

# **THERMOXIDATIVE DECOMPOSITION OF SOME POLYSULFONES UNDER DYNAMIC CONDITIONS OF HEATING**

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## **Abstract**

Kinetic aspects of the first step of thermoxidative decomposition, under dynamic conditions of heating, of some polysulfones have been studied.

The dependence of the kinetic parameters on the heating rate and conversion degree has been established. The compensation effect and conversion function have also been discussed.

Polysulfone decomposes by the breaking of the main chain, a process involving very high activation energy.

Chemically modified polysulfones show the first step of thermoxidative decomposition at relatively low temperatures. This step corresponds to the elimination of functional side – groups for the bromomethylated polysulfone while in the case of the carboxylated polysulfone, the loss of the carboxyl group is probably accompanied by a crosslinking reaction.

**Keywords:** bromomethylated polysulfone, carboxylated polysulfone, kinetics, polysulfone, thermoxidative decomposition

## **Introduction**

Polysulfone is a high performance thermoplastic material known for its high temperature resistance, exceptional resistance to boiling water and steam, excellent close tolerance moldability over a large temperature range and very long periods of time. With these characteristics, polysulfone has replaced metal, glass and ceramic materials in a wide variety of applications with the cost saving advantage.

Because of the excellent retention of properties upon exposure to high temperatures for long period of time, polysulfone is recommended for applications in air at temperatures as high as 422–443 K.

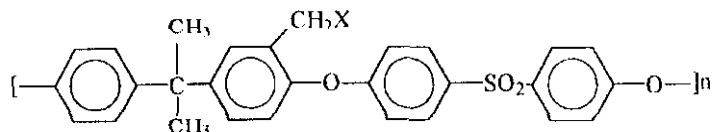
Due to these applications, many studies have been made of the thermal behaviour of polysulfone from the technological point of view [1], but only a few studies [2] are available about its thermoxidative degradation and/or decomposition under non-isothermal conditions of heating.

This paper deals with the thermoxidative decomposition of polysulfone, bromomethylated and carboxylated polysulfone.

## Experimental

### Materials

The following materials were used: polysulfone (Udel 1700 (PSF-1700) and 3500 (PSF-3500), (from Union Carbide, today supplied by AMOCO Corp.) purified by extraction with methanol, bromomethylated (PSF-CH<sub>2</sub>Br) and carboxylated (PSF-COOH) polysulfones obtained under conditions previously described [3] having the following structure:



X = -Br, -COOH, for PSFCH<sub>2</sub>Br and respectively PSF-COOH.

The intrinsic viscosities in dimethylformamide at 20°C were of 0.30; 0.35; 0.45; 53 ml g<sup>-1</sup> for PSF-1700; PSF-3500; PSF-CH<sub>2</sub>Br and PSF-COOH, respectively.

The degree of substitution with X groups for PSF-CH<sub>2</sub>Br and PSF-COOH was 0.9 and 0.77, respectively.

### Method

The TG curves were recorded on a Paulik-Paulik-Erdey-type Derivatograph, MOM Budapest, under the following operational conditions: heating rate ( $\beta$ ) 1, 5, 9 and 12 K min<sup>-1</sup>, (over this heating rate interval the experimental artifacts may be considered as negligible), temperature range 293–873 K, sample mass 50 mg, using film samples, in ceramic crucibles, 30 cm<sup>3</sup> min<sup>-1</sup> air flow. Two TG curves were recorded at each heating rate, ( $\beta$ ). The actual  $\beta$  values were evaluated from the temperature – time curve and so the ( $\beta$ ) calculated values were further employed in evaluating the kinetic parameters.

Three or four repeated readings (temperature and mass loss) were performed on the same TG curve, each reading having at least 15 points.

The kinetic analysis of the TG data was carried out using either a single curve (Coats Redfern [4], Reich-Levi [5] and Swaminathan-Modhavan [6] methods), or several curves recorded at all the above – mentioned heating rates (modified Friedman [7] and Flynn-Wall [8] methods).

This means that both integral (Coats-Redfern, Reich-Levi and Flynn-Wall) and differential (Swaminathan-Modhavan and Friedman) methods of the kinetic parameter evaluation were employed.

