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THERMAL DEGRADATION OF CHALCOGENIDES CONTAINING POLY(METHACRYLATES)

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Thermogravimetric analysis of aromatic poly(methacrylates) containing heterocyclic side chains were carried out. The effect of the substituent introduced into the side chain on the thermal stability of the polymer was investigated. The kinetic parameters of thermal degradation process were analysed. Different thermogravimetric profiles were obtained depending on the structure of the side chain of the polymer.

The effect of the side chain structure on several properties of synthetic macromolecules has been extensively described for a number of systems [1-5]. The incorporation of heteroatoms in the side chain has not been thoroughly investigated yet for aromatic poly (methacrylates). Recently we have reported the solution properties, chain rigidity [6,7] and calorimetric behaviour [8] of Poly (2-Thienylmethyl methacrylate) (PTiM) and Poly(2-Selenolylmethyl methacrylate) (PSeM). The nature and structure of the side chain seems to play an important role over the flexibility of these macromolecules what should be reflected on thermal properties of the polymer, such as glass transition temperature (T_g) or thermal stability. In a previous paper we also reported the thermal degradation of aromatic poly(methacrylates) containing alkyl substituents in the aromatic ring [9], and we did not find a clear correlation between the bulkiness and steric hindrance of the side chain and the thermal decomposition of the polymer.

The aim of this work is to study the thermal decomposition of several poly(methacrylates) in order to determine the kinetic parameters of the

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decomposition and to correlate these parameters with the chemical structure of the polymers. For this purpose we have analysed a new family of chalcogenides containing poly (methacrylates) which have a flexible spacer group $-CH_2-$ in the side chain i.e. poly(benzyl methacrylate) (PBzM), Poly (2-Thienylmethyl methacrylate) (PTiM), Poly(2-Selenolylmethyl methacrylate) (PSeM), poly(furfurylmethyl methacrylate) (PFM), and poly(tetrahydrofurfuryl methacrylate) (PHFM).

Experimental

Polymer samples were characterized using methods reported previously [6-8,10]. Number average molecular weight (Mn), was determined by membrane osmometry. Weight average molecular weight (Mw) and molecular weight distribution (MWD) were determined by size exclusion chromatography (SEC).

Dynamic thermogravimetric analyses were determined using a Perkin-Elmer TGS-1 thermobalance with a Perkin-Elmer UU-1 temperature program control. Samples (5-7 mg) were placed in the platinum sample holder and the thermal degradation measurements were carried out between 323 and 873 K at 20° min^{-1} under N_2.

Results and discussion

Figure 1 shows the thermogravimetric curves for fractions of narrow molecular weight distribution (MWD) and similar molecular weights (Mw $\sim 10^5$) for the five polymers studied, determined in same conditions. These curves represent the dependence of the loss of weight on temperature between 323 and 873 K. According to these profiles, PBzM and PHFM show a qualitative similar behavior in the sense that in both polymers the loss weight apparently follow a single one-stage decomposition process. However, in the case of PTiM, PSeM and PFM the degradation process seems to be more complex. In fact, in these three systems the profile of the thermograms suggest a three-stage weight loss on heating. Moreover, the degradation process in PFM begin earlier than in PTiM and PSeM. It is interesting to remark that these polymers are the three aromatic of the series containing heteroatoms in the side chain. Therefore, this behaviour could be due to the differences in the side chain structure relative to PBzM and PHFM, where the former, being aromatic do not have heteroatom and the second although contain oxygen as heteroatom is aliphatic what should be a significative difference and therefore the thermal behaviour can be different.

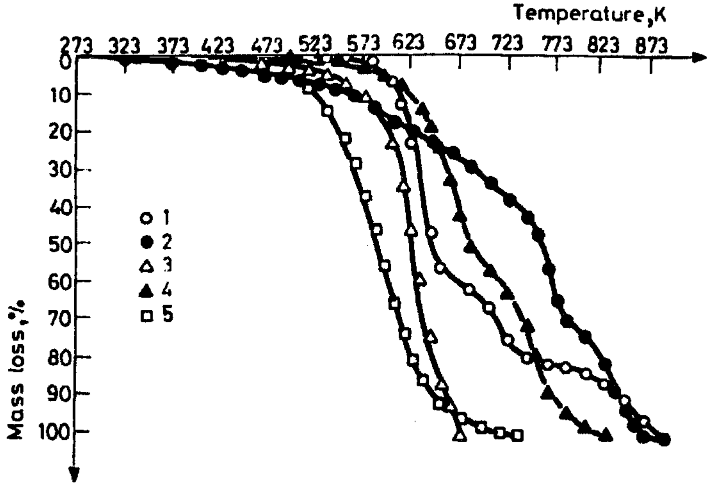

Fig. 1 Thermogravimetric curves of PBzM (+), PTiM (▲), PSeM (o), PFM (●) and PHFM (x)

