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經 Photo-fries ' 重排的新高分子型光安定劑之研究(II)

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**Kinetics and Mechanism of Photo-Fries' Rearrangement of  
Aromatic Polyester, Copolyesters and Copolyester-amides (I)**

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## ABSTRACT

Three aromatic polyesters and two aromatic polyester-amides were synthesized and characterized. They are: poly(bisphenol-A terephthalate) (PBAT), poly(bisphenol-A terephthalate-alt-ethylene terephthalate) (PBATAPET), poly(bisphenol-A terephthalate-co-ethylene terephthalate) (PBATCPET), poly(bisphenol-A terephthalate-alt-hexamethylene terephthalamide) (PBATAPHMTA) and poly(bisphenol-A terephthalate-co-hexamethylene terephthalamide) (PBATCPHMTA). Upon irradiation of ultraviolet light ranging from 275 to 360 nm, these polymers underwent intra-molecular Photo-Fries rearrangement, leading to the formation of o-hydroxybenzophenone moiety at the pendant group, which is believed to be powerful photostabilizer. Kinetic studies of these polymers were investigated using FTIR to monitor the functional group changes. Experimental results revealed a continuous  $\alpha$ -cleavage of the ester group, leading to decreases of ir absorptions at  $\nu_{C=O}$  1742  $\text{cm}^{-1}$  and at  $\nu_{C-O-C}$  1210  $\text{cm}^{-1}$ , and an increase of  $\nu_{C=O}$  absorption at 1632  $\text{cm}^{-1}$  for the formation of o-hydroxybenzophenone moiety. The kinetic data fitted a first-order of reaction, with rate constants of  $5.67 \times 10^{-3} \text{ hr}^{-1}$  for PBAT >  $4.02 \times 10^{-3} \text{ hr}^{-1}$  for PBATCPET >  $3.92 \times 10^{-3} \text{ hr}^{-1}$  for PBATAPET >  $3.90 \times 10^{-3} \text{ hr}^{-1}$  for PBATCPHMTA >  $2.78 \times 10^{-3} \text{ hr}^{-1}$  for PBATAPHMTA, respectively. Of all these polymers, poly(bisphenol-A terephthalate) indicated the highest rate constant and was expected to be the best photostabilizer.

## INTRODUCTION

That o-hydroxybenzophenone and its derivatives are effective photostabilizers have been well known in literature [1,2,3]. This study deals with the photo-fries' rearrangement on aromatic polyesters, copolyesters and aromatic copolyester-amides. Photo-fries' rearrangements of these polymers produce o-hydroxybenzophenone moiety at the pendant group which serves as a uv absorber, and therefore, these polymers are considered as effective polymeric type of photostabilizers. A comparison of the rate constants of photo-fries' rearrangement reveals their relative photostabilization capabilities. Protection of PET by these polymeric type of

photostabilizers will be evaluated in the next chapter.

## EXPERIMENTAL

### Synthesis of 4-(1-{4-[(4-chlorocarbonylbenzoyl)oxy]-phenyl}-1-methyl-ethyl)phenyl 4-chlorocarbonyl-benzoate (TBT adduct)

Terephthaloyl chloride (0.02 mole) and (n-hexane/ethyl acetate 4/6 v/v, 67 ml) were charged into a 250 ml three-necked flask, equipped with a thermometer, a CaCl<sub>2</sub> dry tube, and a magnetic stirrer. The mixture was kept at 65 °C, then the solution containing Bisphenol A (0.01 mole), triethylamine (0.02 mole) and 33ml of solvent was added dropwise. The reaction proceeded for 6 hours. The reaction mixture was filtered to remove any precipitate, and coagulated in n-hexane. The TBT adduct was filtered and dried in a vacuum oven at RT for 12 hours.

### Purification of TBT adduct

The first stage, TBT was dissolved in dichloroethane with small amount of activated carbon, and was refluxed for hours and then was filtered and coagulated from n-hexane. The purified TBT adduct was filtered and dried in a vacuum oven at room temperature for 12 hours. The second stage, TBT was dissolved in anhydrous acetone with small amount of activated carbon. The solution was refluxed for hours and filtered, then concentrated to supersaturated solution. Stored and kept at 4 °C overnight, then was filtered and rinsed with n-hexane to get the white crystal of TBT adduct. This adduct was identified with IR and <sup>1</sup>H NMR to confirm its chemical structure.

### Syntheses of Poly(bisphenol A terephthalate-alt-ethylene terephthalate) (PBATAPET)

The above TBT adduct thus obtained was dissolved in dichloroethane to make a 0.3M solution (75ml), and was added to a 500ml three-necked flask, equipped with a mechanical stirrer and a thermometer. A solution containing triethylamine (0.045mole), ethylene glycol (0.0225mole) in 75ml of dichloroethane, capped with a CaCl<sub>2</sub> dry tube was added dropwise, keeping at 75 °C. Reaction was continued for 24 hours. Then the reaction mixture was coagulated from n-hexane. Polymer thus obtained was filtered and rinsed with deionized water and ethanol, then dried in a

vacuum oven at RT overnight then was characterized.

#### Syntheses of Poly(bisphenol A terephthalate-co-ethylene terephthalate) (PBATCPET)

Terephthaloyl chloride was dissolved in dichloroethane to make a 0.3M solution (50ml), and was added to a 500ml three-necked flask, equipped with a mechanical stirrer and a thermometer. The solution of bisphenol A (0.0075mole), ethylene glycol (0.0075mole) and triethylamine (0.03mole) in 100ml of dichloroethane was capped with CaCl<sub>2</sub> dry tube and was added dropwise to the above solution, keeping at 75 °C. Reaction proceeded for 24 hours, then was coagulated and dried in vacuum oven and characterized.