With the last two methods the general expression of the conversion function was considered:

$$\beta d\alpha / dT = Ae^{-E/RT} \underbrace{[\alpha^m (1-\alpha)^n [-\ln(1-\alpha)]^p]}_{f(\alpha)} \quad (1)$$

where  $\alpha = w_t/w_\infty$  is the conversion degree (ratio of the mass loss at time 't' and at the end of the process);  $T$  – temperature in K,  $A$  – pre-exponential factor,  $E$  – activation energy and  $n$  – reaction order,  $m, p$  – other exponents;  $f(\alpha)$  – differential form of the conversion function.

$m, n, p$  may take different values with respect to the reaction mechanism or physical processes occurring during decomposition. Positive values of the kinetic parameters,  $A$  and  $E$ , might be used as a selection criterion for kinetic parameters. As additional criteria, applied in our studies, mention may be made of the good reproducibility of kinetic parameters for different readings of TG data, maximum value of the correlation coefficient or minimum value of the mean squared error for each experimental point of the DTG or TG curves with respect to the calculated one with the previously evaluated kinetic parameters, etc.

## Results and discussion

### *Variation of the kinetic parameters with the heating rate and conversion degree*

Polysulfone decomposes above 673 K in a single thermogravimetric step – (Fig. 1). It seems that the molecular weight has a small influence on the thermoxidative decomposition pathway.

All chemically modified polysulfones show a DTG peak at a low temperature, which mainly corresponds to the loss of the functional groups (as  $\text{CH}_4$  and  $\text{Br}_2$ ,  $\text{CH}_3\text{Br}$  or  $\text{CO}_2$ ) as it results from the agreement of the calculated and experimental mass losses. After elimination of the functional groups, a less stable structure than that of PSF appears having a peculiar decomposition pathway as a function of the structure of the modified polymer and of the atmosphere employed in the TG apparatus (for comparison, see the curves recorded in a nitrogen flow in Figs 3 and 4, Ref [3])

The instability of PSF- $\text{CH}_2\text{Br}$  in oxidative and especially photooxidative conditions has already been mentioned [3, 9].

In a subsequent paper we will present some considerations of the reaction mechanisms on the basis of EGA results coupled with the analysis of the reaction products.

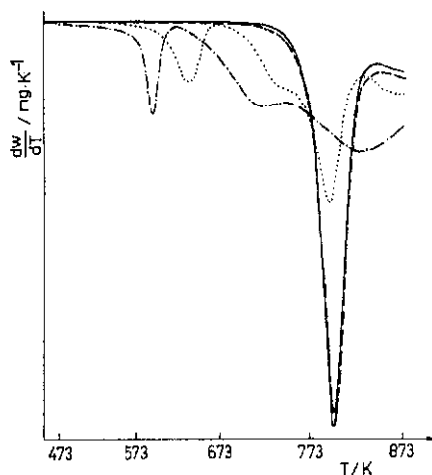


Fig. 1 DTG curves for the thermoxidative decomposition of PSF-3500 (—); PSF-1700 (---) PSF-CH<sub>2</sub>Br (-·-) and PSF-COOH (···)

The kinetic analysis was performed only for the first step of the thermoxidative decomposition of the polysulfones under study.

Commonly, with increasing heating rate, the TG curves are shifted towards higher temperatures (Fig. 2a and b). When no change occurs in the reaction mechanism, the curves are approximately parallel as well as the straight lines from the Flynn-Wall plots over the whole conversion degree region – Fig. 3.

