

Contribution of the solid phase polymerization to the molecular weight distribution in acrylonitrile precipitation copolymerization

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Abstract—Molecular weight distribution of copolyacrylonitrile, which was obtained from precipitation copolymerization without and with using dispersants in mixed solution, is studied. The contribution ratio of liquid phase polymerization and solid phase polymerization under different polymerization conditions could be worked out through the formula, which has been deduced in literature. From the calculated results, common points of each reaction system are, i) contribution ratio (r) of solid phase to liquid phase decreases with the increase of water content; thus the solid phase polymerization is gradually strengthened, which is apt to form chain of high molecular weight, ii) the higher temperature leads to higher compatibility between water and DMSO; thus the solid phase polymerization contribution would decrease, while the value of r is considerably larger. The limit molecular weight distribution of the system without dispersants in 100% water is approaching to 2; thus the corresponding r becomes larger, the molecular weight distribution ratio (Q) decreases in the system with dispersants.

Key words: Molecular Weight Distribution, Polyacrylonitrile, Precipitation Polymerization, Contribution Ratio of Liquid Phase and Solid Phase Polymerization

INTRODUCTION

Polyacrylonitrile (PAN)-based carbon fibers, which are used as one of the reinforcement fibers for advanced composite materials, are irreplaceable high-tech materials in the aerospace and defense industry. However, the PAN precursor with low quality is the bottleneck of carbon fiber development in China. Usually, as far as the polymer homologue with different average molecular weight is concerned, the breaking strength increases with the increase of average molecular weight. Therefore, using high molecular weight resin is one of the main methods in preparation of high modulus fibers. To produce high performance carbon fiber, a PAN precursor of high mechanical performance is needed. Also, using resin of high molecular weight is the most effective way(duplicated) to spinning PAN precursor of high strength [1-4].

At present, polymerization in China is carried out mostly with methyl methacrylate as the second monomer and itaconic acid as the third monomer. Some researchers have studied how the weight ratio of $H_2O/DMSO$, monomer concentration and initiator concentration affects the polymerization. Some researchers studied the influence of polymerization reaction conditions by conducting the ratio of $H_2O/DMSO$ and $H_2O/dimethyl$ formamide (DMF), respectively [5-9]. In general, the dual precipitation copolymerization of PAN with acrylonitrile and the second monomer (such as acrylic acid, itaconic acid, etc.) is the major process in PAN precursor production [10,11]. Qin [12] reported the effect of polymerization on mechanical properties of PAN fibers. Bahrami [13] reported the effect of H_2O/DMF on the conversion rate and intrinsic viscosity

during precipitation polymerization using acrylonitrile and acrylic acid as monomers and H_2O/DMF as mixed solvent system. Ali [14] reported the control of molecular weight distribution of polymer using Ziegler-Natta catalyst. However, there is a lack of theoretical background on the molecular weight distribution during the precipitation polymerization between liquid phase polymerization and solid phase polymerization.

The purpose of this study is the investigation of the contribution of the heterogeneous reaction to the molecular weight distribution during acrylonitrile precipitation polymerization. To achieve the purpose, i) molecular weight distributions (MWD) of PAN precursor obtained from precipitation copolymerization were measured in mixed solvent with and without dispersants, and ii) contribution of the heterogeneous reaction to the PAN MWD during precipitation polymerization was analyzed by using the formula deduced in the literature and the derived theoretical equations.

THEORETICAL

Precipitation polymerization in mixed solution can adjust the molecular weight and MWD by controlling the mixed solution ratio and initiator dosage. A theoretical equation of precipitation polymerization has been derived by considering both liquid phase polymerization and solid phase polymerization. According to statistics theory, defining that the distribution function goes as $N_{xL}=f_L(x)$ in liquid phase, while in solid phase, the distribution function goes as $N_{xS}=f_S(x)$. If the consumption volumes of AN in liquid phase polymerization and solid phase polymerization are V_L and V_S , respectively, and $f_L(x)$, $f_S(x)$ are the molecular number for liquid phase polymerization and solid phase polymerization, respectively. Then $N_x=V_L f_L(x)+V_S f_S(x)$ can be obtained. $V_L/V_S=r$ is the contribution ratio of liquid

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phase polymerization and solid phase polymerization.

