

Thermal analysis of polyarylene ether sulfones and polyimides ^α

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Abstract

Some results on the thermal analysis of polyimides and polyaryl ether sulfones, some reactions and the purity determination of the monomers, and the thermal stability and kinetic analysis of the thermo-oxidative degradation of these polymers are described.

INTRODUCTION

After more than 20 years of sustained research, polysulfones and polyimides still play an important role in the development of heat-resistant aromatic/heterocyclic polymers [1,2]. Thermal analysis techniques are available for studying thermal properties of these polymers.

The present paper deals briefly with some results on the thermal analysis of the monomers and polymers in our laboratory in recent years.

EXPERIMENTAL

A Model CDR-1 differential scanning calorimeter (Shanghai Tienping Instrument Factory) was used to determine the purity of monomers. The conditions were as follows: heating rate, $0.5^{\circ}\text{C min}^{-1}$; chart speed, 1200 mm h^{-1} when approaching the melting points; sample weight, 2 mg; sensitivity, 4.184 mJ s^{-1} . The temperature and calorimetric calibration were carried out with high purity indium as standard. The same instrument was also used to measure differential thermal analysis (DTA) and differential scanning calorimetry (DSC) curves for observing reactions of monomers and polymers: heating rate, 5 or $10^{\circ}\text{C min}^{-1}$; sample weight, 5 mg; sensitivity for DTA, $\pm 100\text{ }\mu\text{V}$; sensitivity for DSC, $\pm 20.92\text{ mJ s}^{-1}$ ($\pm 5\text{ mcal s}^{-1}$).

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A Model LCT-1 differential thermobalance (Beijing Optical Instrument Factory) was employed to measure TG curves: heating rate, $5^{\circ}\text{C min}^{-1}$; sample weight, 10 mg.

Thermomechanical analysis (TMA) experiments were carried out with an RJY-80 thermomechanical analyzer (Chengde Test Machine Factory): heating rate, $2.6^{\circ}\text{C min}^{-1}$; load, 18 kg cm^{-2} .

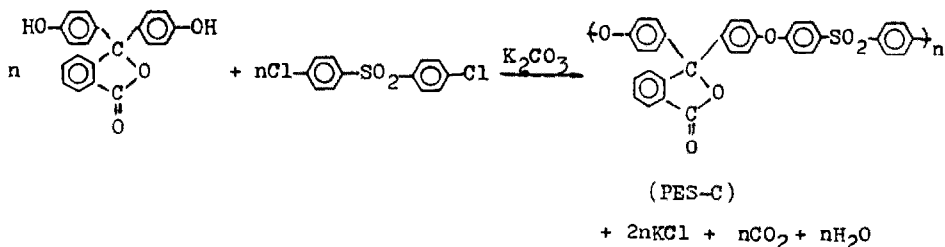
A Model 2305 gas chromatograph (Beijing Analytical Instrument Factory) was used to obtain pyrolysis gas chromatograms. Experimental conditions were as follows: pyrolysis temperature, 650°C ; pyrolysis time, 2.5 min; sample weight, $0.5 \pm 0.05\text{ mg}$.

RESULTS AND DISCUSSION

Reactions and purity determination of monomers of heat-resistant polymers

A new type of polysulfone and purity determination of the monomers

A new type of polyarylene ether sulfone with a cardo side-group (PES-C) was synthesized by a new one-step method. The reaction is shown below:



The advantages of the new method are lower reaction temperature, shorter reaction time for polycondensation, higher molecular weight and higher yield, compared with existing methods.

PES-C has many superior properties, such as thermostability, hydrolysis resistance under water vapor and corrosion resistance against chemicals. It has a glass transition temperature ($T_g = 260^{\circ}\text{C}$) higher than those of other kinds of polysulfone ($T_g = 190\text{--}220^{\circ}\text{C}$). It is employed in many fields as film, plate, pipe, fiber and other structural forms.

The key to this polycondensation reaction is to maintain the stoichiometry of the monomers, 4,4'-dichlorodiphenyl sulfone and phenolphthalein, in the reacting system. In other words, monomers of high purity are required. The results in Table 1 show that the purity of 4,4'-dichlorodiphenyl sulfone has a marked effect on the polycondensation rate as well as on the viscosity of the polymers. For instance, with 4,4'-dichlorodiphenyl sulfone of different purities, such as 99.0 and 99.9 mol.%, by reaction with phenolphthalein by the one-step method, polymers with $\eta_{\text{sp}} = 0.36\text{ c}$ and $\eta_{\text{sp}} = 0.62\text{ c}$ respec-

TABLE 1

Effects of purity of 4,4'-dichlorodiphenyl sulfone on the polycondensation rate and molecular weight of polysulfones

Monomer quality	Purity of monomers by DSC method (mol.%)	Polycondensation		Viscosity of polymers η_{sp} (c)
		Temp. ($^{\circ}$ C)	Time (h)	
Crude sample	—	210	10	Very low
Recrystallized twice from ethanol	99.0	210	8	0.36
Recrystallized three times	99.9	210	5	0.62

tively are obtained. DTA and DSC curves of monomers of different purities were determined with a CDR-1 differential scanning calorimeter, as shown in Figs. 1 and 2. Crude 4,4'-dichlorodiphenyl sulfone showed two peaks, at