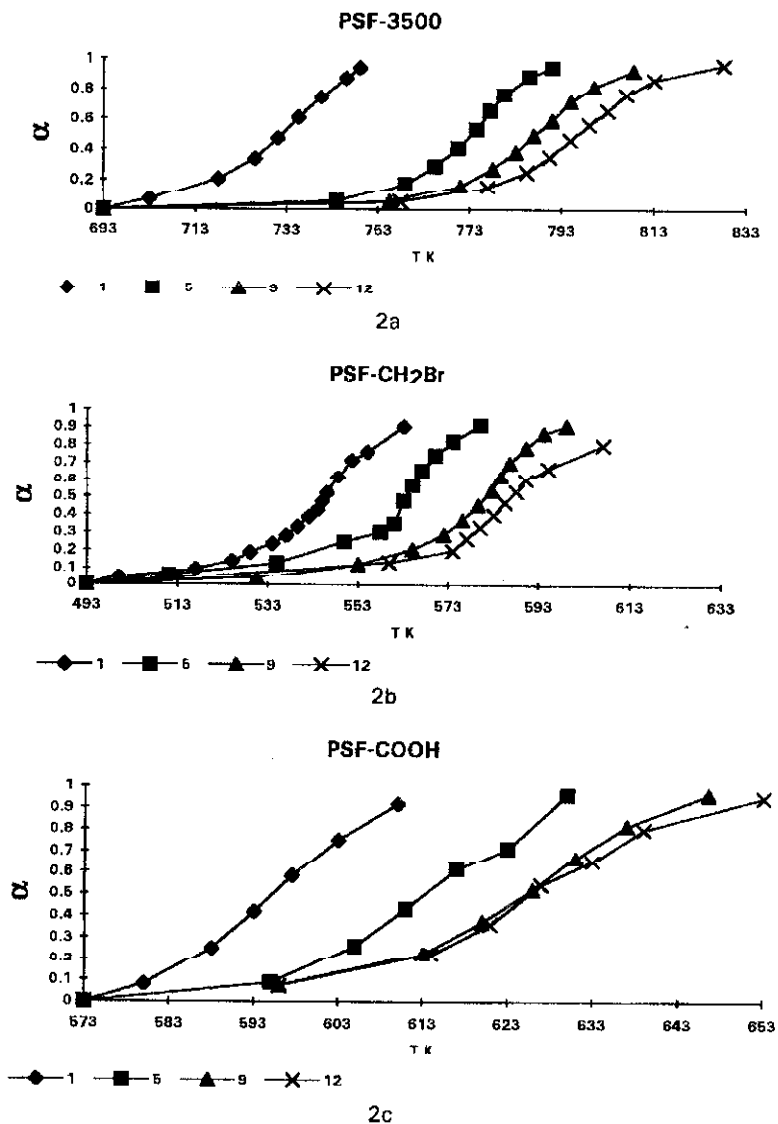
This is the case with the thermoxidative decomposition of PSF (1700 and 3500) and PSF-CH<sub>2</sub>Br while, in the decomposition of PSF-COOH, especially at the beginning of the process, the TG curves overlap at various heating rates (Fig. 2c) and the Flynn-Wall plot shows discontinuous lines for all conversion degrees (Fig. 3c).

Variations of the global activation energy, (evaluated by the Coats-Redfern method,  $E_{CR}$ ) and the values extrapolated to  $\alpha=0$  (from Reich-Levi method  $E_{RL}$ ) are presented in Figs 4 and 5. Both values lie on a straight line for all three polysulfones and there is good agreement between  $E_{CR}$  and  $E_{RL}$ . Within the experimental errors, the constancy of the  $E_{CR}$  and  $E_{RL}$  values for PSF and PSF-CH<sub>2</sub>Br is evident while PSF-COOH shows a pronounced decrease in the activation energy with increasing heating rate (Fig. 4) or conversion degree (Fig. 5c).

At a fast heating many artifacts appear and the activation energies for low conversion degrees cannot be correctly obtained (see the  $E-\alpha$  curve corresponding to  $\beta=12.4 \text{ K min}^{-1}$ ). This decrease in the activation energy with  $\beta$  or  $\alpha$  should indicate that the rate-limiting step of the process is changed only during the decomposition of the PSF-COOH, while the thermoxidative decomposition of the other two polymers (PSF and PSF-CH<sub>2</sub>Br) have the same reaction mechanism over the whole temperature range of decomposition and for all heating conditions.

