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Kinetic study of new AB₃ type hyperbranched poly(amide-ester)

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ABSTRACT

The AB₃ type hyperbranched poly (amide-ester) was synthesized by the condensation polymerization reaction of hexahydrophthalic anhydride and tri(hydroxymethyl) aminomethane. The conversion of monomer can reach 80%. Reaction conditions (time and temperature) have been investigated systemically. The dynamics of condensation polymerization reaction for the AB₃ type hyperbranched poly(amide-ester) was studied as well. Another, the equation of the overall polymerization rate can be written as follows: polycondensation reaction is a third-order and self-catalyst process, the overall activation energy was calculated to $k = -1.12 \times 10^4$, $E_a = 93.07$ kJ/mol. The proof of poly-condensation was obtained from FTIR spectroscopy. And the hyperbranched polymer was characterized by intrinsic viscosity and TGA analysis. The result showed that the hyperbranched polymer have low melt viscosity, good dissolubility and good thermostability.

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KEYWORDS

Hyperbranched poly
(amide-ester);
Synthesis;
Dynamic;
Thermostability.

INTRODUCTION

Dendritic macromolecules can be divided into two types^[1,2]: dendrimers and hyperbranched polymers. Dendrimers are well-defined monodisperse regular structures in which all branched points are utilized^[3,4]. Comparing with linear polymers, they often exhibit unusual and attractive properties, including low melt viscosity, good dissolubility, non-entanglement and a large number of active end groups, but they are made using laborious iterative synthesis^[5,11]. So their commercial use has still been very limited. Compared with dendrimers, hyperbranched polymers have the same properties as well, because they are considered as irregular analogues of dendrimers^[12-19]. At the same time, they can be made by one-pot reactions. Therefore, in

recent years, considerable effort has been devoted to synthesize hyperbranched polymer system. As a consequence, new methods for one-pot reactions to hyperbranched polymers are becoming an increasingly important theme in polymer science. Accordingly, it is very challenging and meaningful to design new mechanisms and monomer systems that permit the facile synthesis of highly branched polymers^[20,21].

In this paper, we have synthesized hyperbranched polymers in one-pot from the cheap and commercially available compound hexahydrophthalic anhydride and tri(hydroxymethyl) aminomethane). The dynamics equation of poly-condensation for the AB₃ type hyperbranched poly(amide-ester) was also studied and the results indicate that this polycondensation reaction is third-order and self-catalyst process. And the

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hyperbranched polymer was characterized by intrinsic viscosity and TGA analysis. The result showed that the hyperbranched polymer have low melt viscosity, good dissolubility and good thermostability.

EXPERIMENTAL

Materials

Tri(hydroxymethyl) aminomethane (Henda Baisheng Chemical Co.BR, 99%), pyridine(Titan Chemicals Co.,Ltd), hexahydrophthalic anhydride(Guangzhou Weibo Chemical Co. =99.0%), The other reagents were all analytical reagent and used without purification.

Measurements

FTIR spectroscopy: The FTIR spectra of AB₃ monomer and hyperbranched poly(amide-ester) are recorded on a VECTOR-22 (Bruker, German) by the potassium bromide pellet method.

TGA: The thermogravimetric analysis(TGA) of hyperbranched polymer which obtained at 150°C,160°C ,170°C is carried out by a Pyris 6 TGA (From PerkinElmer USA) at a heating rate of 20°C/min and air_flow rate of 60ml/min.

VPO: The molecular weight of hyperbranched poly-

mer were obtained by VPO (Knauer, German).

MS: Mass measurement was carried out on VG-70EHF (American).

Synthesis of AB₃ monomer

Tri(hydroxymethyl) aminomethane (0.1mol) was dissolved in appropriate amount of pyridine, and the resulting solution was stirred at 0~5°C for 10 min under nitrogen. A solution of equimolar hexahydrophthalic anhydride in acetone was added to this solution dropwise. The mixture was reacted at 0~5°C for another 8 hours. The AB₃ monomer was obtained after the removal of acetone and pyridine under reduced pressure. Monomer acid value: 203.23mg KOH/g (theoretic acid value: 203.85mg KOH/g)

Synthesis of hyperbranched poly (amide-ester)

The obtained AB₃ monomer, dimethylbenzene were dissolved in appropriate amount of pyridine in wolff bottle. Then the polycondensation was carried out under reduced pressure (30×133.322 Pa) at 150°C, 160°C and 170°C respectively. Products with different number molecular weight were controlled by adjusting the reaction time. The approach of synthesis of hyperbranched poly(amide-ester) shows in figure 1.