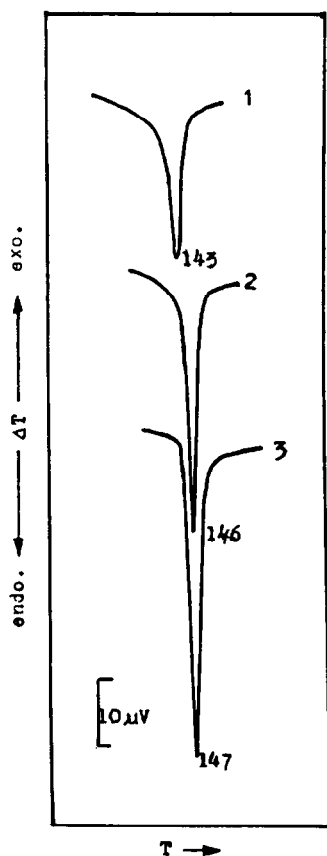


Fig. 1. DTA curves of 4,4'-dichlorodiphenyl sulfone recrystallized from ethanol: curve 1, once; curve 2, twice; curve 3, three times.

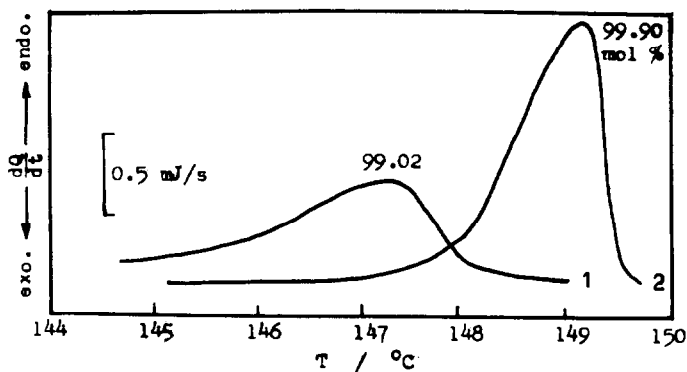
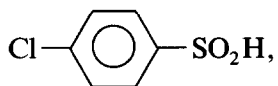


Fig. 2. DSC curves of 4,4'-dichlorodiphenyl sulfone recrystallized from ethanol: curve 1, twice; curve 2, three times.

91°C and at 131°C (see Fig. 3, curve 1); the former is attributed to an impurity, 4-chlorobenzenesulfonic acid



the melting point of which is 93°C [3]. Curve 2 in Fig. 3 is the DTA curve of a sample obtained from a cold extract in ethanol. The presence of a peak at 90°C is associated with the impurity.

Determination of the purity of the monomers by DSC is based on the van't Hoff equation

$$T_s = T_0 - \frac{RT_0^2 x}{H_f} \cdot \frac{1}{F}$$

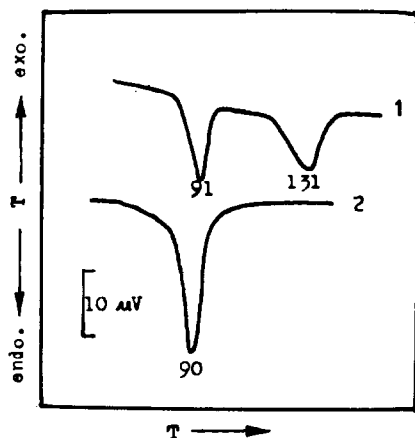


Fig. 3. DTA curves of crude 4,4'-dichlorodiphenyl sulfone sample (curve 1) and of sample obtained from cold extract in ethanol (curve 2).

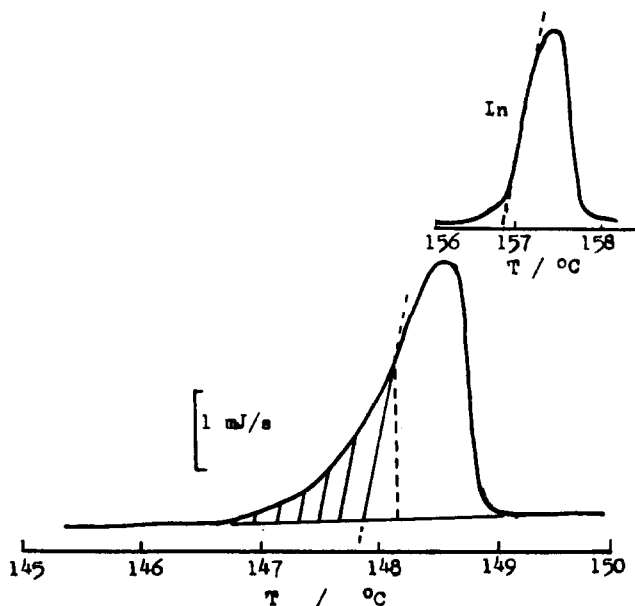


Fig. 4. DSC curves of 4,4'-dichlorodiphenyl sulfone and indium.

where T_s is the sample temperature (K), T_0 the melting point (K) of the pure sample, R the gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), x the mole fraction of impurity, H_f the heat of fusion (J mol^{-1}) of the pure major component and F the area fraction of DSC melting curve at T_s . A typical DSC melting curve and a plot of the sample temperature T_s versus the reciprocal area fraction $1/F$ of 4,4'-dichlorodiphenyl sulfone recrystallized three times from ethanol are shown in Figs. 4 and 5.

