Journal of Thermal Analysis and Calorimetry, Vol. 63 (2001) 153–160

COMPARATIVE THERMOGRAVIMETRIC STUDIES OF POLY(ETHER-KETONE/SULFONE) IMIDES AND THEIR PARENT POLYMERS

I. Poly(ether-ketone/sulfone) ethylimide

Z. Y. Ren[1], *W. Y. Liu*[2], *Y. M. Hou*[3], *Y. Zhu*[3], *L. K. Chang*[3] *and D. Z. Ma*[1]

[1]University of Science and Technology of China, Hefei, Anhui, 230026, P.R. China
[2]Henan Yinge Industrial Investment Holding Co., Ltd. Henan, 450053, P.R. China
[3]Institute of Chemistry of Henan Academy of Sciences, Zhengzhou, Henan, 450002, P.R. China

(Received January 30, 2000; in revised form July 2, 2000)

Abstract

Thermogravimetry (TG) was employed to study the thermal degradation kinetics of poly(ether-ketone/sulfone) ethylimide (PEK-IE and PES-IE). The corresponding decomposition activation energies and reaction orders were obtained and the comparison was made with their parent polymers poly(ether-ketone/sulfone) with Cardo group (PEK-C and PES-C). The results show that the degradation activation energies of PEK-IE and PES-IE were lower than that of PEK-C and PES-C; and two stages of the degradation process were found for all the four polymers. For PEK-IE and PES-IE, the activation energies in the first decomposition stage are much lower than that in the second stage and the two stages can be taken as slow induction and fast degradation, whereas for PEK-C and PES-C the activation energies in the first decomposition stage are larger than that in the second stage, and the two stages can both be taken as two fast degradation stages. The decomposition mechanism of the two stages was also speculated.

Keywords: decomposition mechanism, poly(ether-ketone) with Cardo group (PEK-C), poly(ether-ketone) ethylimide (PEK-IE), poly(ether-sulfone) with Cardo group (PES-C), poly(ether-sulfone) ethylimide (PES-IE), thermogravimetry (TG)

Introduction

Poly(ether-ketone) with Cardo group (PEK-C) and poly(ether-sulfone) with Cardo group (PES-C) are the two heat-resistant polymer materials invented in China [1, 2] and some investigations have been made to deal with their excellent comprehensive properties [3–5]. In order to develop more and better new polymer materials, one of the monomer for PEK-C and PES-C, phenolphthalein, was modified by ethylamine to form a new monomer which then reacted with dichlorobisphenylketon or dichlorobisphenylsulfone to form poly(ether-ketone) ethylimide (PEK-IE) and poly(ethersulfone) ethylimide (PES-IE), respectively. PEK-C and PES-C are referred to as the parent polymers of

1418–2874/2001/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

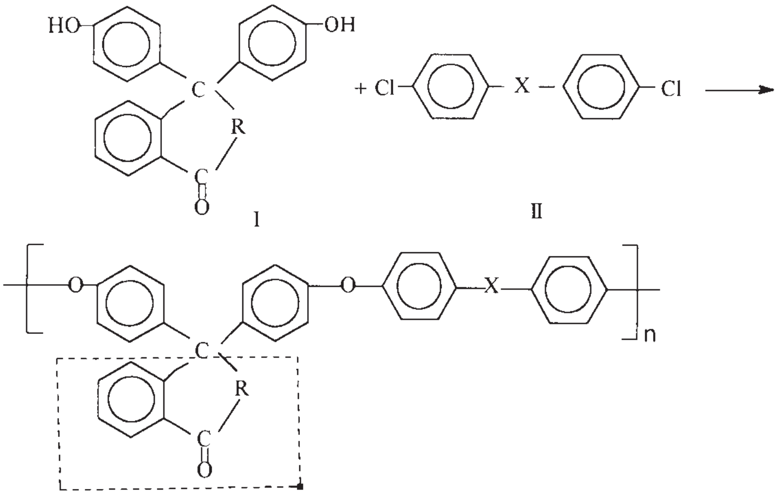
PEK-IE and PES-IE for the later were synthesized from the former-related modified monomers. The research results for the two polymers show that they possess much better gas separation properties than their parent polymers [6], and hence they will be the excellent choice for preparation of ultrafiltration, microfiltration and gas separation membrane materials. Though there have been some articles concerning PEK-C and PES-C, few deal with PEK-IE and PES-IE, and no report so far has been made for the thermal analysis of PEK-IE and PES-IE.

