

# Spectral and thermogravimetric analysis of some poly(carboxybetaine)s polymers

M. STRAT<sup>\*</sup>, S. VASILIU<sup>a</sup>, G. STRAT<sup>b</sup>, C. LUCA<sup>A</sup>, I. GRECU<sup>b</sup>, S. GURLUI, S. I. STRATULAT<sup>c</sup>

<sup>\*</sup>“Al. I. Cuza” University of Iasi, Romania

<sup>a</sup>“P.Poni” Institut of Macromolecular Chemistry Romanian Academy, Iasi, Romania

<sup>b</sup>“Gh.Asachi” Technical University of Iasi, Romania

<sup>c</sup>University of Medicine and Pharmacy of Iasi, Romania

During the past few years, increasing number of papers on physico-chemical properties of poly(betaine)s based on poly(N-vinylimidazole) (PVI) have been reported. It was found that the poly(betaine)s exhibit in water different behaviors: polyelectrolyte, non-polyelectrolyte, or anti-polyelectrolyte. Given their interesting properties, the poly(betaine)s have many applications in medical and industrial areas.

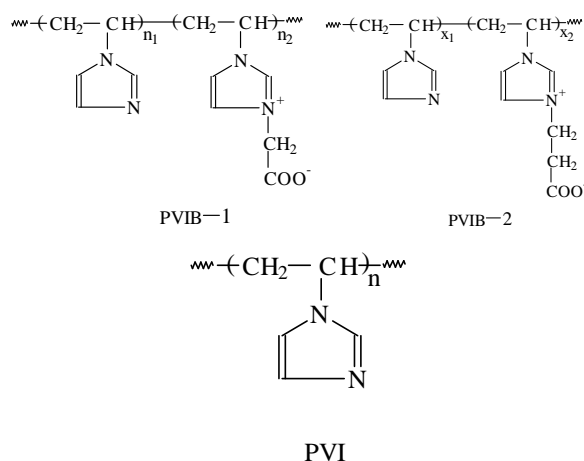
(Received October 14, 2005; accepted January 26, 2006)

**Keywords:** FTIR spectra, Thermogravimetric analysis, Degradation

## 1. Introduction

In this work two poly(betaine)s based on poly(N-vinylimidazole) and their precursor have been studied by means of thermogravimetric analysis and Fourier-transform infrared spectra. It is known that the structural changes have a large influence on the ionic conductivity and dielectric relaxation in such polymer. This analysis can give information about the mechanism of ionic conductivity for the studied polymers [1-6].

The studied substances were synthesized at the “P. Poni” Institute of Macromolecular Chemistry (Romanian Academy) of Iasi, Romania. The chemical structure of the poly(betaine)s based on N-vinylimidazole is given in Scheme I. Scheme 1 shows the obtaining reactions of the two poly(carboxybetaine)s: where  $n_1 + n_2 = n$  and  $x_1 + x_2 = x$ ;  $n_2$  and  $x_2$  are the molar transformation degrees, respectively.



Scheme I. Chemical structure of the studied poly(betaine)s.

## 2. Experimental

### 2.1 Materials

Poly(N-vinylimidazole) (PVI) was synthesized by precipitation polymerization of vinylimidazole as described elsewhere [7].

(PVIB-1) was performed by the quaternization PVI with chloroacetic acid sodium salt (Flucka Chemicals Co.) followed by the dialysis against deionized water of the reaction product.

(PVIB-2) was carried out by the nucleophilic addition of PVI to carbon-carbon double bond from acrylic acid as shown in previous study [8].

### 2.2 Methods

The infrared absorption spectra were obtained by means of the spectrophotometer FT IR BOMEN 104B Canada. The studied polymers were obtained as KBr pellets in which the studied compound amounts at 5 mg per 500 mg KBr.

The thermo-destructive behavior of PVIB-1, PVIB-2 and PVI was evaluated by means of the F. Paulic, J. Paulic Erdey Derivatograph from MOM Budapest on sample weighting 50 mg at 9 °C/ min heating rate in air, having  $\alpha\text{-Al}_2\text{O}_3$  as reference material.

The kinetic parameters of thermal degradation for each step were determined by both Coats Redfern [9] and Levi-Reich [10] integral methods, using software that processes thermogravimetric data up to 900 °C.

## 3. Results and discussions

### 3.1. The FT IR analysis

From the FTIR spectra analysis of the studied polymers, it follow that at room temperature all the

vibration bands are present, characteristic to the groups included in the structure of the studied poly (betaine) [11]. Figs. 1, 2 and 3 illustrate the FT IR spectra of the studied polymers at different temperatures, ranging between the room temperature and 600 °C.

