Thermal degradation behaviour and kinetic parameters of copolymers obtained by copolymerization via zwitterion

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Abstract

The thermal degradation of a series of 18 copolymers corresponding to poly(*p*-methoxyphenylmaleimide-co-2-methyl-2-oxazoline), poly(*p*-methoxyphenylmaleimide-co-2-ethyl-2-oxazoline), poly(*p*-nitrophenylmaleimide-co-2-methyl-2-oxazoline) and poly(*p*-nitrophenylmaleimide-co-2-ethyl-2-oxazoline) has been investigated using thermogravimetry in the temperature range 20–500°C. All the copolymers degrade in one step. The kinetic parameters E_a, n and A have been calculated. The thermal stability depends on the copolymer composition.

INTRODUCTION

Programmed thermogravimetric analysis (TGA) has been widely used to study thermal decomposition. It is particularly useful when applied to homologous series of polymers. In this respect, the kinetic parameters such as activation energy E_a, pre-exponential factor A and reaction order n give a quantitative measure of the thermal stability.

The kinetics of the thermal degradation of poly(*N*-(*n*-alkyl)maleimides) [1–4] and poly(*N*-(aryl)maleimides) [5–7] have been reported. In each case, the thermal stability was considered from different points of view.

Kwiatkowski et al. [8] have reported on bismaleimides, thermosetting resins with a service temperature of 200°C. Their acceptance as the next generation of matrix resins is mainly the result of their easy processability and retention of mechanical properties at high temperatures. These resins are brittle and show poor fracture toughness because of their high cross-link density. Increasing the molecular weight between cross-links helps to reduce brittleness. Different types of maleimides have been synthesized previously with the aim of improving their fracture toughness [9].

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We have recently reported the thermal behaviour of copolymers obtained by zwitterion copolymerization [10]. This paper reports an extension of this work by performing a study of the thermal degradation of poly(p-methoxy-phenylmaleimide-co-2-methyl-2-oxazoline), poly(p-methoxyphenylmalei-mide-co-2-ethyl-2-oxazoline), poly(p-nitrophenylmaleimide-co-2-methyl-2-oxazoline) and poly(p-nitrophenylmaleimide-co-2-ethyl-2-oxazoline) using thermogravimetric analysis to obtain the kinetic parameters involved in this process.

EXPERIMENTAL

The synthesis and characterization of all the copolymers have been reported previously [11,12]. Thermogravimetric analysis was carried out on a Perkin–Elmer TGS-1 thermal analyser system. The measurements were performed under an N_2 atmosphere at a heating rate of $10\,^{\circ}C\ min^{-1}$.

RESULTS AND DISCUSSION

Homopolymerization and copolymerization reactions usually require the presence of an initiator, catalyst or high radiation energy. There have, however, been reports on copolymerization without any added initiator [11–18]. Copolymerization of this type is based on a specific interaction of two monomers: one has nucleophilic reactivity (MN) and the other has electrophilic reactivity (ME). This interaction produces a "genetic zwitte-rion" $^+$MNME$^-$ which is the key intermediate responsible for initiation as
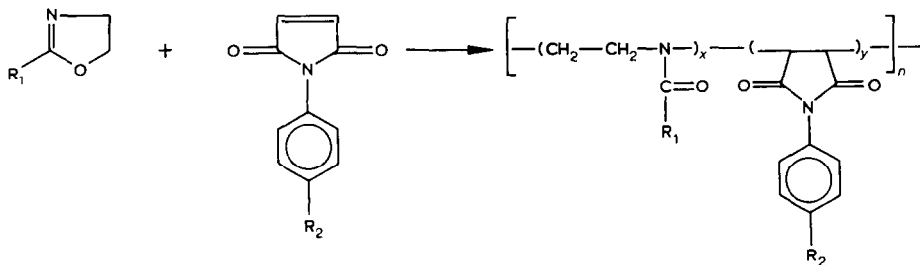
$R_1 = CH_3 (MOX)$ or CH_2CH_3 (ETOX)
$R_2 = OCH_3$ (p-MeOPhMI) or NO_2 (p-NO$_2$PhMI)