#### Syntheses of Poly(bisphenol A terephthalate) (PBAT)

bisphenol A (0.0125mole) and NaOH (0.025 mole) was dissolved in 72.5 ml of deionized water. Tetra-butylammonium bromide (0.00165 mole) in 10ml deionized water was added, and placed to a 1200 ml-autoclave. Then a solution of terephthaloyl chloride (0.0125 mole) in 35 ml of dichloroethane was added quickly under vigorously stirring for 2.5min. Another batch of solution containing terephthaloyl chloride (0.0025 mole) in 7 ml of dichloroethane was added again. Vigorous stirring was continued for another 2 mins. Then the reaction mixture was coagulated from n-hexane, filtered and rinsed with deionized water and acetone, and dried in a vacuum oven at 60 °C overnight and characterized.

#### Syntheses of Poly(bisphenol A terephthalate-alt-hexamethylene terephthalamide) (PBATAPHMTA)

Similar procedure in preparing PBATAPET was employed to make PBATAPHMTA, except using hexamethylene diamine in place of ethylene glycol. PBATAPHMTA thus obtained was dried and characterized.

#### Syntheses of Poly(bisphenol A terephthalate-co-hexamethylene terephthalamide) (PBATCPHMTA)

The syntheses method was similar to that of PBATCPET, except using hexamethylene diamine in place of ethylene glycol. PBATCPHMTA thus obtained was dried and characterized.

Instruments

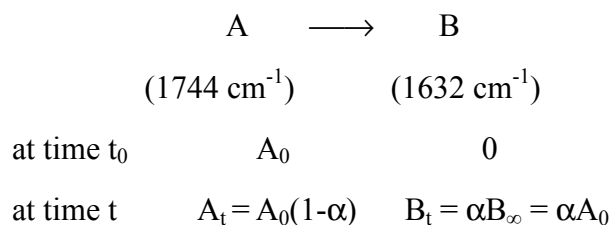
Chemical structure identifications were done with a Bruker AM-300  $^1\text{H-NMR}$  and a Nicolet 520 FTIR with a resolution of  $1\text{ cm}^{-1}$ . Solution viscosity was measured with a Ubbelohde capillary viscometer at  $25\text{ }^\circ\text{C}$ . Glass transition temperatures were obtained with Seiko SSC 5200 DSC. Thermal decomposition was tested with SEIKO TGA/DAT 200

#### Photo-Fries Rearrangement

Commercial UV lamps (UVB-313), emitting UV ranging from 275 to 360 nm with a maximum intensity at 313 nm were selected for this study. The polymer films was spin-coated on Al plates and dried, and were irradiated in a QUV accelerated weathering tester [4] with eight UVB-313 fluorescent UV lamps (with 40 watts of each lamp). The functional group changes at various time were monitored with FTIR by placing the sample in a reflecting type sample cell (Buck Scientific). The conversion,  $\alpha$ , is defined by

$$\alpha = (A_0 - A_t) / (A_0 - A_\infty) \quad (1)$$

considering:



for first –order of reaction, the rate expression can be written as

$$-\ln(1 - \alpha) = kt$$

Where  $A_0$ ,  $A_t$  are the absorbances of  $\nu_{\text{C=O}}$  before irradiation, at irradiation time  $t$ .  $B_0$ ,  $B_t$  and  $B_\infty$  are the corresponding concentrations of the specific group.  $k$  is the rate constant. The difference spectra  $A_0 - A_t$  were obtained by subtracting absorbances before irradiation from that at time  $t$ , using benzene absorption at  $1588\text{ cm}^{-1}$  as internal standard. [5]

## RESULTS AND DISCUSSIONS

The synthesized TBT adduct shows its  $^1\text{H-NMR}$  spectrum in [Figure 1](#).

Integration of peaks at  $\delta$ 8.358 to 8.387 (quartet) shows four protons on the chlorocarbonyl benzoyl phenyl ring. The peaks at  $\delta$ 7.265 to 7.4 (doublet) is attributed to eight protons on the bisphol A ring. The peaks at  $\delta$ 1.774 (singlet) is attributed to six protons on the alkyl group. [Figure 2](#) shows its FTIR spectrum. The chlorocarbonyl group occurs at  $1778\text{ cm}^{-1}$ , the other carbonyl group occurs at  $1735\text{ cm}^{-1}$ , and C-O-C stretching occurs at  $1200\text{ cm}^{-1}$ . The absorption of 1,4-disubstituted benzene ring occurs at  $1014\text{ cm}^{-1}$ . [Figure 3](#) shows the FITR spectrum of poly(bisphenol A terephthalate). Absorptions of  $\nu_{\text{C=O}}$  and  $\nu_{\text{C-O-C}}$  occur at  $1742\text{ cm}^{-1}$  and  $1208\text{ cm}^{-1}$ , respectively. The absorption of 1,4-disubstituted benzene ring occurs at  $1014\text{ cm}^{-1}$ . Missing absorption at  $1735\text{ cm}^{-1}$  indicates the disappearance of  $\nu_{\text{C=O}}$  of chlorocarbonyl group by forming polymer. The structures of poly(bisphenol A terephthalate-alt-ethylene terephthate), poly(bisphenol A terephthalate-co-ethylene terephthalate), poly(bisphol A terephthalate) and poly(bisphenol A terephthalate-alt-hexamethylene terephthalamide) were confirmed by similar spectroscopic analyses. Broad band absorption of  $\nu_{\text{N-H}}$  occurs at 3,200 to 3,500  $\text{cm}^{-1}$ , confirmed the existence of N-H bond in the polyester-amides, and absorptions of  $\nu_{\text{C=O}}$  at  $1743\text{ cm}^{-1}$  and  $1652\text{ cm}^{-1}$  are attributed to carbonyl adjacent to ester and amide group, respectively. Absorption of  $\nu_{\text{C-O-C}}$  occurs at  $1211\text{ cm}^{-1}$  and 1,4-disubstituted benzene ring occurs at  $1014\text{ cm}^{-1}$ . Missing absorption at  $1735\text{ cm}^{-1}$  indicates the disappearance of  $\nu_{\text{C=O}}$  of chlorocarbonyl group by forming polymer. [Figure 4](#) shows the FTIR spectrum of poly(bisphenol A terephthalate-co-hexamethylene terephthalamide), again, a similar absorption to poly(bisphenol A terephthalate-alt-hexamethylene terephthalamide) is noted. The inherent viscosities of these polymers are given in [table 1](#), while their thermal characterization data are given in [Tables 2 and 3](#).