The vibration bands of medium intensity at about 1350  $\text{cm}^{-1}$  and that at about 1560  $\text{cm}^{-1}$  correspond to the,  $>\text{C}=\text{N}-$  group.

There relatively wide absorption band at about 1625  $\text{cm}^{-1}$  is the result of overlapping the vibration band belonging to the  $>\text{C}=\text{N}-$  group from the pentagonal ring, on the band corresponding to the asymmetric strain vibrations of the  $-\text{COO}^{-1}$ , group at about 1610  $\text{cm}^{-1}$ , which is quite intense and wide.

To the,  $>\text{C}=\text{N}^{+}<$ , group in all spectra appear the wide band with its maximum at about 3300  $\text{cm}^{-1}$ , which appears even when the studied samples were at quite high temperatures (500- 600 °C).

In the FTIR spectra are also present the characteristic vibration bands to the carboxyl group  $-\text{COO}^{-}$ , at about 916  $\text{cm}^{-1}$  and 1225  $\text{cm}^{-1}$ .

At temperatures exceeding 400 °C these bands are no longer present in the FTIR spectra. To the carboxyl group also belongs the band at about 1375  $\text{cm}^{-1}$  corresponding to the symmetric valence vibrations of this group.

At lower temperature (up to 100 °C) one can notice that for the PVIB-1 and PVIB-2 samples, the band having its maximum at about 1625  $\text{cm}^{-1}$  gets wider toward the band wings at larger wave numbers (about 1740  $\text{cm}^{-1}$ ). This shoulder can be explained taking into account the strong intermolecular interactions, which occur, in the solid phase. These interactions are of the type of electronic charge transfer (hydrogen bonds) interactions in which the carboxyl groups takes part.

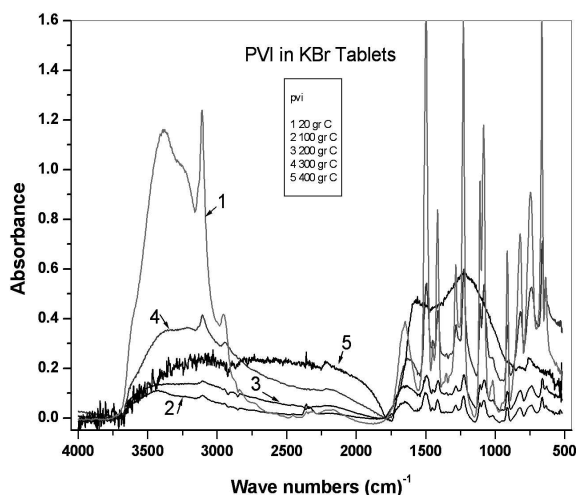


Fig. 1. FT IR spectra of PVI in KBr pellets.

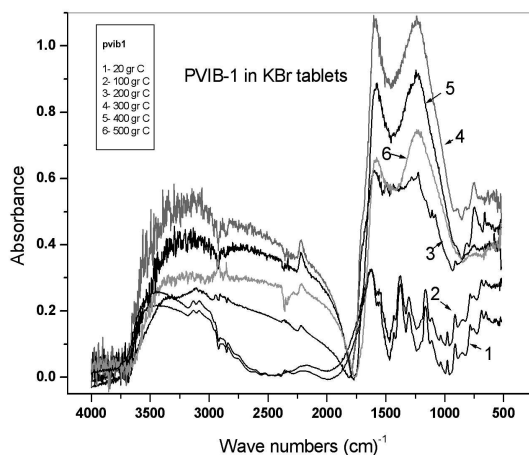


Fig. 2. FT IR spectra of PVIB- 1 in KBr tablets.

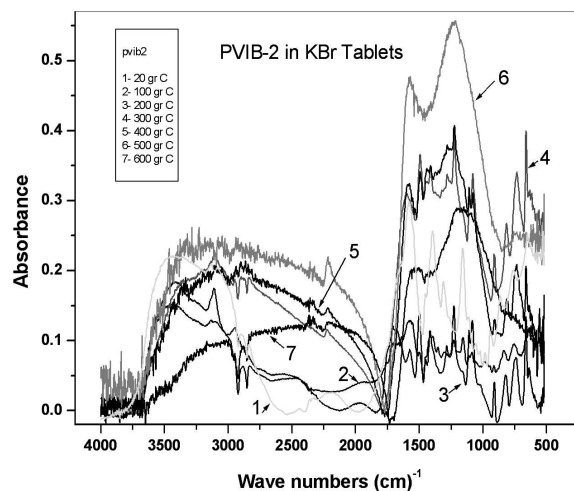


Fig. 3. FT IR spectra of PVIB- 2 in KBr pellets.