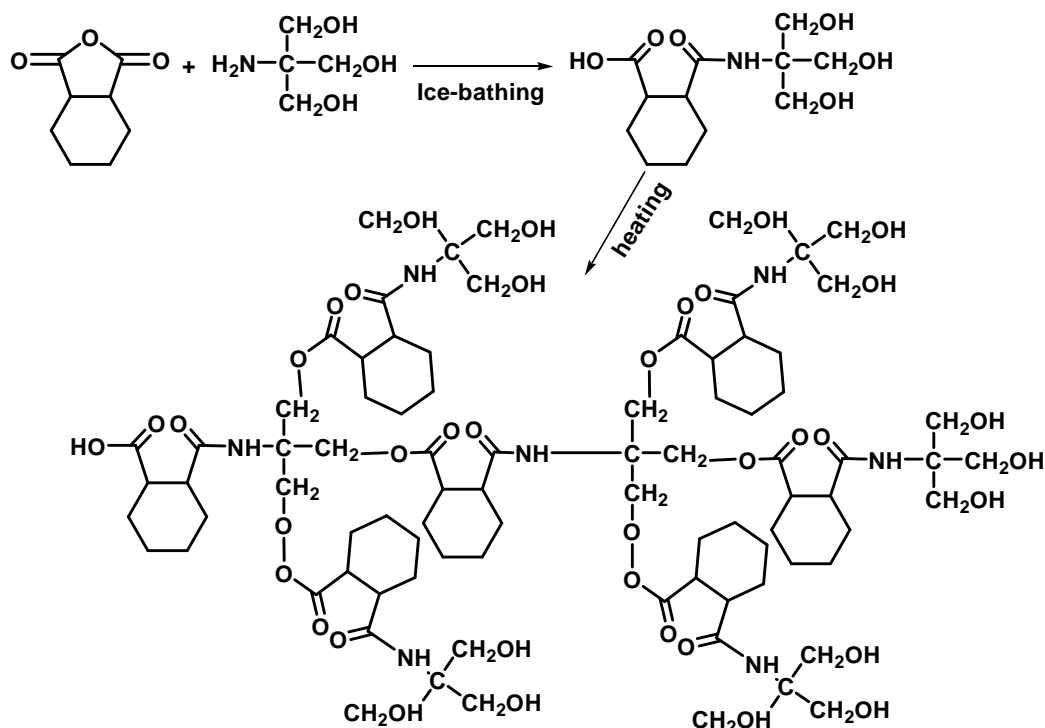


Figure 1 : Synthesis of hyperbranched poly (amide-ester)

Measurement of acid value and conversion

In a conical beaker, hyperbranched polymer was dissolved in dehydrated alcohol. The solution containing phenolphthalein was titrated with 0.1 mol/L KOH solution in dehydrated alcohol until pink appeared, and then the dissipative amount of KOH was recorded. The same procedure was repeated with dehydrated alcohol instead of hyperbranched polymer, carboxyl content of monomer. The acid value C (mol/g) was recorded respectively. Then the conversion was calculated on the basis of $P_a = (1 - C/C_0) \times 100\%$ (P_a , represented carboxyl transformation ratio; C_0 , acid value of monomer; C , acid value of hybranch).

Measurement of inherent viscosity

Inherent viscosity was measured in anhydrous alcohol with an Ubbelohde viscometer. In experimental process, we firstly measured the viscosity of different concentration solution of hyperbranched polymer. Then the viscosity of pure solvent was measured after washing viscometer with pure solvent for 3~5 times, to clear up the influence of adsorption layer on capillary wall on the viscosity.