[Table 1](#) Inherent viscosities of polymers prepared.

Polymer	$\eta_r$	Solvent
Poly(bisphenol-A terephthalate-alt-ethylene	1.17	1,1,2,2-tetrachloro ethane

terephthalate)		
Poly(bisphenol-A terephthalate-co-ethylene terephthalate)	1.21	1,1,2,2-tetrachloro ethane
Poly(bisphenol A terephthalate)	1.34	1,1,2,2-tetrachloro ethane
Poly(bisphenol A terephthalate-alt-hexamethylene terephthalamide)	1.18	m-Cresol
Poly(bisphenol A terephthalate-co-hexamethylene terephthalamide)	1.15	m-Cresol

**Table 2** Glass transitions temperatures of polymers from DSC thermograms

Polymer	Tg
Poly(bisphenol-A terephthalate-alt-ethylene terephthalate)	115.5
Poly(bisphenol-A terephthalate-co-ethylene terephthalate)	110.6
Poly(bisphenol A terephthalate)	154.5
Poly(bisphenol A terephthalate-alt-hexamethylene terephthalamide)	134.9
Poly(bisphenol A terephthalate-co-hexamethylene terephthalamide)	144.5
Poly(ethylene terephthalate)	73.5~74.9

**Table 3** Decomposition temperatures of polymers from TGA thermograms

Polymer	5% wt loss	Decomposition
Poly(bisphenol-A terephthalate-alt-ethylene terephthalate)	363.6	455
Poly(bisphenol-A terephthalate-co-ethylene terephthalate)	390.6	460
Poly(bisphenol A terephthalate)	314.5	475



Poly(bisphenol A terephthalate-alt-hexamethylene terephthalamide)	371.0	410
Poly(bisphenol A terephthalate-co-hexamethylene terephthalamide)	380.3	410
Poly(ethylene terephthalate)	410.8	431.3

During irradiation of ultraviolet ranging 275 to 360 nm, the intra-molecular photo-fries' rearrangement were evidenced from the continuous decreasing absorbances of  $\nu_{C=O}$  at  $1742\text{ cm}^{-1}$  and  $\nu_{C-O-C}$  at  $1210$  and  $1014\text{ cm}^{-1}$  for these polymers (Figure 5). It is noted that a newly increasing absorption of  $\nu_{C=O}$  at  $1632\text{ cm}^{-1}$ , due to the formation of o-hydroxybenzophenone moiety, is observed. Absorbance at  $1632\text{ cm}^{-1}$  of o-hydroxybenzophenone was selected for the kinetic analyses. Integration of  $A_t - A_0$  divided by  $A_\infty - A_0$  gives the conversion,  $\alpha$ , according to equation (1). In general, the kinetic data fit a first-order of reaction, up to a conversion of 60%, according to

