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# Thermodegradation of poly(2-vinylpyridine-co-styrene-co-divinylbenzene) and N-oxide derivatives

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## Abstract

Copolymer networks based on 2-vinylpyridine(2VP)/styrene(STY)/divinylbenzene(DVB) and their N-oxide derivatives have been investigated by thermogravimetric analysis (TG) to evaluate their thermal stability in nitrogen atmosphere at fixed heating rate. Thermal stability was determined from TG curves to investigate the influence of 2VP content and introduction of N-oxide groups. The TG and DTG curves of unmodified copolymers clearly show two thermodegradation stages and the same kinetic pathway. The decomposition temperatures do not depend on the 2VP content and material porosity. The copolymers modified by oxidation present lower thermostability than unmodified showing that the introduction of N-oxide groups modifies their kinetic pathways.

*Keywords:* Thermal stability; Thermogravimetry; Poly(2-vinylpyridine-co-styrene-co-divinylbenzene); 2-Vinylpyridine N-oxide

## 1. Introduction

Copolymer networks with controlled porous structure are widely employed as starting materials for ion exchangers, as specific sorbents, as packing for gel permeation chromatography and as catalyst supports [1–4]. The morphological control of the copolymer beads and their porous structures may result in many advantages concerning removal of metal ions and other pollutants from wastewater. These characteristics have a strong influence on the removal kinetics and flow properties [3]. Crosslinked copolymers based on vinylpyridines (VP) have a great potential for many applications as ion-exchange resins, gas separation membranes, catalyst supports, in the water purification industry, in monitoring heavy metals, and as other useful materials [4–8]. However, there are few studies on thermodegradation of VP crosslinked with divinylbenzene (DVB) [5,9,10]. The VP ring can be chemically modified by oxidation, producing a VP N-oxide. These modified materials could be employed as catalyst supports and ion-exchange resins to remove heavy metals due to presence of VP N-oxide groups [6]. As far as we know, the evaluation of thermodegradation of crosslinked copolymers containing 2VP N-oxide derivatives has not been done. This work deals with the influence of 2VP content of crosslinked copolymers and the introduction of N-oxide groups on their thermal stability.

## 2. Experimental

### 2.1. Materials

Styrene was donated by Petroflex and used as received. Commercial DVB (grade of 45% of DVB, containing a mixture of DVB and ethylvinylbenzene) and 2VP (from Nitriflex, Brazilian Co.) were used as received. α,α'-Azo-bis-isobutyronitrile (AIBN, donated by Metacril, Brazilian Co.) was purified by recrystallization from methanol. 2-Hydroxyethyl-celullose (HEC, Cellosize QP-100MH) was donated by Union Carbide and used as received. The other reagents were commercially purchased, namely gelatin, *n*-butanol, propanone, methanol, NaCl, *n*-heptane, ethyl acetate, hydrogen peroxide (30%

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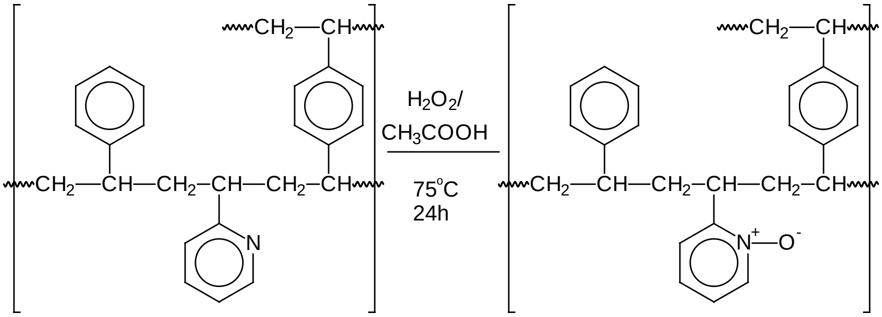

Scheme 1. Oxidation reaction of 2VP copolymer.

w/v), glacial acetic acid, toluene (Vetec Química Fina Ltd., Brazil) with P.A. degree and used as received. Aqueous solutions were prepared using distilled deionized water.

