Thermodegradation of poly(4-vinylpyridine-*co*-crotonic acid-*co*-divinylbenzene) and N-oxide derivatives

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Abstract

Copolymer networks based on 4-vinylpyridine (4VPy)/crotonic acid (CrA)/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 4VPy content and introduction of N-oxide groups. The TG and DTG curves of unmodified copolymers clearly show two thermodegradation stage and the same kinetic pathway. The decomposition temperatures do not depend on the 4VPy content. The copolymers modified by oxidation present lower thermostability than unmodified showing that the introduction of N-oxide groups modifies their kinetic pathways. A kinetic model Ozawa was used to determine the kinetic parameters. The apparent thermal decomposition activation energies (ΔE_d) of the unmodified copolymer under nitrogen was higher than that in modified copolymer. Also, the characterizations of copolymer networks were done by Fourier transform infrared spectroscopy (FTIR).
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1. Introduction

Crosslinked copolymers based on vinylpyridines (VPy) 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 [1–5]. The VPy ring can be chemically modified by oxidation, producing a VPy–N-oxide. These modified materials could be employed as catalyst supports and ion-exchange resins to remove heavy metals due to presence of VPy–N-oxide groups [3]. It has been pointed out that polymers or copolymers containing carboxylic acid groups are highly desirable because such groups represent functionality that is useful for yielding a wide variety of products. Copolymers have the newly available carboxylic acid functional groups, which can be used in any further incorporation of drugs or other bioactive agents [6,7]. However, there are few studies on thermodegradation of VPy crosslinked with divinylbenzene (DVB) [2,8–10]. It is interesting to study how the thermal stabil-

ity of 4VPy-*co*-DVB is affected by incorporating CrA units. It is known that basic polymers such as poly(vinylpyridine)s are miscible with proton-donating polymers through hydrogen bonding interactions. Poly(4-vinylpyridine) (P4VPy), a weakly self-associated basic polymer, is miscible with several self-associated polyacids, such as poly(4-vinylphenol) (P4VPh) [11], poly(acrylic acid) (PAA) [12], poly(methacrylic acid) (PMAA) [13], poly(monoalkyl itaconates) [14], poly(maleic acid) (PMA) [15] and with the strongly self-associated random copolymer ethylene-*co*-methacrylic acid (E-*co*-MAA) [13]. Kinetic of thermal degradation of solids has been investigated from thermogravimetric (TG) thermograms at linear rates of temperature rise in a number of studies. Thermogravimetry is widely used as a method to investigate the thermal degradation of polymers and to determine the kinetic parameters. The thermal stability and degradation depend on the composition [16–18]. The isoconversional methods may be best known through their most popular representatives, the methods of Friedman [19], Ozawa [20], and Flynn and Wall [21]. Interestingly, all three methods were conceived by the researchers working on the thermal degradation of polymers and since then they have been mostly used in polymer kinetic studies. The isoconversional methods require performing a series of experiments at different temperature programs

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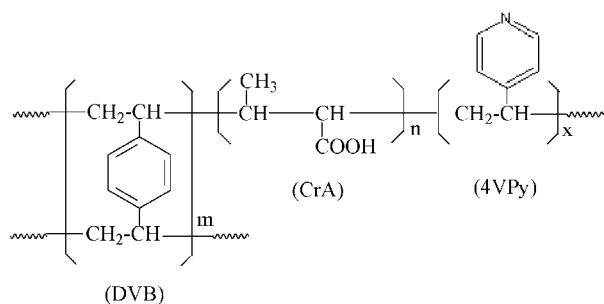
Scheme 1. Structure of 4VPy/CrA/DVB networks.

and yield the values of effective activation energy as a function of conversion. More often than not, the activation energy is found to vary with the extent of conversion. The full potential of the isoconversional methods has been appreciated as Vyazovkin [22,23] brought analysis of the E_a-dependences to the forefront and demonstrated that they can be used for exploring the mechanisms of processes and for predicting kinetics.