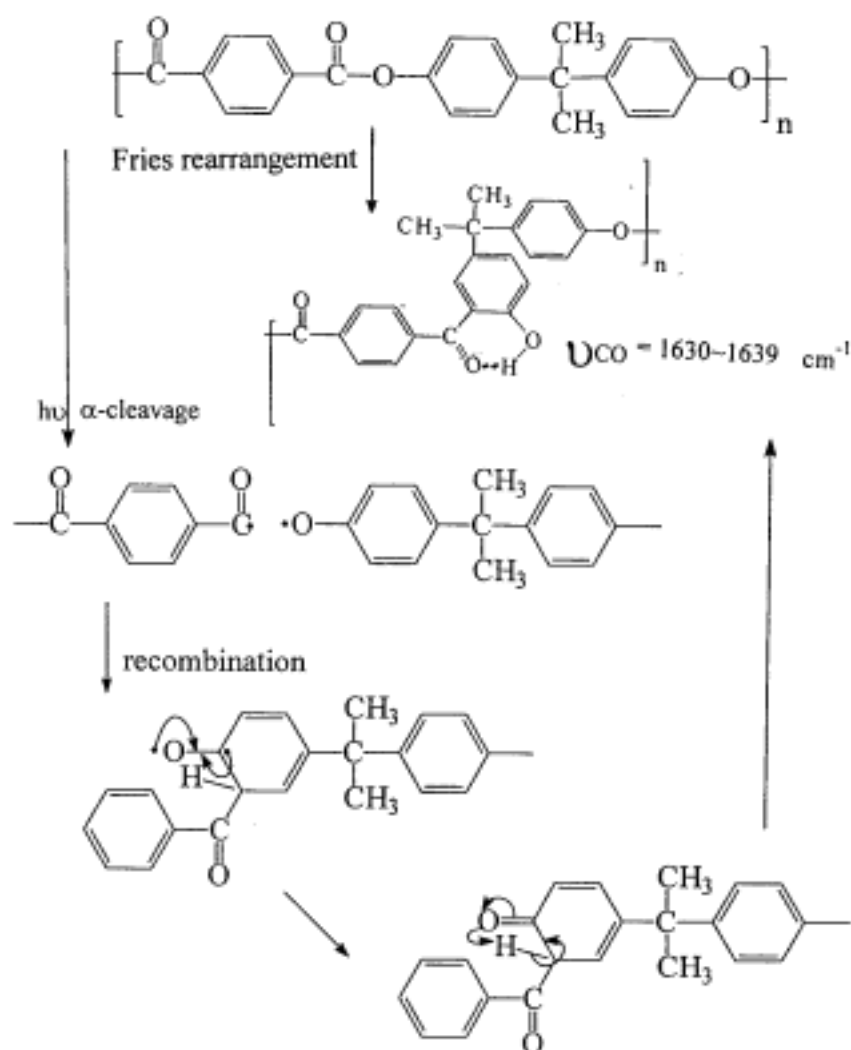
$$-\ln(1 - \alpha) = kt \quad (2)$$

where  $k$  and  $t$  represent the rate constant and irradiation time. A typical plot of  $-\ln(1 - \alpha)$  versus  $t$  for these copolymers is given in Figure 6, from which the rate constants of photo-fries's rearrangement,  $k$ 's, for these copolymers can be obtained and were given in the following order:

PBAT ( $k = 5.67 \times 10^{-3}\text{hr}^{-1}$ ) > PBATCPET ( $k = 4.02 \times 10^{-3}\text{hr}^{-1}$ ) > PBATAPET ( $k = 3.92 \times 10^{-3}\text{hr}^{-1}$ ) > PBATCPHMTA ( $k = 3.90 \times 10^{-3}\text{hr}^{-1}$ ) > PBATAPHMTA ( $k = 2.78 \times 10^{-3}\text{hr}^{-1}$ ).

It is noted that Poly(bisphenol A terephthalate) shows the highest value of rate constant, presumably because it contains larger portion of bisphenol-A terephthalate group which underwent photo-fries' rearrangement, leading to the formation of o-hydroxybenzophenone moiety. It is also noted that PBATCPET and PBATAPET (random and alternating copolymers of bisphenol-A terephthalate and ethylene

terephthalate) show higher rate constants than **PBATCPHMTA** and **PBATAPHMTA** (random and alternating copolymers of bisphenol-A terephthalate and hexamethylene terephthalamide), probably because the hydrogen bonding in copolyester-amides increased the activation energy of the solid phase photo-fries' rearrangement. Lower rate constants for alternating copolyesters and alternating copolyester-amides than the corresponding random copolyesters and random copolyester-amides are also noted, presumably, because the alternating copolymers have more regular chain package and higher crystallinity than random copolymers, and also have higher activation energy of reaction in the solid phase photo-fries' rearrangement.



The mechanism of photo-fries' rearrangement of these copolymer are given in the following scheme: [6-9] It is believed that the only product of photo-fries'

rearrangement [1,2,3] in these polymers is o-hydroxybenzophenone moiety, which is an effective uv absorber. These copolymers can be used as photostabilizer for polymers, like poly(ethylene terephthalate),...,etc. The stabilization capability is expected to increase with the rate constant of the photo-fries' rearrangement. Therefore, as the bisphenol-A terephthalate proportion increases its stabilization effect would be increase, with the PBAT possessing the most stabilization effect for all these polyesters and polyester-amides in this study.

## CONCLUSIONS

Upon irradiation of ultraviolet light ranging from 275 to 360 nm, all these copolymers underwent intramolecular Photo-Fries rearrangement, leading to the formation of o-hydroxybenzophenone moiety in the pendant group. This result was evidenced from the continuously increasing absorbance of  $\nu_{\text{C=O}}$  at  $1632\text{ cm}^{-1}$ , due to the formation of o-hydroxybenzophenone moiety. Plots of  $-\ln(1-)$  versus time revealed a first-order reaction. Poly(bisphol-A terephthalate) showed the highest value of rate constant because it contains the largest portion of bispheno-A terephthalate. Copolyester-amides generally showed lower rate constants than the corresponding copolyesters because copolyester-amides contain intermolecular hydrogen bonding and increased the activation energy in the solid phase photo-fries' rearrangement. Alternating copolyester and alternating copolyester-amide indicated lower rate constants than the corresponding random copolyester and random copolyester-amide because the alternating copolymers have more regular molecular array in the solid state, and hence contain higher crystallinity, therefore, leading to increase of the activation energy of reaction.