Through polymerization dynamical equations,

i) The distribution function of the molecular weight in liquid phase polymerization can be expressed as,

$$f_L(x) = N_{xL} = C_{mL} e^{-C_{mL}x} \quad (1)$$

Where, $C_{mL} = (k_{trL}/k_{pL})$, is the liquid phase chain transfer constant.

ii) The distribution function of the molecular weight in solid phase polymerization can be expressed as,

$$f_S(x) = N_{xS} \approx C_{mS} e^{-C_{mS}x} \quad (2)$$

Where, $C_{mS} = (k_{trS}/k_{pS})$, is the solid phase chain transfer constant.

Therefore, the total distribution function of the molecular weight can be obtained:

$$N_x = V_L C_{mL} e^{-C_{mL}x} + V_S C_{mS} e^{-C_{mS}x} \quad (3)$$

Where, $r = V_L/V_S$, V_L and V_S express liquid phase and solid phase contribution factors separately.

Due to the number distribution function, the integral distribution function of weight will be expressed as the following equation:

$$W_x = N_x \frac{x}{\bar{X}_n} = \frac{x}{\bar{X}_n} (V_L C_{mL} e^{-C_{mL}x} + V_S C_{mS} e^{-C_{mS}x}) \quad (4)$$

$$I_x = \int_0^x W_x dx = \frac{x}{\bar{X}_n} \left\{ \frac{V_L}{C_{mL}} [1 - (1 + C_{mL}x)e^{-C_{mL}x}] + \frac{V_S}{C_{mS}} [1 - (1 + C_{mS}x)e^{-C_{mS}x}] \right\} \quad (5)$$

$$Q = \frac{\bar{X}_w}{\bar{X}_n} = \frac{2 \left(\frac{r}{C_{mL}^2} + \frac{1}{C_{mS}^2} \right) (r+1)}{\left(\frac{r}{C_{mL}} + \frac{1}{C_{mS}} \right)} \quad (6)$$

Where \bar{X}_n , \bar{X}_w are number average degree of polymerization and weight average degree of polymerization, respectively. Therefore, Q is the molecular weight distribution ratio, which can be available through gel permeation chromatography (GPC). C_{mL} and C_{mS} can be obtained from the following formulas. When the solid phase polymerization accounts for 100% of the polymerization, $r=0$, the limit MWD of precipitated phase can be obtained as $Q=2$ from Eq. (6).

From the reaction kinetics theory of the macromolecule one can easily infer that the polymerization degree (\bar{X}_S) of AN in 100% water can be expressed as follows:

$$\bar{X}_{max,S} = \frac{R_p}{R_{tr,m}} \frac{k_p[M][M\bullet]}{k_{tr,m}[M][M\bullet]} = \frac{k_p}{k_{tr,m}} = \frac{1}{C_{mS}} \quad (7)$$

On the other hand, the following equation can be obtained from solution polymerization of AN in DMSO.

$$\frac{1}{\bar{X}_{min,L}} = C_m + C_S \frac{[S]}{[M]} = C_{mL} \quad (8)$$

If $\bar{X}_{max,S}$ ($H_2O/DMSO \rightarrow \infty$) and $\bar{X}_{min,L}$ ($H_2O/DMSO \rightarrow 0$) are known, C_{mS} and C_{mL} can be obtained from Eqs. (7) and (8). The value of r can be obtained when Q is known. Generally, $\bar{X}_{min,L}$ and $\bar{X}_{max,S}$ are all calculated by using the equation $\bar{M}_w/53.06Q = \bar{X}_n$, where the weight-average molecular weight is obtained under limit conditions.

MATERIALS AND METHODS

1. Materials

Acrylonitrile (AN, Beijing Chemical Reagents Co.) was used for polymerization. AN was freed from inhibitors by distillation at 76-78 °C before polymerization. Dimethyl sulfoxide (DMSO, Beijing Chemical Reagents Co.) and deionized water (H_2O) were used as polymerization solvents. α, α' -azobisisobutyronitrile (AIBN, Beijing Chemical Reagents Co.) was used as an initiator. Itaconic acid (IA, Beijing Chemical Reagents Co.) and methyl acrylate (MA, Beijing Chemical Reagents Co.) were used as the second monomer. MA and AIBN were purified by recrystallization. Dimethyl formamide (DMF, Beijing Chemical Reagents Co.) solution was used to measure the intrinsic viscosity of the polymer. Dispersant (PVA, $M \approx 30000$) was supplied by Beijing Chemical Reagents Co.