### 3.2. Thermal characterization

In Fig. 4, one can see TG and DTG curves, characteristic for the precursor PVI. Activation energies ( $E_a$ ) and order of reactions ( $n$ ) were calculated based on the weight loss ( $w$ ).

The degradation stages, weight loss, kinetic parameters and char data for the precursor are given in Table 1.

Table 1. Thermal behavior of PVI.

Stage	$T_i$ (°C)	$T_m$ (°C)	$T_f$ (°C)	w (%)	$E_a$ (kJ/mol)	n
I	20	70	255	6	37	0
II	255	310	355	16	126	1.1
III	355	430	498	54	282	1.9
IV	498	592	620	18	156	0.7

$T_i$  = initial decomposition temperature;  $T_m$  = temperature of maximum rate of weight loss;

$T_f$  = final decomposition temperature.

Data shows in Table 1 indicate that the thermal degradation mechanism of studied sample is complex and occurs in several steps. From Fig. 4 and Table 1 one can see that the degradation process for PVI proceeds in three stages.

The first decomposition stage, between 20 and 255 °C starts with the loss of water.

According to Fig. 4, a strong degradation starts at about 355 °C, the temperature at which the weight loss exceeds 54%. This result is in a very good agreement with the results obtained by FTIR spectra analysis. The FTIR spectrum of the PVI sample at the temperature of 400 °C clearly shows that the substance has degraded. The vibration bands assigned to the atomic groups from the chemical structures of this compound have completely disappeared.

The TG and DTG curves for the PVIB-1 and PVIB- 2 samples are given in the Fig. 5.

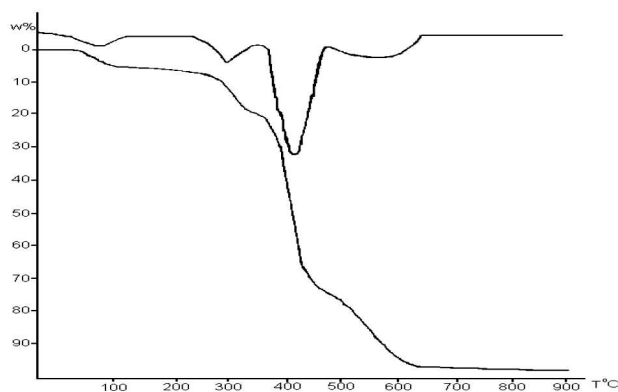


Fig. 4. TG and DTG curves, characteristic for the precursor PVI.

Some thermogravimetric characteristic for poly(carboxybetaine) evaluated by means of the curves plotted in Fig. 5 are listed in Table 2. For PVIB-1 the thermogravimetric analysis reveals that the polymer is strongly degrading starting at 245 °C (see Fig. 5). At this temperature the weight loss exceeds 60%. This result has been confirmed by the analysis of the FTIR spectra at different temperatures. For example, all the characteristic vibration bands belonging to the chemical structure of the studied sample disappear at 300 °C (Fig. 2). This fact obviously indicates that at 300 °C the PVIB-1 product degrades.

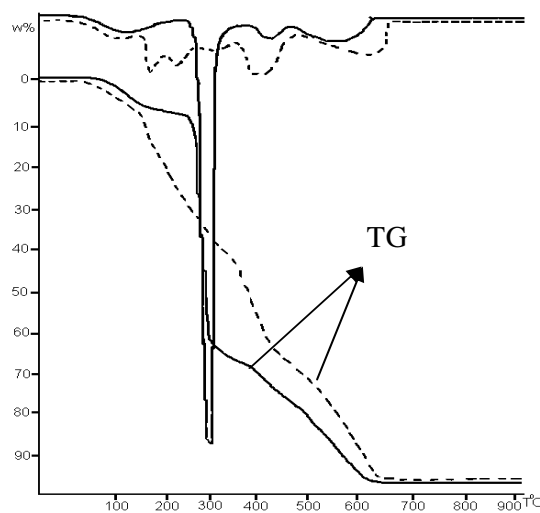


Fig. 5. TG and DTG curves for the PVIB-1( — ) and PVIB-2 ( - - - ).

Table 2. Thermal behavior of PVIB-1 and PVIB-2.