TABLE 1

The copolymers obtained

R_1	R_2	Copolymer	Number
CH_3	OCH_3	p-MeOPhMI/MOX	**1–3**
CH_2CH_3	OCH_3	p-MeOPhMI/ETOX	**4–6**
CH_3	NO_2	p-NO$_2$PhMI/MOX	**7–9**
CH_2CH_3	NO_2	p-NO$_2$PhMI/ETOX	**10–12**

well as for propagation. According to this concept, oxazoline derivatives possess high reactivity as nucleophilic monomers. *N*-phenylmaleimides may, however, be copolymerized as electrophilic monomers owing to the reactivity of the double bond and to the electrophilic effect of the substituent. The copolymers obtained are statisticals (see reaction below and Table 1).

Figures 1(a)–1(d) show the thermograms of *p*-MeOPnMl/MOX, *p*-MeOPhMl/ETOX, *p*-NO$_2$PhMI/MOX and *p*-NO$_2$PhMI/ETOX. Figures 1(e) and 1(f) show the thermograms for *p*-NO$_2$PhMI/MOX and *p*-NO$_2$PhMI/ETOX which were synthesized in solvents with different dielectric constants (CH$_3$CN, CH$_3$CH$_2$COCH$_3$ and C$_6$H$_6$). The primary thermograms of all 18 copolymers show the typical sigmoidal form. All the copolymers degrade continuously in one stage.

Determination of the kinetic parameters

The thermal decomposition kinetics of the thermogravimetric weight-loss can be described by the following kinetic equation

$$-\frac{d\alpha}{dt} = Kn(1-\alpha)^n \qquad (1)$$

where α is the fraction of the sample weight reacted at time t, n is the reaction order and Kn is the specific rate. The reaction rate $d\alpha/dt$ was calculated using a differential technique which allows for the heating rate and uses temperature vs. sample weight-fraction data [19].

The kinetic parameters were calculated according to the equation

$$\beta = \ln\left[-\frac{d\alpha/dt}{v(1-\alpha)^n}\right] = \ln A - \frac{E_a}{RT} \qquad (2)$$

and using a linear multiple regression program by plotting β vs. $1/T$. E_a and A were determined from the slope and intercept (see Figs. 2 and 3 and Tables 2 and 3).

For all the copolymers, the program was run for $n = 0$ and 1. The linear relationship obtained indicated that the reaction is zero order. If $n = 0$, $-dw/dt$ is constant at a specified temperature so that if the sample mass is increased the rate of decrease in mass remains unchanged at that temperature. This can only happen if a constant concentration of volatile material is maintained at the sample surface; this implies that the sample geometry is such that diffusion of volatiles to the sample surface and evaporation from the sample surface are the rate-controlling factors.

The coefficients of linear correlation vary from 0.991 to 0.999. The kinetic parameters E_a and A calculated from these plots are summarized in Tables 2 and 3.