2. Precipitation Polymerization

Precipitation polymerization of AN was carried out in a 1.0 L three-necked glass reactor. The monomer ratio was AN : MA : IA = 96 : 3 : 1 (weight ratio), and monomer concentration was at 30 (wt%). The component of solvent was controlled by changing the volume ratio of H_2O (from 0.1 to 1.0 to the amount of DMSO) and DMSO. 1 wt% AIBN was added as an initiator, which did not affect the volume ratio of solvent. Polymerization was carried out by changing the reaction temperature from 55 °C to 70 °C for 2 h, 30 rpm, under a pure nitrogen atmosphere. During the polymerization, newly produced PAN nanoparticles were precipitated. After certain time, polymerization was terminated. Polymerization slurry was filtered and washed with acetone many times, then vacuum dried at 50 °C one day to get all dry samples. Then the intrinsic viscosity and MWD were measured.

3. Molecular Weight Distribution

Intrinsic viscosity $[\eta]$ of the obtained polymers was measured in DMF solution using an Ubbelohde viscometer in a water bath at constant temperature of 25 ± 0.5 °C following Kashyap's method [15]. The weight-average molecular weight \bar{M}_w was calculated from the following equation:

$$[\eta] = 3.35 \times 10^{-4} \bar{M}_w^{0.72}$$

Use GPC (self-made), DMF be solvent, temperature 25 °C, to test and get the MWD Q.

RESULTS AND DISCUSSION

1. Investigation of r in the Polyacrylonitrile Copolymerization without Using Dispersants

Fig. 1 shows the relationship between average polymerization degree of PAN copolymer and $H_2O/DMSO$ ratio at different temperature. The \bar{X}_n values linearly increased as the increase of $H_2O/DMSO$ ratio and slightly decreased with the increase of temperature. $\bar{X}_{min,L}$ can be obtained from the intercepts when $H_2O/DMSO \rightarrow 0$, and C_{mL} can be obtained from Eq. (8). $\bar{X}_{max,S}$ can be obtained when $H_2O/DMSO \rightarrow \infty$, and C_{mS} can be obtained from Eq. (7). Then using Q measured by GPC, contribution ratio (r) can be obtained from Eq. (6). $\bar{X}_{min,L}$ was 0.17, 0.13, 0.10, and 0.05, respectively, which was reduced as the increase of temperature. All the results showed that the average polymerization degree of PAN copolymer linearly increased with the increase of $H_2O/DMSO$ ratio due to