Over the past decade, the isoconversional kinetic analysis has come a long way, succesfully opening up new opportunities in traditional areas of application such as polymer degradations and curing as well as efficiently delving into uncharted application areas such as glass transition and crystallization. The efficacy of the analysis originates from its ağabeylity of disclosing and handling the complexity of the respective processes. As a matter of fact, the isoconversional analysis provides a fortunate compromise between the oversimplified but widely used single-step Arrhenius kinetic treatments and the prevalent occurrence of processes whose kinetics are multi-step and/or non-Arrhenius. Although the resulting activation energies tend to be effective or composite values and tend to vary with the extent of conversion and temperature, they can be employed to make reliable kinetic predictions, to get information about complex mechanisms, and, ultimately, to Access intrinsic kinetic parameters. The present work reports the influence of 4VPy content of crosslinked copolymers and the introduction of N-oxide groups on their thermal stability.

2. Experimental

2.1. Materials

Crotonic acid (CrA) (Aldrich) was used after recrystallization from distilled water, m.p. 72–74 °C, divinylbenzene (Merck)

and 4-vinylpyridine (4VPy) (Aldrich) were used as received. α,α'-Azobisisobutyronitrile (AIBN) (Merck) was purified by recrystallization from methanol. The other reagents were commercially purchased, namely *n*-butanol, propanone, methanol, NaCl, *n*-heptane, ethyl acetate, hydrogen peroxide (H_2O_2) (30%, w/v), glacial acetic acid, toluene used as received. Aqueous solutions were prepared using distilled deionized water.
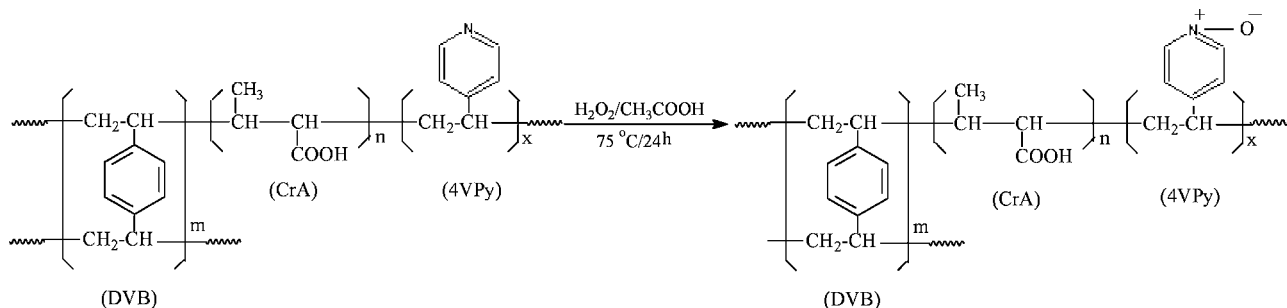
2.2. Synthesis of networks

The synthesis of the 4VPy/CrA/DVB networks was carried out with a radical initiator (Scheme 1). To a polymerization flask, the two appropriate monomers 4VPy and CrA, the crosslinking reagent DVB, and the initiator AIBN were added. The system was kept under N_2 for 3 h at 60 ± 0.1 °C. Subsequently, the resins was filtered and washed with abundant distilled water and dried in vacuo at 50 °C until a constant weight was obtained. The conversion of monomer to polymer (yield) was determined by gravimetric method. The amounts of monomeric units in the copolymers were determined by elemental analysis (N content for 4VPy).

2.3. Oxidation of pyridine rings

The oxidation reaction of 4VPy crosslinked copolymers (Scheme 2) was carried out in *n*-bütanol. The polymers 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 [7,18]. The modified networks was filtered off, thoroughly washed with water and propanone to remove excess reagents and then dried at 50 °C for 24 h.

