# **Thermal Degradation of Poly(sulfobetaines)**

### J. CARDOSO,<sup>1</sup> L. RUBIO,<sup>1</sup> M. ALBORES-VELASCO<sup>2</sup>

<sup>1</sup> UAM-I, CBI, Depto. de Física, Apdo. Postal 55-534, C.P.09340 México, D.F., Mexico

<sup>2</sup> Facultad de Química, UNAM, Circuito Interior, C.U., 04510 México, D.F., México

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ABSTRACT: Due to their interesting properties, zwitterionic polymers have been extensively studied; however, only a few reports discuss their thermal degradation. The objective of this work was to study the pattern of thermal degradation of three poly-(sulfobetaines) with different lateral chain lengths and the relationship between structure and degradation mechanism of the polymers. Because the initial decomposition temperatures are not significantly different in polymers with different ethylene glycol residues, it was possible to study the thermal behavior of these polymers at the same temperature range. The apparent activation energies of the degradation for polymers, calculated by the Ozawa method, was different for each poly(sulfobetaine). A decomposition mechanism is suggested, which included a Hoffman elimination of the quaternary amine giving vinyl ethers, which in turn, decompose to carboxylic acids, which can suffer and intramolecular cyclization reaction, and finally produce a polypropylene like chain. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 1409–1414, 1999

**Key words:** thermal decomposition; poly(sulfobetaines); degradation mechanism; parameters kinetics; thermogravimetric analysis

# INTRODUCTION

Zwitterionic polymers have been extensively studied by many groups of investigation: Galin and coworkers<sup>1–5</sup> have reported on poly(ammonium sulfopropylbetaines) and recently on poly- $(ammonio alkoxydicyano ethenolates)^5$  physical chemistry properties. Cardoso and coworkers<sup>6–9</sup> have worked on poly(sulfobetaines), poly(carboxybetaines), and poly(N-oxides). Huglin and Rego,<sup>10</sup> on the other hand, have used zwitterionic polymers in blends with poly(vinylpyridines). Zwitterionic polymers show specific and unique properties, for example, "antipolyelectrolyte" behavior, strong binding capacity, and high solvation power of the glassy polymeric matrixes toward salts of widely different lattice energies.<sup>5</sup> All

these interesting properties are due to the high dipole moments exhibited by this kind of polymers. Some possible applications as flocculants, and as solid electrolytes for high-energy batteries have been envisioned for these polymers.

Despite these attractive properties, there are only a few reports on thermal degradation of poly-(zwitterionic) materials. Liaw and Lee,<sup>11,12</sup> and recently Galin et al.,<sup>13</sup> studied the thermal degradation of samples of poly(sulfobetaines) [named, poly-(DMAPS)], both in nitrogen and in air. They showed that the temperature of thermal degradation of poly(DMAPS) in air is lower than in nitrogen at a high heating rate. They also found thermal degradation of such a polymer to occur in two and three stages in nitrogen or air atmosphere, respectively.

On the other hand, the change in length of the lateral chain between the nitrogen atom and sulfonate group or between the backbone chain and the nitrogen atom drastically changes some properties of poly(sulfobetaines), i.e., solubility,<sup>5</sup> glass

Correspondence to: J. Cardoso.

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transition temperatures,<sup>9</sup> dipolar moments,<sup>14</sup> etc. The objective of this work was to study the pattern of thermal degradation of poly(sulfobetaines) with different lengths of the lateral chain and the relation between their mechanisms of degradation and their structures. The determination of the kinetics parameters for their thermal decomposition is also discussed.