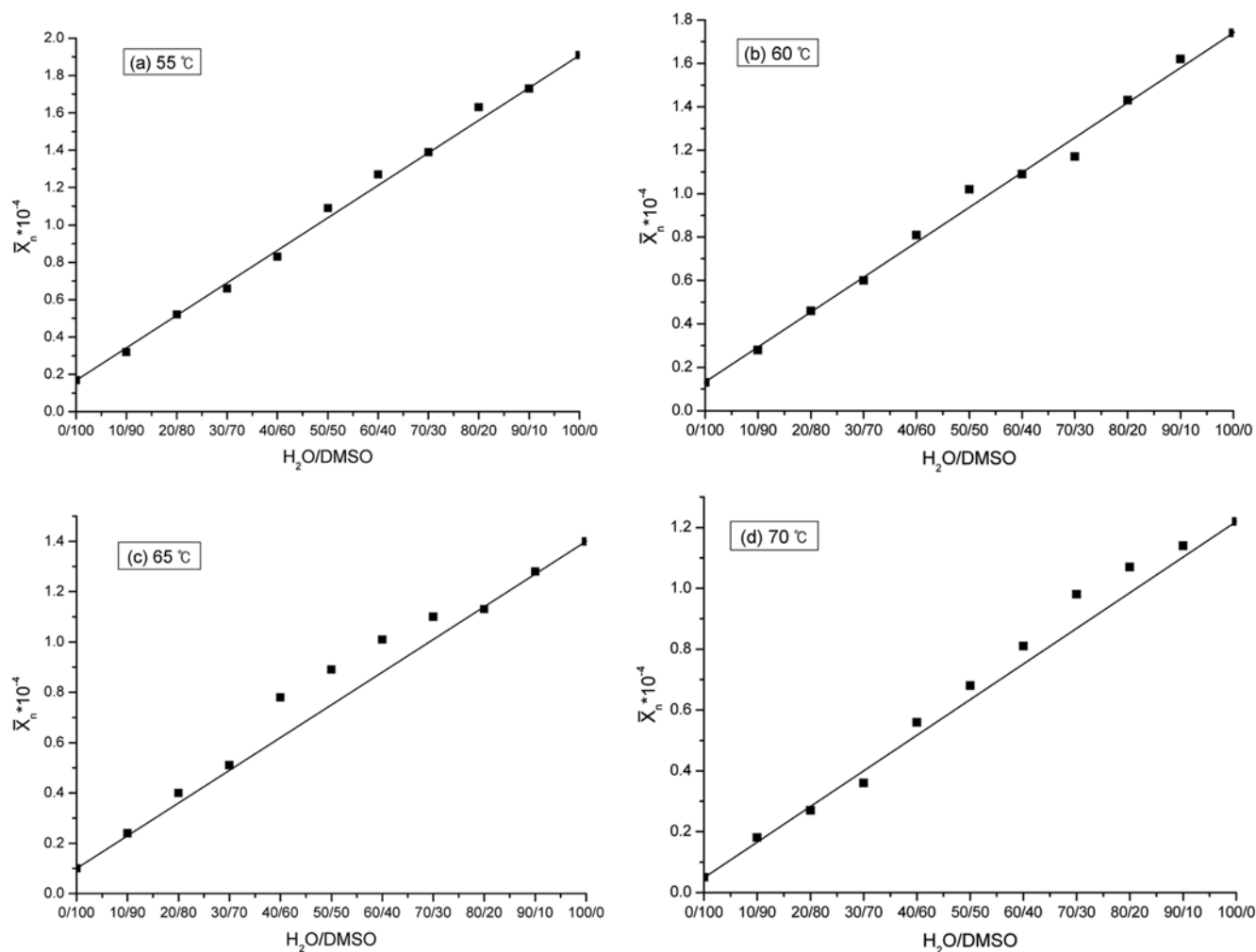


Fig. 1. Relationship between average polymerization degree and $H_2O/DMSO$ ratio: (a) 55 °C, (b) 60 °C, (c) 65 °C, and (d) 70 °C.

the increase of solid phase polymerization. Table 1 shows the molecular weights, the average polymerization degree, contribution ratio (r), and molecular weight distribution (Q) of PAN copolymer with increasing the $H_2O/DMSO$ ratio at different temperature.

From Table 1, some conclusions could be obtained as follows. Flash polymerization might occur at high temperature, so several points were above the baseline at 65 °C and 70 °C (see Fig. 1(c) and (d)). Contribution ratio (r) and MWD (Q) decreased with the increase of H_2O ratio, and along with the increase of water content, Q was approaching to 2. With the increase of water, solid phase polymerization gradually predominated in the process of precipitation polymerization. Under such condition, the termination or transfer of inner chain of solid phase polymerization was more difficult than that of liquid phase polymerization, so it was apt to form chain of high molecular weight. The precipitation copolymerization of PAN had the same change laws with different solution ratios as the precipitation homopolymerization of PAN. It showed that competitive polymerization existing between monomers did not change the model of liquid-solid phase polymerization, and PAN precipitation copolymerization in mixed solutions could be analyzed and guided by the derived theory.

Comparing r and Q separately, r and Q were smaller in copoly-

merization than these in homopolymerization at the same temperature and the same $H_2O/DMSO$ ratio. Namely, the proportion of copolymer of solid phase polymerization was larger than the one of homopolymer of solid phase polymerization under the same precipitation polymerization conditions, and the MWD of the copolymer was relatively narrower than the one of homopolymer.

2. Investigation of r in Mixed-solution Precipitation Copolymerization with Using Dispersants

In addition, since Wang [16] studied precipitation copolymerization with using dispersants in mixed solutions, the reference polymerization data were calculated, discussed and analyzed in this paper.