### 2.2. *Oxidation of pyridine rings*

The oxidation reaction of 2VP crosslinked copolymers (Scheme 1) was carried out with beads swollen in *n*-butanol. The swollen beads were heated at 75 °C in glacial acetic acid (5.25 mol) with $H_2O_2$ (1 mol using 30% w/v $H_2O_2$ solution) under mechanical stirring for 24 h [6,11]. The modified resin was filtered off, thoroughly washed with water and propanone to remove excess reagents and then dried at 60 °C for 24 h.

### 2.3. *Characterization*

Modified and unmodified copolymers were analysed by Fourier transform infrared spectrophotometry (FT-IR—Perkin-Elmer mod. 1710×) using KBr pellets. The TG analyses were carried out with powdered resin beads based on poly(2-vinylpyridine-co-styrene) crosslinked with 30 mol% divinylbenzene with varied 2VP and STY contents (Table 1). The unmodified copolymers were prepared and porous structure characterized earlier [12].

Thermal analyses of modified and unmodified copolymers were conducted with a Shimadzu TG-50 at a heating rate of 10 °C min$^{-1}$ under nitrogen (99.99% purity) with a platinum pan at temperatures from ambient (~25 °C) to 900 °C. The powered sample, about 3 mg in weight was packed into the platinum pan and the gas flow rate was kept at 30 mL min$^{-1}$. The specific surface area (*S*, in m$^2$/g) of unmodified beads was determined by mercury porosimetry (Quantachrome Autoscan equipment) or BET method from low-temperature nitrogen adsorption isotherms (ASAP Micromeritics 2010), which were obtained at 77 K using a high-vacuum volumetric apparatus. The samples were degassed at 100 °C/1 mPa for 3 h.

## 3. Results and discussions

Table 1 shows 2VP/STY/DVB resins with different porous structures are readily prepared by the suspension technique in the presence of different porogenic agents. The porosity of the unmodified polymers depends on the 2VP content, diluent and dilution degree [12]. The DVB content was the same for all copolymers. The nitrogen content of the copolymers was determined by elemental analysis (Table 1). The yield values and elemental analysis data for the copolymers obtained agree with the theoretical values calculated from the monomer amounts in the feed.

Comparing the *S* values of the resins shown in Table 1, the R1, R2 and R3 resins generally present lower *S* values

Table 1
Synthesis parameters, chemical analysis and specific surface area of copolymer networks

| Resin | Diluent system[a] (volume ratio = 7:3) | Feed monomers (mol%) 2VP/STY/DVB[b] | N from elemental analysis (%) (theoretical value) | Yield (%) | *S* (m$^2$/g) |
|---|---|---|---|---|---|
| R1[c] | Hep/Tol | 30/40/30 | 3.8 (3.7) | 94 | 72[e] |
| R2[c] | Hep/Tol | 40/30/30 | 4.9 (5.0) | 94 | 51[e] |
| R3[c] | Hep/Tol | 50/20/30 | 6.1 (6.2) | 92 | 4[f] |
| R4[d] | Hep/AcOEt | 30/40/30 | 4.1 (3.7) | 92 | 78[e] |
| R5[d] | Hep/AcOEt | 40/30/30 | 5.3 (5.0) | 93 | 75[e] |
| R6[d] | Hep/AcOEt | 50/20/30 | 6.5 (6.2) | 94 | 43[e] |

[a] Hep = *n*-heptane, Tol = toluene, AcOEt = ethyl acetate.
[b] 2VP = 2-vinylpyridine, STY = styrene, DVB = divinylbenzene.
[c] Dilution degree = 150% (dilution in relation to total volume of monomers).
[d] Dilution degree = 100% (dilution in relation to total volume of monomers).
[e] From BET equation from ASAP analysis.
[f] From mercury porosimetry.

