

Thermal degradation and determination of kinetic parameters by dynamic thermogravimetry of copolymers synthesized without initiator

B.L. Rivas ^{a,1}, G. del C. Pizarro ^a, R.E. Catalán ^a and L.H. Tagle ^b

^a *Polímeros, Departamento de Química, Facultad de Ciencias, Universidad de Concepción, Casilla 3-C, Concepción (Chile)*

^b *Facultad de Química, Pontificia Universidad Católica de Chile, Casilla 6177, Santiago (Chile)*

(Received 4 January 1991)

Abstract

The thermal degradation of a series of 18 copolymers of 2-methylaziridine and 1-(2-hydroxyethyl)aziridine with *N*-phenylmaleimide and derivatives obtained without added catalyst, was investigated using thermogravimetry (TGA) under a dynamic nitrogen atmosphere over a temperature range from 20 to 500 °C. Almost all the copolymers degrade in one step. The kinetic parameters E_a , n and A were obtained following one method of thermogravimetric analysis. The thermal stability depends on the copolymer composition which was determined from the ¹H NMR spectra. The most stable material was poly(*p*-nitrophenylmaleimide-co-2-methylaziridine).

INTRODUCTION

The technique of thermogravimetric analysis (TGA) has been widely used in polymer characterization, and in thermal stability and degradation studies. It is particularly useful when applied to a homologous series of polymers. Kinetic parameters such as activation energy E_a , pre-exponential factor A and reaction order n give a quantitative measure of the thermal stability [1].

Copolymers of *N*-phenylmaleimide with styrene, vinyl acetate and methyl methacrylate showed better thermal stability than the vinyl homopolymers; the thermal stability increased as a function of the maleimide content [2]. The same was found to be true in previous work on the improvement of the thermal stability of acrylonitrile copolymerized with various *N*-substituted maleimides [3]. Moreover, Hoering et al. [4] noticed that the glass tempera-

¹ Author to whom correspondence should be addressed.

tures of vinyl chloride/*N*-phenylmaleimide and vinyl chloride/*N*-cyclohexylmaleimide copolymers increase linearly with increasing maleimide content.

The aforementioned properties of *N*-substituted maleimides in improving the thermal stability of a variety of vinyl polymers, together with the highly conjugated nature of these molecules, allow them to act in the radical degradation processes of poly(vinyl chloride) (PVC) [5]; furthermore, because they are good dienophiles, they can interact with the conjugated double bonds of the degraded PVC.

The copolymerization of vinyl monomers with cyclic monomers is of great interest; however, it is difficult to achieve owing to their different polymerization reactivities and mechanisms. Although new types of polymers would be produced by copolymerization of these two extremely different types of monomer and new areas of application would result, only a few reports have been published in this field so far [6–12].

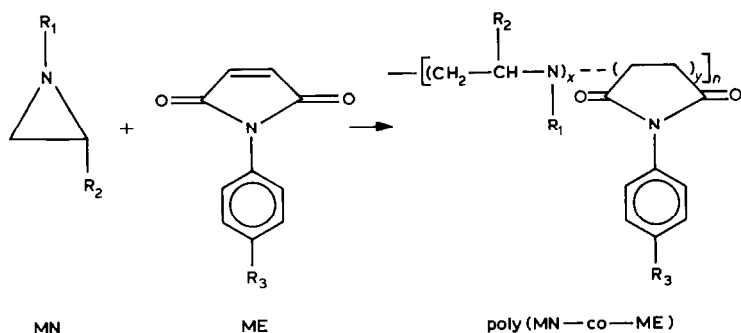
The kinetics of the thermal degradation of poly[*N*-(*n*-alkyl)maleimides] [13–16] and poly[*N*-(aryl)maleimides] [17,18], as well as those of copolymers of *N*-phenylmaleimides and their derivatives with oxazoline monomers [19], have been investigated. In each case, the thermal stability has been considered from different points of view.