For the *p*-MeOPhMI/MOX, *p*-MeOPhMI/ETOX, *p*-NO$_2$PhMI/MOX and *p*-NO$_2$PhMI/ETOX copolymers, it is interesting to observe the effect
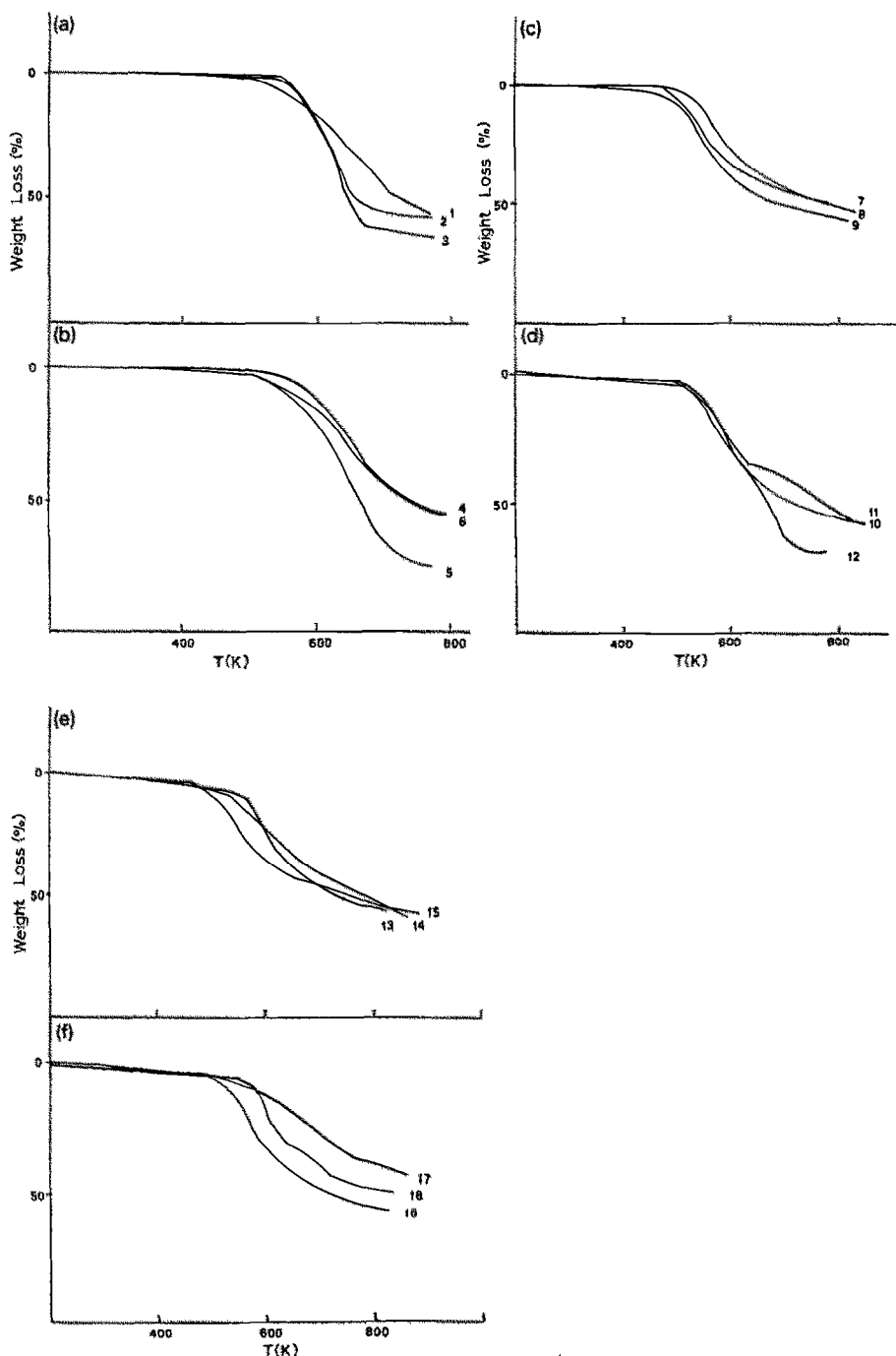
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Fig. 1. Thermograms (heating rate, $10\,^{\circ}C$ min^{-1}; nitrogen atmosphere) for (a) p-MeOPhMI/MOX, copolymers **1–3**; (b) p-MeOPhMI/ETOX, copolymers **4–6**; (c) p-NO$_2$PhMI/MOX, copolymers **7–9**; (d) p-NO$_2$PhMI/ETOX, copolymers **10–12**; (e) p-NO$_2$PhMI/MOX, copolymers **13–15**; and (f) p-NO$_2$PhMI/ETOX, copolymers **16–18** obtained in different copolymerization solvents.
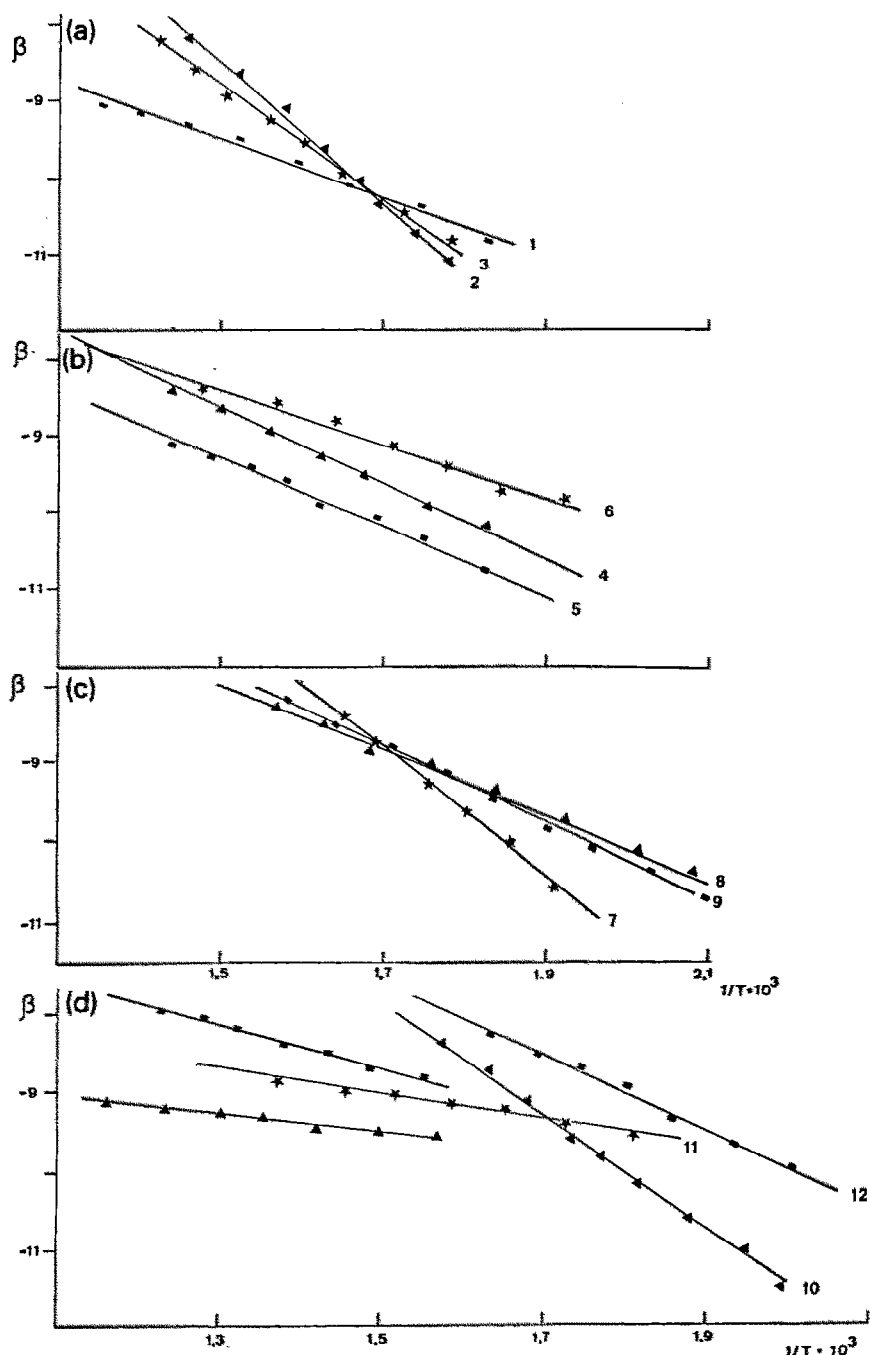
Fig. 2. Plot β vs. $1/T$ for (a) p-MeOPhMI/MOX, copolymers **1–3**; (b) p-MeOPhMI/ETOX, copolymers **4–6**; (c) p-NO$_2$PhMI/MOX, copolymers **7–9**; and (d) p-NO$_2$PhMI/ETOX, copolymers **10–12**.
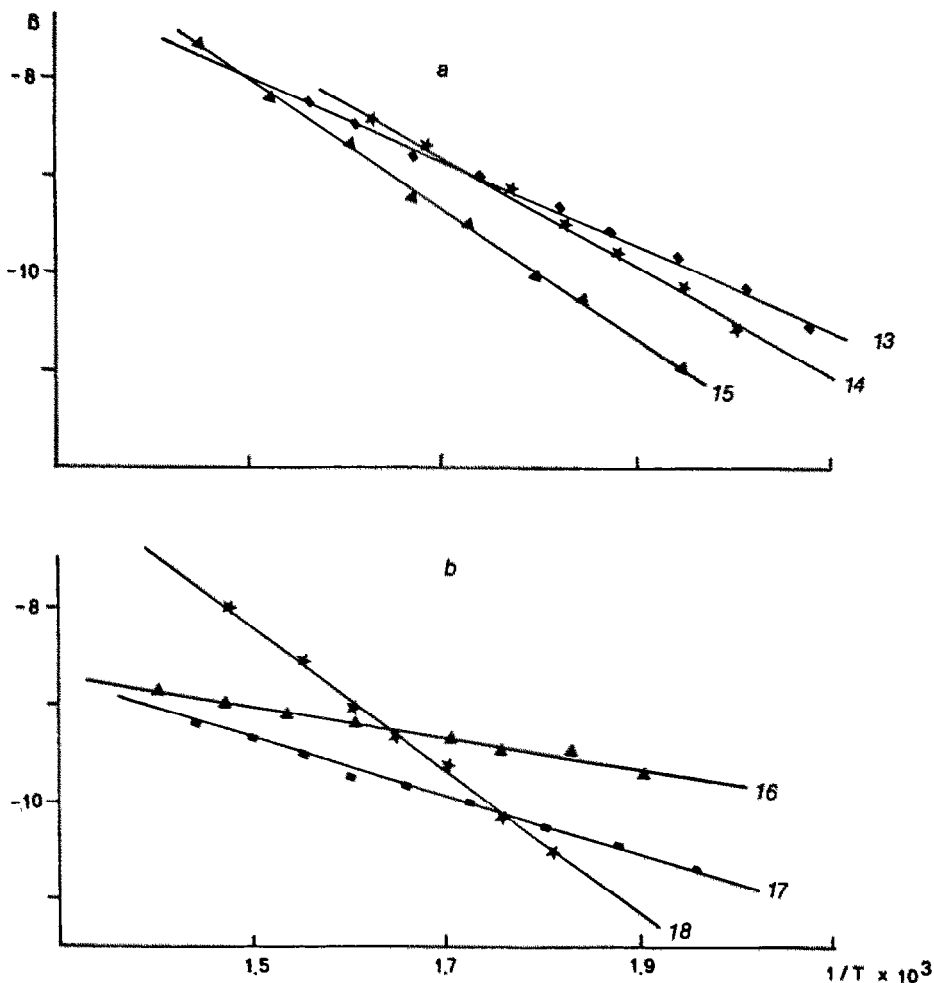
Fig. 3. Plot of β vs. $1/T$ for (a) p-NO$_2$PhMI/MOX, copolymers **13–15**, and (b) p-NO$_2$PhMI/ETOX, copolymers **16–18** obtained in different copolymerization solvents. Heating rate, $10\,^\circ$C min^{-1}; nitrogen atmosphere.

