phase diagram shown in Fig.1 indicates it is hard to pass through critical point to realize spinodal decomposition mechanism for polymer volume fraction of 0.2, whereas it is easy to form nuclei of the minor phase interspersed in the matrix of the major phase taking place within the metastable region. The nuclei growth mechanism is separated into two categories including initial nuclei-formed and droplet coarsening. If the time of mass transferring through metastable region is shorter than nucleation time, the composition of polymer solution enters unstable region of phase diagram to undergo spinodal decomposition.

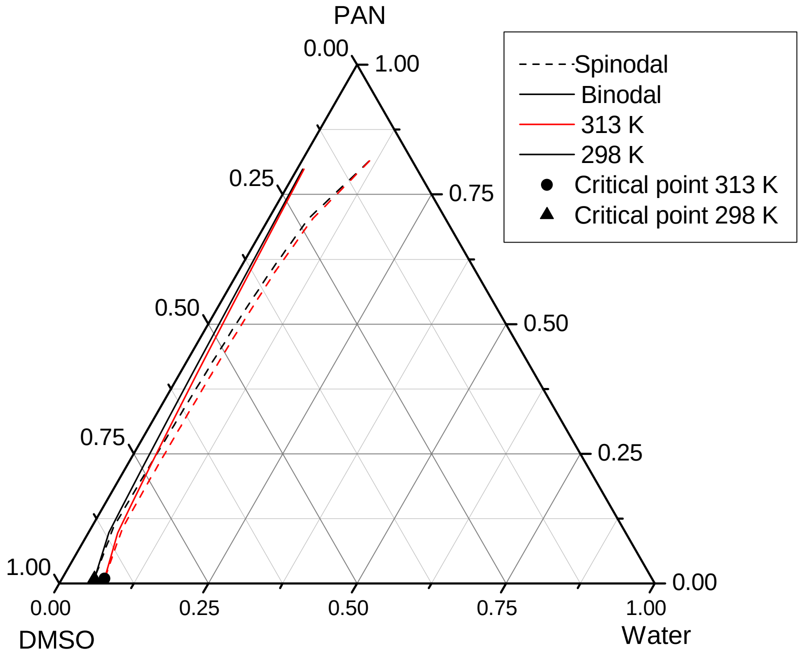

Fig. 1. Phase diagram of PAN/DMSO/Water system.

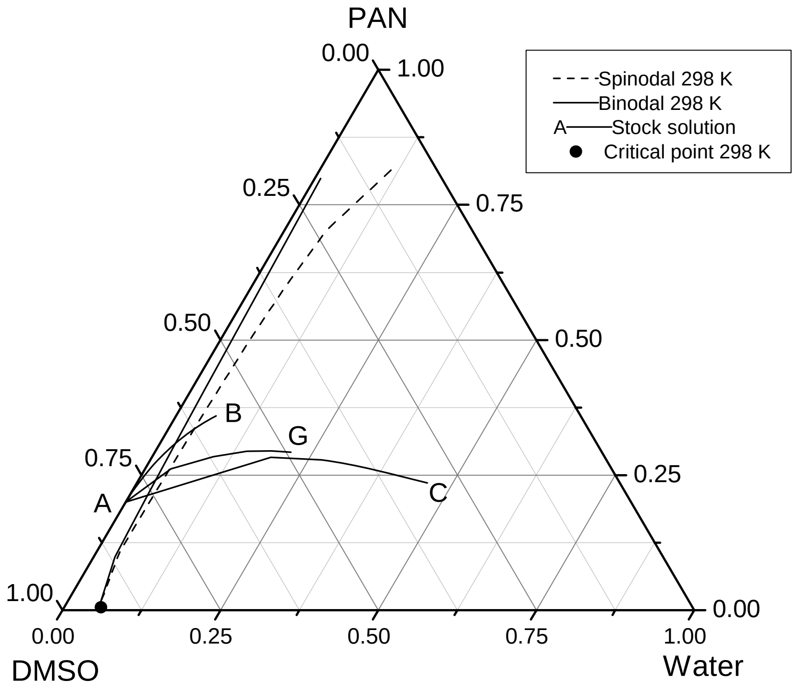

Fig. 2. Paths of different layers of fiber at coagulation bath (298 K). During phase inversion, paths of AB, AG, and AC represent the varied compositions of the third layer, the eleventh layer, and the outermost layer respectively.