We have reported previously the thermal behaviour for copolymers obtained by zwitterion copolymerization [19,20]. In this study, samples of poly[*N*-phenylmaleimide-co-1-(2-hydroxyethyl)aziridine] (P(*N*-PhMI-co-HEA)), poly[*p*-methyl-phenylmaleimide-co-1-(2-hydroxyethyl)aziridine] (P(*p*-MePhMI-co-HEA)), poly[*p*-methoxyphenylmaleimide-co-1-(2-hydroxyethyl)aziridine] (P(*p*-MeOPhMI-co-HEA)), poly[*p*-nitrophenylmaleimide-co-1-(2-hydroxyethyl)aziridine] (P(*p*-NO₂PhMI-co-HEA)), poly[*N*-phenylmaleimide-co-2-methylaziridine] (P(*N*-PhMI-co-MAZ)) and poly(*p*-nitrophenylmaleimide-co-2-methylaziridine) (P(*p*-NO₂PhMI-co-MAZ)) obtained by copolymerization via the zwitterion [21], were degraded under dynamic conditions. This paper reports the data on the thermal stability of these polymers obtained by TGA. The investigation also involves the variation of the kinetic parameters of the thermal degradation of copolymer samples with the type of substituent and with the copolymer composition.

EXPERIMENTAL

Samples

All copolymer samples were obtained by copolymerization via the zwitterion without an added catalyst [21]. The copolymer composition was determined from ¹H NMR spectra.



Thermogravimetric analysis

The TGA thermograms were obtained using a Perkin-Elmer thermobalance TGS-1. Samples of about 3–6 mg were degraded under a dynamic nitrogen atmosphere at $10^\circ\text{C min}^{-1}$.

RESULTS AND DISCUSSION

On the basis of the concept of spontaneous copolymerization the copolymers were synthesized without added initiator. The *N*-phenylmaleimides and their derivatives, as electrophilic monomers (ME), and the aziridine derivatives, as nucleophilic monomers (MN), were copolymerized respectively. Almost all the copolymers are statisticals [21]; they are listed in Table 1.

Figures 1–3 show the thermograms of the 18 copolymers recorded under dynamic conditions; the plots show the typical sigmoidal form. All the copolymers degrade continuously in one stage, except copolymer 18 which degrades in two stages.

Table 2 shows the values of the thermal decomposition temperatures (TDTs) for each copolymer. These were taken as the first marked change in

TABLE 1
The copolymers synthesized

| R ₁ | R ₂ | R ₃ | Copolymer | Number |
|------------------------------------|-----------------|------------------|---|---------|
| CH ₂ CH ₂ OH | H | H | P(<i>N</i> -PhMI-co-HEA) | (1–3) |
| CH ₂ CH ₂ OH | H | CH ₃ | P(<i>p</i> -MePhMI-co-HEA) | (4–6) |
| CH ₂ CH ₂ OH | H | OCH ₃ | P(<i>p</i> -MeOPhMI-co-HEA) | (7–9) |
| CH ₂ CH ₂ OH | H | NO ₂ | P(<i>p</i> -NO ₂ PhMI-co-HEA) | (10–12) |
| H | CH ₃ | H | P(<i>N</i> -PhMI-co-MAZ) | (13–15) |
| H | CH ₃ | NO ₂ | P(<i>N</i> -PhMI-co-MAZ) | (16–18) |