on the thermal stability of the substituent on the C-2 oxazoline ring as well as the electronic effect of the substituent in the N-phenylmaleimide. Thus, a volume increase in the lateral chain on the oxazoline ring decreases the thermal stability (see Table 2; copolymers **3** and **4** have an E_a of 15.4 and 8.9 kcal mol^{-1} respectively. A similar effect is also observed when the copolymer chain has greater amounts of p-MeOPhMI.

Of the p-MeOPhMI/MOX copolymers, copolymer **1** is the more stable with $E_a = 17.3$ kcal mol^{-1}. This behaviour may be correlated with the copolymer composition. In general, the p-MeOPhMI/MOX copolymers with a slight excess of p-MeOPhMI (1.2:1.0, 1.5:1.0) are the most stable. However, a high incorporation of p-MeOPhMI in the copolymeric chain

TABLE 2

Thermal decomposition temperatures and kinetic parameters for the copolymers

Copolymer	A (s^{-1})	TDT (°C)	E_a (kcal mol^{-1})	Monomer feed ratio (ME/MN)	Copolymer composition (ME/MN) [a]
p-MeOPhMI/MOX					
1	86.900	300	17.3	1:2	1.5:1.0
2	0.020	230	7.6	2:1	3.5:1.0
3	17.000	260	15.4	1:1	1.2:1.0
p-MeOPhMI/ETOX					
4	0.070	215	8.9	1:1	3.0:1.0
5	0.070	220	10.9	2:1	3.7:1.0
6	0.170	200	8.7	1:2	1.9:1.0
p-NO$_2$PhMI/MOX					
7	0.280	200	8.8	1:1	1.0:1.0
8	0.750	200	10.1	1:2	1.0:1.3
9	124.200	200	16.0	2:1	1.1:1.0
p-NO$_2$PhMI/ETOX					
10	1.870	200	10.7	1:2	0.5:1.0
11	209.000	200	11.9	2:1	2.3:1.0
12	0.003	200	4.0	1:1	1.1:1.0

[a] Determined from ^{1}H NMR spectra.

decreases the activation energy, e.g. copolymer 2 (3.5 : 1.0) has an E_a of 7.6 kcal mol^{-1} (see Table 2).

Comparing the p-MeOPhMI/MOX and p-MeOPhMI/ETOX copolymers, the latter is richer in p-MeOPhMI owing to the low nucleophilic reactivity of ETOX, producing copolymers with the lowest activation energy (E_a = 8.7–10.9 kcal mol^{-1}).

For the p-NO$_2$PhMI/MOX and p-NO$_2$PhMI/ETOX copolymers, the presence of a nitro group on the N-phenylmaleimide decreases the electro-

TABLE 3

Thermal decomposition temperatures and kinetic parameters for p-NO$_2$PhMI/MOX and p-NO$_2$PhMI/ETOX copolymers obtained in different polymerization solvents

Copolymer	Solvent	Copolymer composition (ME/MN) [a]	A (s^{-1})	TDT (°C)	E_a (kcal mol^{-1})
p-NO$_2$PhMI/MOX					
13	CH$_3$CN	1.0:1.1	0.290	230	8.9
14	CH$_3$CH$_2$COCH$_3$	1.0:2.6	0.626	230	10.0
15	C$_6$H$_6$	1.0:1.3	16.720	280	14.3
p-NO$_2$PhMI/ETOX					
16	CH$_3$CN	1.0:0.9	0.003	240	4.0
17	CH$_3$CH$_2$COCH$_3$	1.0:0.8	0.005	240	5.4
18	C$_6$H$_6$	1.0:1.3	11.544	300	14.2

[a] Determined from ^{1}H NMR spectra.

philic reactivity forming copolymers of about $1.0:1.0$ or with an excess of oxazoline monomers, with the exception of copolymer **11**. Thus, copolymer **9** with a copolymer composition of $1.1:1.0$ has an E_a of 16.0 kcal mol^{-1}.

In general, substitution on the N-phenylmaleimide monomer does not produce a marked effect. Nevertheless, the copolymer compositions are not the same even though the activation energy for these polymers are similar (see for example copolymers **3** and **9**).

In order to find the best synthesis conditions and to obtain more information about the effect of the copolymer composition on the thermal stability copolymerization reactions in solvents of different dielectric constants were carried out for p-NO$_2$PhMI/MOX and p-NO$_2$PhMI/ETOX. The results are summarized in Table 3.

As expected, owing to the presence of an ionic growing species during polymerization, a polar solvent such as CH$_3$CN favours the dipole–dipole reaction between both monomers producing a copolymer with a composition of around $1:1$; for solvents with low dielectric constants such as acetone and benzene, the homopropagation reaction of the less polar monomer is favoured forming statistical polymers rich in p-NO$_2$PhMI. Thus, with benzene as polymerization solvent, the copolymer composition is $1.0:1.3$ and the activation energy is 14.3 and 14.2 kcal mol^{-1} (see Table 3, copolymers **15** and **18**).

CONCLUSIONS

From these results it is possible to conclude that copolymers rich in ME have the highest thermal stability although a great excess of this monomer along the copolymer backbone decreases the thermal stability. Therefore, it is suggested that an ideal copolymer composition exists. An increase in MN size causes the copolymer chain to lose thermal stability. For all copolymers, the decomposition reaction was found to be of zero order, $n = 0$.

ACKNOWLEDGEMENTS

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