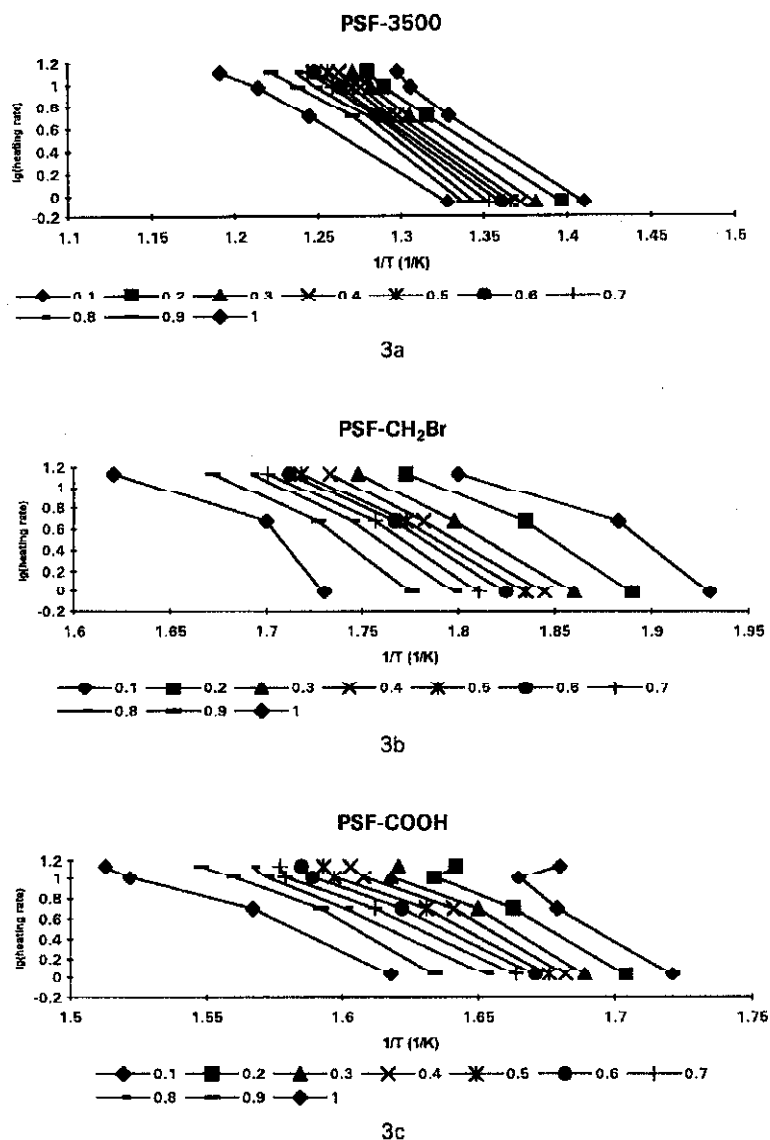
This conclusion is also supported by the variation with the conversion degree of the activation energies as evaluated by the Reich-Levi ( $E_{RL}$ ) and Friedman's modified method ( $E_F$ ) and preexponential factor ( $\ln A$ ) as well (Fig. 5).

A similar dependence of the kinetic parameters on the conversion degree was obtained by considering either a single decomposition process over the tempera-



**Fig. 2** TG curves for the thermoxidative decomposition of PSF-3500 (a); PSF-CH<sub>2</sub>Br (b) and PSF-COOH (c) at various heating rates; 1; 5; 9 and 12 K min<sup>-1</sup> (see legend)

ture range 693–842 K for PSF, 493–623 K for PSF-CH<sub>2</sub>Br and 573–663 K for PSF-COOH at each heating rate, or at all heating rates, although the two methods (Reich Levi and Friedman) employed gave different values. No constant values were obtained at various conversion degrees for PSF-COOH. Moreover, for this modified polysulfone, Friedman's isoconversional method cannot be ap-



**Fig. 3** Flynn-Wall plots for the thermoxidative decomposition of PSF-3500 (a); PSF-CH<sub>2</sub>Br (b) and PSF-COOH (c). Constant values of the conversion degree are 0.1; 0.2; 0.3; 0.4; 0.5; 0.6; 0.7; 0.8; 0.9; 1.0 (see legend)