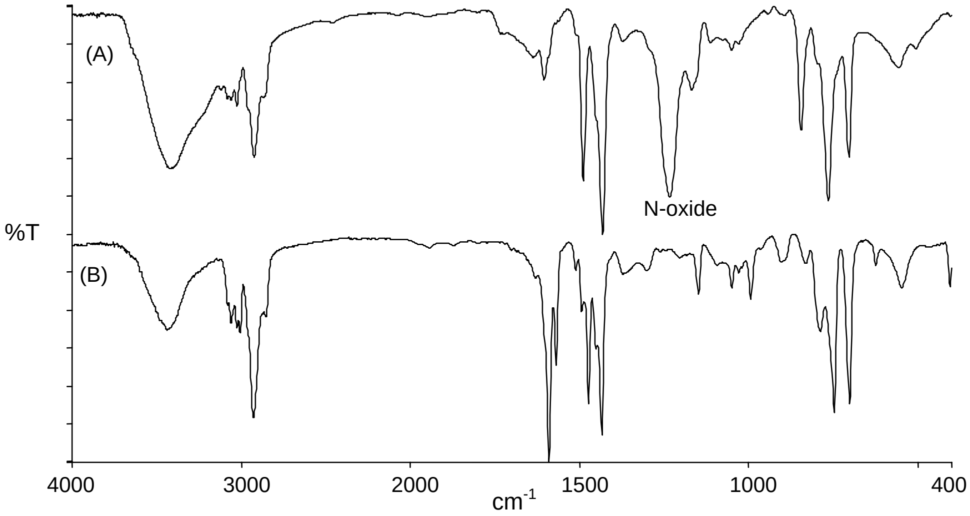

Fig. 1. FT-IR spectra of the 2VP N-oxide (A) and 2VP (B) copolymers.

than the copolymers R4, R5 and R6 synthesized with same 2VP content. Hence, R1, R2 and R3 present larger pores than the R4, R5 and R6, respectively [12].

The FT-IR spectra of all unmodified copolymers have an absorption band at 747 $cm^{-1}$ attributed to C–H out-of-plane bending vibration of the pyridine ring in 2VP chain units, confirming the incorporation of 2VP into the copolymer structure [13]. The FT-IR spectra of the copolymers modified by oxidation with peracetic acid display the N-oxide stretching band (~1230 $cm^{-1}$) [6,13]. Fig. 1 shows typical spectra of modified (Fig. 1A) and unmodified (Fig. 1B) copolymers. The elemental analyses of modified copolymers evidenced that all pyridine units were oxidized to N-oxide. The N:O ratio was 1:1, therefore the conversion of pyridine to N-oxide was not dependent on the porosity.

Fig. 2A and B shows the TG and DTG curves of the R1, R2 and R3 resins based on unmodified 2VP/STY/DVB copolymers. Fig. 3A and B shows the TG and DTG curves of the R4, R5 and R6 resins based on unmodified 2VP/STY/DVB copolymers. The data presented in Table 2 show thermodegradation of copolymer is independent of the 2VP content or porosity.

All copolymers are thermodegraded in two stages and completely crumbled around 750 °C showing the same kinetic pathway. The least stable stage ($T_{dm}$) may be due to the scissions of head-to-head linkages, the scissions of