## ACKNOWLEDGEMENT

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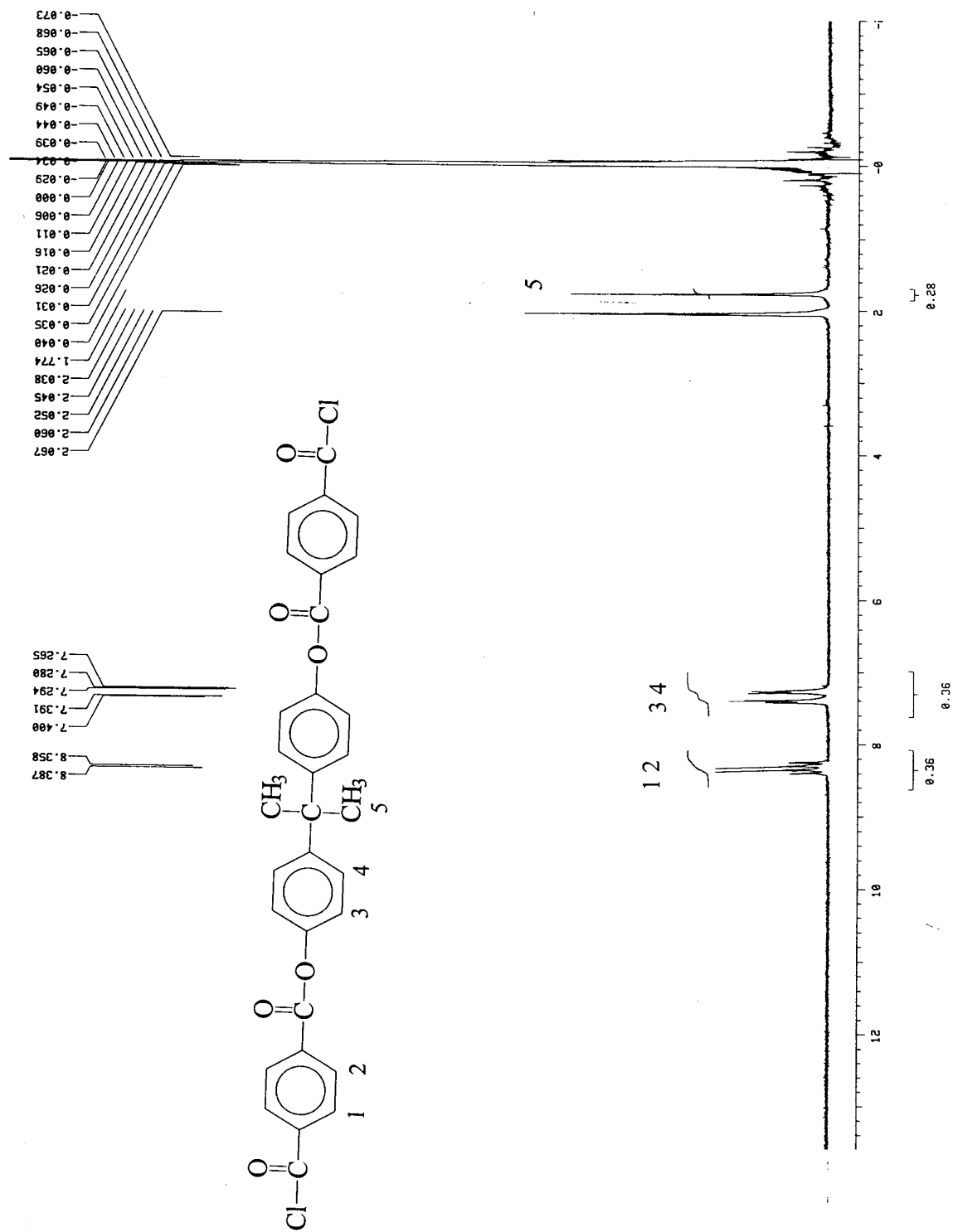


Figure 1  $^1\text{H}$  NMR spectrum of TBT adduct.

