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THERMAL DECOMPOSITION TEMPERATURES AND KINETIC PARAMETERS OF COPOLYMERS FROM *N*-PHENYLMALEIMIDE AND OXAZOLINE DERIVATIVES

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ABSTRACT

The thermal stabilities of 15 copolymers of varying comonomer structure based on *N*-phenylmaleimide and oxazoline derivatives have been studied by programmed thermogravimetric analysis over a temperature range from 20 to 500 ° C under a flow of nitrogen. All the copolymers are stable below 130 ° C. Only three of the copolymers undergo degradation in two stages.

Kinetic parameters such as the pre-exponential factor, activation energy and reaction order were evaluated. All the reactions were found to be zero order under the experimental conditions used. Possible effects of copolymer composition on the kinetic parameters are discussed.

INTRODUCTION

The development of such branches of modern industry as electronics and aircraft manufacture necessitates the synthesis of polymers with adequate mechanical properties and the capacity to perform at high temperatures for prolonged periods. The development of new thermostable polymers is thus an important field of reasearch.

Programmed thermogravimetric (TG) analysis has been widely used as a method for investigating the thermal stability of polymers, and characteristics of their thermal decomposition. Kinetic parameters such as activation

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energy, pre-exponential factor and reaction order provide a quantitative measure of thermal stability [1].

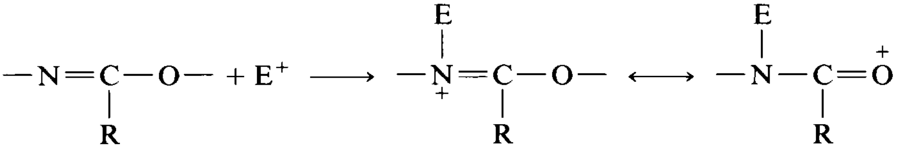
Other workers have studied the kinetics of the thermal degradation of poly(*n*-alkylmaleimides) [2–6], poly(*N*-arylmaleimides) [7,8] and bismaleimides [9]. The present work reports on a study of the thermal degradation of copolymers from *N*-phenylmaleimide and oxazoline derivatives. Thermogravimetric analysis was used to determine the kinetic parameters of this process.

EXPERIMENTAL

The methods of synthesis and characterization of these copolymers have been reported in previous works [10–12]. Thermogravimetric analyses were carried out using a Perkin–Elmer thermobalance. Samples (3–6 mg) were heated in a platinum sample holder between 20 °C and 500 °C at 10 °C min^{-1} under a nitrogen atmosphere.

RESULTS AND DISCUSSION

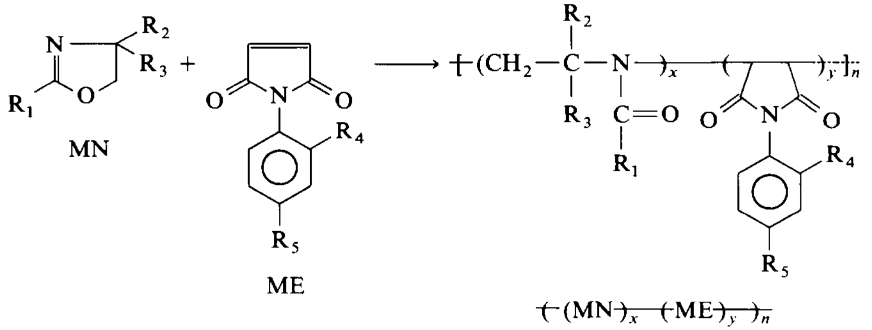
According to the new concept of 'spontaneous copolymerization', the high reactivity of nucleophilic monomers such as cyclic iminoether is attributable to the stability of the products of interaction with an electrophilic monomer. These are stabilized by resonance structures between ammonium and oxonium species.



$$-N{=}\underset{R}{C}-O- + E^+ \longrightarrow -\overset{E}{\underset{+}{N}}{=}\underset{R}{C}-O- \longleftrightarrow -\overset{E}{N}-\underset{R}{C}{=}\overset{+}{O} \qquad (1)$$

On the other hand, copolymerization of the *N*-phenylmaleimides may be a result of the reactivity of the double bond and the basic electronic effect of the substituent.

On the basis of concept and the properties of the monomers, copolymers were synthesized without the addition of any initiator. The interaction of the two monomers, nucleophilic (MN) and electrophilic (ME), produces a 'genetic zwitterion' $^+$MNME$^-$ which is the species responsible for the initiation and propagation reactions. The copolymers are statistical.



