

STUDY ON THE CHAIN-EXTENDING REACTION OF POLY (ETHYLENE TEREPHTHALATE) WITH 2,2'-BIS (4H-3, 1-BENZOXAZIN-4-ONE)

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ABSTRACT

2,2'-Bis (4H-3, 1-benzoxazin-4-one) (BBON) has been proved to be an effective chain extender for poly (ethylene terephthalate) (PET). In order to study the reaction mechanism and kinetics of chain-extending reaction, β -bishydroxyethylene terephthalate (BHET) was selected as model compound. The NMR data, IR spectra and number average molecular weight ($\overline{M}_n$) of the products obtained from the reaction of BBON and BHET verify that BBON is a hydroxyl-reactive extender. The mechanism was discussed. Kinetics data indicate that extending reaction is a second order reaction, and BBON has high reactivity. The activation energy (E_a) was measured.

INTRODUCTION

For practical use of poly (ethylene terephthalate) (PET), it is well known that increasing molecular weight and decreasing the number of the carboxylic and hydroxyl end group per weight of PET will improve significantly the physical and thermal properties of PET products. One of the methods for achieving this purpose was to use the so-called "chain extender" which can react with the end groups of the polymers readily, resulting in the increase of molecular weight of the obtained polymers^[1,2]. It was reported that 2,2'-bis (4H-3, 1-benzoxazin-4-one) (BBON) was one of the effective hydroxyl reactive chain extenders and the reaction mechanism was proposed^[3] but without adequate experimental evidence. In our research, we confirm that BBON is an effective hydroxyl reactive chain extender, the intrinsic viscosity of PET raise from 0.69 to 0.91 under nitrogen atmosphere. The reaction mechanism and kinetics were studied from the results of reactions between the model compound with end hydroxyl group and BBON.

EXPERIMENTAL

^1H and ^{13}C NMR spectra were measured on Varian EM-360L and FQ-90 NMR spectrometer, respectively. IR was performed on Shimadzu-440 instrument.

Materials

PET was obtained from Yanshan Petroleum Chemical Company. 1,2-Ethanediol, anthranilic acid and oxalyl chloride were commercial products without further purification. Terephthaloyl chloride was prepared by the reaction of terephthalic acid and thionyl chloride. Chloroform, N,N-dimethylformamide (DMF) and pyridine were purified before use.

(1) Preparation of β -bishydroxyethylene terephthalate (BHET)

A solution of terephthaloyl chloride (20.3g, 0.1mol) in 100 ml of chloroform was dropwise added into 1,2-ethanediol (14ml, 0.25mol). The mixture was stirred at 90°C for 8h. After removing the unreacted 1,2-ethanediol under reduced pressure, a crude product was obtained, then crystallized from cyclohexane, a white solid (15.5g; yield, 61%) was obtained. m.p. 108.4°C .

^1H NMR (in d-DMSO), δ (ppm): 3.42 ($-\text{OH}$, 2H); 3.85 ($-\text{CH}_2-$, 4H); 4.37 ($-\text{COOCH}_2-$, 4H); 8.19 (phenylene, 4H).

(2) Preparation of 2,2'-bis (4H—3, 1-benzoxazin—4-one) (BBON)

A solution of oxalyl chloride (8.6 ml, 0.1 mol) in 30 ml of chloroform was added into a solution of anthranilic acid (27.4 g, 0.2mol) in 70ml of pyridine. The mixture was stirred at $50-60^\circ\text{C}$ for 6h. The reaction mixture was poured into cold water while stirring, then the solution was acidified with concentrated hydrochloric acid. The precipitate was filtered and dried in vacuum oven at 60°C . The obtained solid was dissolved in 180ml of acetic anhydride and refluxed for 12h. After cooling the reaction mixture, the precipitate formed was filtered out and then recrystallized from DMF, 16.1g (yield, 56%) of product was obtained. m.p. 376°C .

Elementary Analysis for $\text{C}_{16}\text{H}_8\text{N}_2\text{O}_4$: Calcd.: C, 65.75%; H, 2.74%; N, 9.59%

Found: C, 65.23%; H, 2.92%, N, 9.62%

Chain-extending reaction

BHET (0.154g, 0.001mol) and BBON (0.08g, 0.0005mol) were ground and mixed. The glass tube with the mixture was sealed under nitrogen atmosphere, then put into a salt bath at a presetting temperature. The glass tubes were taken out at a definite time interval and chilled immediately.