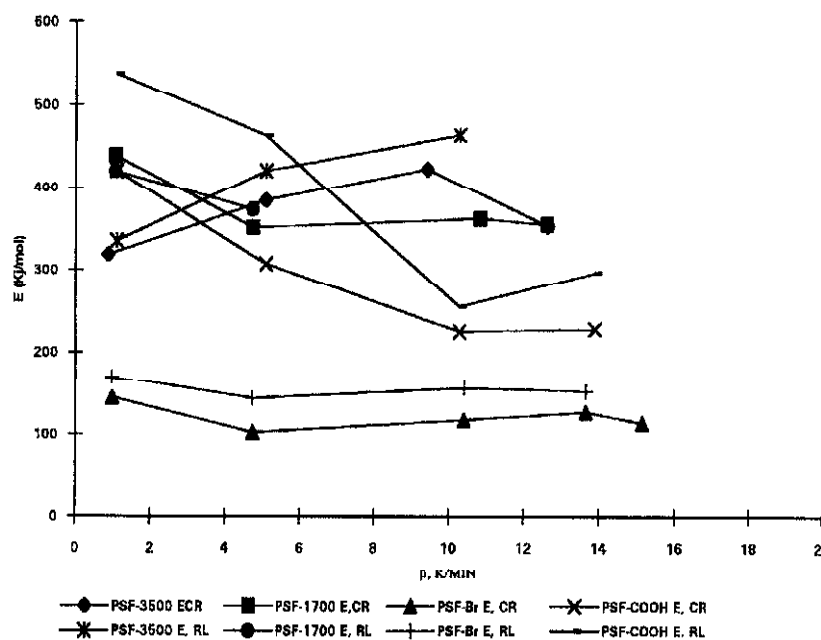


Fig. 4  $E_{CR}$  and  $E_{RL, \alpha=0}$  vs. heating rate ( $\beta$ ) for PSF-1700 and PSF-3500; PSF-CH<sub>2</sub>Br and PSF-COOH (see legend)

plied, as most evaluations over different conversion degree intervals gave no solution for the kinetic parameters or the conversion function.

### Compensation effect

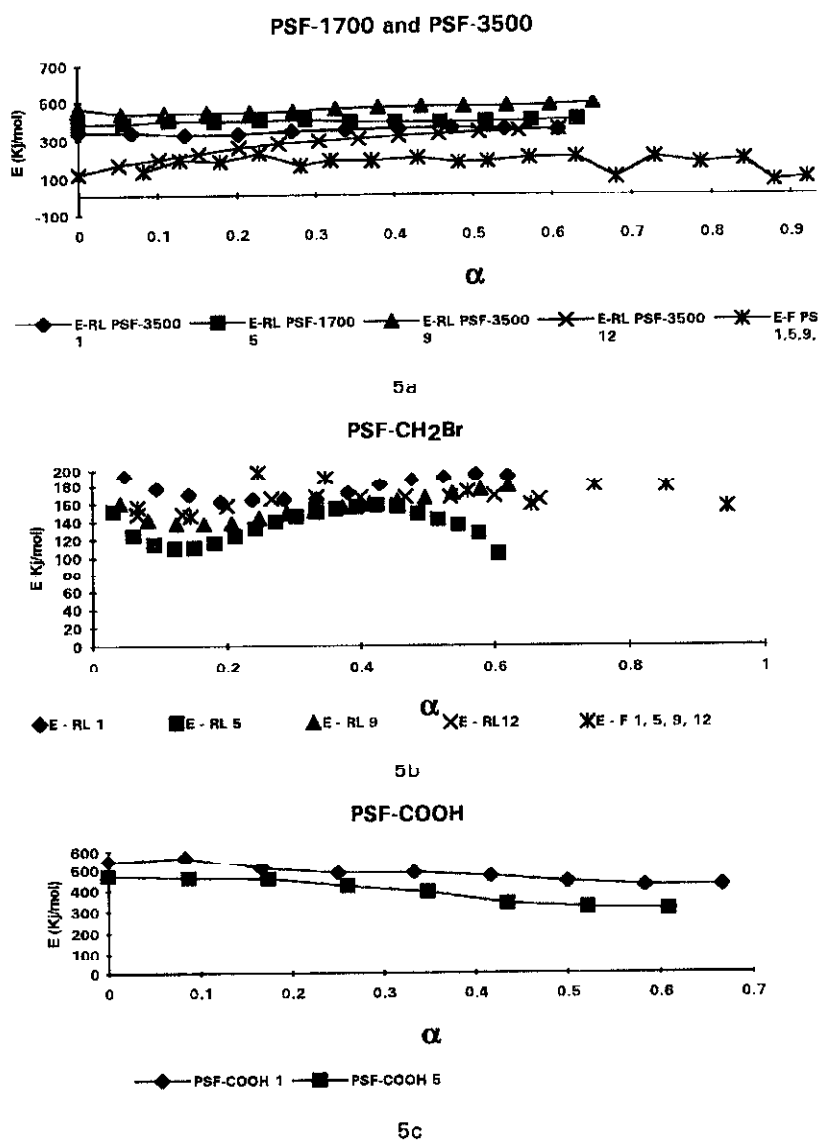
The  $a$  and  $b$  parameters of the isokinetic relation:

$$\ln A = a + bE \quad (2)$$

(where  $b=1/RT_{iso}$ ,  $R$  is the gas constant,  $T_{iso}$  the isokinetic temperature), describing the compensation effect, are given in Table 1.

For the thermoxidative decomposition of polysulfone a small variation of  $a$  and  $b$  values with the heating rate is recorded and also a relatively small difference between  $T_{iso}$  and  $T_{m,DTG}$  (temperature at the maximum of the DTG peak), which is probably due to the large shift of TG curves with increasing heating rates (Fig. 2).