Table 1 Initial decomposition temperature TD^i, temperature where 50% of residual weight is observed $TD^{50\%}$, molar volume of the side group V, activation energy Ea, the reaction order n, and the frequency factor for the degradation of PBzM, PTiM, PSeM, PFM and PHFM

Polymer	TD^i K	$TD^{50\%}$ K	V cm^3	E_a Kcal/mol	Z S^{-1}	n
PBzH	583	623	88.8	22.2^c	$1.8x10^{4c}$	0
PSeM	604	645	85.2	38.0^c	$3.6x10^{9c}$	0
				3.1^d	$3.4x10^{-3d}$	0
				2.4^e	$1.5x10^{-3e}$	0
PTiM	628	683	78.9	21.0^c	$1.8x10^{3c}$	0
				3.3^d	$3.2x10^{-3d}$	0
				11.0^e	0.6^e	0
PFM	511^a	751	72.6	8.0^c	$2.1x10^{-1c}$	0
	687^b			5.0^d	$8.0x10^{-3d}$	0
				15.0^e	5^e	0
PHFM	531	586	-	13.1^c	$2.6x10^{2c}$	0

a: temperature range 423-613K; b: temperature range 653-783K; c: first step; d: second step; e: third step

Table 1 summarizes the values for the initial decomposition temperature (TD^i) and the temperature at which 50% weight residual was observed ($TD^{50\%}$). In this Table the values of the molar volume (V) of the side groups of the polymer are also listed. According to these results, the stability of the polymers decreases in the following order: PFM > > PTiM > > PSeM > > PBzM > > PHFM, and all the polymers can be considered as thermally stable. As it can be seen the thermal stability of the polymers decreases as the molar volume of the side chain increases, at least in the group of aromatic polymers, what agree with the results found for other polymers such as poly(alkyl methacrylates) [11], poly (alkyl acrylates) [12] and poly(N(n-alkyl)maleimides) [13]. Therefore, in this family of polymers tnere is a correlation between the temperatures of the decomposition and the polymer structure.

In order to obtain the kinetic parameters of the decomposition of the polymers studied we have considered that this reaction is irreversible, therefore the reaction rate $d\alpha/dt$, can be expressed as function of the degree of conversion α, according to:

$$d\alpha / dt = kf(\alpha) \tag{1}$$

where k is the specific rate constant and $f(\alpha)$ is a function of the degree of conversion for a single reaction of the type: A → P and $f(\alpha)$ can be expresed in the form $f(\alpha) = (1-\alpha)^n$ where n is the order of the reaction. Therefore by replacing $f(\alpha)$ in equation 1 we obtain:

$$-d\alpha / dt = k(1-\alpha)^n \tag{2}$$

where α is the fraction of the sample weight reacted at time t, and it can be obtained directly from the thermogram. The reaction rates $d\alpha/dt$ were calculated using a differential technique and directly incorporating the heating rate ($20^\circ\ min^{-1}$) into the data of temperature vs. sample weight fraction [14]. The specific rate constants were obtained from the Arrhenius relation:

$$k = Ze^{-(E_a/RT)} \tag{3}$$

where Z is the frequency factor, E_a the energy of activation, T is the absolute temperature and R the gas constant.

By combining eqn. (2) and (3) and using the logarithm form we obtain:

$$\beta = \ln[(-\mathrm{d}\alpha/\mathrm{d}t)/(1-\alpha)^n] = LnZ - E_a/RT \tag{4}$$

In order to determine the kinetic parameters for thermal decomposition we have used a linear multiple regression program which allow to calculate E_a and Z from a linear least-square fit of the data in a semilogarithmic plot of β vs. 1/T. Following this procedure we find a zero order kinetic model for all the polymers studied.

Figures 2, 3 and 4 show the plots of β vs. 1/T for PBzM and PHFM, PTiM and PSeM, and PFM respectively. As it can be seen good straight lines are