S Stage	Sample	T <sub>i</sub> (°C)	T <sub>m</sub> (°C)	T <sub>f</sub> (°C)	w (%)	E <sub>a</sub> (kJ/mol)	n
I	PVIB-1	70	115	245	6	28	1.7
	PVIB-2	60	115	170	11	156	0.7
II	PVIB-1	245	295	355	60	147	0
	PVIB-2	170	200	220	9	126	0.8
III	PVIB-1	355	425	480	10	254	2.7
	PVIB-2	220	255	292	11	190	1.2
IV	PVIB-1	480	570	625	18	144	0.7
	PVIB-2	292	315	355	11	190	1.7
V	PVIB-1	-	-	-	-	-	-
	PVIB-2	355	400	485	26	156	1.5
VI	PVIB-1	-	-	-	-	-	-
	PVIB-2	485	620	650	26	128	0.8

T<sub>i</sub> = initial decomposition temperature; T<sub>m</sub> = temperature of maximum rate of weight loss; T<sub>f</sub> = final decomposition temperature.

The thermogravimetric analysis of the PVIB-2 product shows that the weight loss becomes slower when the temperature increase (Fig. 5), getting then larger starting with 355 °C. The result of the thermogravimetric analysis completely agrees with the FTIR spectra analysis carried out at different temperature for this product too. The FTIR spectra of the PVIB-2 polymer presented in Fig. 3 reveal an advanced degradation process starting at 400 °C.

Important modification of E<sub>a</sub> as against the conversion for the polymers can be observed in Fig. 6.

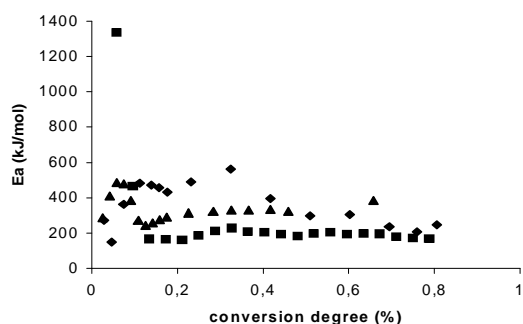


Fig. 6. The dependence of transformation degree ( $\alpha$ ) on the  $E_a$  for the PVIB-1, PVIB-2 and PVI samples:  $\blacklozenge$  PVI;  $\blacksquare$  PVIB-2;  $\blacktriangle$  PVBI-1.

The PVIB-1 shows a increase of  $E_a$  up to 0.14 conversion than a decrease of  $E_a$  up to 0.18 followed by a slightly increase. The PVIB-2 has a decrease of the  $E_a$  for a conversion up to 0.14 and than  $E_a$  remains constant up to 0.4. Dependence of  $E_a$  on conversion for PVI shows the peculiar behavior indicating many changes in the degradation process.

#### 4. Conclusions

The results of the spectral and thermogravimetric analysis concerning the stability and degradation of the two poly(betaine) polymers are in a very good agreement.

The PVIB-1 compound can be used in non-conventional technological applications up to 200 °C while PVIB-2 can be used up to 290 °C.

#### References

- [1] J. Galin, Polyzwitterions, Polymeric materials Encyclopedia, Ed. Salamone, J.C., Ed. CRC Press, Boca Raton, F.L. **9**, 7189 (1996).
- [2] J. C. Salamone, W. C. Rice, Polyampholytes: J. I. Kroschwitz, editor 2<sup>nd</sup>, Encyclopedia of Polymer Science and Technology, New York, Wiley Interscience **11**, 514 (1988).
- [3] S. E. Kudaibergenov, Adv.Polym.Sci. **144**, 115 (1999).
- [4] T. A. Wielema, J. B. F. Engberts, Eur. Polym. J. **23**(12), 947 (1987).
- [5] T. A. Wielema, J. B. F. Engberts, Eur. Polym. J. **26**, 639 (1990).
- [6] A. Niu, D. J. Liaw, H. C. Sang, C. Wu, Macromolecules **33**, 3492 (2000).
- [7] C. Luca, S. Mihailescu, M. Popa, Eur. Polym. J. **38**, 1501 (2002).
- [8] V. Barboiu, E. Streba, M. N. Holerca, C. Luca, J. Macromol. Sci.-Pure Appl. Chem. A. **32**(8-9), 1385 (1995).
- [9] A. W. Coats, J. P. Redfern, Nature **201**, 68 (1964).
- [10] L. Reich, D. W. Levi, Makromol. Chem. **66**, 102 (1963).
- [11] Margareta Avram, Infrared spectroscopy (roum.), Technical Publ. House, Bucharest (1976).

\* Corresponding author: mstrat@uaic.ro