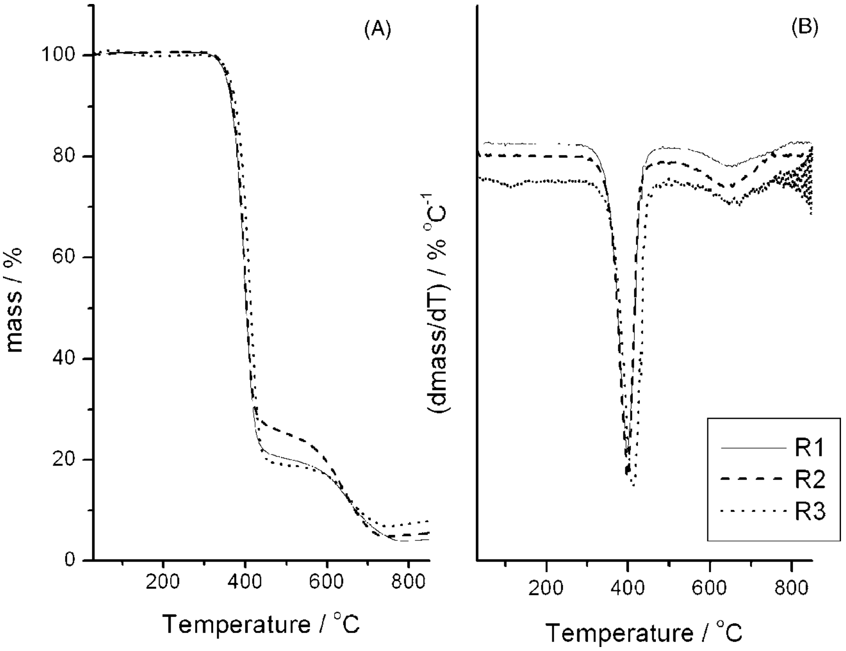

Fig. 2. TG (A) and DTG (B) curves of the unmodified 2VP/STY/DVB copolymers (R1, R2 and R3 resins) under nitrogen at heating rate of 10 °C $min^{-1}$.

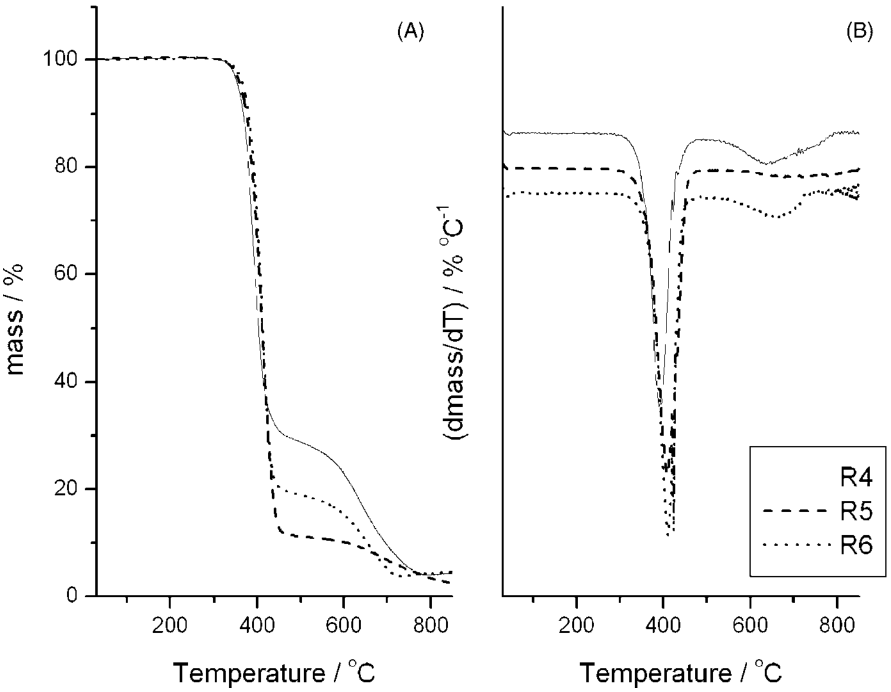

Fig. 3. TG (A) and DTG (B) curves of the unmodified 2VP/STY/DVB copolymers (R4, R5 and R6 resins) under nitrogen at heating rate of 10 °C $\text{min}^{-1}$.

crosslinked bonds and the most stable step related to the random scissions of the poly-2VP polymer chain [10]. The last stable stage (Figs. 2B and 3B) may be due to the thermo-oxidative degradation of poly-2VP polymer chain by the low oxygen content in the nitrogen gas employed in this analysis [5,10].