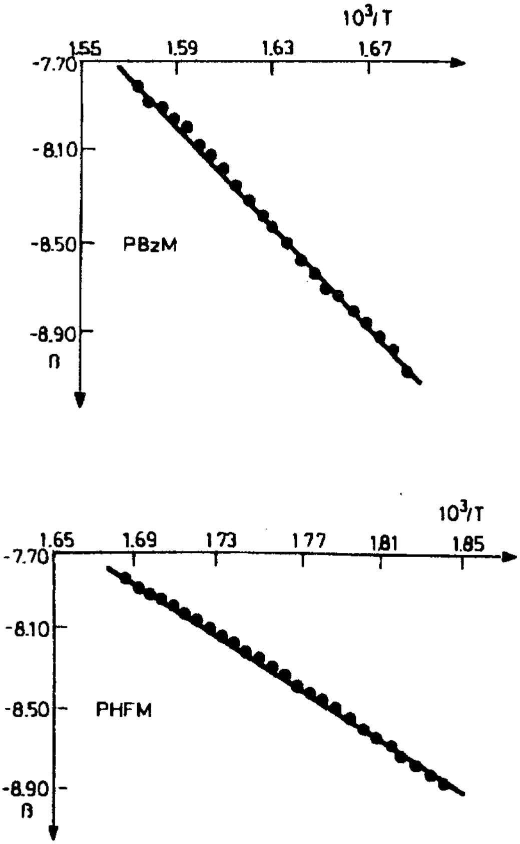

Fig. 2 Plots of β as function of 1/T for PBzM and PHFM

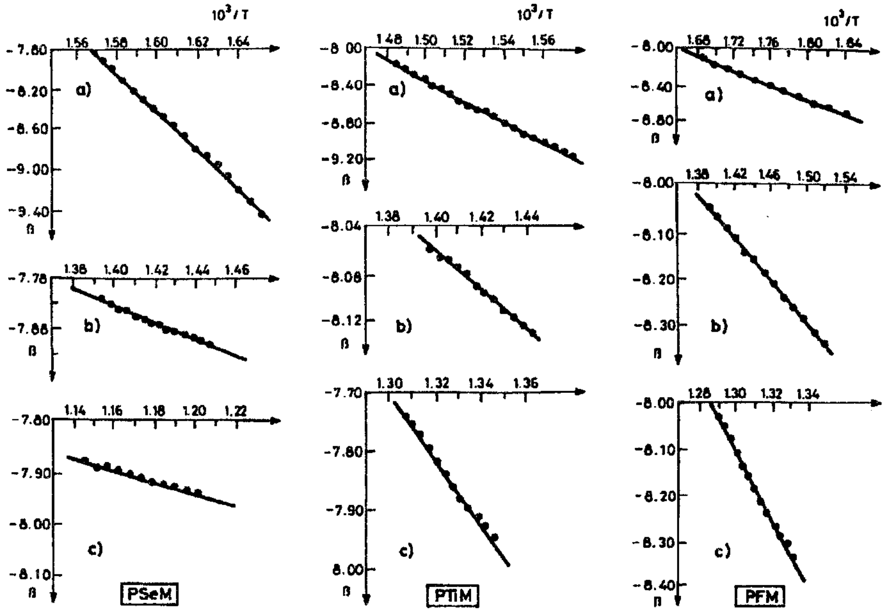

Fig. 3 Plots of β as function of 1/T for PSeM, PTiM and PMF a: first stage, b: second stage, c: third stage

obtained in all cases for a zero order kinetic model. Table 2 summarizes the kinetic parameters obtained from these plots.

The activation energies obtained from the first stage of the degradation for all polymers studied show that E_a increases as the molar volumen of the side group increases, except for PBzM. This particular behaviour could be explained by taking into account that PBzM is a very flexible polymer according to the results of δ (the rigidity factor) obtained from solution, therefore we could expect that not only the molar volume of the side chain affect the kinetic parameters but also the structure of the polymer. Similar results have been reported for other systems but not in terms of δ but in terms of steric repulsions [11-17] what are similar. The final value of E_a would be affected at least by two different factors which would excert opposite effects. By one hand the increases of the volume of the lateral group (V) which would enlarge the value of the activation energy for decomposition and on the other hand the rigidity of the chain (δ), which would contribute to diminish the activation energy for the thermal degradation of the polymer.

The values of the frequency factor Z, are low but are in good agreement with those found generally for a zero order kinetics [8,18]. There is not a clear correlation between Z and E_a, what have been also reported for other poly(methacrylates) [9].

The values of the activation energy and the frequency factor for the second and third step for PTiM, PSeM and PFM are also summarized in Table 1. As it can be seen E_a and Z for the second step are lower than for the first, increasing for the third step.

Finally we can conclude that in all cases the thermal decomposition of chalcogenides containing polymers follow a zero order kinetic model and that there is a correlation between the structure of the side chain and the degradation temperature.

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Zusammenfassung - Es wurden TG-Untersuchungen an aromatischen Polymethacrylaten mit heterocyclischen Seitenketten durchgefürt. Dabei wurde der Einfluß des Substituenten der Seitenkette auf die termische Stabilität der Polymere untersucht. Die kinetischen Parameter des thermischen Zersetzungsprozesses wurden untersucht. In Abhängigkeit von der Struktur der Seitenkette des Polymeres konnten verschiedene TG-Profile erhalten werden.