RESULTS AND DISCUSSION

Chain-extending reactions

trolled by varying the mole ratio of reactants. The polyesters were collected at different reaction time intervals without further purification and measured on proton NMR instrument in CF_3COOH solvent. From Fig. 2, it was found that the peak at $\delta = 4.2$ ppm corresponding to protons of methylene group adjacent to hydroxyl group of compound BHET was decreased, and the peak at $\delta = 4.7$ ppm representing methylene group of ester was increased as the reaction temperature raised gradually. This fact demonstrated that the end hydroxyl group of BHET was converted to ester groups.

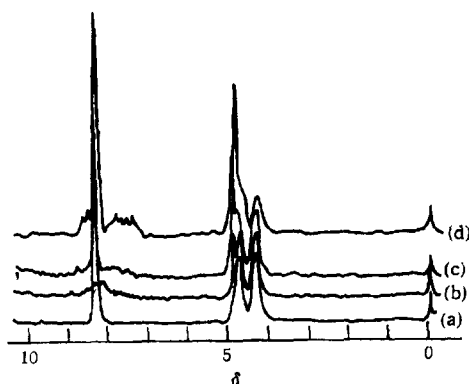


Fig. 2 ^1H NMR spectra of BHET and the chain-extending reaction products (solvent: CF_3COOH) (a) BHET (b) 250°C , 1 min. (c) 250°C , 3 min. (d) 270°C , 5 min

The moles of unreacted hydroxyl group (X) and reacted hydroxyl group (Y) of an extending sample can be obtained according to equation 3 and 4:

$$X = \text{Ha} \quad (3)$$

$$X + 2Y = \text{Hb} \quad (4)$$

The conversion of hydroxyl group in BHET (P%) and the number average molecular weight of the sample can be calculated based on equation 5 and 6:

$$P = Y(X + Y)100\% \quad (5)$$

$$\overline{M}_n = 800/(3 - 4P) \quad (6)$$

When 2 moles of BHET reacts completely with 1 mole of BBON, the $\overline{M}_n$ of obtained polyester is 800, thus equation 6 was deduced. The conversions of BBON can be calculated from NMR data and $\overline{M}_n$ respectively. The results are listed in Table 1. Complete conversion of BBON at 270°C within 5 min (see Table 1) indicates its high reactivity. Almost the same value of the calculated and measured

$\overline{M}_n$ implies that only addition reaction occurs without the formation of by-product during extending reaction.

Table 1 The result of chain extending reaction between PET and BBON under N_2 atmosphere

No.	Mole ratio of BHET/BBON	Temp. (°C)	Time (min)	$\overline{M}_n$		BBON Conv. ^{b)} (%)
				Calc.	Measured ¹⁾	
1	2:1	200	5	800	419	55
2	2:1	230	6	800	612	85
3	2:1	250	5	800	622	86
4	2:1	270	5	800	800	100

a) Calculated based on proton NMR data of the polyesters after extending reaction

b) Calculated based on the data of the number average molecular weight of polyesters after extending reaction

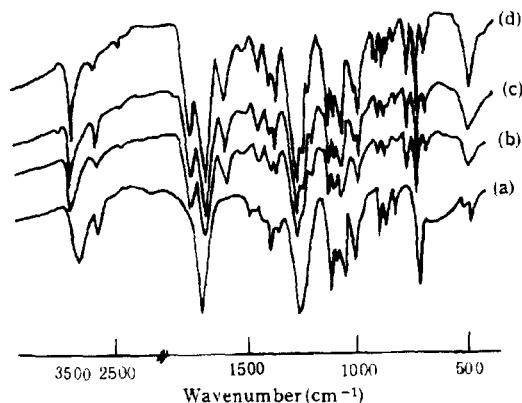


Fig. 3 IR spectra of BHET and the chain-extending reaction products

(a) BHET, (b) 200°C, 2 min, (c) 230°C, 2 min, (d) 270°C, 1 min

The reactivity of BBON with hydroxyl groups was also verified by IR spectra of the extending BHET samples (see Fig. 3). The hydroxyl absorption band of BHET at $\nu = 3300\text{cm}^{-1}$ gradually disappeared as the reaction proceeded, while the absorption peak for acylamide group at $\nu = 3500\text{cm}^{-1}$ appeared, and became stronger as the reaction temperature increased from 200°C to 270°C. The appearance of two absorption peaks at $\nu = 1683\text{cm}^{-1}$ and 1750cm^{-1} on the spectra of the samples implies the formation of acylamide and ester groups respectively during the extending reaction. According to these facts, the mechanism of extending reaction was proposed as reaction 2:

This mechanism was also confirmed by ^{13}C NMR data of the extending polyesters.