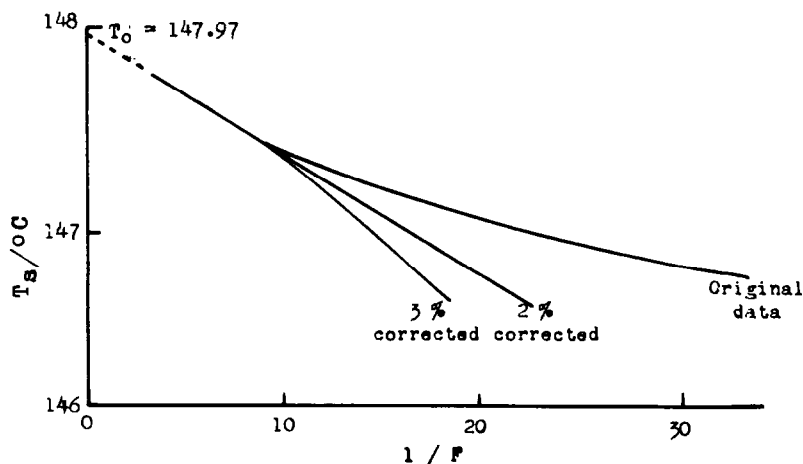
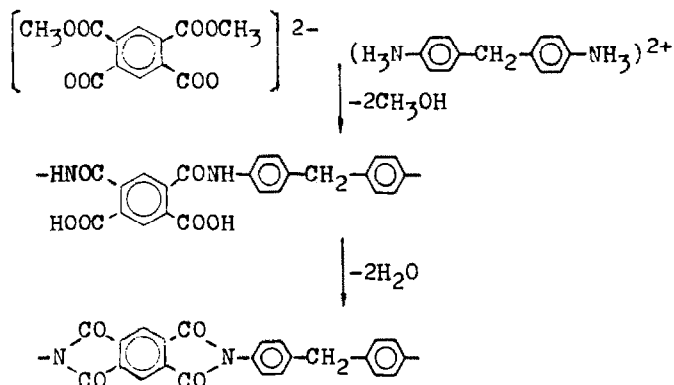


Fig. 5. Plot of T_s vs. $1/F$ for 4,4'-dichlorodiphenyl sulfone.



The main points of this method are that the sample temperature should be programmed from well below the melting point at a slow heating rate ($0.5^\circ\text{C min}^{-1}$) and the sample size should be small (about 2.0 mg) to ensure the thermal equilibrium of the sample being analyzed. Using a closed container, this method is suitable for determinations of the purity of monomers with little sublimation or vaporization when heated. For example, the purity values determined in this method for 4,4'-dichlorodiphenyl ketone and phenolphthalein are 99.7 mol.% and 98.94 mol.% respectively.

Amidation and imidization (A-I) reaction of amine salts of aromatic tetracarboxylic acids, their esters and a diamine

The main findings on the A-I reaction for amine salts of aromatic tetracarboxylic acids and a diamine are as follows [4].

- (1) The extent of cyclization estimated from TG data is 87–93 mol.%.
- (2) The A-I processes are obviously not segregative and the imidization process closely follows the amidation reaction.

For diamine salts of partially esterified aromatic tetracarboxylic acids, which are formed as bis esters according to the thermogravimetric (TG) data, the A-I reaction with diaminodiphenylmethane as an example is as follows:

We have determined the TG and DSC curves of several amine salts, as shown in Figs. 6 and 7. The results from the TG and DSC curves for these amine salts are listed in Table 2.

Both the reaction temperature range and the apparent activation energy of diamine salts of partially esterified aromatic tetracarboxylic acids are lower than those of diamine salts of aromatic tetracarboxylic acids (as mentioned above). Also, it can be seen that the polyimides formed from amine salts are excellent heat-resistant polymers, their initial temperature of decomposition being near 500°C .

TABLE 2

TG and DSC studies of the A-I reaction for several salts of partially esterified aromatic tetracarboxylic acids and a diamine

Abbreviated symbol of salt	Structural formula	DSC A-I		TG A-I		A-I activation energy E (mJ mol ⁻¹)
		Peak temp. (°C)	Temp. range (°C)	Temp. range (°C)	temp. range (°C)	
B ₂ j		124, 140	115-156	124.7-272	46	
L ₂ j		117-127	109-145	111.2-261.5	42	
LB ₂ j		117	108-149	104.5-285.6	51	
L ₂ 'j		142.5	109-167.5	107.4-266.3	43	
T ₂ j		148	110-170	97.7-273	109	

