STUDY ON THERMAL STABLIZATION AND HYDROPHILICITY OF POLY(ACRYLONITRILE-*co*-β -MONOISOBUTYL ITACONATE)

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Introduction

Because of the regular chain structure, high crystal degree, and large cohesive energy density, polyacrylonitrile releases heat in a short time in thermal stabilization process and shows bad spinnability, which go against its application of carbon fiber precursor. To solve the problems above, currently many PAN-based carbon fiber companies prepare dope using acrylonitrile/ acid/ vinyl ester ter-polymer. As co-monomer, effect of acid is to lower cyclization temperature, broaden exothermic peak and decrease heat release rate in thermal stabilization---all in a word, soothing the exothermic reaction; effect of vinyl ester is to lower cohesive energy of PAN using volume effect of ester group, and then improving spinnability and oxygen permeability, restraining the formation of "sheath-core" structure. Itaconic acid, acrylic acid, methylacrylic acid and acrylamide [1-3] are mainly adopted for acid, and methyl acrylate, methyl methacrylate [4] are mainly adopted for vinyl ester. But hard control of sequence distribution of ter-polymerization will result in bad chain uniformity and then microgel in the dope, which has bad influence on spinning. So, developing a new co-monomer that have functions of both acid and vinyl ester, changing the traditional ter-polymerization to binary polymerization is necessary. Besides, the sequence distribution of binary copolymer can be controlled by synthesis techniques like method of refilling active monomers which provides the possibility of improving chain uniformity, restraining formation of microgel, increasing content of acrylonitrile in the copolymer, and finally improving mechanical property of carbon fiber.

We synthesized a new type of itaconate ester: β-monoisobutyl itaconate(MIBI), and measured the apparent reactivity ratio of AN/MIBI copolymerization system in N,N-dimethylformamide at 70℃. MIBI's effect on the exothermic property of PAN copolymer, chain regularity, chain flexibility was investigated.

Experimental

Solution copolymerization

13~19mg AIBN, 5mL AN, 0.7~7.0g MIBI, and 10mL DMF were put in a Schlenk flask. The amount of initiator was 0.1% of total amount of monomers. The volume ratio of solution and monomer was 2:1. Implemented freeze, vacuumize, melt and then connect nitrogen operation for three times to remove oxygen. The polymerization was carried out in 70℃ under nitrogen protection. After a short time (the conversion were controlled to be less than 10%), the reaction was terminated with liquid nitrogen and was drop to water to precipitate. After vacuum drying, purified the copolymer twice with dissolve-precipitation method (DMF as solvent, water as precipitant), washed the copolymer 3 times with methanol, and then vacuum dried to constant weight. A series of copolymerization with different monomer ratio were implemented with the method above.

Thermal analysis experiment

In the atmospheres of air or N_2 (the flow rate was 20mL/min), heated and scanned from 35℃ to 400℃, the rate was 5℃/min, 10℃/min, 15℃/min and 20℃/min. when changed atmosphere or heat rate, scanned the baseline again with empty crucible in corresponding temperature region.

Results and Discussion

Fineman-Ross[5] method is a simple and illustrative method to measure the reactivity ratio among many methods. It is adopted here to calculate the reactivity ratios.

According to Mayo-Lewis equation:

$$\frac{dM_1}{dM_2} = \frac{m_1}{m_2} = \frac{M_1}{M_2} \times \frac{r_1 M_1 + M_2}{r_2 M_2 + M_1}$$

m_1, m_2-----Monomer molar ratio in the copolymer;

M_1, M_2----- Monomer molar fraction in feed;

r_1, r_2----- Reactivity ratio of $M_1$and M_2, respectively.

If $X = \frac{M_1}{M_2}$; $Y = \frac{m_1}{m_2}$; $G = \frac{X(Y-1)}{Y}$; $H = \frac{X^2}{Y}$

it can be calculated that: $G = r_1 H - r_2$, and this formula is the equation to calculate reactivity ratio by Fineman-Ross method.

Table 1 shows monomer molar fraction in feed, Nitrogen content N% got from elementary analysis, the copolymer composition calculated, G and H deduced.

