

# SYNTHESIS OF SERIES OF $\beta$ -MONOALKYL ITACONATE AND DETERMINATION OF APPARENT REACTIVITY RATIO OF COPOLYMERIZATION WITH ACRYLONITRILE

Ma Sai, Bai Hui-Tao, Zhao-Kun Ma, Jieying Liang, Liu Jie\*

Key Laboratory of carbon fiber and functional polymers, Ministry of Education, Chao-Yang District, Beijing 100029, China

## Introduction

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 improve spinnability and oxygen permeability, restrain the formation of "sheath-core" structure. Itaconic acid, acrylic acid, methacrylic 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 the copolymer by ter-polymerization always results a bad chain uniformity and then micro-gel in the dope, which is not conducive to spinning. So it is necessary to develop a new multifunctional co-monomer that combines of the acid and the vinyl ester, converting the traditional ter-polymerization into the binary polymerization to provide the possibility of improving chain uniformity, restrain formation of micro-gel, increase content of acrylonitrile in the copolymer, and finally improving mechanical property of carbon fiber.

## Experiment

Itaconic acid (0.50mol), R-OH (5.00mol) and benzoyl chloride (0.050mol) were combine and the mixture was stirred 180 min at 70°C to give the  $\beta$ -monoalkyl itaconate ( $\beta$ -MAI).

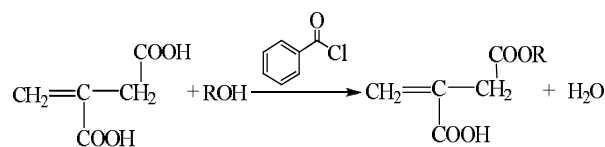
AIBN, AN,  $\beta$ -MAI, DMF were put in a Schlenk flask. The amount of initiator was 0.1% of total amount of monomers. The volume ratio of solution and monomer was 2:1. Implement Schlenk method for three times to remove oxygen. The

polymerization was carried out in 70°C 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.

## Results and Discussion

### Synthesis and characterization of $\beta$ -monoalkyl itaconate

The new series itaconate monomer, including  $\beta$ -monomethyl itaconate ( $\beta$ -MMI),  $\beta$ -monoethyl itaconate ( $\beta$ -MEI),  $\beta$ -monopropyl itaconate ( $\beta$ -MPI),  $\beta$ -monoisopropyl itaconate ( $\beta$ -MIPI),  $\beta$ -monobutyl itaconate ( $\beta$ -MBI) and  $\beta$ -monoisobutyl itaconate ( $\beta$ -MIBI), were synthesized by selective esterification showed in Equ. 1 [5]. And Table 1 shows the  $^1\text{H}$  NMR parameters of  $\beta$ -MAI.



Equ. 1 Synthesis of  $\beta$ -MAI

Table 1.  $^1\text{H}$  NMR Parameters of  $\beta$ -MAI

$\beta$ -MAI	$^1\text{H}$ NMR ( $\delta$ )
$\beta$ -MMI	3.35 (2H, s), 3.71 (3H, s), 5.85 (1H, s), 6.5 (1H, s), 11.25 (1H, s)
$\beta$ -MEI	1.3 (3H, t), 3.3 (2H, s), 4.2 (2H, q), 5.83 (1H, s), 6.46 (1H, s), 10.7 (1H, s)
$\beta$ -MPI	0.90 (3H, t), 1.59-1.65 (2H, sextet), 3.3 (2H, s), 4.0 (2H, t), 5.8 (1H, s), 6.43 (1H, s), 12.0 (1H, s)
$\beta$ -MIPI	1.224-1.235 (6H, d), 3.30 (2H, s), 5.01-5.03 (1H, quintet), 5.813 (1H, s), 6.446 (1H, s)
$\beta$ -MBI	0.90-0.925 (3H, t), 1.33-1.39 (2H, sextet), 1.58-1.62 (2H, quint), 3.33 (2H, s), 4.09-4.11 (2H, t), 5.825 (1H, s), 6.46 (1H, s), 11.90 (1H, s)
$\beta$ -MIBI	0.91, 0.92 (6H, d), 1.88-1.969 (1H, multi), 3.35 (2H, s), 3.88, 3.89 (2H, d), 5.83 (1H, s), 6.46 (1H, s), 11.68 (1H, s)

### Determination of reactivity ratios of AN/ $\beta$ -MAI copolymerizations

The reactivity ratio of AN/ $\beta$ -MAI copolymerization was determined by Fineman-Ross method [6].

Table 2 shows the monomer molar fraction in feed, Nitrogen content N% got from elementary analysis, the copolymer composition calculated, G and H deduced.