## Theory

Thermogravimetric (TGA) experiments at different heating rate,

$$\beta = \frac{dT}{dt}$$

allows determination of kinetic parameters of polymers degradation. If the conversion C at a constant temperature is defined as the relative loss of weight:

$$C = \frac{1 - w}{w_0}$$

where  $w_0$  and w represent the initial weight and weight after at a time (*t*), respectively, then the rate of chemical reaction can be expressed as a function of conversion *C* by the kinetic equation:

$$\frac{dC}{dt} = kf(C) \tag{1}$$

The rate of conversion depends on C according to the equation:

$$f(C) = (1 - C)^n$$
 (2)

where n is the order of reaction. If k is represented by the Arrhenius equation, it can be substituted in eq. (1), taking in consideration eq. (2) to get:

$$\frac{dC}{dt} = A(1-C)^n e^{-E/RT}$$
(3)

In TGA experiments, the rate of heating  $\beta$  is kept constant; finally, eq. (3) can be written as:

$$\frac{dC}{(1-C)^n} = \frac{A}{\beta} e^{-E/RT} dT$$
(4)

The integration of eq. (4) was developed by Doyle<sup>15</sup> and Ozawa,<sup>16</sup> giving the following form:

$$-\log \beta_1 - 0.457 \, \frac{E}{RT_1} = -\log \beta_2 - 0.457 \, \frac{E}{RT_2} \quad (5)$$

where R is the universal constant of gases,  $T_1$  and  $T_2$  are absolute temperatures associated with the different heating rates,  $\beta_{1,}$  and  $\beta_{2,}$  at the same weight loss.

The determination of the order of the reaction was obtained by using the relationship<sup>11,12</sup> between C and n:

$$\log \beta = \begin{cases} \log[(1-C)^{1-n} - 1] \text{ for } n \neq 1\\ \log|\ln(1-C)| \text{ for } n = 1 \end{cases}$$
(6)

## **EXPERIMENTAL**

The synthesis of monomers was carried out according to the technique used by Cardoso and Albores.<sup>9</sup> Polymers were synthesized by aqueous solution polymerization according to Monroy and Galin.<sup>1</sup> FTIR Spectroscopy (Perkin-Elmer 1615 FTIR Spectrometer); <sup>1</sup>H-NMR (Brucker DMX500, 500 MHz) and Elemental Analysis (Desert Analytics) showed the authenticity of the samples.<sup>9</sup> Molecular weights of the polymers were determined by light scattering at room temperature on a Dawn-F (Wyatt Tech.) apparatus at  $\lambda = 6320$  Å in trifluoroethanol.

Thermal analysis was made on a 931 TGA Du-Pont thermobalance linked to a Thermal Analyzer 2100 microprocesser. The heating rate ( $\beta$ ) was set to 2, 5, 10, 20, and 40 K/min; the size of samples was 4.8  $\pm$  0.5 mg, and all experiments were performed under nitrogen conditions using a 50 mL/min flow rate.

## RESULTS

The characterization of synthesized polymers: PMBS-1, PMBS-2, and PMBS-3 (see Fig. 1) showed the following values: molecular weights (by LS) were  $M_w$  (10<sup>-6</sup>) = 3.06, 0.71, and 0.59, and glass transition temperature (by DSC)  $T_g$  (K) = 527, 368, and 300 for PMBS-1, PMBS-2, and PMBS-3, respectively. Molecular weights and glass transition temperatures decrease as x (ethoxy groups number) increases. Glass transition temperature showed a linear relationship as

$$\begin{array}{c} \mathsf{CH}_{3} \\ \cdot (\mathsf{CH}_{2} \cdot \mathbf{C}_{-}) \cdot & \mathsf{R} \\ & & \mathsf{I} \\ \mathsf{O} = \mathsf{C} \cdot (\mathsf{OCH}_{2} \mathsf{CH}_{2}) \cdot \mathsf{N} \cdot \mathsf{CH}_{2} \mathsf{CH}_{2} \mathsf{CH}_{2} \mathsf{CH}_{2} \mathsf{CH}_{2} \mathsf{SO}_{3} \\ & & \mathsf{R} \end{array}$$

$$\mathbf{R} = \mathsf{CH}_{3}, \quad \mathbf{x} = \mathbf{1} \implies \mathsf{PMBS-1}$$

$$\mathbf{R} = \mathsf{CH}_{2} \mathsf{CH}_{3}, \mathbf{x} = \mathbf{2} \implies \mathsf{PMBS-2}$$