Fig. 4A and B shows the TG and DTG curves of the R1-NO, R2-NO and R3-NO resins based on modified 2VP/STY/DVB copolymers, respectively. Fig. 5A and B shows the TG and DTG curves of the R4-NO, R5-NO and R6-NO resins based on modified 2VP/STY/DVB copolymers, respectively. All modified copolymers are thermodegraded in two stages and not completely crumbled until 900 °C, differing from the unmodified copolymers. In addition, the thermodegradation kinetic pathways of modified copolymers are different compared to the unmodified ones. The kinetic pathway of modified copolymers is dependent of N-oxide content. After the thermoanalysis, a residue was observed inside the crucible and confirmed by the char yield formed of 6–15% (Table 3). The $T_{\text{dm}}$ values (Tables 2 and 3) of the modified resins are lower than the unmodified ones. The least stable stage displays two steps as seen in the DTG curves shown in Figs. 4B and 5B. This result evidences an effective chemical modification of 2VP units. The $T_{\text{dm}}$ values around 310 °C could be attributed to the thermoscission of N-oxide bonds. Comparing the DTG curves (Fig. 4B), the weight loss attributed to thermodecomposition of the N-oxide bond ($T_{\text{dm}}$ 309 °C) is more accentuated in the R3-NO resin compared to the others. This result could be explained by the larger 2VP content of R3 resin (see Table 1). The same behavior was verified for the R4-NO, R5-NO and R6-NO resins.

The $T_{\text{dm}}$ values (Table 3) indicate that the N-oxide group influences the thermal stability of the modified copolymer.

Table 2
Thermal decomposition temperatures of the unmodified copolymers

| Resin | $T_{\text{dm}}$[a] (°C) (±3 °C) | Mass loss (%) |
|---|---|---|
| R1 | 398 | −79 |
| R2 | 399 | −73 |
| R3 | 410 | −81 |
| R4 | 394 | −68 |
| R5 | 413 | −88 |
| R6 | 412 | −80 |

[a] $T_{\text{dm}}$ = temperature at the maximum weight-loss rate from DTG curves.

Table 3
Thermal decomposition temperatures of the modified copolymers

| Resin | $T_{\text{dm1}}$[a] (°C) (±3 °C) | $T_{\text{dm2}}$[a] (°C) (±3 °C) | Total weight loss (%) | Char yield at 900 °C (%) |
|---|---|---|---|---|
| R1-NO | 315 | 389 | 67 | 8 |
| R2-NO | 312 | 388 | 56 | 8 |
| R3-NO | 309 | 360 | 39 | 10 |
| R4-NO | 313 | 406 | 67 | 15 |
| R5-NO | 309 | 381 | 57 | 12 |
| R6-NO | 310 | 365 | 41 | 6 |

[a] $T_{\text{dm}}$ = temperature at the maximum weight-loss rate.