2.4. Characterization

Modified and unmodified copolymers were analysed by Fourier transform infrared spectroscopy (Jasco 460 Plus FTIR spectrometer) using KBr pellets in 4000–400 cm^{-1} range, where 10 scans were taken at 4 cm^{-1} resolution. Thermal analyses of modified and unmodified copolymers were conducted with a Setaram labsys TG-DSC/DTA 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 600 °C. The powdered sample, about 5–8 mg in weight was packet into the platinum pan and the gas flow rate was kept at 5 L h^{-1}. Elemental analyses were carried out by a LECO-932 microanalyzer.

Scheme 2. Oxidation reaction of 4VPy/CrA/DVB networks.

Table 1
Synthesis parameters and chemical analysis of the investigated copolymer networks

Resin	Feed monomers (mol%) 4VPy/CrA/DVB[a]	N from elemental analysis (%) (theoretical value)	Yield (%)
R2	30/40/30	3.6 (3.5)	94
R4	40/30/30	4.7 (4.7)	95
R6	50/20/30	5.8 (5.9)	95

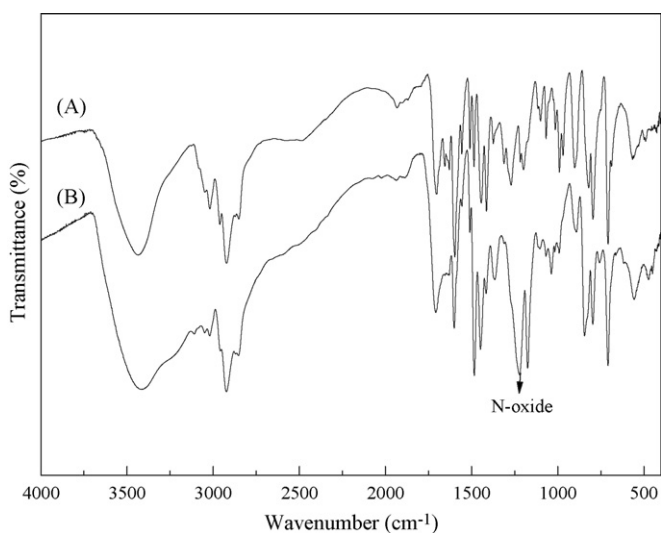[a] 4VPy = 4-vinylpyridine; CrA = crotonic acid; DVB = divinylbenzene.

Fig. 1. FTIR spectra of the (A) 4VPy/CrA/DVB and (B) 4VPy/CrA/DVB-N-oxide network.

3. Results and discussion

Table 1 shows 4VPy/CrA/DVB networks with different compositions are prepared by the radical polymerization technique. The nitrogen content of the copolymers was determined by elemental analysis (Table 1). The FT-IR spectra of all unmodified copolymers have an absorption band at $745\,cm^{-1}$ attributed to C–H out-of-plane bending vibration of the pyridine ring in 4VPy chain units, confirming the incorporation of 4VPy into the copolymer structure [24]. The FT-IR spectra of the copolymers modified by oxidation with peracetic acid dis-

play the N-oxide stretching band ($\sim$1230 cm^{-1}) [7,18]. Fig. 1 shows typical spectra of unmodified (Fig. 1A) and modified (Fig. 1B) copolymers. The FT-IR spectra shows a broad band with $\upsilon_{max} = 3425\,cm^{-1}$ due to strong intramolecular and intermolecular hydrogen bonds. The carbonyl stretching band for CrA units lies at $1715\,cm^{-1}$, while the C–O stretching couples with the O–H bending deformation resulting in two bands, one at $1420\,cm^{-1}$ and second in the $1300\,cm^{-1}$.