#### R=-CH $_2$ CH $_3$ , x = 3 $\implies$ PMBS- 3

**Figure 1** Structure of synthesized polymers, named PMBS-1, PMBS-2, and PMBS-3.

a function of the carbon atom number for the synthesized polymers.<sup>9</sup> Polymers are quite hygroscopic; therefore, they were dried in a vacuum oven for 24 h before the TGA experiments. Evolved water of 8  $\pm$  1%, 3  $\pm$  1%, and 2  $\pm$  1% for PMBS-1, PMBS-2, and PMBS-3, respectively, was obtained by heating the polymers at a rate of 10 K/min up to 473 K in a TGA apparatus. Because water affinity of polysulfobetaines has been extensively studied by Galin and coworkers,<sup>5</sup> it is possible to consider that the hygroscopicity decreases as x (number of ethoxy groups) in the synthesized polymers increases. Taking into account that PMBS-2 and PMBS-3 have ethyl groups on the nitrogen atom, which are slightly more hydrophobic than the methyl group in PMBS-1 together with the change of x, these results can be explained.<sup>9</sup>

The temperature at which intensive degradation is initiated  $(T_i)$  at various heating rates was taken as a criterion of heat stability of the studied polymers. The decomposition temperature of the synthesized polymers is shown in Table I. It is clear in the table that these temperatures are not significantly dependent on the number of ethylene glycol residues; therefore, it is possible to study the thermal behavior of all samples in the same temperature range. The initial size of each sample was almost the same; this allowed us to compare the initial decomposition temperature of the polymers. The results of thermogravimetry at various heating rates under nitrogen atmosphere for PMBS-1 are plotted as a function of temperature (see Fig. 2). The graph clearly illustrates the strong influence of heating rates on the thermal

Table IDecomposition Temperature ofSynthesized Polymers

	Stage 1		Stage 2	
β (°C/min)	$\Delta T$ (K)	C%	$\Delta T$ (K)	C%
	PM	BS-1		
2	543 - 601	59	646-699	17
5	551 - 623	60	667 - 717	18
10	561 - 645	62	682 - 732	18
20	572 - 654	62	695 - 743	18
40	582 - 675	59	702 - 750	18
	PM	BS-2		
2	479-602	66	610 - 679	17
5	502 - 591	59	640-698	18
10	517 - 614	60	666 - 715	16
20	521 - 622	60	660 - 722	18
40	518 - 673	69	673 - 752	18
	PM	BS-3		
10	509-627	30	627 - 773	20
20	497-641	29	617-773	_
40	527-645	28	645 - 773	24

decomposition behavior of the polymers: when the heating rate was increased from 2 to 40 K, an increase of 39 K in the initial thermal decomposition temperature was measured. Figure 2 also shows that the decomposition process is performed in two stages at different rates under a nitrogen atmosphere. The first stage starts at 543 K, and is increased to 675 K, and the second one initiates between 646 and 750 K, as the heating



Figure 2 TGA curves of PMBS-1 at various heating rates under a  $\rm N_2$  atmosphere.



Figure 3 TGA and its derivative curves of PMBS-2 at 10 K/min under an  $N_2$  atmosphere.

rate is increased from 2 to 40 K/min. Liaw and Lee<sup>12</sup> reported the decomposition of a sulfobetaine polymer in two stages by heating under nitrogen almost at the same range; PMBS-2 and PMBS-3, however, decompose in more than two stages, which are not clearly distinguished (see, e.g., Fig. 3, the thermogram and its derivative curve for PMBS-3). In the case of PMBS-2, initial temperatures of each stage are around 517 and 682 K at  $\beta = 10 \text{ K/min}$ . In the same way, PMBS-3 shows initial temperature decomposition of 517 and 666 K at  $\beta = 10$  K/min. These values change according to  $\beta$ . In some cases it is not possible to clearly indicate the end of one stage and the start the following. In Table I the most representatives values for  $T_i$  and % lost weights are shown.