R_1	R_2	R_3	R_4	R_5	Copolymer (numbers)
$-CH_3$	-H	-H	-H	-H	*N*-PhMI/MOX (**I–III**)
$-CH_2CH_3$	-H	-H	-H	-H	*N*-PhMI/ETOX (**IV–VI**)
$-CH_3$	$-CH_3$	$-CH_3$	-H	-H	*N*-PhMI/TMOX (**VII–IX**)
$-CH_2CH_3$	-H	-H	$-CH_3$	-H	*o*-MePhMI/ETOX (**X–XIII**)
$-CH_2CH_3$	-H	-H	-H	$-CH_3$	*p*-MePhMI/ETOX (**XIII–XV**)

Figure 1 shows five plots of three thermograms, corresponding to the individual copolymers within the five copolymer systems analysed.

The primary thermograms of all 15 copolymers have a typical sigmoidal shape.

The copolymers degrade continuously in one stage except for the *N*-PhMI/TMOX copolymers, which degrade in two stages. This last observation indicates that other preferred or competitive processes occur simultaneously at this temperature.

Table 1 shows the values of the thermal decomposition temperatures (TDTs) obtained for each copolymer. These were taken as the first strong change in the slope of the TG curve.

Values of TDT $\geqq 200\,°C$ were obtained for all the copolymers which degrade in only one stage, except for copolymer **III** (TDT 160 °C). In the case of the copolymers which degrade in two stages, similar values were obtained for both TDTs.

Determination of the kinetic parameters

The thermal decomposition kinetics of the thermogravimetric weight loss were determined using the kinetic equation

$$-(\mathrm{d}\alpha/\mathrm{d}t) = K_n(1-\alpha)^n \qquad (2)$$

where α is the fraction of the sample weight reacted at time t, n is the reaction order, and K_n is the specific rate. The reaction rate $\mathrm{d}\alpha/\mathrm{d}t$ was calculated using a differential technique and taking account of the heating rate (5 or 10 °C min^{-1}), using data from plots of temperature vs. sample

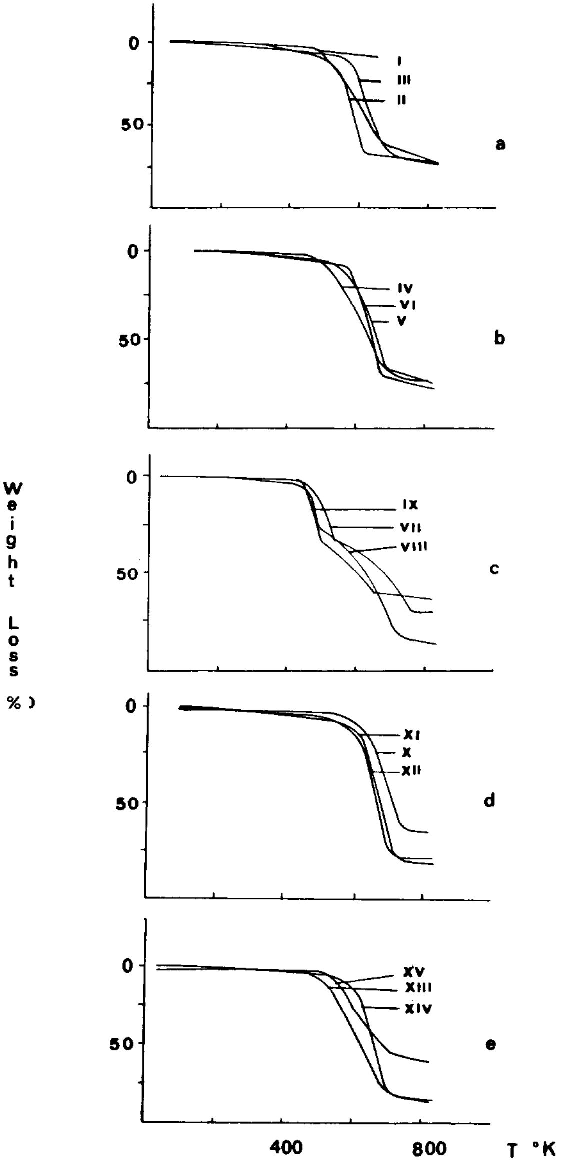


Fig. 1. Primary thermograms obtained under nitrogen atmosphere at a heating rate of 5 °C min^{-1} for copolymers: a, *N*-PhMI/MOX; b, *N*-PhMI/ETOX; c, *N*-PhMI/TMOX; d, *p*-MePhMI/ETOX; e, *o*-MePhMI/ETOX.

weight fraction [13]. The specific rate K_n was obtained using the Arrhenius relation

$$K_n = A \exp(-E/RT) \qquad (3)$$

where A is the pre-exponential coefficient, E is the activation energy, T is the absolute temperature, and R is the gas constant. Combining the equa-

TABLE 1

Values of thermal decomposition temperature (TDT) for copolymers of phenylmaleimide derivatives with oxazoline monomers