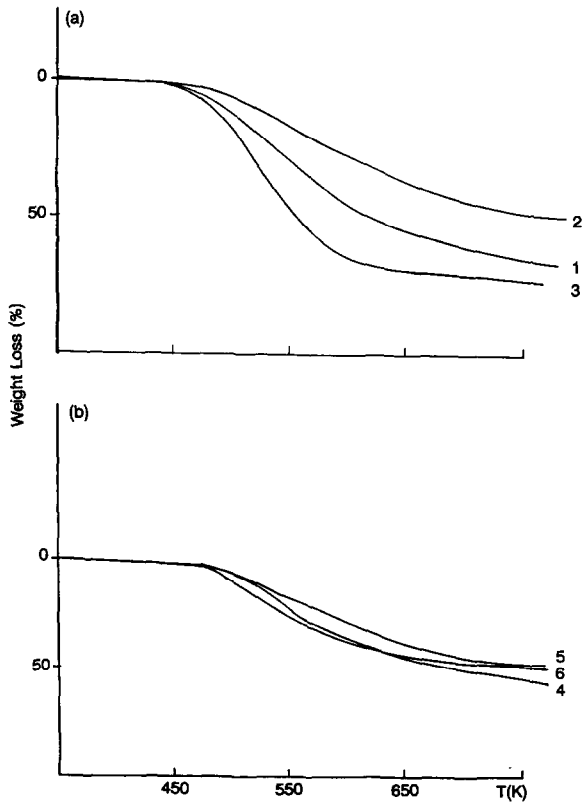


Fig. 1. Thermograms for (a) P(*N*-PhMI-co-HEA) and (b) P(*p*-MePhMI-co-HEA) copolymers. Heating rate, $10^{\circ}\text{C min}^{-1}$; nitrogen atmosphere.

the slope of the TG curve. The copolymers have a TDT equal to or greater than 440 K, the P(*p*-NO₂PhMI-co-MAZ) copolymer having the highest, 520 K.

Determination of the kinetic parameters

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

$$-d\alpha/dt = K_n(1 - \alpha)^n$$

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, $d\alpha/dt$, was determined using a differential technique and including the heating rate v . The specific rate K_n was obtained from the Arrhenius relation:

$$K_n = A \exp(-E_a/RT)$$

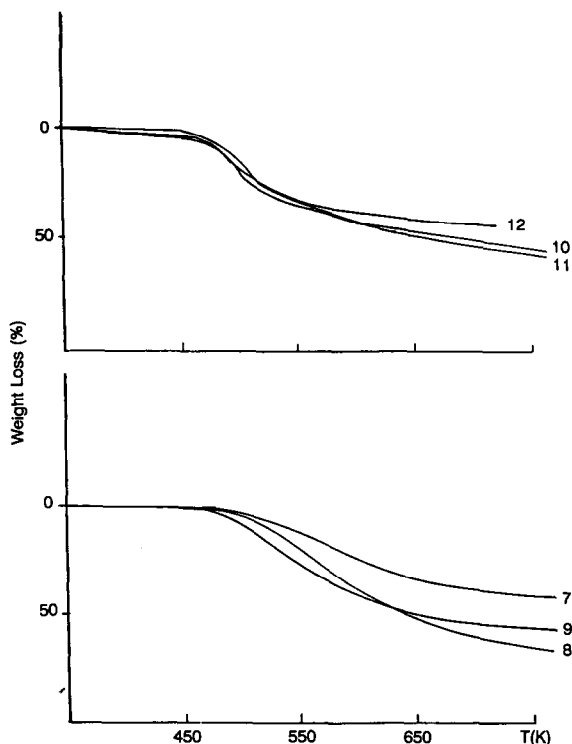


Fig. 2. Thermograms for (a) P(*p*-MeOPhMI-co-HEA) and (b) P(*p*-NO₂-PhMI-co-HEA) copolymers. Heating rate, 10 °C min⁻¹; nitrogen atmosphere.

On combining both equations, incorporating the heating rate v and using a logarithmic form, the following equation is obtained:

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

Finally, to calculate the kinetic parameters E_a and A , a linear multiple regression program was used. From a plot of β vs. $1/T$, E_a and A were determined from the slope and intercept respectively (see Figs. 4–6).

For all the copolymers, the program was run for $n=0$ and $n=1$. According to the results, the reaction order is zero, which infers that the sample geometry is such that diffusion of volatiles to the sample surface and their evaporation are the rate-controlling factors. The coefficient of linear correlation varied from 0.999 to 0.993 for $n=0$. The E_a and A values are summarized in Table 2.