#### **Chemical Mechanism of Degradation**

For PMBS-1, the first stage could correspond to a Hoffman elimination of the quaternary amine, probably giving place to a residual vinyl methacrylate in the molecule, while the second stage would correspond to the scission of the lateral chain of the polymer due to a electrocyclic elimination of acetylene, leaving a carboxylic acid that might form an anhydride and is finally decarboxylated to give a saturated polypropylene-like chain. The same loss of dialkylaminobutyl sulphonic acid can be suggested for the other two



**Figure 4** Decomposition chemical mechanism suggested of Poly(sulfobetaines).

polymers, followed by a gradual loss of vinyl alcohol to finally give the same vinyl ester that would follow the same pattern of degradation as PMBS-1. Indeed, Figure 3 shows that there are about three stages in the decomposition process for PMBS-2 and PMBS-3, and Figure 4 shows the general proposal of the decomposition mechanism for PMBS-1, PMBS-2, and PMBS-3. Table I shows only two decomposition stages for each polymer. In the case of PMBS-2 and PMBS-3, the second stage is considered as a whole of the different chemical process they had. Table II shows the

Table II	<b>Comparation between the Proposed</b>
Mechanis	m and Experimental Data

	Stag Loss W	Stage 1 Loss Weight		Stage 2 Loss Weight	
Polymer	Exp.	Theo.	Exp.	Theo.	
PMBS-1 PMBS-2 PMBS-3	$egin{array}{c} 60 \pm 2 \ 65 \pm 2 \ 67 \pm 2 \end{array}$	61 69 72	$25 \pm 2 \\ 18 \pm 2 \\ 22 \pm 2$	23 19 17	



**Figure 5** FTIR spectra of the residual polymers after heating of the three polymer samples at 10 K/min up to 633–653 K, which is the final temperatures of the first stage in nitrogen atmosphere.

agreement between the proposed mechanism and experimental data for the studied polymers. A final observation in the thermoghams is that the residual mass percent obtained by heating the polymers up to 773 K is not significantly dependent on the number of ethylene glycol residues (x)increment, i.e., around 6-8% of solid residues.

The FTIR spectra (Fig. 5) of the residual polymers after heating any of the three PMBS-1, PMBS-2, and PMBS-3 polymer samples at 10 K/min up to 633–653 K, which is the final temperature of the first stage in nitrogen atmosphere, seems to support the degradation proposal, because the spectra show bands at 1805 and 1762 cm<sup>-1</sup> (anhydride absorption) beside the C=O stretching at 1728 cm<sup>-1</sup> and the C-O st and C-H at 1149 and 1016, and 1458 cm<sup>-1</sup>, respectively.

#### **Determination of Kinetic Parameters**

Kinetic parameters of polymers degradation from TGA data are strongly dependent on the method of calculation. The apparent activation energy of the process can seldom be assessed correctly from a single TGA curve. The method of calculation of activation energy, proposed by Ozawa, requires several TGA curves at different heating rates. Representative results are shown in Figures 6 and 7 for PMBS-I and PMBS-3, respectively, at several heating rates (2, 5, 10, 20, and 40 K/min).

To determine the reaction order "*n*" of the chemical decomposition, we used the Ozawa's method. In the case of n = 1, the relationship must be linear when log  $[\ln(1-C)]$  vs. log  $\beta$  is plotted, according to eq. (5). As it is observed (see Fig. 6), PMBS-1 shows a linear relationship for



**Figure 6** The plot of logarithms of  $\beta$  vs. the reciprocal absolute temperature for the indicate conversion, *C*, of the degradation of PMBS-1 of the first stage under an N<sub>2</sub> atmosphere.

the first stage of decomposition, but PMBS-2 shows only linear behavior up to C = 0.4 (see Fig. 7). The chemical reaction's order of the other stages for each polymer were obtained in a similar way. Table III shows the results taking into account three stages for PMBS-2 and PMBS-3.