A single isokinetic relation was found for the first step of the thermoxidative decomposition of PSF-CH<sub>2</sub>Br as seen both graphically (Fig. 6) and by the application of the method of least squares, while two isokinetic relations were found for the decomposition of PSF-COOH corresponding to a heating rate of



**Fig. 5**  $E_{RL}$  and  $E_F$  vs. conversion degree for the thermoxidative decomposition of PSF-3500 (a); PSF-CH<sub>2</sub>Br (b) and PSF-COOH (c) at various heating rates ( $\beta$ ): 1; 5; 9; 12 K min<sup>-1</sup> (see legend)

1 K min<sup>-1</sup> and 5–12 min<sup>-1</sup>, respectively. Isokinetic temperatures are close to  $T_{10,DTG}$  at 10 K min<sup>-1</sup> similarly to the decomposition of PSF-CH<sub>2</sub>Br.

The change in the 'b' parameter is significant for the decomposition of PSF and PSF-COOH at a heating rate of 1 K min<sup>-1</sup> which means that at slow heating



**Table 1** Isokinetic relations for the thermoxidative decomposition of polysulfone and chemically modified polysulfones

Polysulfone	$\beta/K \text{ min}^{-1}$	$\ln A$	$T_{iso}/K$	$T_{m,DTG}/K$	$\Delta W/\%$
PSF-3500	0.87	0.1624E-2.4883	741	735	37
	5.07	0.1536E-0.7013	783	775	42.5
	9.40	0.1531E+0.1228	785	793	46
	12.61	0.1509E+0.5028	797	798	49.5
PSF-1700	1.07	0.1648E-2.5834	729	736	25
	4.73	0.1593E-0.9021	779	775	43.5
	10.82	0.1533E-0.4878	784	789	48
	12.61	0.1522E-0.7881	790	795	48
PSF-CH <sub>2</sub> Br	0.98			550	15.5
	4.73	0.2053E-0.6107	585	566	16.5
	10.40			581	12.1
	13.64			588	14.3
PSF-COOH	1.09	0.2024E-1.8158	594	601	5.25
	5.07			618	6.13
	10.27	0.1919E-0.0999	626	623	6.75
	13.87			633	6.87

another chemical or physical process may occur in parallel with the thermoxidative decomposition.

Another proof of such behaviour is the smaller mass loss at this heating rate. Probably, cross-linking reactions take place, thus diminishing the mass loss. Studies on the aging of PSF have shown that the tensile strength, modulus of elasticity and heat distortion temperature increase at the beginning of aging, followed by stabilization of both polymer and its properties [1]. This behaviour should be correlated with the occurrence of certain cross-linking reactions.

Cross-linking and decomposition reactions occurring by a free radical mechanism have also been evidenced by Danilina [2] and Levantovskaia *et al.* [10].

### Conversion function

The most probably differential form of the conversion function (Eq. (1)) is given in Table 2 for various heating rates.

For the thermoxidative decomposition of PSF-1700 and PSF-3500, two forms of the conversion function, namely:

$$(1-\alpha)^n \text{ or } (1-\alpha)^n [-\ln(1-\alpha)]^p$$

adequately describe the TG curve. The latter form seems to correct the former one for the occurrence of diffusion processes, including  $[-\ln(1-\alpha)]^p$  for a small difference in the  $n$  values. The two exponents increase with increasing heating rate.

The thermoxidative decomposition of PSF-CH<sub>2</sub>Br can be described, for all the heating rates employed, by a single conversion function involving  $n=0.65$ .

For the thermoxidative decomposition of PSF-COOH mention should be made on the variation of not only the exponents with the change in the heating