Under the condition of water volume fraction of 0.7, as shown Fig. 2, the path AC of composition of outermost layer travels from binodal line to spinodal line taking 3 milliseconds according to Fig. 3; the water volume fraction of outermost layer is varying with time. The formed morphology of skin is compact without pores attributed to spinodal decomposition. Path AG for the eleventh layer and path AB for the third layer, Within the metastable region in phase diagram, take 15 milliseconds and 1 s respectively. If the eleventh layer forms pores, it could be deduced that the nucleation time is about 4~14 milliseconds. Though the composition of third layer enters the unstable region, phase separation is attributed to nucleation mechanism resulting in bigger pores for long time in metastable region.

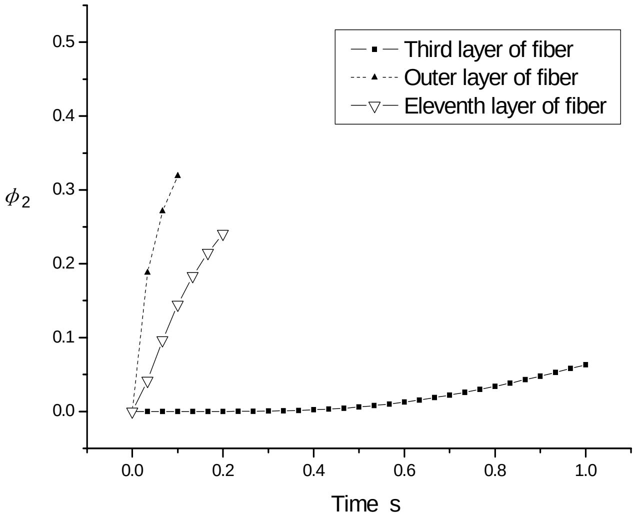

Fig. 3. Water volume fractions ($\phi 2$) of different layers varying with time.

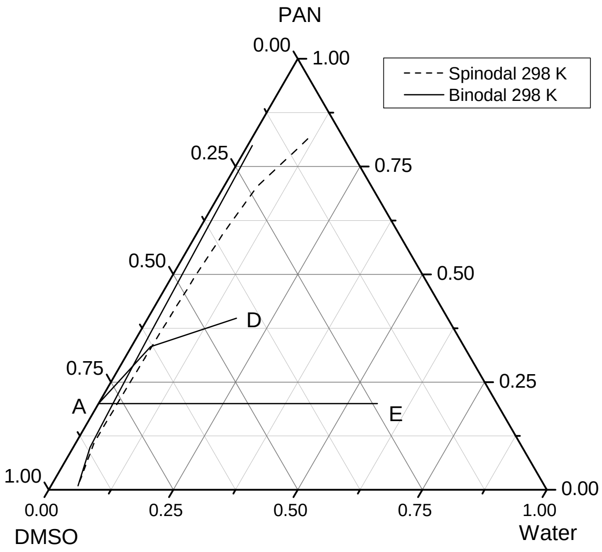

Fig. 4. Paths of the third layer of fiber with different radii at coagulation bath (298 K). path AD:10 microns, path AE:2 microns

The volume fraction of PAN in Fig. 2 on close analysis of paths, increases first and then decreases with time during phase inversion. Due to constant mole number of PAN in every layer, at the first stage of mass transferring, solvent decreases quickly and nonsolvent increases slowly, which is equivalent to the increase in volume fraction of PAN. At the later stage of mass transferring, the volume fraction of PAN decreases with increasing nonsolvent.

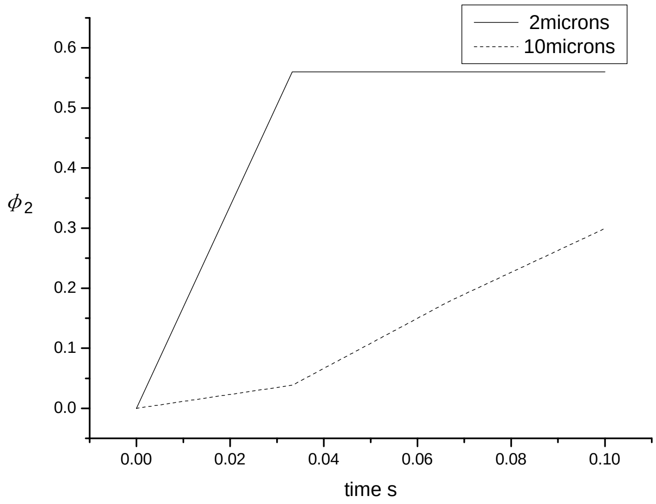

Fig. 5. Water volume fraction ($\phi 2$) of the third layer of fiber varying with time. Fiber radii: 2 microns, 10 microns respectively.