In the present paper, TG was used to study the degradation of the new polymers and the comparison was made between PEK-IE, PES-IE and PEK-C, PES-C.

Experimental

Samples and their structure

PEK-IE and PES-IE were obtained from the condense-polymerization of monomer I and monomer II (Scheme I). Due to the introduction of phenolphthalein, a lateral 'ring' group (as indicated in Scheme 1) was hanged on the body chain and the phenolphthalein lateral group or its chemically modified group is known as Cardo group (from Latin language). That is what C in PEK-C and PES-C means. When some modified reactions are made inside Cardo group, we name them according to the introduced group to replace the letter C in order to stress the difference more specifically. Hence here IE stands for the imide formed by N and ethyl. In the future, series of articles will be written concerning other imides formed from N and methyl, butyl etc. which will be represented by IM and IB etc. The concrete synthesis procedure for these polymers and their characterizations made by element analysis, IR and NMR were seen elsewhere [6], which showed the synthesized polymers were well consistent with the theoretical analysis.



Scheme 1 The structure of four polymers

Polymer	*X*	*R*
PEK-IE	CO	N–CH_2CH_3
PES-IE	SO_2	N–CH_2CH_3
PEK-C	CO	O
PES-C	SO_2	O

Experiment apparatus and conditions

TG experiments were carried out on a Perkin Elmer TG-7 thermogravimetric analyzer, in a nitrogen atmosphere (80 ml min^{-1}) and a heating rate of 10°C min^{-1}. The sample masses were 8–10 mg.

Results and discussion

Thermal decomposition stages

The TG curves of four polymers are shown in Fig. 1 and the corresponding data are listed in Table 1. It can be seen that PEK-C and PES-C are stable before about 450°C whereas PEK-IE and PES-IE begin to lose mass at about 380°C. It seems that the modified polymers possess lower thermal stability than their parent polymers, i.e. -IE series are less stable than -C series, which may be due to the weaker bond energy of C–N than that of C–O. It can also be found that PEK-C curve is similar to PES-C, and PEK-IE is similar to PES-IE. There is an obvious turning point in the whole degradation temperature range of PEK-C and PES-C curves, and a distinct slope change exists before and after the point.

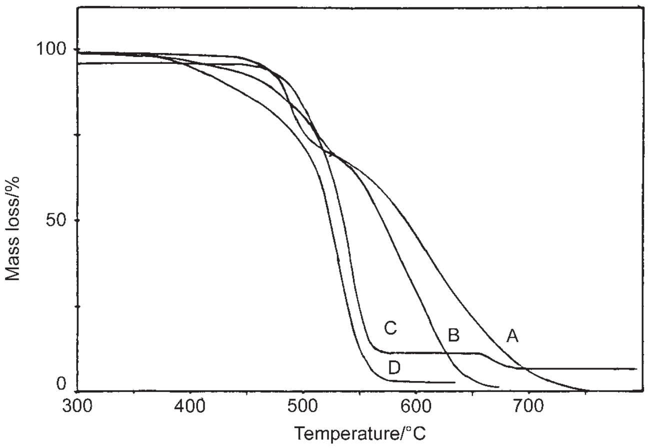


Fig. 1 TG-DTG curves of four samples; A – PEK-C; B – PES-C; C – PEK-IE; D – PES-IE

It can be taken that there exists two stages for the degradation of PEK-C and PES-C. The curve before the slope change in the lower temperature range can be taken as the first stage and the curve after the slope change in the higher temperature range as the second stage (Table 1). Though there are not such a turning point in PEK-IE and PES-IE curves, the degradation rate increase sharply after 490 and 500°C, respectively. As Table 1 shows that the mass loss percentage are only 18.25 and 13.29% before 501 and 490°C although the related degradation temperature range ΔT come to 120 and 104°C, respectively. Whereas after 501 and 490°C, the mass loss percentage reach 67.1 and 70.67% although the degradation temperature range ΔT are only 61 and 73°C. Hence, it may be postulated that in case of PEK-IE and PES-IE also two stages exist.