Both kinetic parameters depend on the copolymer composition. For copolymers 1–12, the higher values of E_a were obtained for those statistical copolymers richer in the nucleophilic monomer, HEA.

The P(*N*-PhMI-co-HEA) and P(*p*-MePhMI-co-HEA) copolymers have the highest E_a values of 18.6 kcal mol⁻¹ and 18.9 kcal mol⁻¹ for copolymer

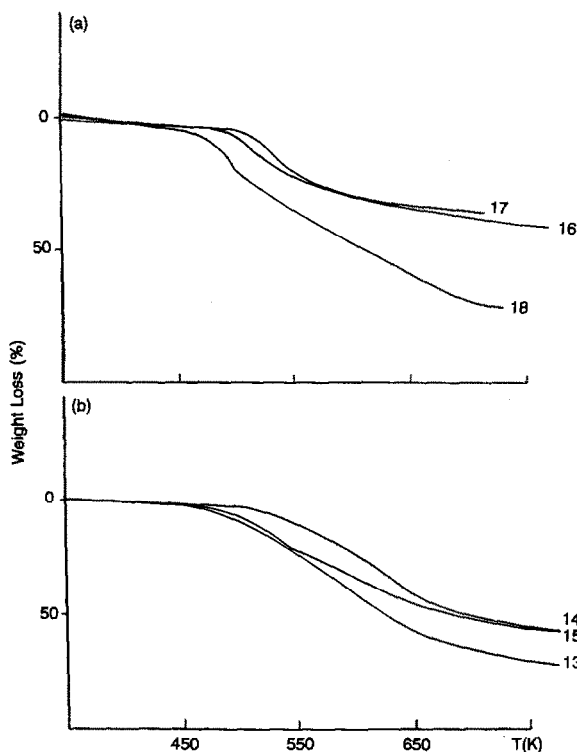


Fig. 3. Thermograms for (a) P(*N*-PhMI-co-MAZ and (b) P(*p*-NO₂-PhMI-co-MAZ) copolymers. Heating rate, 10°C min⁻¹; nitrogen atmosphere.

compositions 1.0:2.3 and 1.0:1.5 respectively. For copolymers with a similar copolymer composition, however, the effect of the substituent on the phenylmaleimide ring is not so marked. For instance, copolymers 1 and 8 with compositions 1.7:1.0 and 1.5:1.0 respectively have E_a values of 12.0 kcal mol⁻¹ and 13.3 kcal mol⁻¹ respectively.

Copolymers 13–18 show a different behaviour, the most stable being the P(*p*-NO₂PhMI-co-MAZ) copolymer, sample 16, which has an E_a value of 21.7 kcal mol⁻¹. The backbone has a copolymer composition of 2.0:1.0, rich in *p*-NO₂PhMI, which is the same as the feed monomer ratio.

In general, the statistical copolymers rich in *N*-phenylmaleimide are the most stable. Increasing the 2-methylaziridine content in the copolymer chain decreases the E_a (see copolymers 13 and 18).

CONCLUSIONS

The copolymer composition depended on the substituent in the *para* position of the *N*-phenylmaleimide ring. For the -NO₂ group, the homopropagation reaction of 1-(2-hydroxyethyl)aziridine is favoured over the