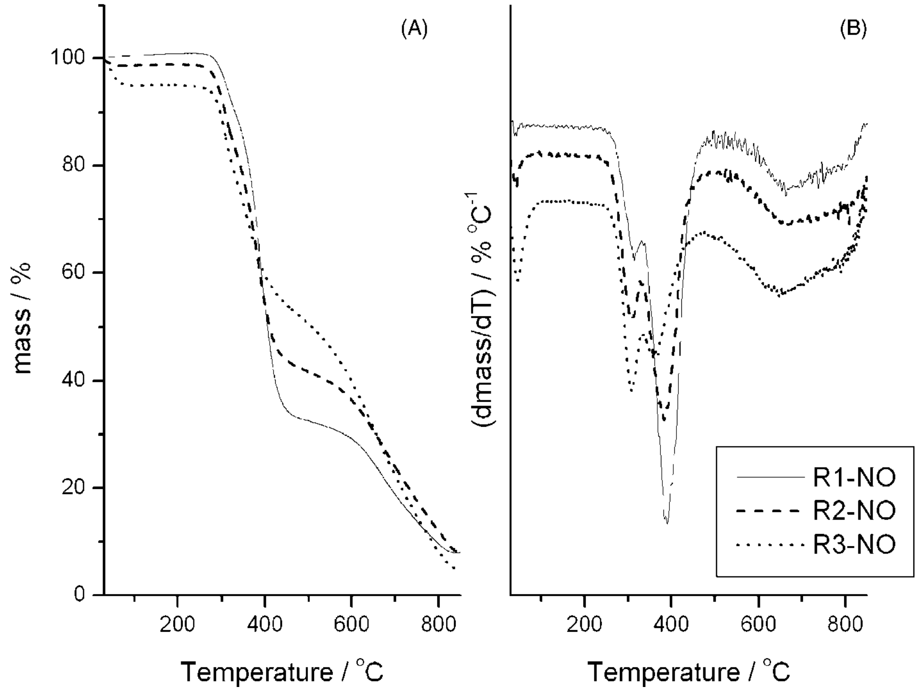

Fig. 4. TG (A) and DTG (B) curves of the modified 2VP/STY/DVB copolymers (R1-NO, R2-NO and R3-NO resins) under nitrogen at heating rate of 10 °C min$^{-1}$.

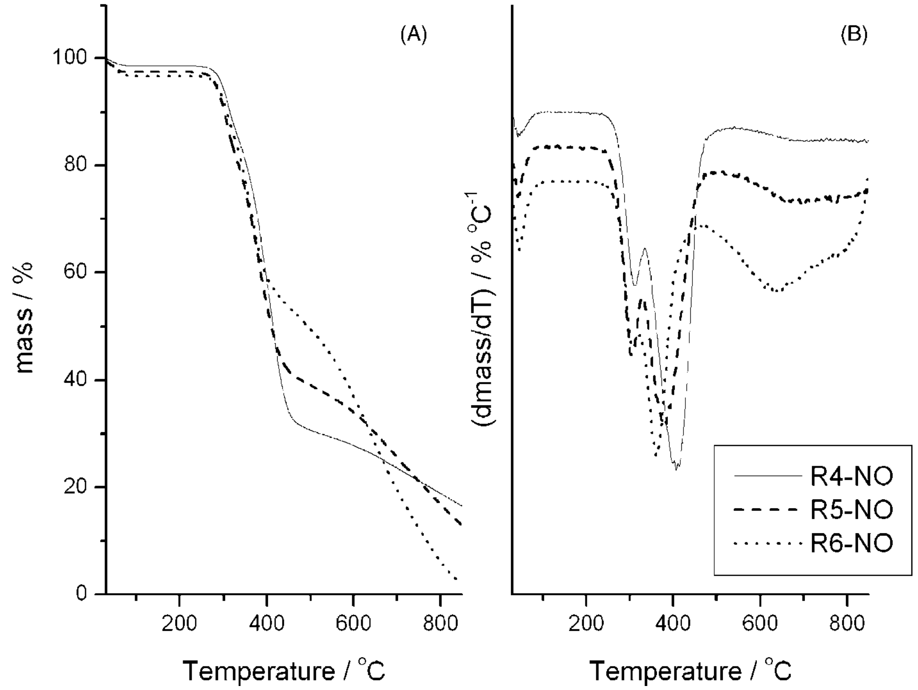

Fig. 5. TG (A) and DTG (B) curves of the modified 2VP/STY/DVB copolymers (R4-NO, R5-NO and R6-NO resins) under nitrogen at heating rate of 10 °C min$^{-1}$.

The last stable stage (Figs. 4B and 5B) of modified resins may also be due to the thermo-oxidative degradation of poly-2VP polymer chain. The lower $T_{dm}$ values of modified resins could be explained by the lower thermostability of the oxidized pyridine rings [14–16].

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