Table 1 TG data of the four polymers

Polymer	Temp. range*/°C	ΔT/°C	ΔW/°C
PEK-IE	381–501 501–562	120 61	18.25 67.1
PES-IE	351–455 490–563	104 73	13.29 70.67
PEK-C	434–525 535–715	91 180	28.48 63.54
PES-C	460–532 534–647	72 113	27.26 63.67

*Temperature range includes two groups of numbers, the above one standing for first stage of degradation and the second one for the second stage of degradation

For the first stage of PEK-C and PES-C, relatively small temperature ranges (ΔT=91 and 72°C) lead to nearly 30% of mass loss, whereas for PEK-IE and PES-IE, relatively large temperature range (ΔT=120 and 104°C) lead to less than 20%. Therefore, the two stages of PEK-C and PES-C can both be taken as the fast degradation stages but the first stage of PEK-IE and PES-IE can be taken as the slower degradation stage, which is reasonable to be regarded as an induction decomposition stage. The second stage, on the other hand, can be taken as the fast decomposition stage. The possible reason will be explained below.

Kinetics of the thermal decomposition

There are some ways to deal with the decomposition kinetics, and for a reaction in which the reaction order (n) is unknown, the following expression was derived [7] and can be used [8]:

$$\log\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right]=\log\frac{AR}{\beta E}\left[1-\frac{2RT}{E}\right]-\frac{E}{2.3RT}$$

where α is the fraction of the sample decomposed at time t, and β is the heating rate.

Plotting $\log[1-(1-\alpha)^{1-n}/T^2(1-n)]$ *vs.* $1/T$, a straight line with the intercept of $-E/2.3R$, the reaction order n, activation energy E and frequency factor A can be obtained and calculated (Fig. 2). The thermal decomposition kinetics data obtained with Coats–Redfern method are listed in Table 2, where n_1, n_2 and E_1, E_2 stand for the reaction orders, the activation energy of the first and second stages, respectively.

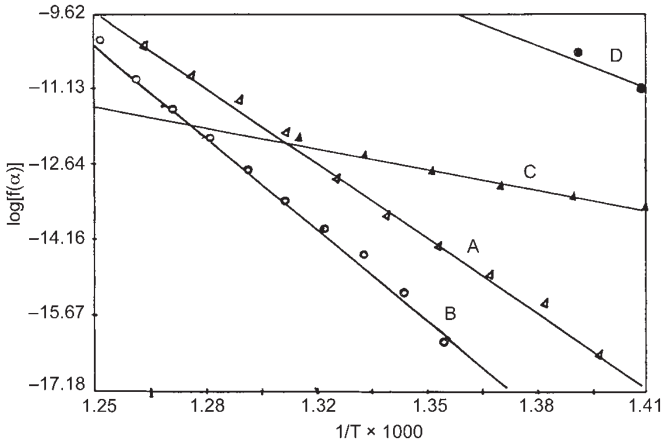


Fig. 2 Relationship between $\log[f(\alpha)]$ and $1/T$ of four samples: A – PEK-C; B – PES-C; C – PEK-IE; D – PES-IE