Copolymer	Number	TDT (°C)	Copolymer composition (ME:MN)
N-PhMI/MOX	**I**	200	3.2:1.0
N-PhMI/MOX	**II**	200	1.6:1.0
N-PhMI/MOX	**III**	160	1.0:1.0
N-PhMI/ETOX	**IV**	200	4.0:1.0
N-PhMI/ETOX	**V**	220	1.6:1.0
N-PhMI/ETOX	**VI**	270	1.0:1.0
N-PhMI/TMOX	**VII** [a]	140 230	2.7:10
N-PhMI/TMOX	**VIII** [a]	170 230	2.2:1.0
N-PhMI/TMOX	**IX** [a]	150 220	1.2:1.0
o-MePhMI/ETOX	**X**	300	2.8:1.0
o-MePhMI/ETOX	**XI**	230	2.0:1.0
o-MePhMI/ETOX	**XII**	240	1.2:1.0
p-MePhMI/ETOX	**XIII**	200	2.2:1.0
p-MePhMI/ETOX	**XIV**	200	1.6:1.0
p-MePhMI/ETOX	**XV**	200	1.4:1.0

[a] Undergoes degradation in two stages.

tions, incorporating v and adopting the logarithmic form, we obtain

$$\beta = \ln\{-(\mathrm{d}\alpha/\mathrm{d}T)/[v(1-\alpha)^n]\} = \ln A - (E/RT) \tag{4}$$

A linear multiple regression program was used to calculate the kinetic parameters E and A. Plotting β vs. $1/T$ should give a straight line, and E and A are determined from the slope and intercept (see Figs. 2–3).

For all the copolymers, the program was run for $n = 0$ and $n = 1$. The linear relationships obtained indicated that the reaction is of order 0. The coefficients of linear correlation varied from 0.990 to 0.999.

The kinetic parameters E and A calculated from these plots are collected in Table 2 for comparative purposes.

We are interested in establishing the possible effects of copolymer composition on kinetic parameters such as E and A. Now copolymer composition is determined by other factors, such as the size of the alkyl group on the nucleophilic monomer, and the electronic effect of the substituent in *ortho* and *para* positions on the electrophilic monomer. So, the copolymer compositions were determined from ^{1}H NMR spectra by comparing equivalent areas of protons in the nucleophilic and electrophilic monomeric units incorporated into the copolymer [10–12].

It is interesting to note the relation between activation energy, copolymer composition, monomer–backbone structure, and position of the methyl

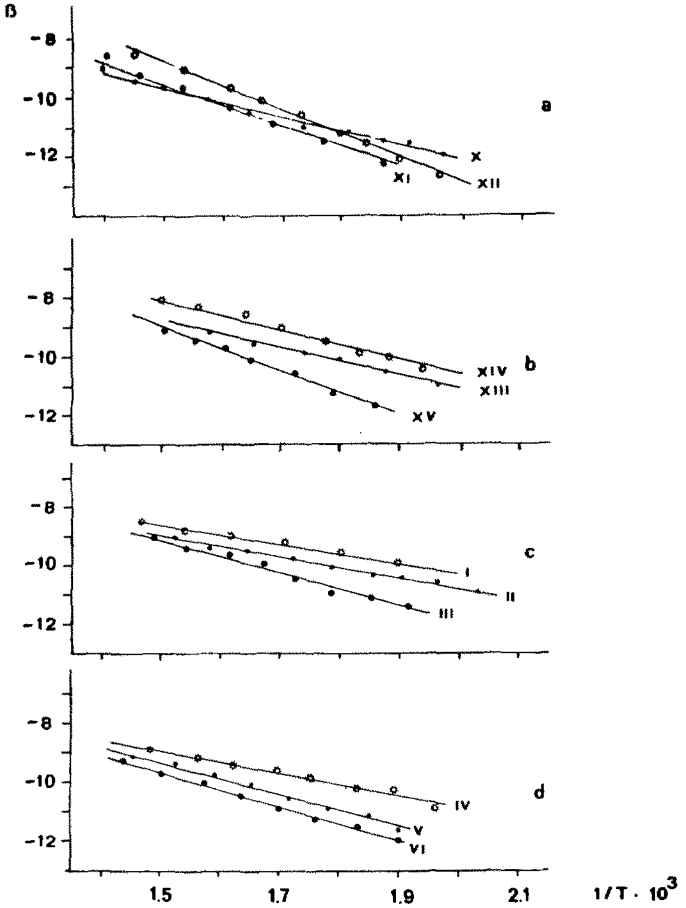


Fig. 2. Arrhenius plots for the thermal degradation of copolymers **I–VI** and **X–XV**. a, *N*-PhMI/MOX; b, *N*-PhMI/ETOX; c, *p*-MePhMI/ETOX; d, *o*-MePhMI/ETOX.

group on the monomer. From Table 2, the following conclusions can be drawn, regarding similar copolymer compositions.