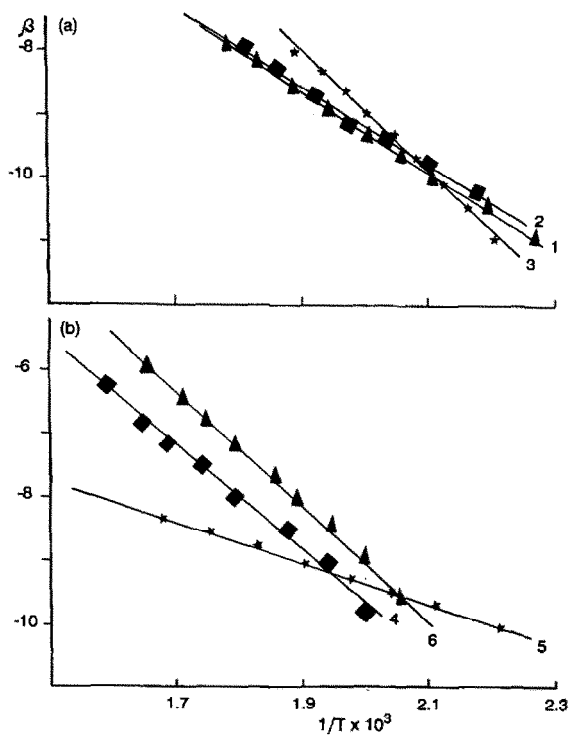


Fig. 4. Plots of β vs. $1/T$ for (a) P(*N*-PhMI-co-HEA) and (b) P(*p*-MePhMI-co-HEA) copolymers.

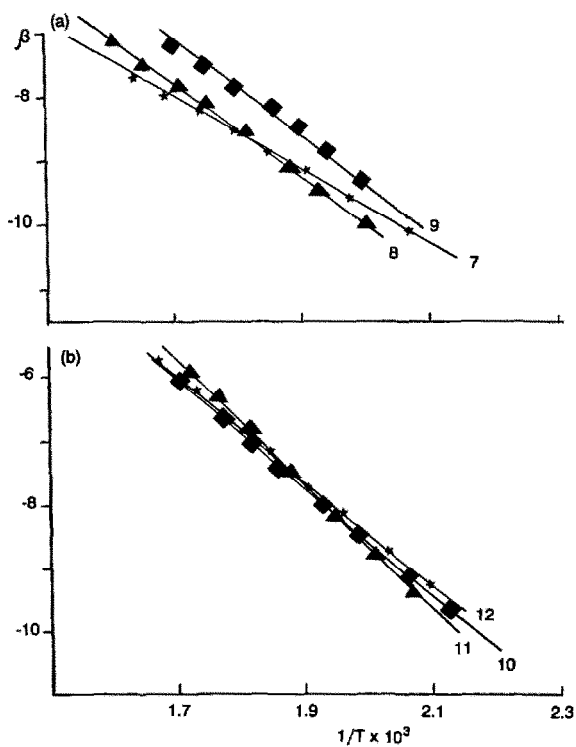


Fig. 5. Plots of β vs. $1/T$ for (a) P(*p*-MeOPhMI-co-HEA) and (b) P(*p*-NO₂-PhMI-co-HEA) copolymers.