**Table 2. Feed of Monomers and Values of G and H**

Sample	M <sub>1</sub> (AN)/mol	M <sub>2</sub> (MIBI)/mol	N/%	Conversion/%	G	H
β-MMI	0.0764	0.00382	20.89	7.92	18.05	38.94
	0.0764	0.00437	19.92	3.05	15.38	36.68
	0.0764	0.00521	19.35	4.21	12.69	28.90
	0.0764	0.00617	17.92	4.17	10.22	26.75
	0.0764	0.00694	18.08	2.87	9.141	20.56
β-MEI	0.0764	0.00380	20.13	2.75	18.00	42.34
	0.0764	0.00437	19.37	4.09	15.35	37.29
	0.0764	0.00506	19.17	5.09	13.18	28.90
	0.0764	0.00617	17.86	2.43	10.39	24.64
	0.0764	0.00759	17.05	2.44	8.211	18.67
β-MPI	0.0764	0.00384	20.43	3.89	18.10	35.73
	0.0764	0.00437	19.51	4.51	15.58	33.33
	0.0764	0.00512	18.67	3.05	13.01	28.46
	0.0764	0.00617	17.74	2.34	10.52	23.10
	0.0764	0.00761	17.58	2.71	8.485	15.61
β-MIPI	0.0764	0.00384	19.79	2.80	17.84	40.83
	0.0764	0.00437	19.05	8.00	15.40	36.41
	0.0764	0.00512	18.35	2.60	12.90	30.16
	0.0764	0.00617	17.17	3.85	10.33	25.44
	0.0764	0.00761	16.48	4.03	8.174	18.72
β-MBI	0.0764	0.00382	19.37	3.44	17.93	41.46
	0.0764	0.00437	18.73	6.36	15.44	35.74
	0.0764	0.00511	18.28	2.25	13.06	28.35
	0.0764	0.00617	16.91	4.60	10.40	24.56
	0.0764	0.00763	15.86	1.44	8.114	19.01
β-MIBI	0.0764	0.00382	19.97	3.33	18.16	36.79
	0.0764	0.00437	19.25	3.46	15.63	32.42
	0.0764	0.00511	18.19	3.39	13.02	28.80
	0.0764	0.00617	16.08	2.93	10.11	28.08
	0.0764	0.00763	16.34	2.58	8.254	17.62

**Table 3. Reactivity Ratio of β-MAI**

Sample	r <sub>1</sub> (AN)	r <sub>2</sub> (β-MAI)
β-MMI	0.457	1.316
β-MEI	0.404	0.744
β-MPI	0.463	0.524
β-MIPI	0.440	0.398
β-MBI	0.436	0.008
β-MIBI	0.523	2.001

Linear fit with G and H, and the reactivity ratios is showed in Table 3. As the Table 3 shows, the monomer reactivity ratio changes with the different ester, which is controlled by steric effect and electronic effect. It is known from  $r_1 \times r_2$ , that the AN/β-MBI polymerization system approaches the alternating copolymerization and the AN/β-MIBI polymerization system approaches the general ideal copolymerization, while other systems approach the non-ideal copolymerization.

### Conclusions

New series itaconate monomers were synthesized using itaconate as starting material by selective esterification. This monomers were copolymerized with acrylonitrile in DMF at 70°C. The apparent reactivity ratios of AN/β-MAI copolymerization systems were calculated by Fineman-Ross method respectively. This result may provide a reference to benefit the PAN-based carbon fiber precursor copolymer synthesis.

**Acknowledgment.** The authors thank the supports from the National Natural Science Foundation of China (Grant No.: 50333070 and 50673011),

### References

- [1] Bajaj P, Sreekumar TV, Sen K. Thermal behaviour of acrylonitrile copolymers having methacrylic and itaconic acid comonomers. *Polymer* 2001;42(4):1707-1718.
- [2] Hajir Bahrami S, Bajaj P, Sen K. Thermal behavior of acrylonitrile carboxylic acid copolymers. *J. Appl. Polym. Sci* 2003;88(3):685-698.
- [3] Gupta AK, Paliwal DK, Bajaj P. Effect of the nature and mole fraction of acidic comonomer on the stabilization of polyacrylonitrile. *J. Appl. Polym. Sci* 1996; 59(12): 1819-1826.
- [4] Bang YH, Lee S, Cho HH. Effect of methyl acrylate composition on the microstructure changes of highmolecular weight polyacrylonitrile for heat treatment. *J. Appl. Polym. Sci* 1998; 68(13):2205-2213.
- [5] Zewang Feng, Xinqi Zhao, Hua Bi. Selective esterification of non-conjugated carboxylic acids in the presence of conjugated or aromatic car-boxylic acids over active carbon supported methane-sulfonic acid ; *Science in China Series B: Chemistry*. 2008; 51(10): 990-992.
- [6] Finemann M, Ross SD. Linear method for determining monomer reactivity ratios in copolymerization; *J. Polym. Sci* 1950; 5:259-262.