Some measures might be taken to reduce the time crossing over the metastable region between binodal line and spinodal line. However, the increase in water concentration of coagulation bath would result in skin-core structure in fiber. The increase in temperature of coagulation bath would result in turbulent morphology. Fig. 4 and Fig. 5 show the path for the third layer of fiber with different radius. When the radius of fiber is 10 microns, under conditions of coagulation bath temperature of 298 K and water volume fraction of 0.7, path AD shows the time between binodal line and spinodal line as about 10 milliseconds according to Fig. 5. While the radius is reduced to 2 microns, path AE shows the time about 1.4 milliseconds lower than the nucleation time. In fact, it is difficult to obtain such a slender fiber at the initial stage of spinning.

Step-mass-thermal transferring for PAN/DMSO/Water system

As discussed above, it is difficult to obtain morphology by spinodal decomposition from core to surface in fiber, while easy to form skin-core structure. Bigger pores are regarded as flaws. Small pores in outmost layer are favorable for gas diffusion during fiber preoxidation [12]. In metastable region, only the droplet beyond critical size can further grow. The growth of droplet is explained using coarsening phenomena [13, 14] which includes coalescence mechanism and Ostwald ripening mechanism. The radii of droplets have an exponential relationship with time related to PAN concentration or bath temperature. In view of spinnability of polymer solution, there is a limit to the increase in PAN concentration. Maybe temperature is a good choice to control the growth of droplet.

As shown Fig. 6, under conditions of PAN volume fraction of 0.2, stock solution temperature of 353 K, and fiber radius of 50 microns, without regard to thermoresistance, temperature (353 K) of the third layer of fiber reduces to the temperatures of coagulation bath in 0.033 s respectively. The lower temperature of coagulation bath, the more quickly temperature of the third layer reduces. The time of 0.033 s corresponds to the nucleation time, so temperature reduction can control the growth of droplet. Whereas the result of temperature reduction makes solvent difficult to be extracted from fiber due to decreasing diffusion coefficients of both solvent and nonsolvent, several consecutive coagulation baths with different concentration and temperature are designed to control phase separation by step-mass-thermal transferring.

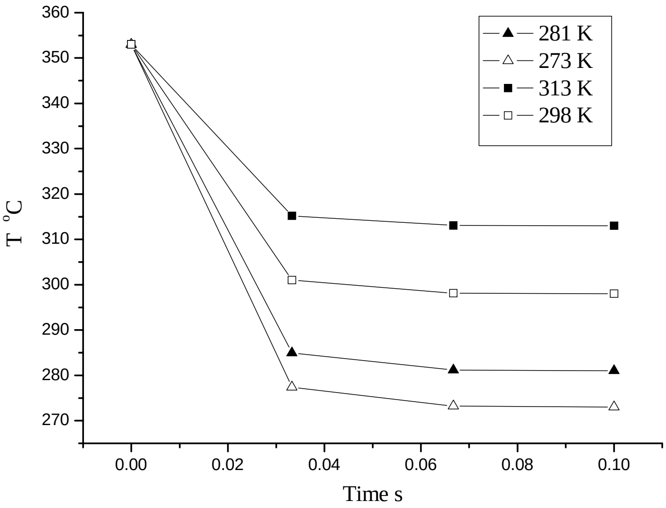

Fig. 6. Temperature reduction of the third layer of fiber at coagulation bath with temperatures of 273 K, 281K, 298 K, and 313 K respectively.