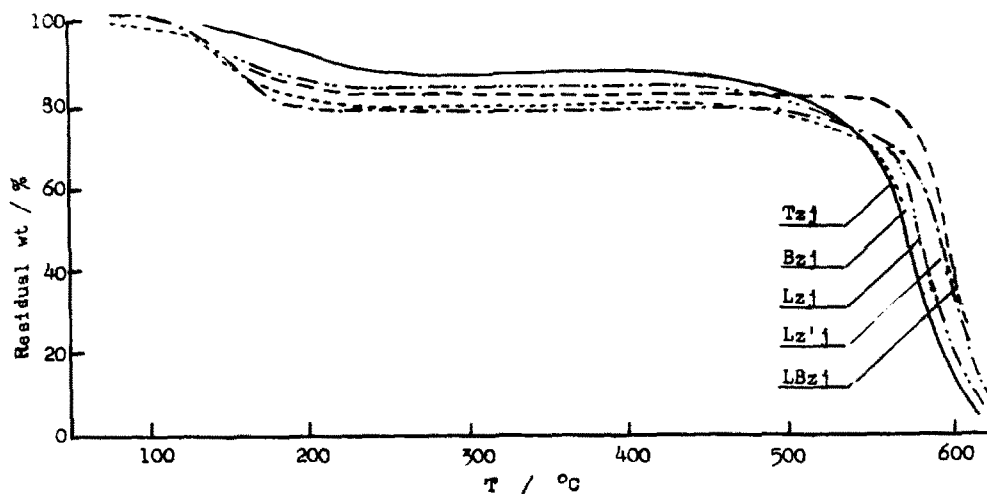


Fig. 6. TG curves of diamine salts of partially esterified aromatic tetracarboxylic acids.

Thermal stability of polyimides

Thermo-oxidative stability of polyimides

The TG curves and DTA curves for the different polyimides have been recorded in air and in nitrogen. Some of the results in air are shown in Table 3. From these results we can draw the following conclusions. (1) When the

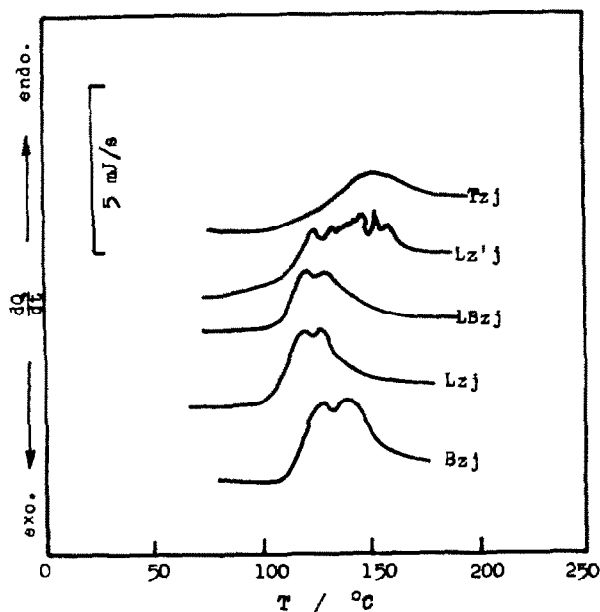


Fig. 7. DSC curves of diamine salts of partially esterified aromatic tetracarboxylic acids.

TABLE 3

TG data of polyimides of different structures

No.	Structural formula	Temp. for given wt. loss (°C)			Wt. loss at given temp. (%)		
		10%	20%	30%	350°C	450°C	550°C
		I		567	588	598	-
II		554	574	588	-	-	9
III		568	585	590	-	-	6.5
IV		550	574	588	-	-	10
V		544	565	581	-	-	12.5
VI		496	544	569	-	3.5	22
VII		489	531	550	-	5	30
VIII		468	484	502	-	4.5	39
IX		419	458	515	-	18	47
X		352	382	409	9.5	47	89

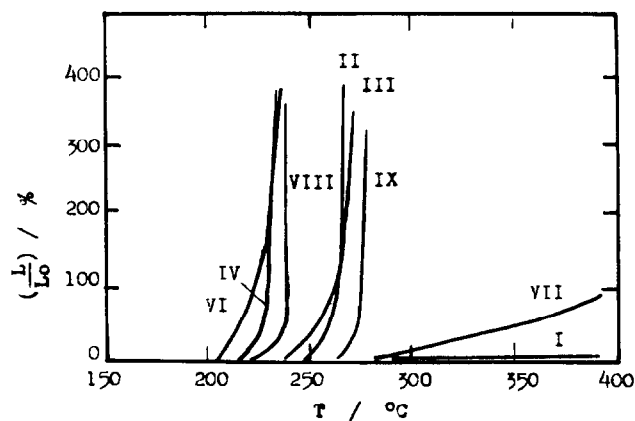


Fig. 8. Thermomechanical curves of polyimides.

oxygen bridge $-O-$ (II, IV) in the dianhydride is replaced by the thioether bridge $-S-$ (III) or the sulfone linkage $-SO_2-$ (V), no obvious change is observed in the dynamic TG curves. However, from the kinetic study discussed below, the apparent activation energy of thermal degradation for III is rather low, because the bond energy between aromatic carbon and sulfur atoms is low. (2) Polyimide IX has a lower thermal stability than the others because the dianhydride, from which the polyimide is derived, contains alicyclic rings and methylene linkages in the chain. (3) In the presence of an aliphatic chain in the backbone (VI, VII, IX, X) the longer the aliphatic chain the less thermally stable it is.