In general, all the copolymers possess low activation energy. Incorporat-

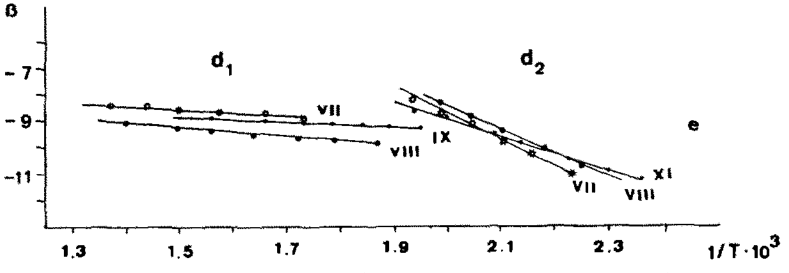


Fig. 3. Arrhenius plots for the thermal degradation of copolymers **VII–IX**. d$_1$ and d$_2$ correspond to the first and second stages of the degradation process for e, *N*-PhMI/TMOX.

TABLE 2

Kinetic parameters for the copolymers **I–XV**

Copolymer	Copolymer composition[a] (ME:MN)	A (s^{-1})	E (kcal mol^{-1})	Temperature range (°C)
I	3.2:1.0	5.3×10^{-2}	7.40	225–360
II	1.6:1.0	15.2×10^{-2}	6.42	260–405
III	1.0:1.0	2.3	12.98	220–410
IV	4.0:1.0	2.3×10^{-2}	6.93	235–410
V	1.6:1.0	33.2×10^{-2}	10.79	290–295
VI	1.0:1.0	31.2	16.34	250–425
VII	2.7:1.0	32.8×10^{-2}	14.85	170–250
		1.37×10^{-3}	2.68	240–375
VIII	2.2:1.0	55.4	12.8	170–260
		6.4×10^{-4}	3.6	305–470
IX	1.2:1.0	11.94×10^{2}	15.61	150–240
		3.86×10^{4}	1.47	230–460
X	2.8:1.0	14.9×10^{-2}	10.16	280–430
XI	2.0:1.0	5.54	14.79	230–445
XII	1.2:1.0	19.4	15.62	245–430
XIII	2.2:1.0	5.3×10^{-2}	7.99	250–450
XIV	1.6:1.0	31.4×10^{-2}	9.25	230–410
XV	1.4:1.0	62×10^{-2}	12.03	245–400

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

ing more *N*-phenylmaleimide into the copolymer decreases the activation energy. Optimal copolymer compositions (compositions for which the highest values of A are observed) are 1.0 : 1.0, 1.0 : 1.0, 1.2 : 1.0, 1.2 : 1.0 and 1.4 : 1.0 for copolymers **III, VI, IX, XII** and **XV**, respectively.

For copolymers with the same copolymer composition, the size of the alkyl group on the oxazoline derivative has an effect. Copolymer **III** has $E = 12.98$ kcal mol^{-1}; copolymer **VI** has $E = 16.34$ kcal mol^{-1}. In other words, E increases when the methyl group on the oxazoline is replaced by an ethyl group. The copolymers *N*-PhMI/TMOX are not comparable because they do not have the same copolymer composition, but it is possible that incorporation of three methyl groups onto the oxazoline ring will increase E (see Table 2, copolymers **I–IX**).

The presence of a methyl group in the *ortho* or *para* position on the *N*-phenylmaleimide also has an effect on stability. The statistical copolymers which are richer in *o*- and *p*-methyl-phenylmaleimide (copolymers *o*- and *p*-MePhMI/ETOX) have greater E than does copolymer *N*-PhMI/ETOX. For copolymer **V**, $E = 10.79$ kcal mol^{-1}; for copolymer **XIV**, $E = 9.25$ kcal mol^{-1}.

For copolymers **XI** and **XIII**, which have a similar copolymer composition (2.0 : 1.0 and 2.2 : 1.0, respectively), the energy activation value obtained is greatest ($E = 14.79$ kcal mol^{-1}) if the methyl group is in the *ortho* position on the *N*-phenylmaleimide ring. This is probably due to structural effects and/or resonance effects stabilizing the bonds of the lateral or main chain.

CONCLUSIONS

From these results, regarding thermal decomposition and energy activation values, the following conclusions may be drawn.

Copolymer composition does influence thermal decomposition and energy activation.

For all the copolymers considered, the decomposition reaction was found to be zero order.

The nucleophilic monomers with one (MOX) or two (ETOX) methyl groups undergo thermal degradation in one step; but TMOX, which has three methyl groups, degrades in two steps.

Copolymers with the same or similar copolymer composition have highest activation energy if the methyl group is in *ortho* or *para* position on the *N*-phenylmaleimide ring.

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