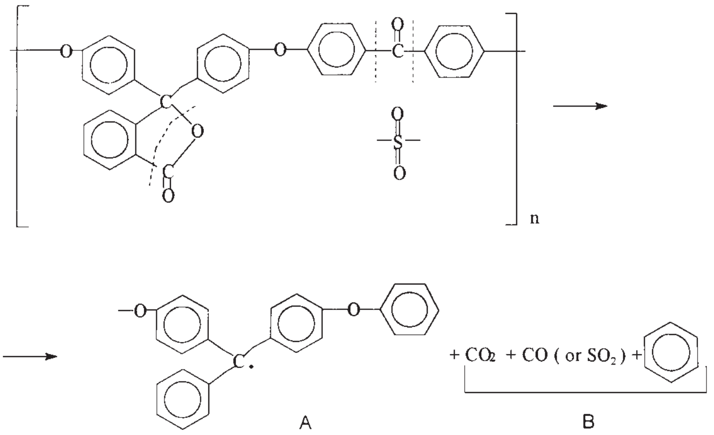
Judged from n values, none of the four thermal decomposition reactions belongs to the base-reaction. For PEK-C and PES-C, E_2 is less than E_1, which shows that the two polymers will be easier to be decomposed in the second stage than in the first one. But for PEK-IE and PES-IE, E_2 is larger than E_1. Such a phenomenon would be closely correlated with the mechanism of their thermal decomposition. During the first stage of the thermal decomposition the body chain of PEK-C and PES-C should have broken, hence the further decomposition will need only lower activation energy, whereas for PEK-IE and PES-IE the body chain should not have been destroyed after the first stage and would be broken during the second decomposition stage. Hence the activation energy for the second stage is higher than that of the first stage.

Table 2 The treated TG data for the four polymers

Polymer	n_1	E_1/kJ mol^{-1}	n_2	E_2/kJ mol^{-1}
PEK-C	1.6	390.27	1.7	196.46
PES-C	1.8	482.72	1.6	301.29
PEK-IE	0.6	110.4	1.3	481.076
PES-IE	1.8	223.64	1.6	452.44

Thermal decomposition mechanism

With TG curve, bond energy, the samples structure and also taking MS studies [9] for PEK-IB and PES-IB (IB stands for butylimide) as reference (Table 3), it can be thought that during the first breaking stage, C=O or O=S=O would be deleted from the body chain and meanwhile the heterocyclic ring would break, too, resulting from the breaks of C–O and Ph–C for PEK-C and PES-C during the first breaking stage, as the structure indicated (Scheme 2).



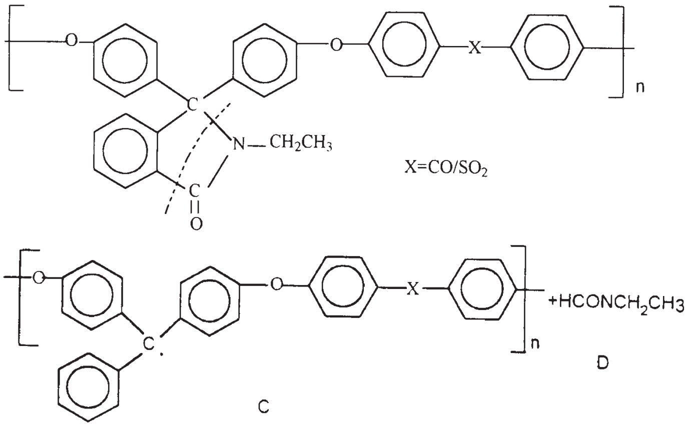
Scheme 2

Table 3 MS pyrolysis parts for PEK-IB and PES-IB

Formula	M_w	Formula	M_w	Formula	M_w
CO_2	44	Ph	78	Ph–CH_3	92
$HCON(CH_3)_2$	73	Ph–CN	103	H_3C–Ph–NC	117
Ph–OH	94	Ph–O–Ph	170	C_3H_7CN	69
Ph–O–Ph–CH_3	184	SO_2	64	CH_3–CH=CH–CH_3	56

‘A’ will be split into small fragments during the second stage. The molecular mass of PEK-C fragment B is 148, and the calculated decomposition percentage is 148/496=29.8%, which is almost equivalent with the first stage decomposition 28.48% (Table 1); whereas PES-C fragment B has the molecular mass of 184, and the calculated decomposition percentage is 184/532=34.6%, which is also closed to 27.26% of TG result. Therefore, the proposed mechanism is possibly reasonable. As for PEK-IE and PES-IE, it can be thought that the first decomposition stage would lead to the breaks of C–N and Ph–C instead of the body chain since C–N bond is easier to break as the figure indicated below (Scheme 3).