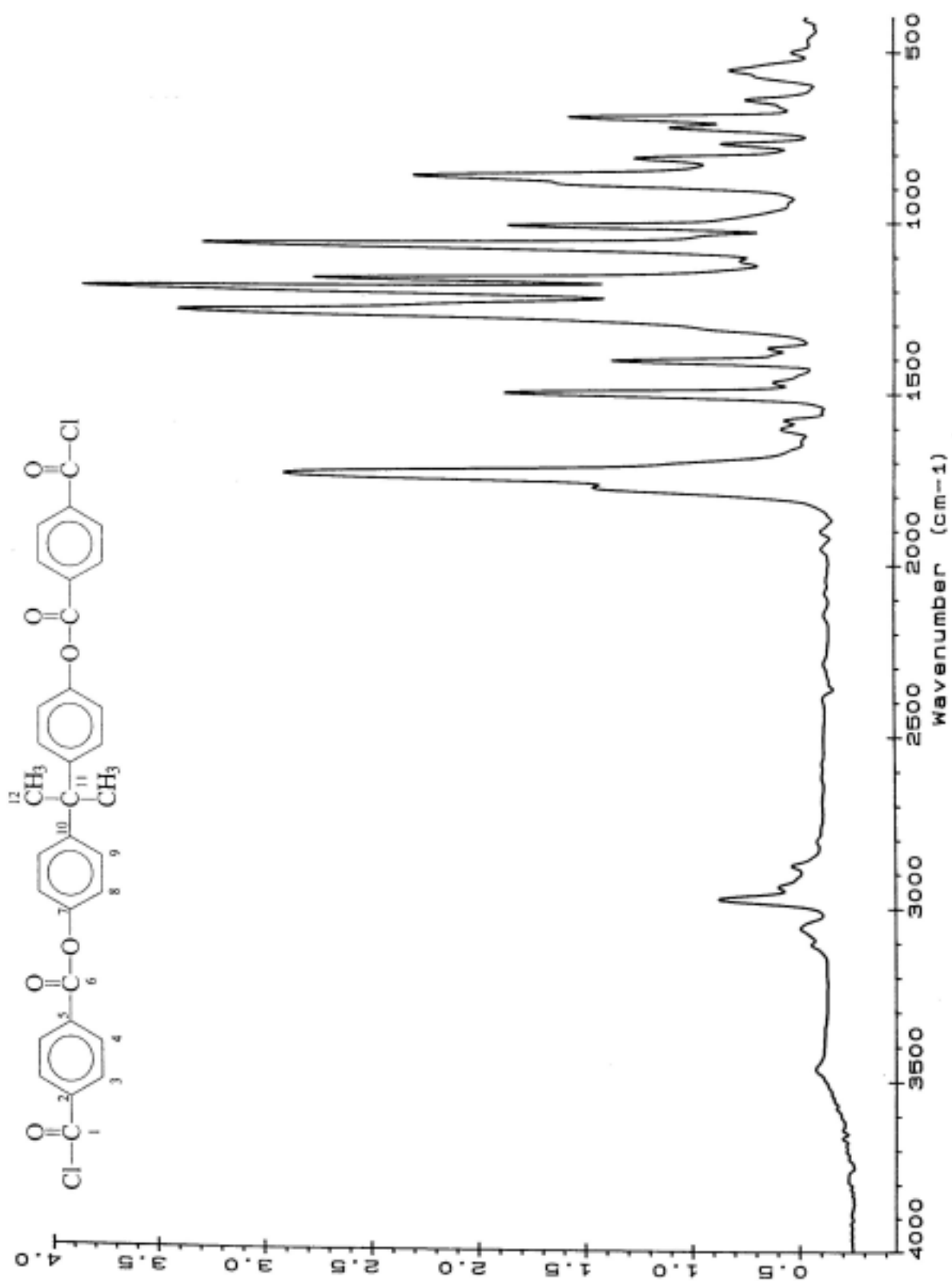


Figure 2 FTIR spectrum of TBT adduct.

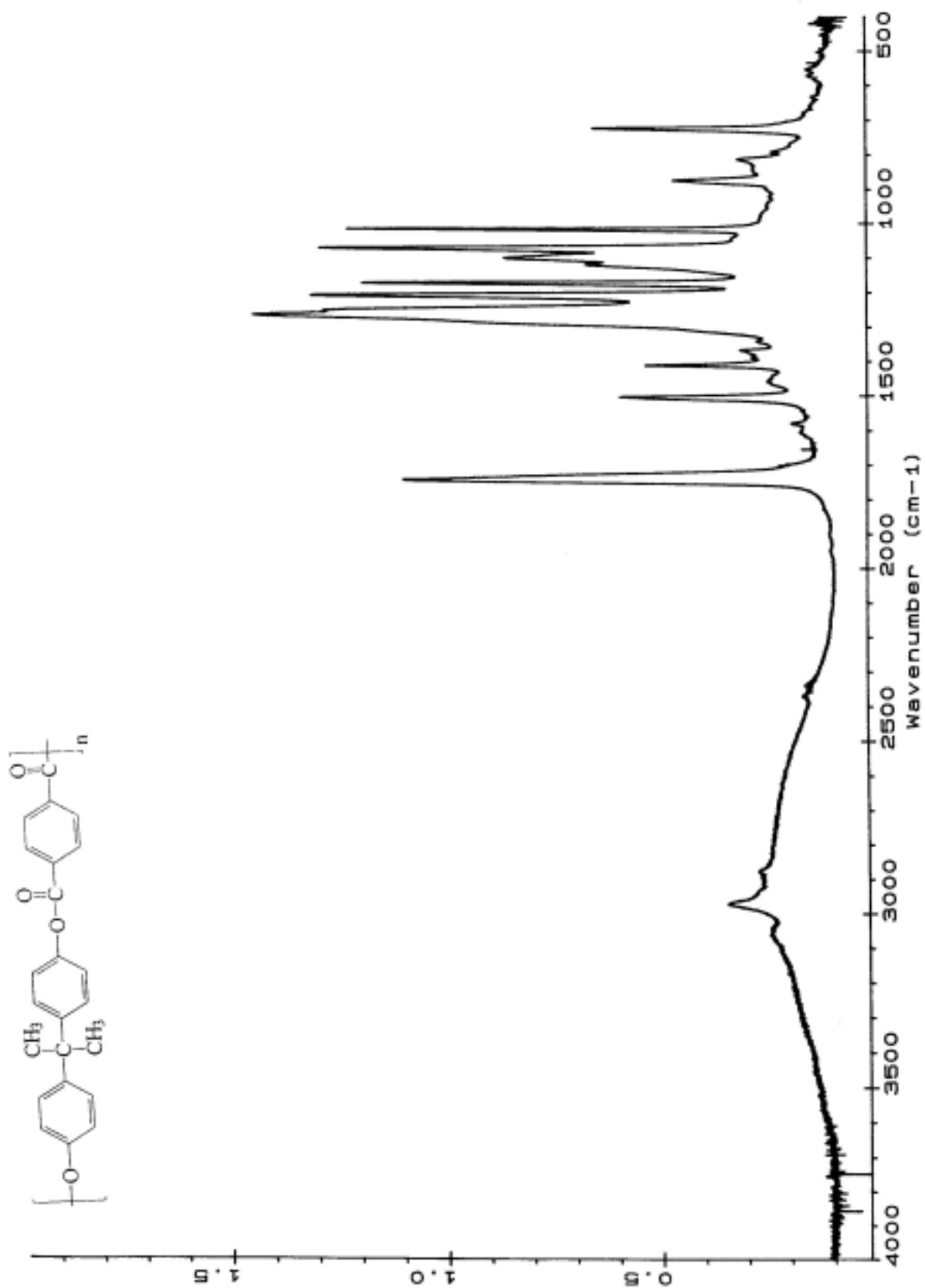


Figure 3 FTIR spectra of poly(bisphenol A terephthalate).