**Figure 7** The plot of logarithms of  $\beta$  vs. the reciprocal absolute temperature for the indicate conversion of the degradation of PMBS-3 of the first stage under a N<sub>2</sub> atmosphere.

	Stage 1				Stage 2	
	$\Delta E$ (kJ/	/mol)	$\log A$	$\Delta E$	(kJ/mol)	$\log A$
PMBS-1	159	)	13.6		209	13.6
	Stage 1		Stage 2		Stage 3	
	$\Delta E$ (kJ/mol)	$\log A$	$\Delta E$ (kJ/mol)	$\log A$	$\Delta E$ (kJ/mol)	$\log A$
PMBS-2 PMBS-3	163 105	$\begin{array}{c} 13.9 \\ 1.82 \end{array}$	$\begin{array}{c} 163\\ 360\end{array}$	$13.9\\1.83$	219 317	$\begin{array}{c} 13.9\\ 2.17\end{array}$

Table IIIApparent Activation Energies and Preexponential Factors of the Degradation of<br/>Poly(sulfobetaines)

The apparent activation energy determined by the Ozawa's method for a given value of the conversion *C*, at constant temperature, when log  $\beta$  is plotted as a function of the reciprocal absolute temperature, is shown in Figure 6 for PMBS-1. The apparent activation energy and preexponential factors of the first stage of PMBS-1, PMBS-2, and PMBS-3 degradation in nitrogen atmosphere were 159, 163, and 105 kJ/mol and log A = 13.6, 13.9, and 1.86, respectively. These values are higher than those reported by Liaw and Lee<sup>11,12</sup> for poly(DMAPS) (103.3 kJ/mol and log A = 8.8 ) in similar conditions.

## CONCLUSIONS

Zwitterionic polymers with different lengths in the lateral chain showed almost the same initial decomposition temperature. They showed at the last two stages of decomposition. Both of them had a reaction order "n" of chemical decomposition equal to 1. The apparent activation energy and preexponential factor for each stage were calculate using Ozawa's method. A possible decomposition mechanism through a vinyl ether, vinyl metacrylate, and anhydride groups was proposed. IR spectra seem to support the mechanism.

#### REFERENCES

- 1. Monroy-Soto, V. M.; Galin, J. C. Polymer 1984, 25, 121.
- Galin, M.; Monroy-Soto, V. M.; Galin, J. C. Polymer 1984, 25, 254.
- Galin, M.; Marshal, E.; Mathis, A.; Meorer, B.; Monroy-Soto, V. M.; Galin, J. C. Polymer 1987, 28, 1937.
- Galin, J. C.; Galin, M. J Polym Sci Part B Polym Phys 1992, 30, 1113.
- Galin, M.; Galin, J. C. J Polym Sci Part B Polym Phys 1995, 33, 2033.
- 6. Cardoso, J.; Manero, O. J Polym Sci Part B Polym Phys 1991, 29, 639.
- Montiel, R.; Cardoso, J.; Manero, O. J Mater Res 1995, 10, 1.
- Cardoso, J.; Manero, O. In The Polymer Material Encyclopedia; Salamone, J. C., Ed.; CRC Press, Boca Raton, FL, 1996, p. p. 8841, vol. 11.
- Cardoso, J.; Manrique, R.; Albores-Velasco, M.; Huanosta, A. J Polym Sci Part B Polym Phys 1997, 35, 479.
- 10. Huglin, M.; Rego, J. Polymer 1990, 31, 1269.
- Liaw, D. J.; Lee, W. F. J Appl Polym Sci 1985, 30, 4697.
- 12. Lee, W. F. J Appl Polym Sci 1989, 37, 3263.
- 13. Ehrmann, M.; Galin, J. C. Polymer 1993, 33, 859.
- Salcedo, R.; Alcalá, T.; Cardoso, J.; Manero, O. Polymer 1991, 32, 2300.
- 15. Doyle, C. D. J Appl Polym Sci 1961, 5, 285.
- 16. Ozawa, T. Bull Chem Doc Jpn 1965, 38, 1881.