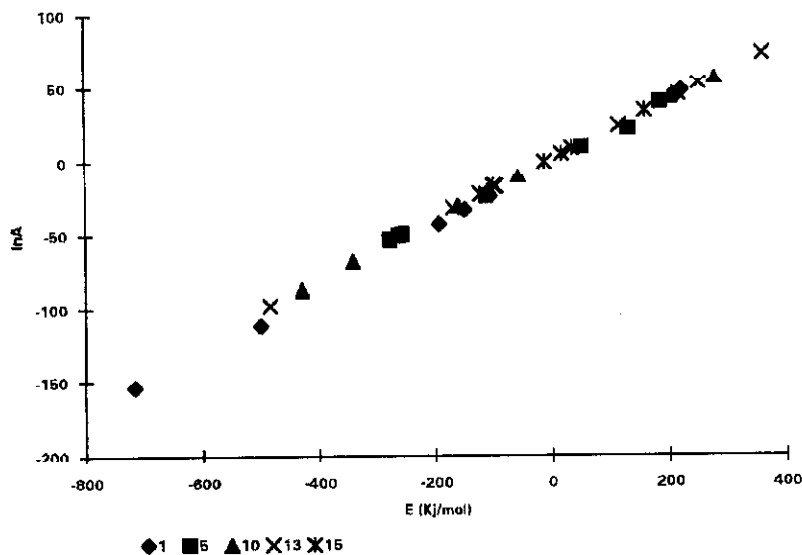


Fig. 6  $\ln A$  vs.  $E$  for the thermoxidative decomposition of PSF-CH<sub>2</sub>Br at various heating rates 1; 5; 10; 12 K min<sup>-1</sup> (see legend)

Table 2 Differential form of the conversion functions for the thermoxidative decomposition of some polysulfones

Polymer	$\beta/\text{K min}^{-1}$	Conversion function
PSF-3500	0.8-1	$(1-\alpha)^{0.65}$ or $(1-\alpha)^{0.8}[-\ln(1-\alpha)]^{-0.3}$
and	1-5	$(1-\alpha)^{1.4}$
PSF-1700	5-10	$(1-\alpha)^{1.75}$ or $(1-\alpha)^{1.5}[-\ln(1-\alpha)]^{0.4}$
	10-12	$(1-\alpha)^2$ or $(1-\alpha)^{1.5}[-\ln(1-\alpha)]^{1.2}$
PSF-CH <sub>2</sub> Br	1-15	$(1-\alpha)^{0.65}$
PSF-COOH	1-5	$\alpha^3$
	5-10	$(1-\alpha)^{0.71}$ or $(1-\alpha)^{1.2}[-\ln(1-\alpha)]^{0.96}$
	10-14	$(1-\alpha)^{1.6}$

rate but especially of the form of the conversion function, applied only over the narrow heating rate interval.

## Conclusions

The kinetic parameters of the thermoxidative decomposition of polysulfone do not vary with the heating rate and conversion degree. The differential conversion function is of the form  $(1-\alpha)^n[-\ln(1-\alpha)]^p$ .

Chemical modifications of polysulfone essentially change its thermal behaviour.

Chemically modified polysulfones decompose in two thermogravimetric steps. The first thermoxidative decomposition step occurs at low temperatures. It corresponds to the elimination of functional groups. The kinetic parameters of this process are nearly constant for the thermoxidative decomposition of PSF-Cl<sub>2</sub>Br, but they change with the heating rate and conversion degree for the decomposition of PSF-COOH. Probably in the last case the elimination of side groups is accompanied by other reactions.

## References

- 1 Udel Polysulfone, Union Carbide Firma Papers 1977-1981.
- 2 L. I. Danilina, E. N. Teleshov and A. N. Pravednikov, *Vysokomol. Soedn. A-16* (1970) 581.
- 3 A. Warshawsky, N. Kahana, A. Deshe, H. E. Gottlieb and R. Arad-Yellin, *J. Polym. Sci.: Polym. Chem. Ed.*, 28 (1990) 2885.
- 4 A. W. Coats and J. T. Redfern, *Nature (London)* 201 (1964) 68.
- 5 L. Reich and D. W. Levi, *Makromol. Chem.*, 66 (1963) 102.
- 6 V. Swaminathan and N. S. Modhavan, *J. Anal. Appl. Pyrolysis*, 3 (1981) 131.
- 7 H. L. Friedman, *J. Polym. Sci. C-6* (1963-1964) 47.
- 8 L. A. Wall, *Nat. Bur. Standards. Spec. Publ.*, 357 (1970) 183.
- 9 F. Gugumus, Chap. 3 'Light Stabilizers' in 'Plastics Additives' Eds. R. Gächter, H. Müller, P. P. Klemchuk, Hanser Publishers, Munnich, Viena 1990 p. 173-175.
- 10 I. I. Levantovskaya, G. V. Draľyuk, O. A. Mochalova, I. A. Yurkova, M. S. Akutin and V. M. Kovarskaia, *Vysokomol Soedn. A-13* (1971) 8.