RESULTS AND DISCUSSION

FTIR and mass of AB₃ monomer

Figure 2 shows the IR spectra of monomer. The FTIR spectrogram shows characteristic absorption bands of carboxyl and hydroxy at 3200 cm⁻¹ (ν_{O-H}). The stretching bands of C-H stretching is found at 2980 cm⁻¹. And the absorption around 1630 cm⁻¹ is considered to belong to amide. In addition, the bands around 1717 cm⁻¹ is attributed to the vibration band of C=O of carboxyl groups, and the bands around 1066 cm⁻¹ is

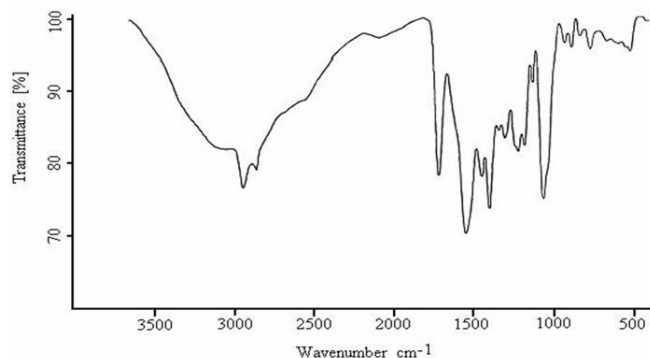


Figure 2 : The IR spectra of monomer

attributed to the vibration band of primary alcohol.

As shown in figure 3, quasimolecular ion absorption ($m/e=275$) is found and polymer ion absorption was not found. On the other hand Monomer acid value and theoretic acid value were 203.23mg KOH/g and 203.85 mg KOH/g, respectively. According to above analysis, we conclude that the product is what we expected.

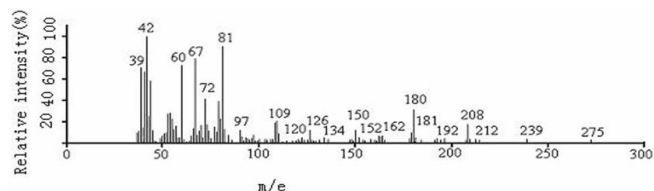


Figure 3 : The mass spectra of monomer.

FTIR of AB₃ hyperbranched polymer

In Figure 4, the bands around 1716 cm⁻¹, 1630 cm⁻¹, 1066 cm⁻¹ can still be found. Additionally, the O-H stretching band of hydroxyl around 3401 cm⁻¹ shows the polymer with a large hydroxyl groups. And C-O vibration band around 1313 cm⁻¹~1042 cm⁻¹ shows that the esterification reaction takes place. Figure 4 resembles Figure 2, because characteristic functional groups do not change after polymerization reaction. With polymerization processing, the number of carboxyl decreases and that of hydroxyl increases.

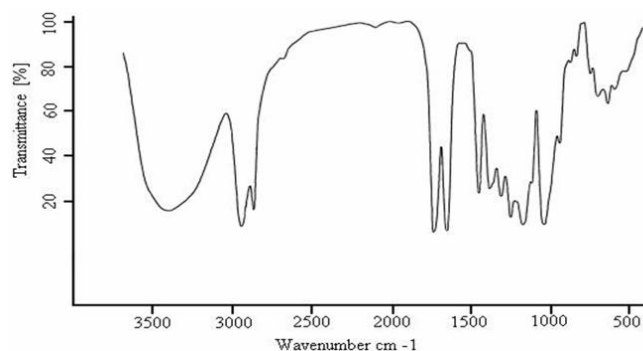


Figure 4 : The FTIR of AB₃ hyperbranched polymer

In Figure 4, the stretching bands of OH around 3401 cm⁻¹ strengthen clearly, but that of C=O in amide around 1630 cm⁻¹ do not change almostly. According to above analysis, we can conclude that the product is the hyperbranched polymer we prospect in Figure 1.

Thermogravimetric analysis

Figure 5 is the thermogravimetric analysis of the hyperbranched polymer obtained at 150°C, 160°C,

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170°C respectively, within the same reaction time. In Figure 5(a), there are three weight losses: the first loss from 170°C to 280°C, may be caused by the condensation of prepolymer, the rate of weight loss is 11.62%; the second distinct loss from 280°C to 490°C, may be caused by the abruption of ester linkage and amide linkage, the rate of weight loss is 67.67%; the third rate of weight loss is 17.08% to 600°C, caused by the oxidative decomposition and carbonization of remained hyperbranched polymer.