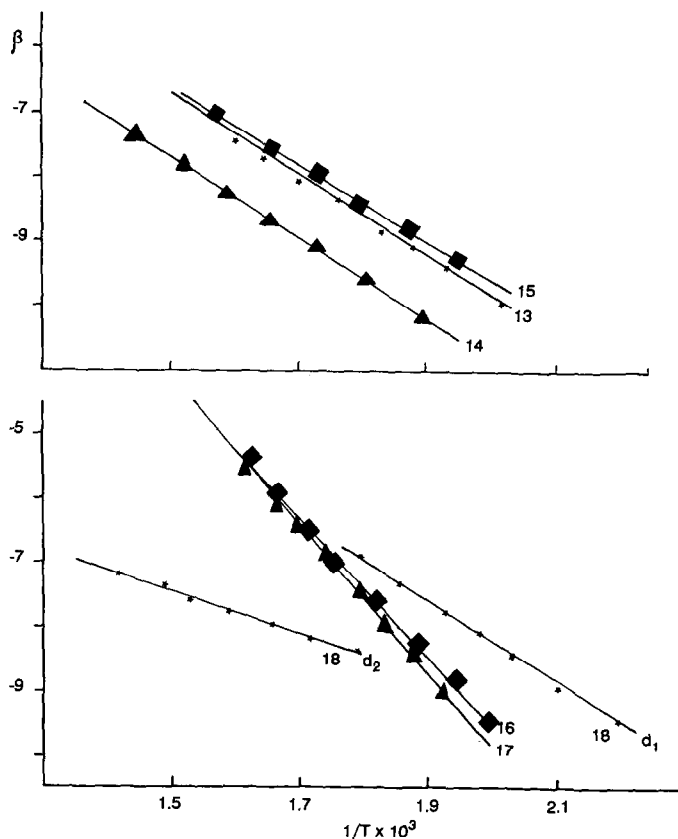


Fig. 6. Plots of β vs. $1/T$ for (a) $P(N\text{-PhMI-co-MAZ})$ and (b) $P(p\text{-NO}_2\text{-PhMI-co-MAZ})$ copolymers.

copolymerization reaction. In contrast, for the $-\text{OCH}_3$ p -group, all the copolymers were statistical richest in p -methoxyphenylmaleimide.

The thermal decomposition temperature and the kinetic parameters depended on the copolymer composition. An effect of to the nucleophilic monomer was also observed. The higher thermally stable copolymers were those obtained using 2-methylaziridine rather than 1-(2-hydroxyethyl)aziridine monomer. Thus, copolymers 15 and 16, with copolymer compositions 1.9:1.0 and 2.0:1.0, respectively had a TDT of 510 K and 520 K respectively.

For all copolymers, the decomposition reaction was zero order, $n = 0$.

ACKNOWLEDGEMENTS

We thank the Dirección de Investigación, Universidad de Concepción, for financial support (Grant No. 20.13.49). G. del C. Pizarro thanks CONICYT for a Fellowship.

TABLE 2

Relationship between copolymer composition, thermal decomposition temperature and kinetic parameters

| Copolymer | A (s^{-1}) | TDT (K) | E_a (kcal mol^{-1}) | Copolymer composition ME:MN ^a |
|---|---------------------|------------|--------------------------------|--|
| P(<i>N</i> -PhMI-co-HEA) | | | | |
| 1 | 16.60 | 460 | 12.0 | 1.7:1.0 |
| 2 | 205.40 | 450 | 18.6 | 1.0:2.3 |
| 3 | 9.70 | 440 | 11.3 | 1.0:1.1 |
| P(<i>p</i> -MePhMI-co-HEA) | | | | |
| 4 | 1197.60 | 470 | 16.7 | 1.3:1.0 |
| 5 | 0.09 | 450 | 6.9 | 2.3:1.0 |
| 6 | 21384.00 | 450 | 18.9 | 1.0:1.5 |
| P(<i>p</i> -MeOPhMI-co-HEA) | | | | |
| 7 | 7.70 | 480 | 11.7 | 2.7:1.0 |
| 8 | 60.50 | 480 | 13.3 | 1.5:1.0 |
| 9 | 0.20 | 480 | 8.3 | 3.9:1.0 |
| P(<i>p</i> -NO ₂ PhMI-co-HEA) | | | | |
| 10 | 829.60 | 470 | 15.1 | 1.0:5.7 |
| 11 | 984.70 | 470 | 15.1 | 1.0:5.2 |
| 12 | 19.80 | 460 | 18.6 | 1.0:4.7 |
| P(<i>N</i> -PhMI-co-MAZ) | | | | |
| 13 | 2.60 | 460 | 10.4 | 1.0:2.4 |
| 14 | 56.60 | 460 | 14.1 | 1.0:1.4 |
| 15 | 5.10 | 510 | 12.3 | 1.9:1.0 |
| P(<i>p</i> -NO ₂ PhMI-co-MAZ) | | | | |
| 16 | 0.0020 | 520 | 21.7 | 2.0:1.0 |
| 17 | 0.0004 | 470 | 10.1 | 1.1:1.0 |
| 18 | 95.4000 | 460 | 12.7 | 1.0:1.7 |

^a Determined from ¹H NMR spectra.

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