Fig. 2A and B shows the TG and DTG curves of the networks based on unmodified 4VPy/CrA/DVB copolymers. They degrade in a manner similar to each other, so it can be considered as two-stage process at $600\,°C$ with weight loss around 75% showing the same kinetic pathway. In the region from 100 to $150\,°C$; a peak is detected, which is assigned to the dehydration of partially degraded of acid groups. In the second temperature region from 380 to $470\,°C$, there is a peak, connected probably with some decarboxylation and carbonization processes and the anhydride ring formation in the CrA units chain [25]. The least stable stage (T_{dm}) may be due to the scissions of head-to-head linkages, the scissions of crosslinked bonds and the most stable step related to the random scissions of the poly-4VPy polymer chain [12]. The last stable stage (Fig. 2B) may be due to the thermo-oxidative degradation of poly-4VPy polymer chain by the low oxygen content in the nitrogen gas employed in this analysis [2,12].

Fig. 3A and B shows the TG and DTG curves of the resins based on modified 4VPy/CrA/DVB copolymers. All modified copolymers are thermodegraded in three stages and completely crumbled until $600\,°C$ with weight loss around 80%, 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. The T_{dm} values of the modified resins and the unmodified resins are seen in Table 2. The least stable stage display a step as seen in the DTG curves shown in Fig. 3B. This result evidences an effective chemical modification of 4VPy units. The T_{dm} values around $300\,°C$ could be attributed to the thermoscission of N-oxide bonds. The T_{dm} values (Table 2) indicate that the N-oxide group influences the thermal stability of the modified copolymer. The last stable stage (Fig. 3B) of modified networks
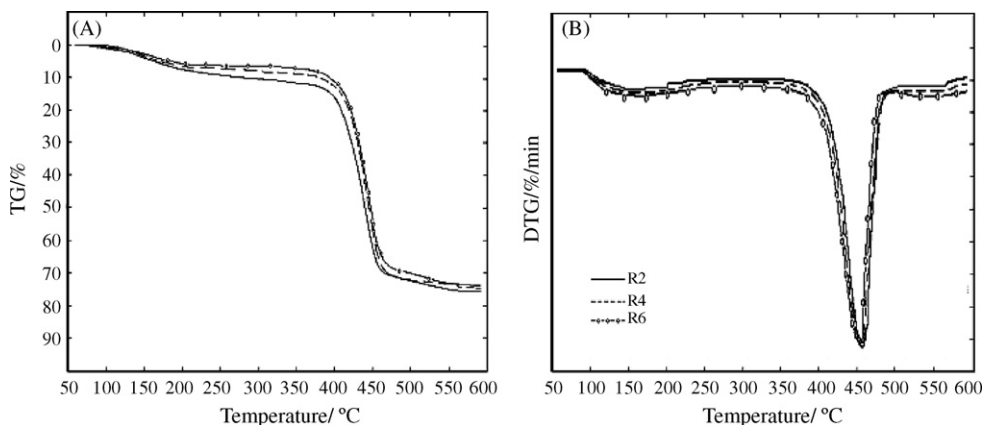

Fig. 2. (A) TG and (B) DTG curves of the unmodified 4VPy/CrA/DVB networks (R2, R4 and R6) under nitrogen at heating rate of $10\,°C\,min^{-1}$.
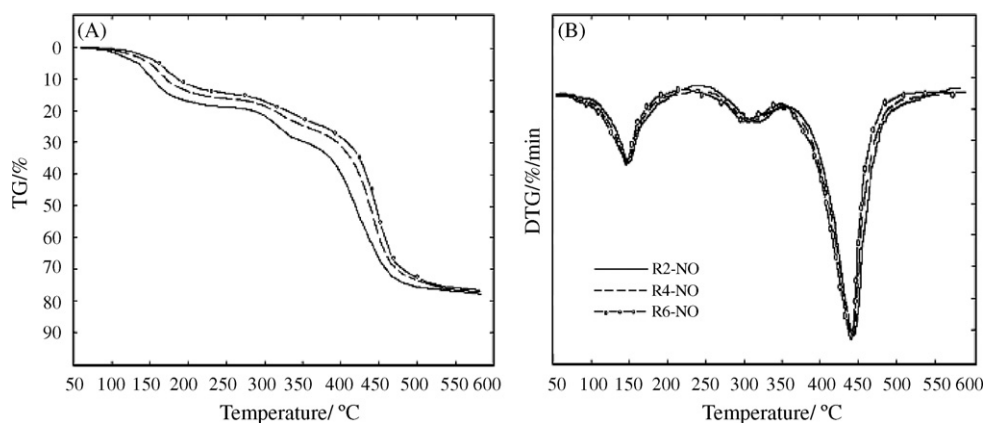
Fig. 3. (A) TG and (B) DTG curves of the modified 4VPy/CrA/DVB networks (R2, R4 and R6) under nitrogen at heating rate of $10\,^{\circ}\text{C min}^{-1}$.