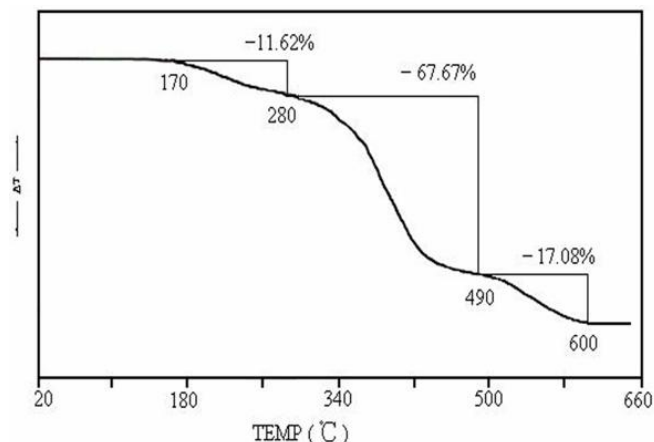


Figure 5 : (a, 150°C) The thermogravimetric analysis of the hyperbranched polymer

In Figure 5(b) and Figure (c), there is not obvious weight loss from 170°C to 240°C. This indicated few prepolymer remained in polymer after the increasing reaction temperature. In Figure 5(b), the first distinct weight loss is 78.12%, from 240°C to 490°C; In Figure 5(c), the first distinct weight loss is 70.03%, from 280°C to 490°C. The second rate of weight loss in Figure 5(b) and Figure 5(c) are respective 16.87% and 12.68%, caused by the oxidative decomposition and carboniza-

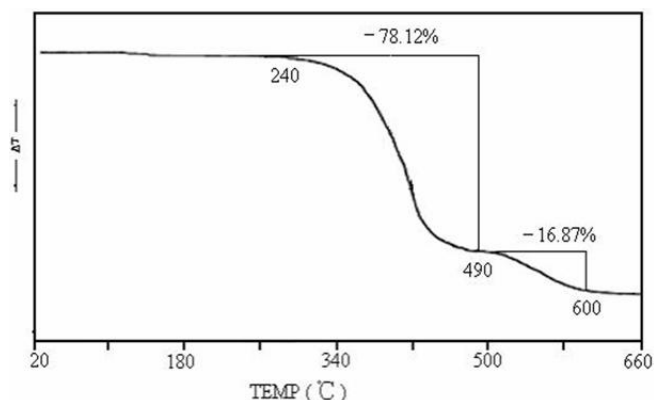


Figure 5 : (b, 160°C) The thermogravimetric analysis of the hyperbranched polymer

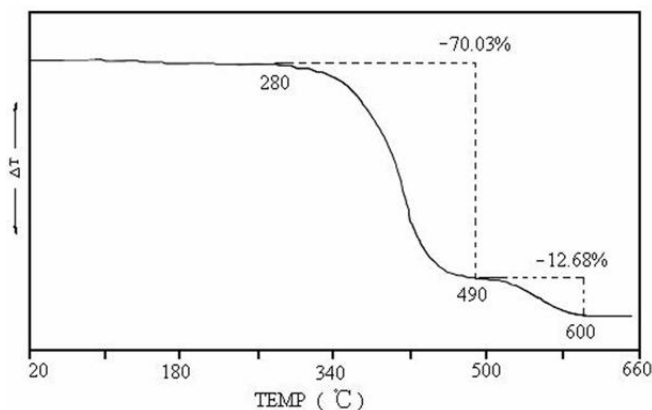


Figure 5 : (c, 170°C) The thermogravimetric analysis of the hyperbranched polymer

tion of remained hyperbranched polymer. The analysis indicate hyperbranched poly(amide-ester) obtained at 170°C possess the best thermostability. Its first decomposed temperature can reach 280°C

Effect of molecular weight on acid value and intrinsic viscosity

The effect of the molecular weight on acid value and intrinsic viscosity is depicted in TABLE 1. From TABLE 1, we find that the inherent viscosity of the hyperbranched polymer change distinctly with the number molecular weight increasing from 2300g/mol to 8500g/mol. However this current flattens out when the number molecular weight is above 8500 g/mol. Due to the similar torispherical as dendrimer, the increase of number molecular weight of hyperbranched polymer do not affect the hydrodynamics radius obviously.