Three carbonyl absorption peaks were observed on the spectrum of the sample 4 (see Fig. 4). One peak appears at $\delta = 165.72$ ppm corresponding to carbonyl group of BHET, and another two at $\delta = 164.46$ and 157.27 ppm represent ester and acyl-amide groups respectively, which are the results of BBON ring-opening extending reaction.

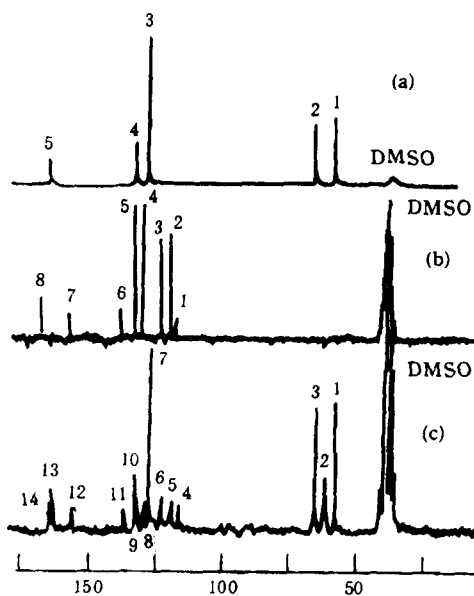
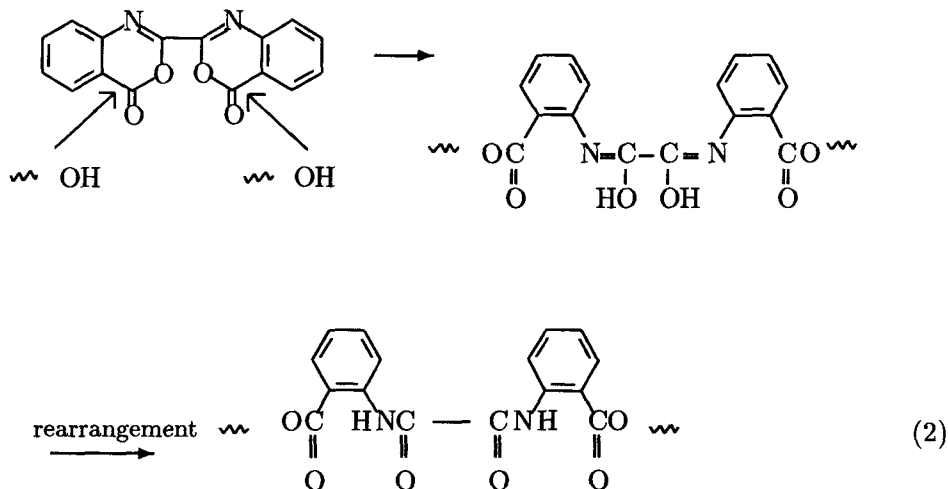


Fig. 4 ^{13}C NMR spectra of (a) BHET, (b) BBON, and (c) sample 4

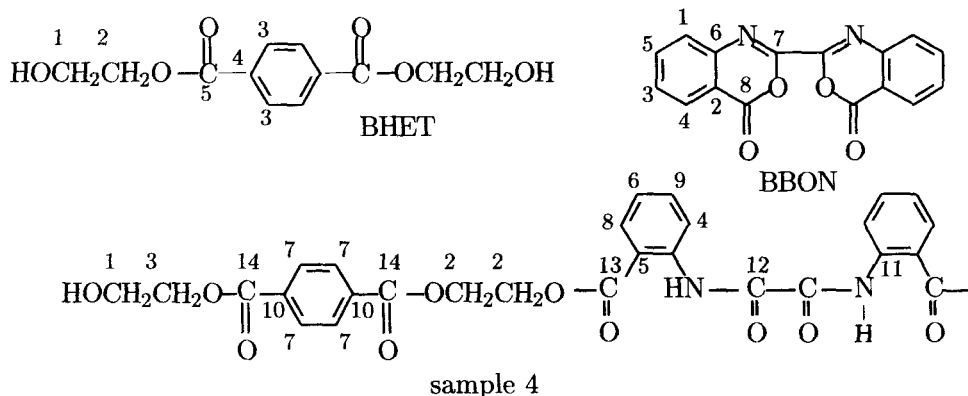
Reaction kinetics

Based on the mechanism of extending reaction, the rate of reaction (R_p) can be expressed as equation 7:

$$R_p = -d[\text{BHET}]/dt = k_2[\text{BHET}][\text{BBON}] \quad (7)$$

Because $[\text{BBON}] = [\text{BHET}]/2$

$$-d[\text{BHET}]/[\text{BHET}]^2 = 0.5k_2dt \quad (8)$$



After integration, the equation 9 was obtained:

$$Y/X = 0.5[\text{BHET}]_0 k_2 t = kt \quad (9)$$

By plotting Y/X against t , straight lines were obtained (see Fig. 5), indicating that the extending reaction is a second order reaction. The rate constants at various temperatures were obtained from the slope of each line, and were tabulated in Table 2.

Table 2 The results of extending reaction of BHET with BBON

No.	Mole ratio of BHET/BBON	Temp. (°C)	$k \times 10^3$ (s ⁻¹)
5	2:1	200	1.180
6	2:1	230	2.083
7	2:1	250	2.547
8	2:1	270	3.333

Based on Arrhenius equation 10, equation 11 was obtained after integration:

$$d \ln k / dt = E_a / (RT^2) \quad (10)$$

$$\ln k = -E_a/(RT) + \ln(0.5k_0[\text{BHET}]_0) \quad (11)$$

Where E_a is the activation energy, R is the gas constant. By plotting $\ln k$ against $1/T$, a straight line was obtained (see Fig. 6), and E_a could be obtained from the slope of the line. The low activation energy ($E_a = 28.82\text{kJ/mole}$) proves the high reactivity of BBON toward hydroxyl group.

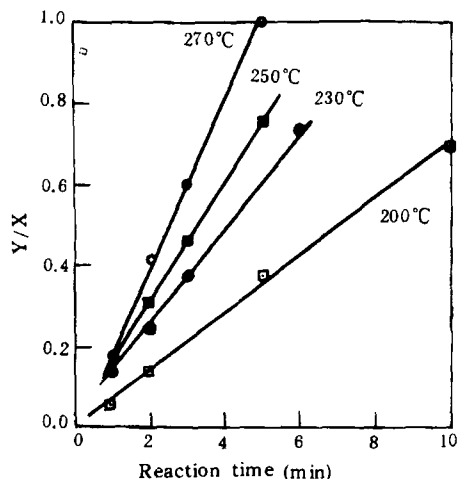


Fig. 5 The curve of Y/X against reaction time

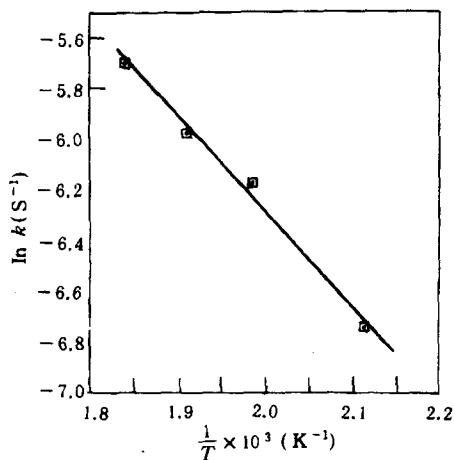


Fig. 6 The curve of $\ln k$ against $1/T$

CONCLUSION

β -Bis (hydroxyethylene terephthalate) was used as a model compound for studying the chain-extending reaction of PET with bis (4H-3, 1-benzoxazin-4-one)s. The results prove that the BBON is a highly efficient hydroxyl-reactive chain extender. Kinetics studies indicate that the extending reaction is a second order reaction with an activation energy of 28.82 kJ/mole.

Keywords:

2,2'-Bis (4H-3, 1-benzoxazin-4-one), Chain-extending reaction of PET, Mechanism, Kinetics.

REFERENCES

- [1] Shima, T.; Urasaki, T. and Oka, I., *Adv. Chem. Ser.*, **1973**, 128: 183.
- [2] Dijkstra, A.J.; Goodman, I. and Reid, J.A.W., *U.S.Pat.*, 3, 553, 157, **1971**.
- [3] Inata, H. and Matsumura, S., *J. Appl. Polym. Sci.*, **1986**, 32: 4581.