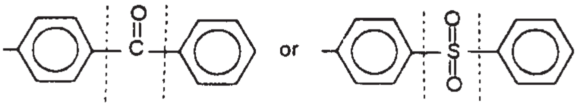
The molecular mass of PES-IE fragment D is 71, and the calculated decomposition percentage is 71/559=12.7%, which is almost equivalent with the first stage de-



Scheme 3

composition 13.29% (Table 1); PEK-IE fragment D has the calculated decomposition percentage =71/523=13.6%, and the experimental result indicates 18.25%, which has not a big difference. In a word, the calculated decomposition percentage of PEK-C and PES-IE corresponds very well with the experimental decomposition fragment percentage whereas the bit of difference between the experimental and calculated values of PES-C and PEK-IE are to be further investigated.

It can be thought that it is the different structure between PEK-C, PES-C and PEK-IE, PES-IE that leads to the different decomposition mechanism as mentioned above. It is no doubt that C–N bond in PEK-IE and PES-IE is easier to be decomposed, which explains that the decomposition stage starts earlier than that of PEK-C and PES-C. Hence the energy needed for breaking the lateral heterocyclic ring containing C–N and for breaking Ph–C and Ph–S in the body chain shown in the above two-structure (Scheme 4) from a corresponding temperature gradient.



Scheme 4

The so-called induction decomposition correspond just to the C–N breaking. However, such a fragment only occupies a small part. As long as the temperature is raised high enough, the other fragments would be further decomposed continuously and quickly, as the differences of the decomposition activation energy among other bonds would not be big according to their structure. Therefore, the breaks of these two kinds of bonds would be mixed with the body chain, which should be broken earlier compared with the similar structure in PEK-C and PES-C. The free radical decomposed from C–N related fragments must have accelerated the other parts of decomposition process due to the earlier break of C–N bond. Whereas for PEK-C and

PES-C without C–N bonds, the breaks of the lateral heterocyclic ring containing C–O, and the breaks of Ph–C containing C=O, O=S=O in the body chain shown in the above structure would occur within the close temperature range as their possible close decomposition energy, which form the obvious first breaking stage range compared with decomposing the more stable free radicals formed by the tri-phenyl structure. As a result, the decomposition process of PEK-IE and PES-IE make the whole decomposition process ends earlier than their parent polymer, and make the other part of fragment decompose earlier than the structure without C–N bonds. These are the possible reasons that there is a relatively smooth curve in the decomposition curve of PEK-IE and PES IE but there is a distinct turning point in the decomposition curve of PEK-C and PES-C.

Conclusions

As the introduction of ethyl group in the Cardo position, the heat stability of the new polymers slightly decreases compared with their parent polymers, but they still possess very good mechanical [6] and thermal property. The two polymers can hardly keep mass loss below 400°C. At the same time, the modified polymers with the introduction NR group had greatly improved the selectivity of gas permeation than their parent polymers [6].

References

1 K. J. Liu, H. C. Zhang and T. L. Chen, China Patent 85101721.
2 H. C. Zhang and T. L. Chen, China Patent 85108751.
3 F. Y. Jing, H. Y. Jiang and T. L. Chen, Chinese Journal of Analytical Chemistry, 26 (1998) 461.
4 H. W. Xie and B. Y. Lie, Chinese Journal of Applied Chemistry, (1996) 95.
5 Z. G. Wang, T. L. Chen and J. P. Xu, Chemical Journal of Chinese Universities, (1996) 1796.
6 W. Y. Liu, Doctoral Dissertation, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 1989.
7 A. W. Coats and J. P. Redfern, Nature, 201 (1964) 68.
8 Y. Zhu, L. K. Chang and S. Z. Yu, J. Thermal Anal., 49 (1997) 1513.
9 Y. P. Ji and W. Y. Liu, Chinese Journal of Analytical Chemistry, 20 (1992) 28.