TABLE 1 : Data of AB₃ type hyperbranched poly(amide-ester) with different molecular weights, *p* conversion of carboxyl groups, acid value and intrinsic viscosity.

| Time of reaction (h) | \overline{M}_n | <i>p</i> (%) | Acid value (mg KOH/g) | Intrinsic viscosity (ml/g) |
|----------------------|------------------|--------------|-----------------------|----------------------------|
| 2 | 2300 | 88.21 | 23.96 | 2.15 |
| 4 | 4150 | 93.66 | 12.82 | 3.05 |
| 6 | 6800 | 96.01 | 8.11 | 4.42 |
| 8 | 8500 | 97.21 | 5.67 | 6.83 |
| 10 | 10800 | 97.54 | 4.99 | 7.61 |
| 11 | 11600 | 97.67 | 4.74 | 8.01 |

Solubility

The hyperbranched polymer can be dissolved in polar CH₃OH, C₂H₅OH, DMF, DMSO, NMP with all propotion and not dissolved in nonpolar THF, cy-

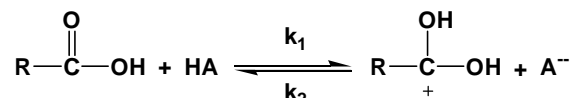
clohexane and benzene. This can be explained by the easy solvation of molecular chain because of a mount of amido bond and hydroxyl groups.

Kinetic of polycondensation

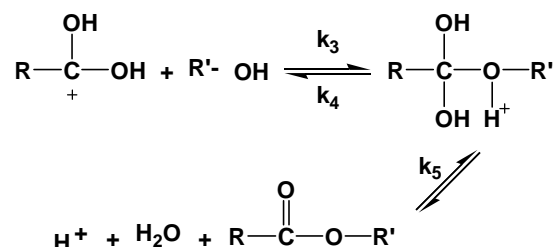
Equation foundation of kinetic polycondensation

In AB_3 system, it is inclined to form polymer by removing micromolecular outgrowth and reaction is non-reversible estification. Following is the reaction process:

Firstly, carboxylic acid was protonated:



Secondly, polyester is formed by reaction of the protonated product and alcohols.



in above equation, k_1 , k_2 and k_5 are all greater than k_3 . When micromolecular outgrowth is removed by de-compression, the above reaction is nonreversible and k_4 can be neglected. When acid is added as catalyst, the rate of estification include two sections: one is autocatalysis and the other is adscititious acid catalysis. The kinetic equation is:

$$-\frac{d[COOH]}{dt} = k''[COOH][OH][COOH] + k_a[COOH][OH][H^+] \quad (1)$$

k'' is rate constant of autocatalysis, k_a is rate constant of adscititious acid catalysis.

If this reaction is adscititious acid catalysis, equation (1) can be rewritten as:

$$-\frac{d[COOH]}{dt} = k_a[COOH][OH][H^+] \quad (2)$$

For $k_a[H^+][COOH][OH] \gg k''[COOH][OH][COOH]$ comes into existence.

If this reaction is autocatalysis, equation (1) can be rewritten as:

$$-\frac{d[COOH]}{dt} = k''[COOH][OH][COOH] \quad (3)$$

Now, assuming $K_a[H^+] = k$, $[COOH] = C$, the originated concentration of carboxyl groups is C_0 , the concentration of carboxyl and hydroxyl groups are respective P_a and P_b after t time. $[COOH] = C_0(1-P_a)$, $[OH] = 3C_0(1-P_b)$. In the AB_3 system, $P_a = 3P_b$, $-dC = C_0 dP_a$. The equations (2) and (3) can be respectively rewritten as:

$$\frac{dP_a}{dt} = kC_0(1-P_a)(3-P_a) \quad (4)$$

$$\frac{dP_a}{dt} = kC_0^2(1-P_a)^2(3-P_a) \quad (5)$$

Integrate equation (4) and (5):

$$\ln\left(\frac{3-P_a}{3-3P_a}\right) = 2kC_0t \quad (6)$$

$$\frac{1}{2(1-P_a)} + \frac{1}{4} \ln \frac{1-P_a}{3-P_a} = kC_0^2t + C' \quad (7)$$