Table 2 shows the results of precipitation copolymerization of PAN performed at the condition of 0.12 wt% initiator (AIBN) concentration, 20 wt% monomer (AN) concentration (monomer ratio AN : NVP = 98 : 2), 0.02 wt% dispersant (PVA) concentration for 2 hours, 150 rpm by changing the $H_2O/DMSO$ ratio at 60 °C. \bar{X}_n s were calculated from the above-mentioned method. When $H_2O/DMSO \rightarrow 0$, $\bar{X}_{n,L}$ was $0.33 \cdot 10^{-4}$ and when $H_2O/DMSO \rightarrow \infty$, $\bar{X}_{n,S}$ was $0.79 \cdot 10^{-4}$. Also, C_{mi} and C_{ms} were obtained from the Eqs. (7) and (8). The way of obtaining contribution ratio (r) was the same as in Table 1.

Table 2 shows that precipitation copolymerization in mixed solu-

Table 1. Average polymerization degree, contribution ratio (r), and molecular weight distribution (Q) of PAN copolymer as increasing the H₂O/DMSO ratio in precipitation polymerization without using dispersants at different temperature

at 55 °C						at 60 °C					
H ₂ O/DMSO	[η]	$\overline{M}_w \cdot 10^{-4}$	$\overline{X}_n \cdot 10^{-4}$	Q	r	H ₂ O/DMSO	[η]	$\overline{M}_w \cdot 10^{-4}$	$\overline{X}_n \cdot 10^{-4}$	Q	R
10/90	7.65	113.08	0.32	6.66	10.60	10/90	7.63	112.76	0.28	7.59	9.73
20/80	9.57	154.51	0.52	5.60	3.97	20/80	9.20	146.20	0.46	5.99	3.88
30/70	10.19	168.44	0.66	4.81	2.55	30/70	9.75	158.54	0.60	4.98	2.43
40/60	10.65	179.24	0.83	4.07	1.64	40/60	10.21	168.91	0.81	3.93	1.37
50/50	11.07	189.12	1.09	3.27	0.89	50/50	10.46	174.81	1.02	3.23	0.81
60/40	11.25	193.40	1.27	2.87	0.58	60/40	10.53	176.40	1.09	3.05	0.68
70/30	11.37	196.18	1.39	2.66	0.43	70/30	10.61	178.17	1.17	2.87	0.55
80/20	11.52	199.79	1.63	2.31	0.19	80/20	10.74	181.34	1.43	2.39	0.24
90/10	11.57	201.03	1.73	2.19	0.12	90/10	10.85	183.95	1.62	2.14	0.08
100/0			1.91			100/0			1.74		

at 65 °C						at 70 °C					
H ₂ O/DMSO	[η]	$\overline{M}_w \cdot 10^{-4}$	$\overline{X}_n \cdot 10^{-4}$	Q	r	H ₂ O/DMSO	[η]	$\overline{M}_w \cdot 10^{-4}$	$\overline{X}_n \cdot 10^{-4}$	Q	R
10/90	6.86	97.29	0.24	7.64	8.29	10/90	6.94	98.85	0.18	10.35	8.00
20/80	8.08	122.04	0.40	5.75	3.33	20/80	7.53	110.74	0.27	7.73	4.32
30/70	8.55	132.06	0.51	4.88	2.25	30/70	7.82	116.71	0.36	6.11	2.77
40/60	8.78	136.99	0.78	3.31	0.86	40/60	8.12	123.01	0.56	4.14	1.29
50/50	8.97	141.20	0.89	2.99	0.63	50/50	8.23	125.20	0.68	3.47	0.86
60/40	9.18	145.77	1.01	2.72	0.44	60/40	8.30	126.79	0.81	2.95	0.54
70/30	9.19	145.92	1.10	2.50	0.30	70/30	8.36	127.92	0.98	2.46	0.26
80/20	9.20	146.30	1.13	2.44	0.26	80/20	8.40	128.88	1.07	2.27	0.15
90/10	9.25	147.38	1.28	2.17	0.10	90/10	8.40	128.84	1.14	2.13	0.07
100/0			1.40	-	-	100/0			1.22	-	-

Table 2. Relationship between H₂O/DMSO ratio and r of PAN copolymer in precipitation polymerization with using dispersants at 60 °C

H ₂ O/DMSO	$\overline{M}_w \cdot 10^{-4}$	$\overline{X}_n \cdot 10^{-4}$	Q	r
0 : 100	17.25	0.33	4.7	
10 : 90	20.83	0.39	3.26	3.8
20 : 80	23.82	0.45	3.15	2.31
30 : 70	25.95	0.49	3.1	2.02
40 : 60	27.84	0.52	3.03	1.71
50 : 50	28.94	0.55	2.98	1.53
60 : 40	30.24	0.57	2.94	1.41
70 : 30	34.63	0.65	2.83	1.12
80 : 20	36.82	0.69	2.78	1.01
90 : 10	38.91	0.73	2.71	0.87
100 : 0	41.78	0.79	2.65	