may also be due to the thermo-oxidative degradation of poly-4VPy polymer chain. The lower T_{dm} values of modified resins could be explained by the lower thermostability of the oxidized pyridine rings [26–28]. On heating, polymers degrade forming low molecular products. The process involves breaking of the bonds between individual atoms forming a polymer chain. For typical vinyl polymers [e.g., polystyrene (PS), polyethylene (PE), polypropylene (PP) degradation involves breaking of C–C bonds whose bond energy is around $350\,\text{kJ mol}^{-1}$. Although this is a large energy, thermal degradation of vinyl polymers readily occurs above $200\text{–}300\,^{\circ}\text{C}$. Thermal degradation starts rather easily because of the weak link sites inherent with the polymer chain. Typical weak sites include head-to-head links, hydroperoxy, and peroxy structures. These sites serve as spots where thermal degradation is initiated. Once macro radicals are formed, further degradation occurs via various radical pathways whose activation energies are markedly smaller than the C–C bond energy. For this reason, the effective activation energy of thermal degradation of many polymers varies throughout the process. At earlier stages it tends to be lower representing the process of initiation at the weak links. Once the weak links have given way to initiation, the effective activation energy increases that typically occurs at the later stages of degradation. This tendency has been clearly demonstrated by Peterson et al. [29] by applying an advanced isoconversional method to the TGA data on the thermal degradation of PS, PE, and PP.

In the presence of oxygen, polymers undergo thermo-oxidative degradation. Oxygen alters the pathways of thermal degradation by initiating reactions of lower activation energy. Thermo-oxidative degradation occurs at temperatures about $100\,^{\circ}\text{C}$ lower than the regular thermal degradation under nitrogen. For vinyl polymers, thermo-oxidative degradation involves the hydroperoxide radical in the propagation step of the degradation. Because of this, many oxygen-initiated degradations have activation energies in the range of $80\text{–}110\,\text{kJ mol}^{-1}$ that are typical for bimolecular decomposition of organic hydroperoxides.

3.1. Thermogravimetry experiments and decomposition kinetics

For the study on the kinetics of thermal degradation of polymer networks, we can select the isothermal thermogravimetry (ITG) or the thermogravimetry at various heating rates [30]. ITG is superior to obtain an accurate activation energy for thermal degradation, although it is time-consuming. In the case of thermal degradation of polymer networks, in which depolymerization is competing with cyclization or crosslinking due to the side groups, the TG at various heating rates is much more convenient than ITG for the investigation of thermal degradation kinetics. Therefore, in the present work TG curves at various heating rates were obtained and the activation energies (E_a) for thermal degradation of polymer networks were calculated by Ozawa's plot, which is a widely used method. Degradations were performed in the scanning mode, from 35 up to $600\,^{\circ}\text{C}$, under nitrogen flow ($5\,\text{L h}^{-1}$), at various heating rates (β: 5.0, 7.0, 10.0, 12.5., and $15.0\,^{\circ}\text{C min}^{-1}$). In Fig. 4, the TG and DTG thermograms of R4-NO are shown. Samples of 5–8 mg held in alumina open crucibles, were used and their weights were measured as a function of temperature and stored in the list of data of the appropriate built-in program of the processor. The TGA