Moreover, the physico-thermal stability of polymers can also be estimated from TMA curves. Figure 8 illustrates some of the TMA curves of polyimides.

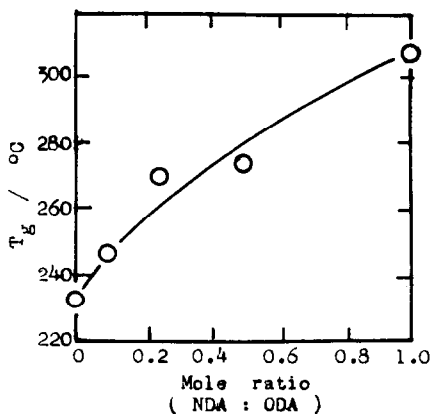


Fig. 9. The T_g of different copolyimides.

From the TMA curves it can be seen that the polyimides (II, III), prepared from 3,3',4,4'-diphenyloxidetetra-carboxylic acid and 3,3',4,4'-diphenylsulfidetetra-carboxylic acid, instead of pyromellitic acid, with 4,4'-diaminodiphenyloxide, have an obvious glass transition T_g at 255°C and 250°C respectively. In the case of polyimide IV, the T_g is 230°C. These polyimides with ether or thioether linkages are fusible. The T_g of polypyromellitimide is 400°C, determined by a linear thermodilatometer. The compound does not melt at high temperature. By copolycondensation of a diamine and a dianhydride with different chain rigidities, T_g could be adjusted over a wide temperature range. For instance, by copolycondensation of 3,3',4,4'-triphenyldioxidetetra-carboxylic acid with two diamines, 4,4'-diaminodiphenyloxide (ODA) and diamionaphthalene (NDA), T_g is increased from 234 to 308°C on increasing the diamionaphthalene concentration in the copolymers (Fig. 9).

Cross-linking reaction of polyimides at high temperature

A study of cross-linking reactions of aromatic heterocyclic polymers, which could take place at high temperature, is important in their processing and application. The cross-linking leads to double peaks on the DTA curve at 550–570°C and a break in the TG curve at the same temperature for the polyaryl sulfone, as proved by dissolution testing [5].

The cross-linking reaction for aromatic heterocyclic polymers after thermal treatment has been observed from the obvious increase in the glass

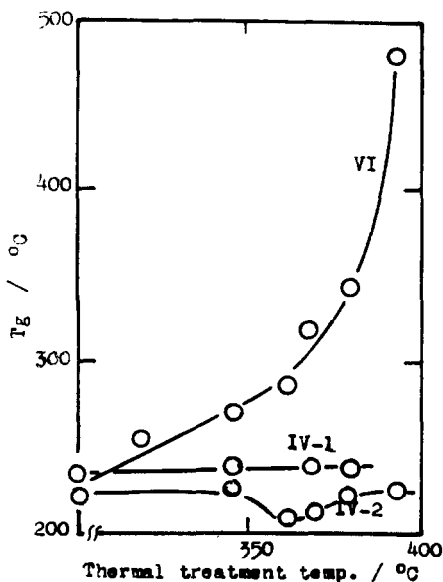


Fig. 10. The T_g of polyimides after thermal treatment at different temperatures in air: IV-1, high molecular weight sample; IV-2, low molecular weight sample.

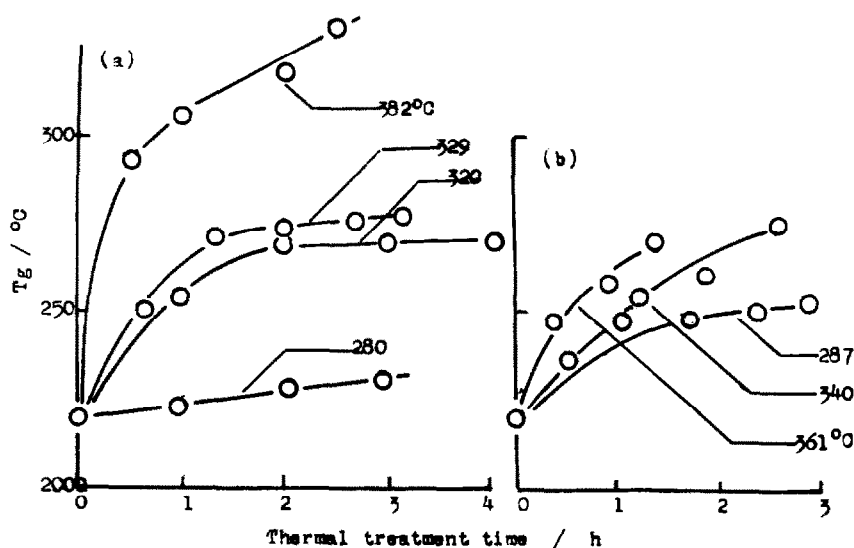


Fig. 11. The cross-linking rate of polyimide IV with time at different temperatures in air (a) and in nitrogen (b).

transition temperature T_g , as determined by the TMA curve. The increase in T_g has been used as a measure of the cross-linking rate. Some polyimide samples were heated in air at a given temperature for 1 h, and then the T_g change was determined (Fig. 10). The result indicated that the cross-linking reaction takes place more easily for VI than for IV.