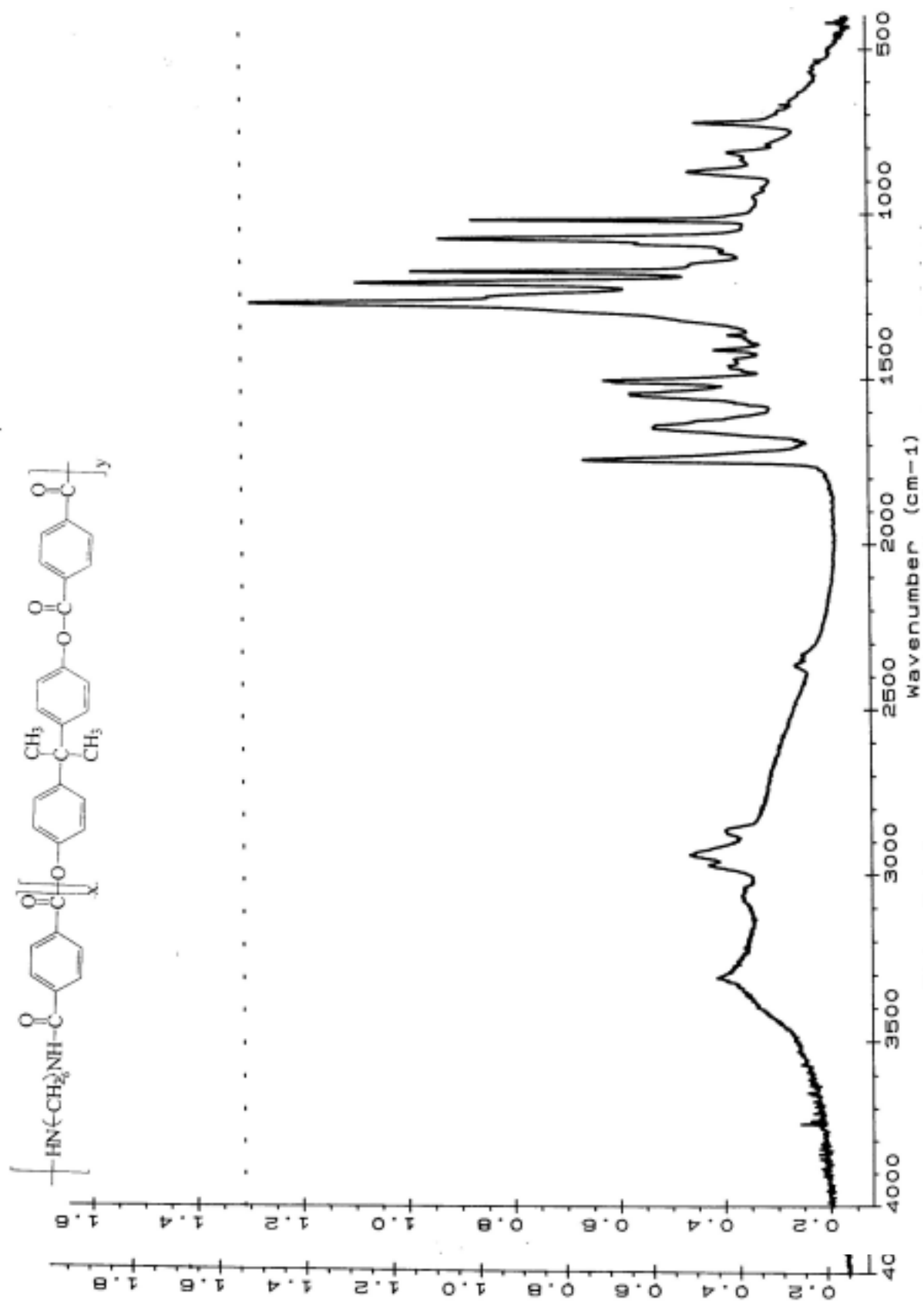
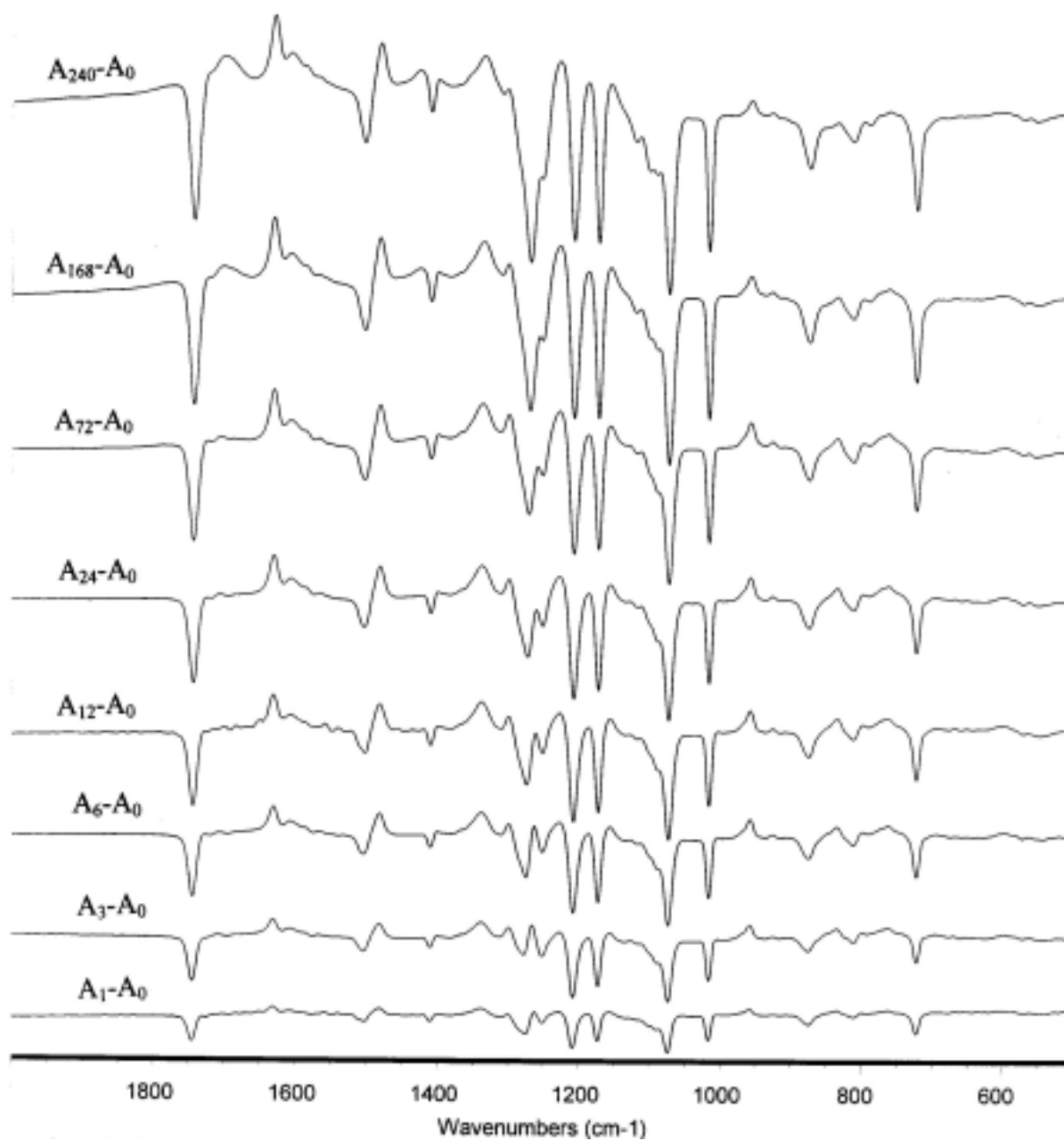
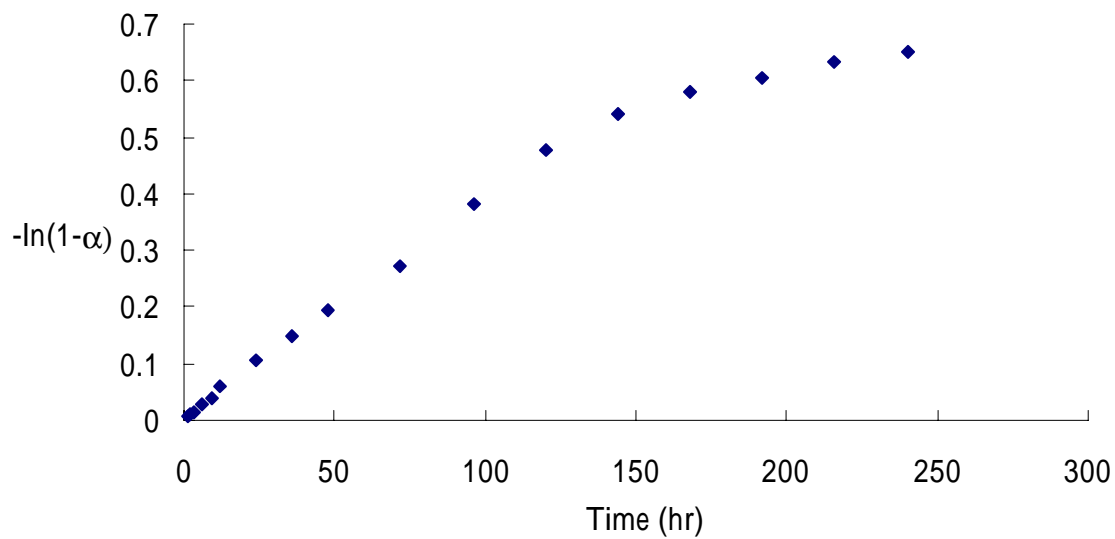


Figure 4 FTIR spectra of poly(bisphenol A terephthalate-co-hexamethylene terephthalamide).





**Figure 5** Typical difference spectra of poly(bisphenol-A terephthalate-co-ethylene terephthalate),  $A_t - A_0$  ( $t$  in hours), using benzene absorbance at  $1588\text{ cm}^{-1}$  as internal standard.



**Fig. 6 Typical plot of  $-\ln(1-\alpha)$  versus time  $t$  during photo-fries' rearrangement.**