Table 2
Thermal decomposition temperatures and activation energies of the unmodified and modified copolymers

Resin	T_{dm1}[a] (°C) (±3 °C)	T_{dm2}[a] (°C) (±3 °C)	T_{dm3}[a] (°C) (±3 °C)	Total weight loss (%)	E_a (kJ mol^{-1})
R2	124	462	–	75	138
R4	125	460	–	74	143
R6	125	459	–	73	144
R2-NO	140	300	490	77	116
R4-NO	142	302	491	78	120
R6-NO	143	305	493	78	122

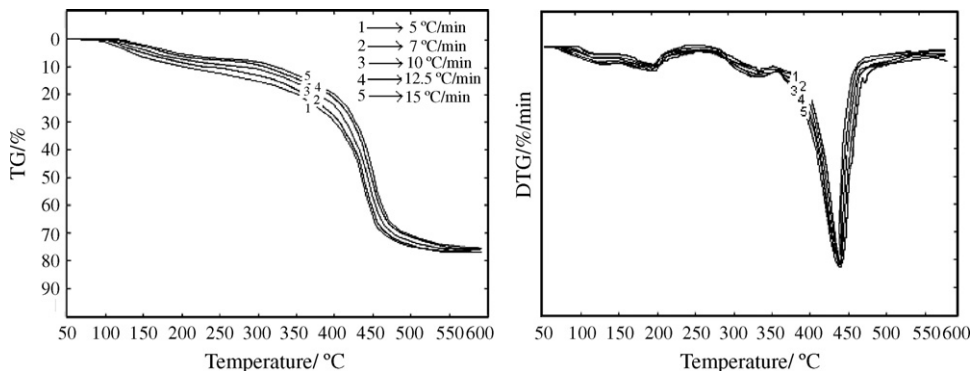[a] T_{dm} = temperature at the maximum weight-loss rate from DTG curves.

Fig. 4. The thermal degradation curves of 4VPy/CrA/DVB network (R4-NO) at different heating rates.

curves were immediately printed at the end of each experiment and the weights of the sample were then transferred to a PC at various temperatures.

According to the method of Ozawa [20], the apparent thermal decomposition activation energy, E_a, can be determined from the TG thermograms under various heating rates, such as in Fig. 4, and the following equation:

$$E_a = -\frac{R}{b}\left[\frac{\mathrm{d}\log\beta}{\mathrm{d}(1/T)}\right] \tag{1}$$

where R is the gas constant, b, a constant (0.4567); and β is the heating rate (°C min^{-1}). According to Eq. (1), the activation energy of degradation can be determined from the slope of the linear relationship between log β and $1/T$, as shown in Fig. 5 (for R4-NO); the E_a values for polymers are given in Table 2. Figs. 6 and 7 show the E_a-dependencies extent of conversion (α) in TGA experiments under nitrogen. Analysis of the E_a-dependences proves generally to be very helpful in exploring an effect of the structure or a composition of a polymer material on its degradation kinetics. The E_a-dependencies obtained for the thermal degradation of these samples exhibit significant difference for the early degradation stages associated with initiation, whereas the later stages ($\alpha > 0.4$) demonstrate almost