The T_g changes for sample VI heated either in air or in nitrogen at 280–390°C for different periods were examined by means of TMA curves (see Fig. 11). The results show that the cross-linking reaction caused by the thermal treatment is dominant for polyimides.

From pyrolysis gas chromatography, it is shown that the toluene content in the pyrolysis products decreased with increasing time of thermal treatment, because dehydrogenation cross-linking has taken place between methylene groups in addition to the combination of phenyl groups.

The assignment of certain peaks on thermal analysis curves for polyimides

The distinction between the DTA and DSC curves for organic compounds, such as macromolecular materials, is not as obvious as for inorganic materials. It is difficult to assign certain peaks on the thermal analysis curves. As a scientific study, one can design a heating-cooling cycle to differentiate a reversible reaction of a material from an irreversible one. We have used a similar method in thermal analysis by using repeated heating-cooling cycles to eliminate peaks due to irreversible reactions. Peaks were assigned according to the chemical composition of the material. We called this method the heating-eliminating method [6]. It is undoubtedly an effective method for the explanation of reaction processes on heating a material.

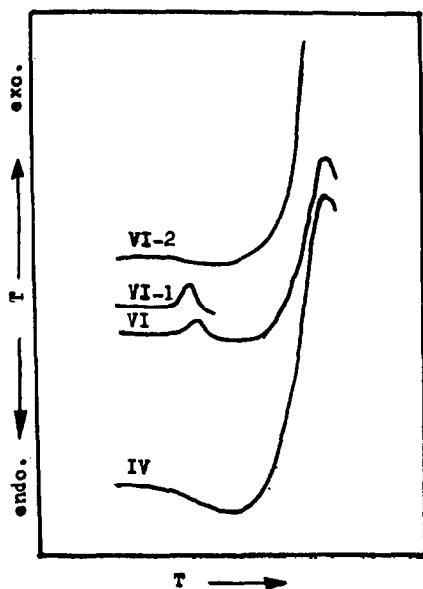


Fig. 12. DTA curves for poly-*p*-triphenyldioxidetetracarboxyl-4,4'-diphenyl ether imide (IV) and poly-*p*-triphenyldioxidetetracarboxyl-4,4'-diphenylmethane imide (VI).

The nature of the first exothermic peak on the thermal analysis curves for polyimides has been determined successfully with this method by comparing the results from different chemical structures and different chemical composition ratios. For example, when the diphenyl ether in the polyether imide IV is replaced by diphenylmethane (VI), a new exothermic peak at 305°C is observed on the DTA curve, but it disappears when the same sample is

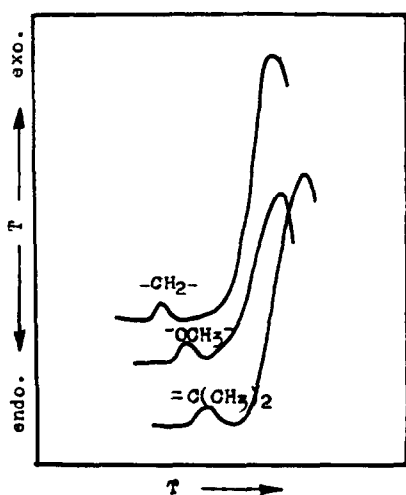


Fig. 13. DTA curves for some polyimides containing aliphatic groups.

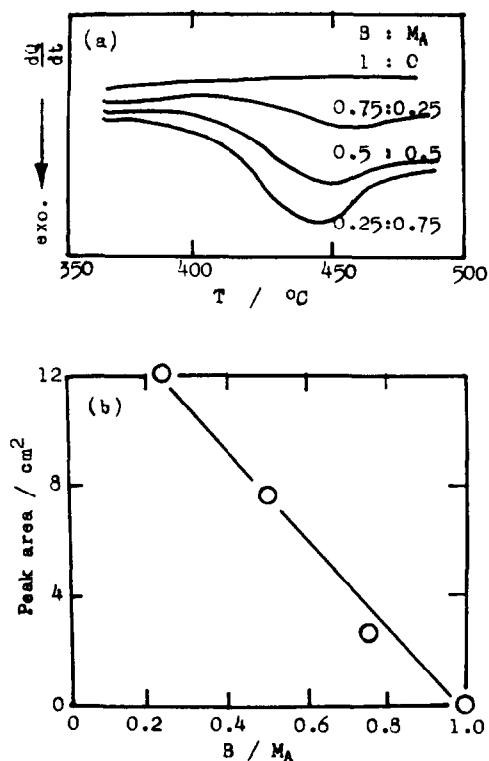
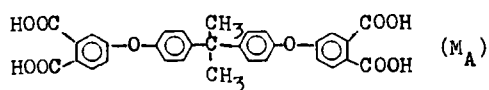


Fig. 14. (a) DSC curves of copolyimides; (b) relationship between oxidative peak area and copolymer composition.