Notes: \overline{M}_w : viscosity-average molecular weight, $\overline{M}_w \cdot 10^{-4}$, $\overline{X}_n \cdot 10^{-4}$, Q were referenced, r was calculated

tion with using dispersants has the same basic laws as the system without using dispersants. In addition, some results could be concluded as follows by comparing the two conditions. The average polymerization degree of the PAN copolymer was in the range of $0.33\text{--}0.79 \cdot 10^4$ when using dispersants, which had a narrower zone than that of $0.23\text{--}1.74 \cdot 10^4$ without using dispersants at 60 °C. Values of r (0.87–3.80) using dispersants also had a narrower zone than

Table 3. Influence of temperature in precipitation copolymerization with using dispersants at H₂O/DMSO=80 : 20

Temperature/°C	$\overline{M}_w \cdot 10^{-4}$	$\overline{X}_n \cdot 10^{-4}$	Q	r
50	50.21	0.95	2.42	0.49
55	42.92	0.81	2.60	0.79
60	36.82	0.69	2.78	1.01
65	30.73	0.58	2.99	1.39
70	21.64	0.41	3.18	1.61

Notes: \overline{M}_w : viscosity-average molecular weight, $\overline{M}_w \cdot 10^{-4}$, $\overline{X}_n \cdot 10^{-4}$, Q were referenced, r was calculated

that of 0.08–9.73 without using dispersants. These showed the following: when the solid phase polymerization predominated, dispersants protected the liquid phase polymerization, and the liquid phase reaction ratio increased, so limit MWD (Q) of the totally solid phase polymerization was not approaching the theoretical value 2, but some other value greater than 2. When the liquid polymerization predominated, dispersants protected the solid phase polymerization, and the solid phase reaction ratio increased, so the MWD was relatively larger than in the system without using dispersants. Dispersants protected the dispersed phase and increased its reaction degree, so the MWD in the system with using dispersants was more uniform.

Table 3 shows the effect of temperature in precipitation copolymerization with using dispersants at H₂O/DMSO=80 : 20. The aver-

age molecular weight decreased as the temperature increased and in the range of $0.95\text{--}0.41 \times 10^4$. The way of obtaining contribution ratio (r) was the same as in Table 1. Value of r increased with the increase of temperature, which showed that the reaction rate increased as the increase of temperature, and the chain transfer degree of AN free radicals in DMSO increased. So the relative molecular weight was reduced, and the MWD grew wider. This indicated that the liquid phase polymerization under the protection of dispersants strengthened with the increase of temperature. Comparing with the results of same precipitation agent content and different temperature, it was found that the higher the reaction temperature, solvent activity and miscibility with water were bigger. So it's easier for the solvent effect to appear among precipitate particles by solvent interacting with particles. Higher temperature can strengthen the solution, and then the effect of liquid phase polymerization was further strengthened. As a result, the value of r became larger, and at the same time particles easily formed large particles by conglutination. Therefore, high temperature and high solvent content on precipitation polymerization had a similar effect.

CONCLUSIONS

The above experiments show that polymerization systems without and with using dispersants are more complex, but liquid phase and solid phase polymerization contribution ratio r of these systems still can be deduced from the theoretical formula, and the change rule of reaction systems will be guided. Precipitation polymerization can be divided into three areas according to the different mixed solution ratio. The first area is the dominant area of DMSO, water content below 30%. In this region, the homogeneous reaction system in pure DMSO belongs to solution polymerization at beginning. With the increased amount of H_2O , the homogeneous reaction changes slowly into precipitation polymerization in mixed solvent. The second area, water content between 30–60%, has more water content compared with the first area. Along with the increase of the water content, the nascent precipitate particles' concentration increases. Thus the in situ polymerization in the nascent particles and con-

densed matter reaches the highest level, and the monomers, which are immersed in precipitation clearance and adsorbed on the surface of the precipitation particles, can continue to polymerize. The third area is the dominant area of H_2O , the precipitation agent. When H_2O dominates in the reaction environment, and DMSO rarely exists, the nascent precipitation particles are easily formed and a further reaction will proceed in precipitation particles.

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