identical E_a values of around 135 kJ mol^{-1}. Comparison of the E_a-dependencies related to individual degradation products with the E_a-dependence derived from the mass loss data allowed for mechanistic insights into the origin of the latter dependence. E_a calculated from the Ozawa method is superior to other methods
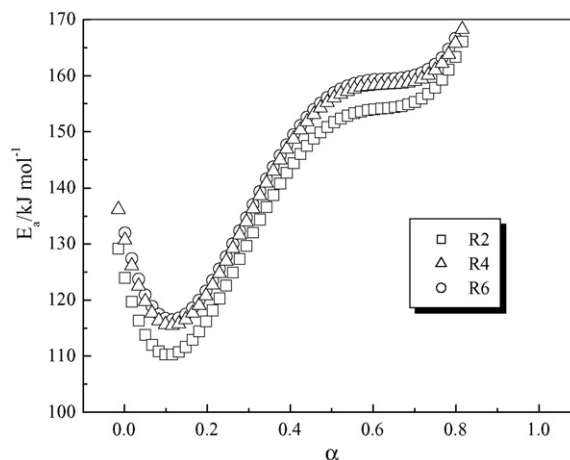

Fig. 6. The E_a-dependencies obtained for the thermal degradation of 4VPy/CrA/DVB networks (R2, R4 and R6) studied in TGA experiments under nitrogen.
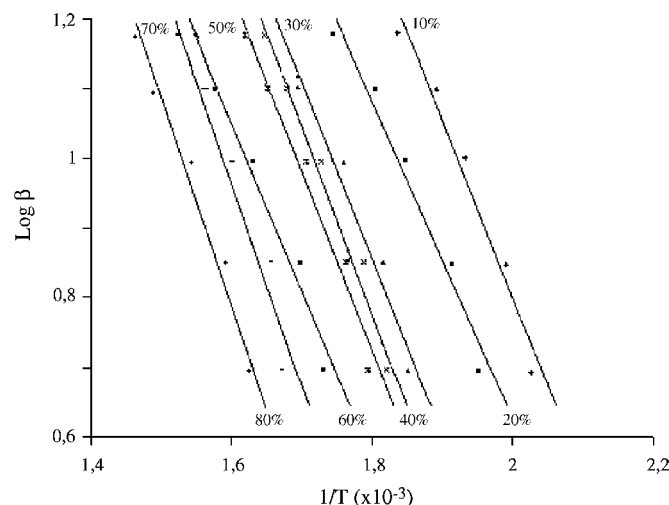

Fig. 5. Ozawa's plots of logarithm of heating rate (β) versus reciprocal temperature ($1/T$) at different conversions for a 4VPy/CrA/DVB network (R4-NO).
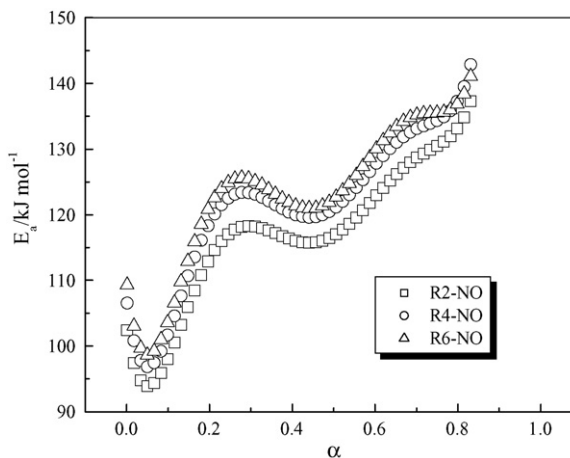

Fig. 7. The E_a-dependencies obtained for the thermal degradation of 4VPy/CrA/DVB networks (R2-NO, R4-NO and R6-NO) studied in TGA experiments under nitrogen.

for complex degradation, since it does not use the reaction order in the calculation of the decomposition activation energy [31]. Therefore, E_a calculated from the Ozawa method was superior to the former methods for complex degradation.

4. Conclusion

The thermal degradation of poly(4-VPy/CrA/DVB) networks was investigated by a study with two stages, unmodified and N-oxide modified from ambient temperature to 600 °C. The thermal stability of the copolymer networks were decreased with the N-oxidation procedure. The apparent activation energy of the unmodified copolymer networks were decreased abouth $20 \, \text{kJ mol}^{-1}$ as compared with that in unmodified copolymer networks.

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