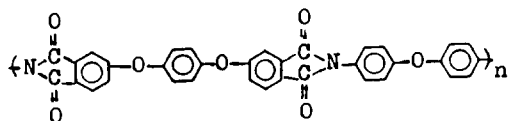
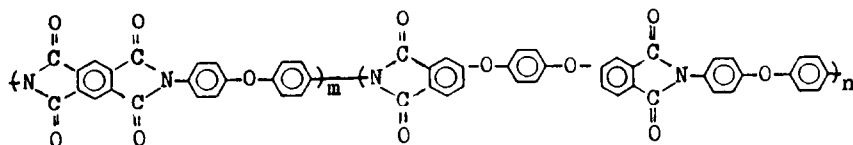
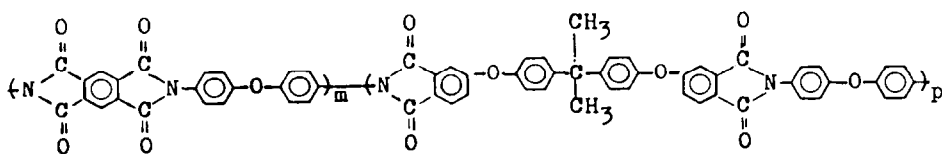
subjected to a second heating-cooling cycle (see Fig. 12). This peak can thus be assigned to the oxidation of the $-\text{CH}_2-$ group.

Similar phenomena were also observed for polyimides with methoxy ($\text{CH}_3\text{O}-$) and isopropyl ($-\text{C}(\text{CH}_3)_2-$) groups. For simplicity, characteristic aliphatic groups only are shown in Fig. 13 (the chemical structure of the polyimide with a methene group differs slightly from VI in Fig. 12). The respective peaks at 322°C , 394°C and 437°C on the thermal analysis curves correspond to the oxidation of the methyl, methoxy and isopropyl groups in the polymers.

Figure 14 indicates the first exothermic peaks on the DSC curves for copolyimides synthesized from



and pyromellitic acid (B) with diaminodiphenyl ether. The peaks are due to the oxidation of the aliphatic groups.

M_2m (IV)

 BmM_2m

 BmM_Am


Pyrolysis gas chromatography of copolyimides

Studies in the analysis of volatile degradation products of polyimides have been reported in the literature [1]. The CO, CO₂, H₂O, NH₃ and HCN usually found in the pyrolysis products could not be identified in our experiments, but the hydrocarbons benzene and toluene, phenylnitrile, phenylamine, phenol and diphenyl ether were found in the pyrolysis products and identified by mass spectrometry.

The structures of the homopolymers and copolymers being studied are as follows.

A typical pyrolysis gas chromatogram is given in Fig. 15. The results indicate that (1) pyrolysis processes for both homopolyimides and copolyimides are random degradations, (2) the pyrolysis product diphenyl ether originates from the diamine component in the polyimide, (3) the relative contents of the components in the pyrolysis products are closely related to the copolymer composition. For example, the phenol content (%) increases with the copolymer composition (or M_A/B). As shown in Fig. 16, the higher the phenoxy group content in the polymer, the higher the phenol content in the product.

Kinetic analysis of thermo-oxidative degradation for polyimides and polyaryl ether sulfone

The thermal degradation energies for polyimides and polyaryl ether sulfone have been determined at different heating rates and also at several

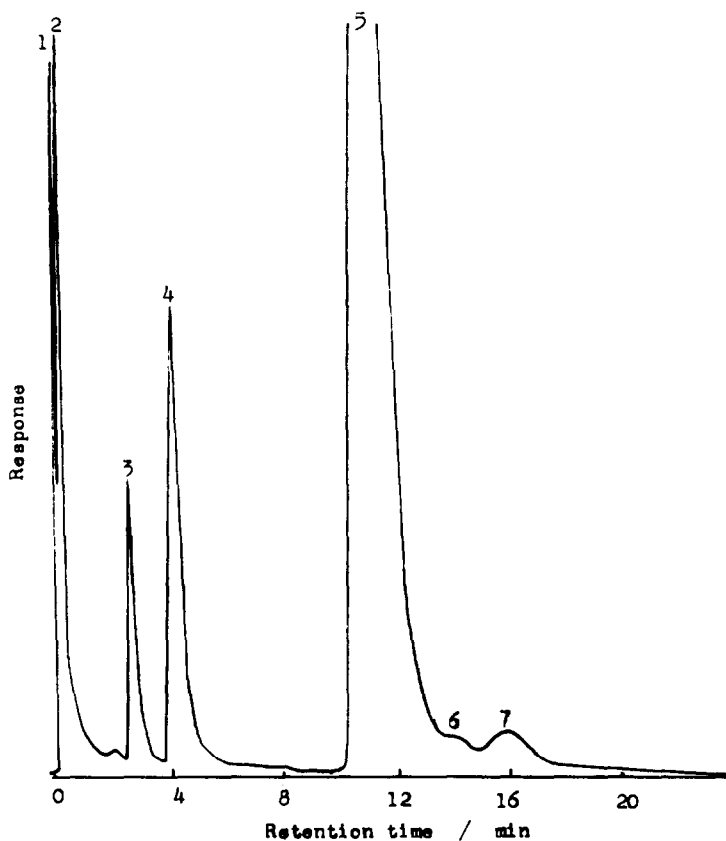


Fig. 15. Pyrolysis gas chromatogram of polyether imide IV: peak 1, hydrocarbon; peak 2, benzene; peak 3, phenylnitrile; peak 4, phenylamine; peak 5, phenol; peak 6, diphenyl ether; peak 7, cresol.