If the reaction is adscititious acid catalysis, from equation (6), the beeline slope of $\ln\left(\frac{3-P_a}{3-3P_a}\right)$ vs t should

be $2kC_0$, then rate constant k can be obtained by calculation. If the reaction is autocatalysis, from equation

(7), the beeline slope of $\frac{1}{2(1-P_a)} + \frac{1}{4} \ln \frac{1-P_a}{3-P_a}$ vs t is the

rate constant k . From Arrhenius equation $\ln k = -E_a/RT + C$, the beeline slope of $\ln k$ vs $1/T$ is $-E_a/R$, E_a can be obtained by calculation.

From Arrhenius equation $\ln k = -E_a/RT + C$, the beeline slope of $\ln k$ vs $1/T$ is $-E_a/R$, E_a can be obtained by calculation.

Data processing

Effect of reaction time on conversion and molecular weight

From figure 6, the conversion of carboxyl groups is above 80% at the beginning and prolong of reaction time do not effect on it, only on molecular weight. The phenomena suggest the prepolymer, formed at the beginning, do not combine to high molecular weight polymer until reaction end. This complies with the mechanism of polycondensation.

Kinetic polycondensation

The data is analyzed on the basis of equation (6), (7) result in Figure 7 and Figure 8 respectively. In Figure 7, the curve of $\ln[(3P_a)/(3-3P_a)]$ vs t is not simple the beeline, so the reaction process mismatch the

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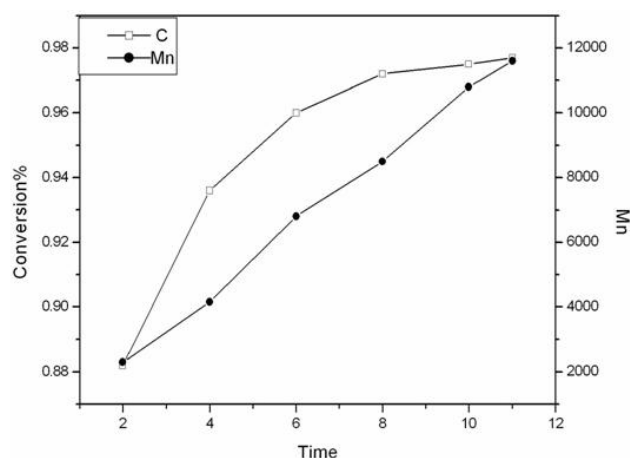