Table 1 Feed of monomers and Values of G and H

No.	M_1(AN)/mol	M_2(MIBI)/mol	N/%	Conversion/%	G	H
P1	0.0764	0.00382	19.97	3.33	18.1	36.79
P2	0.0764	0.00437	19.25	3.46	15.6	32.42
P3	0.0764	0.00511	18.19	3.39	13.0	28.80
P4	0.0764	0.00617	16.08	2.93	10.1	28.08
P5	0.0764	0.00763	16.34	2.58	8.25	17.62

Linear fit with G and H, and then: r_1(AN)= 0.523, r_2(MIBI)= 2.001. For $r_1 \times r_2$=1.047≈1, AN/MIBI copolymerization system approaches general ideal copolymerization.

Table 2 Feed details of monomers

No.	Polymer	AIBN/ mg	M_2/g	M_1(AN)/mL	DMF/ mL	f_2/%	F_2/%
P_1'	AN-*co*-MIBI	12.60	0.0714	5	10	0.500	1.00
P_2'	AN-*co*-MIBI	12.70	0.1440	5	10	1.00	1.90
P_3'	AN-*co*-MIBI	12.80	0.2900	5	10	2.00	3.80
P_4'	AN-*co*-MIBI	13.10	0.5910	5	10	4.00	7.40
P_0	AN	12.50	/	5	10	/	/

Table 2 shows monomers feed details of DSC polymers. The effect of MIBI's content, atmosphere, and temperature rise speed in the thermal stabilization process is studied by differential scanning calorimetry(DSC). It can be seen from Fig. 1 that MIBI could significantly lower copolymer's exothermic onset temperature, broaden exothermic peak and decrease heat release rate. It indicates that cyclization is caused by ion mechanism and then oxidation occures in thermal stabilization process. With the

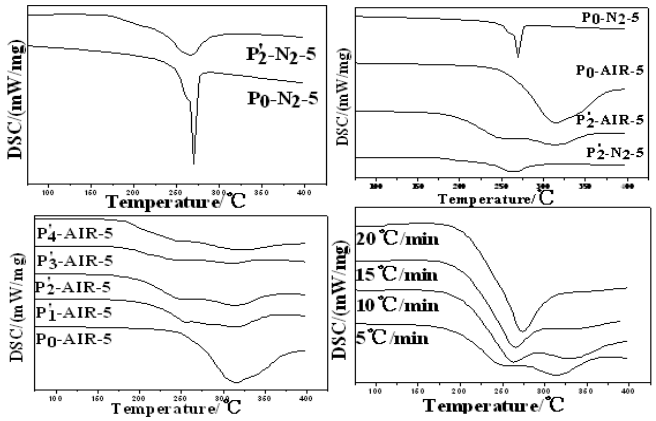

Fig.1 DSC curves of polymers under different conditions

increase of temperature rise speed, exothermic onset temperature moved to high temperature region, heat release amount decreased, and peak shape changed gradually from double broadened peaks to one peak.

It is can be seen from table 3 that polymers' contact angle increase with the increase of MIBI's content which indicates that MIBI is hydrophobic, and its addition can't improve the hydrophilcity problem.

Table 3 Contact Angle of copolymers containing different contents of MIBI

Polymer	No.	Contact Angle
PAN	P_0	62.5 °
P(AN-*co*-MIBI)	P_3	74.5 °
P(AN-*co*-MIBI)	P_4	78.9 °
P(AN-*co*-MIBI)	P_5	80.5 °

Conclusion

The apparent reactivity ratios of MIBI and AN are 2.001 and 0.523, respectively. It is known from $r_1 \times r_2$=1.047≈1 that AN/MIBI copolymerization system approaches general ideal copolymerization. MIBI can initiate cyano group's cyclization at a low temperature by ion mechanism, and then broaden exothermic region and lower heat release rate of cyclization reaction. Heat release amount of P(AN-co-MIBI) copolymer in air is larger than in nitrogen for oxidation reaction. MIBI can efficiently lower exothermic onset temperature, heat release amount and heat release rate. With the raise of temperature rise speed, reaction onset temperature moves to high-temperature region, heat release amount decreases and peak shape changes from broadened double peaks to single peak. MIBI is hydrophobic, and its addition can't improve the hydrophilcity problem.

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