constant temperatures. It has been found that the activation energies of thermo-oxidative degradation are not constant throughout the entire process (see Figs. 17 and 18). It is apparent that the overall process is not controlled

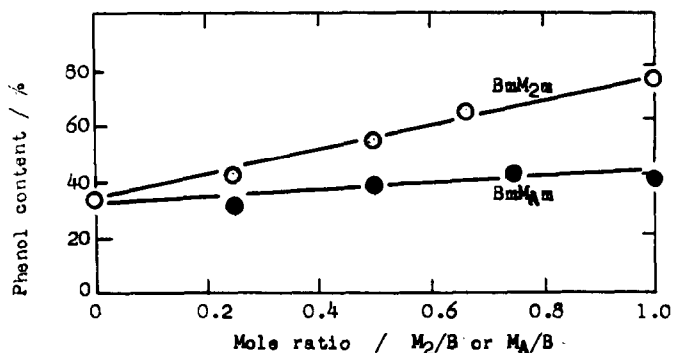


Fig. 16. Phenol content in pyrolytic gases of copolyimides from two aromatic dianhydrides.

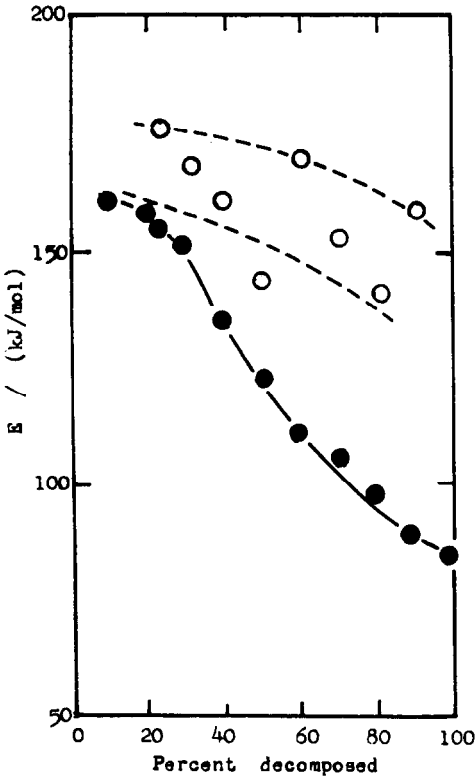


Fig. 17. Decrease in apparent activation energies of thermo-oxidative degradation of polyimide I at increasing extents of pyrolysis: ●, dynamic heating data; ○, constant temperature data.

by a simple reaction; thus the kinetic equation is not universally applicable to the entire process. It is difficult to differentiate the reactions by the TG curves. However, the activation energies of thermal degradation of these

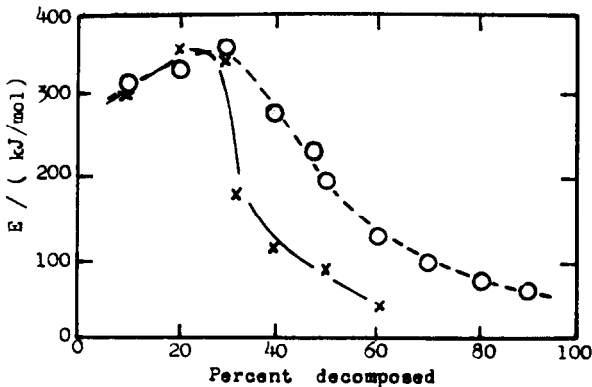


Fig. 18. Change in apparent activation energies of thermo-oxidative degradation of polyarylene ether sulfone at increasing extents of pyrolysis: ×, Friedman method; ○, Ozawa method.

TABLE 4

Apparent activation energy E_a for the thermal degradation of polyimides

No. ^a	E_a (kJ mol ⁻¹)
I	289 ± 8
II	251 ± 25
III	201 ± 17
IV	297 ± 21
V	-
VI	531 ± 38
VII	427 ± 42
VIII	322 ± 42
IX	180 ± 4
X	251 ± 13

^a Numbers I–X are the same as in Table 3.

polymers remain constant throughout the entire process. The results are given in Table 4; the E_a values obtained from the TG curves for polyether imides (**I**, **II**, **IV**, **VIII**, **X**), polysulfide imide (**III**) and polyimides with a $-\text{CH}_2-$ group in the main chain (**VI**, **VII**) are 250–320 kJ mol⁻¹, 200 kJ mol⁻¹ and 430–530 kJ mol⁻¹ respectively. The E_a values for the first kind of polyimide are consistent with those found in the literature. The difference in thermal degradation energies of these three kinds of polyimide may also be interpreted for the other two types of polyimide. The low E_a for **III** is attributed to the low bond energy of $\text{C}_{\text{aryl}}-\text{S}$, and the high E_a for **VI** and **VII** is due to the cross-linking reaction of the $-\text{CH}_2-$ group.

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