Figure 6 : Effect of reaction time on conversion and molecular weight

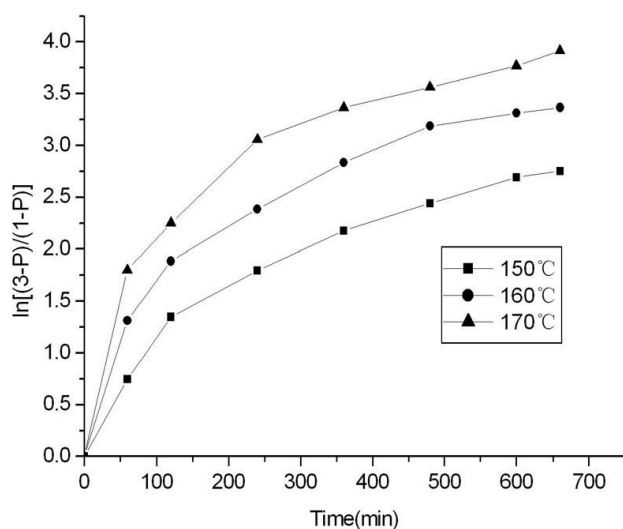


Figure 7 : The curve of $\ln[(3-P)/(1-P)]$ vs t

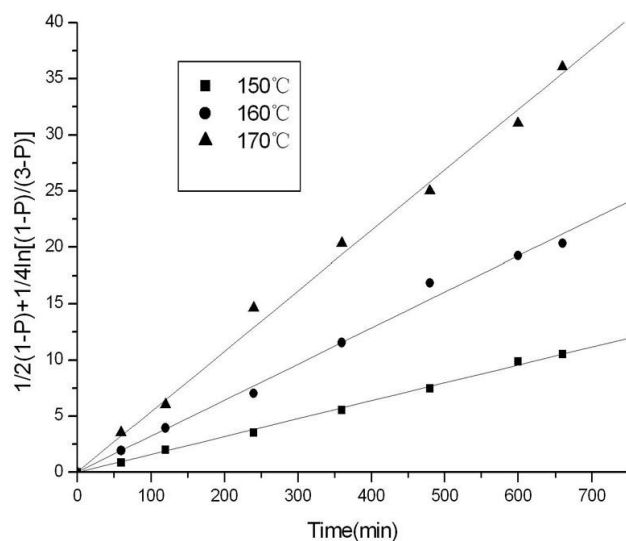


Figure 8 : The curve of $\frac{1}{2(1-P_a)} + \frac{1}{4} \ln \frac{1-P_a}{3-P_a}$ vs t

adsorbent acid catalysis mechanism. However, in Fig-

ure 8, the curve of $\frac{1}{2(1-P_a)} + \frac{1}{4} \ln \frac{1-P_a}{3-P_a}$ vs t present good linear relationship, so the reaction process is autocatalysis mechanism and rate constant can be obtained from the slope of beeline, data in TABLE 2.

TABLE 2 : Reaction temperature and rate constant

| Temperature(°C) | k [(kg/mol) ² min ⁻¹] |
|-----------------|--|
| 150 | 0.213 |
| 160 | 0.424 |
| 170 | 0.700 |

Kinetic equation is correct conditionally for polyestification, but it is correct in any condition for the HBP system. In polymer process of forming linear polyester, the change of medium polarity obviously effected on the rate constant. However, the medium polarity could not change in process of forming HBP for the strong polarity of HBP. In addition, the macromolecule is still easily removed for the low inherent viscosity of HBP, so the hypothesis of unreversible reaction and equal reactivity of functional groups is correct in the whole polymer process.

Arrhenius parameter calculation

We analyzed the data in TABLE 2 on the basis of Arrhenius equation. The curve of $\ln k$ vs $1/T$ is showed in figure 9. The slope of the beeline $k = -1.12 \times 10^4$, $E_a = -R \times k = 8.31 \times 1.12 \times 10^4 = 93.07$ kJ/mol. The reaction energy is high, so the prolong of time in low temperature do not obviously affect the molecular weight of HBP.

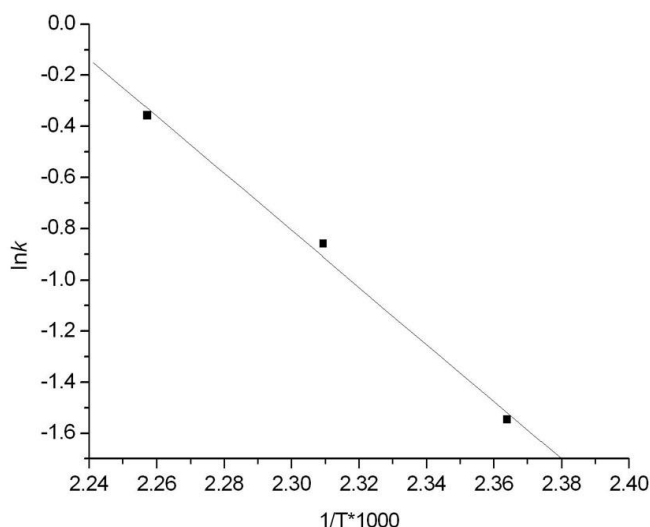


Figure 9 : Logarithm of rate constant versus $1/T$

CONCLUSION

As a satisfactory results, hyperbranched polymers have been synthesized in one-pot from the cheap and commercially available compound hexahydrophthalic anhydride and tri(hydroxymethyl) aminomethane. The equation of dynamics of poly-condensation for the AB₃ type hyperbranched poly(amide-ester) is also studied and the results indicate that this polycondensation reaction is a third-order and self-catalyst process. The reaction energy is 93.07 kJ/ mol. The proof of polycondensation was obtained from FTIR spectroscopy. Anther the hyperbranched polymer have low melt viscosity, good dissolubility and good thermostability which were confirmed by low intrinsic viscosity and TGA analysis.

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