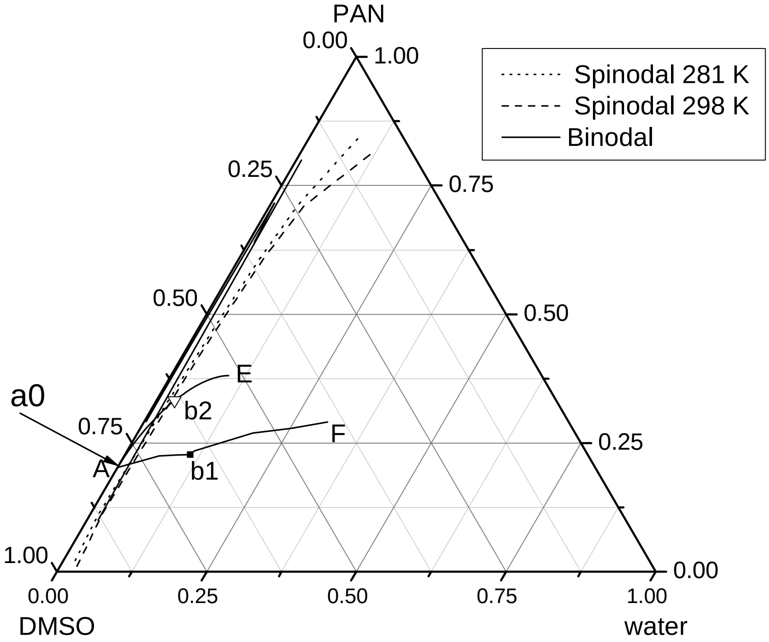

Fig. 7. Step-mass-thermal transferring of fiber at consecutive coagulation baths, path AE: the third layer of fiber , path AF: the outer layer of fiber.

As shown in Fig. 7 and Fig. 8, at the first coagulation bath, in view of higher water concentration resulting in skin-core structure and lower concentration resulting in rough surface, the nonsolvent volume fraction is fixed at 0.3. Bath temperature is fixed at 281 K in order to make quick temperature reduction of polymer solution. It is 0.1 s from 353 k to 281 k for both outermost layer (AF) and the third layer (AE). The time from A to b1 is 0.1 s measured according to Fig.8 and the time within the metastable region for 298 K is about 4 milliseconds. Tiny pores can be formed in the outmost layer. The third layer doesn't change within 0.1 s corresponding to point a0 in Fig. 8 without passing through spinodal line for 281 K.

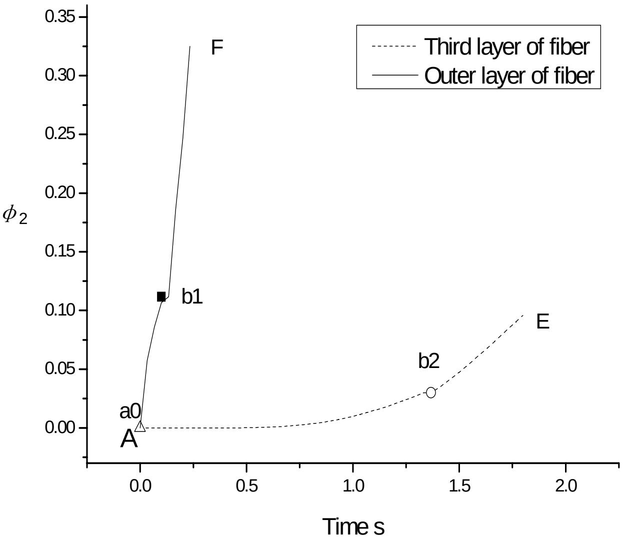

Fig. 8. Water volume fractions (ϕ_2) of different layers of fiber varying with time.

Solvent in fiber is extracted in the second coagulation bath with 281 K and water volume fraction of 0.7. Because pores in skin have been formed at the first bath, higher water concentration of the second bath does not make the skin densified. The outmost layer changes from b1 to F. The third layer reaches point b2 in 0.9 s passing through spinodal line for 298 k. The time between binodal and spinodal line for 298K is about 0.16 s, which results in nucleation mechanism, growth of droplets is related to temperature of 281 k.

At the third coagulation bath with 298 k and water volume fraction of 0.5, the third layer changes from b2 to E. Due to the difference between nucleation mechanism and spinodal decomposition, insitu-growth of droplets is changed because of the present composition of the third layer deep into unstable region of phase diagram for 298 K. Morphology of every layer of entire fiber might evolve into hybrid microstructure arising from the mixing effect of nucleation growth combined with spinodal decomposition. If the composition of fiber is at metastable region for 298 k, droplets would undergo insitu-growth to form bigger pores during phase separation. At following baths, solvent is further extracted from fiber.

The principal points of step-mass-thermal transferring are summed up. The coarsening of droplets is controlled by lower temperature. During phase separation in new coagulation bath, the time should be intercepted during PAN volume fraction increase, which is equivalent to the increase in PAN concentration of polymer solution. The composition of fiber in the third bath should be at unstable region of phase diagram in order to change insitu-growth of droplets.

Conclusions

By analysis of phase diagram and mass-thermal transferring, it is difficult to obtain the morphology by spinodal decomposition from centre to surface of fiber, while it is easy to form skin-core structure. A new way of step-mass-thermal transferring for PAN/DMSO/Water system was proposed to control the morphology of fiber. Step-mass-thermal transferring meant several coagulation baths with different concentration and temperature to control the kinetics of phase separation and droplet ripening.

Acknowledgements

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