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Synthesis of Crosslinked Copolymers based on Acrylonitrile Containing Carboxyl and Amidrazone Groups

Erika Carneiro Riqueza[1], Alcino Palermo de Aguiar[1] (✉),
Mônica R.M.P. Aguiar[2], Luiz C. de Santa Maria[2] (✉)

[1]Departamento de Engenharia Química, Instituto Militar de Engenharia, Pç General Tibúrcio, 80, 22290-270, Rio de Janeiro, RJ, Brazil
[2]Departamento de Química Orgânica, Instituto de Química, Universidade do Estado do Rio de Janeiro, Rua São Francisco Xavier 524, 20559-900, Rio de Janeiro, RJ, Brazil

E-mail: alcino@ime.eb.br

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Summary

Chelating networks based on modified chemically acrylonitrile with hydrazine at alkaline solution were synthesized. The resin beads with different porosities were obtained by aqueous suspension copolymerization of acrylonitrile (AN) and divinylbenzene (DVB). The unmodified and modified resins were characterized by bulk density, surface area, average pore diameter, elemental analysis (CHN), FTIR, ^{13}C CP/MAS NMR and scanning electronic microscopy. Elemental analyses were used to observe the increasing of nitrogen and oxygen contents due to chemical modification. Spectroscopic techniques (FTIR and ^{13}C CP/MAS NMR) were employed to study the structural changes provoked by the modification with hydrazine. The contents of carboxyl and amidrazone group into the copolymer structure were dependent on the reaction conditions.

Introduction

The literature has pointed out that it is possible to modify chemically different kinds of materials based on polyacrylonitrile, e.g.: homopolymers, beads, fibers and membranes [1-6]. However the hydrazine modification of beads based on acrylonitrile crosslinked copolymers has not been studied yet. The copolymer networks with controlled morphology and porous structure are widely employed as starting materials for ion exchangers, as specific sorbents, as packings for gel permeation chromatography and as catalyst support [7-9]. The copolymer bead morphological control and their porous structures may result in many advantages concerning the removal process of metal ions and other pollutants of wastewater. These characteristics have a strong influence on the removal kinetics and flow properties [9-10]. It is well known the chelating groups are introduced by chemical modification in the polyacrylonitrile, e.g. carboxyl [3,11], amidrazone [12,13] and hydrazidine groups [14] which may be produced by hydrazine reactions with copolymer containing ciano groups. The aim of this work is to synthesize and characterize crosslinked copolymer beads based on acrylonitrile with suitable porous structure for modifying them chemically by using the hydrazine reaction.

Experimental section

Materials

Acrylonitrile (AN) and divinylbenzene (DVB, grade of 45%, containing a mixture of DVB isomers and ethylvinylbenzene) were kindly offered by Nitriflex (Brazilian Co.) and used as received. α,α'-Azo-bis-isobutyronitrile (AIBN) was donated by *Metacril do Brasil* and was recrystallized in methanol. Hydrazine aqueous solution (65 wt-%) and 2-hydroxyethyl-celullose (HEC, Dow Chemicals donation) used as received. Hydrazine dihydrochloride, gelatin, propanone, Na_3PO_4, NaOH, HCl, n-heptane, anisole and methanol were purchased from *Vetec* (Brazilian Co.) PA degree.

Preparation of beads based on acrylonitrile

Two AN/DVB copolymers (Table 1) were obtained in a typical glass reactor (1000 mL) fitted with mechanical stirrer using the aqueous suspension polymerization technique. Aqueous phase (AP) was composed by gelatin and 2-hydroxyethyl-celullose (both at 0.3 wt.-% with respect to AP) and Na_3PO_4 (2 wt.-% in relation to AP). The organic phase (OP) was composed by monomers mixture (0.56 mol of AN, and 0.14 mol of DVB, diluent, namely n-heptane and anisole, mixed or not (dilution of 150% v/v in relation to the monomers) and AIBN used as initiator (1.0 mol -% with respect to the monomers). OP was added slowly to AP previously prepared under stirring at room temperature, employing AP/OP ratio = 3/1. These two phases were maintained under stirring (300 rpm) at room temperature during 10 min. Hence, the suspension copolymerization system was kept under stirring at 70°C during 24 hours. The resin beads were thoroughly washed with hot water (8 portions of 500 mL), extracted with propanone (Soxhlet extractor) and dried at 60°C. The yields of copolymers beads were around 43-60% and they have presented a narrow particle size distribution (50-140 µm).

Table 1. Synthesis parameters of the resins

SAMPLE	Monomer in the feed (ACR/DVB mol%)	Diluents System[a]
R1	80 / 20	ANI
R2		7 ANI / 3 HEP

[a] Volumetric ratio (HEP = n-heptane; ANI = anisole)

Chemical modification of resin

Hydrazine reaction – In a flask fitted with a condenser, the modification reactions was conducted by reacting directly the copolymer beads (0.5 g) with a fresh aqueous solution of free hydrazine. The pH of the reaction solution was varied and maintained at alkaline range (pH 9-12) by adding NaOH aqueous solution. The modified resin was thoroughly washed with water, propanone and then dried during 24 h at 60°C. Table 2 shows the reactions conditions (M1-M11). This reaction was carried out with two kind of hydrazine: a) employed $NH_2NH_2.2HCl$: the free hydrazine solution was prepared from dihydrochloride salt, which was dissolved in water. The HCl of $NH_2NH_2.2HCl$ was neutralized by NaOH followed by methanol addition and the NaCl precipitated was removed by filtration. b) Hydrazine aqueous solution (65 wt.-%) was employed as receive (M12, Table 2).

Hydrolysis reaction – 0.5 g of resin was added to a NaOH solution prepared with 1.44 g of NaOH dissolved in 50 mL of water or 30 mL of water and 20 mL of methanol (Table 2). The reaction was carried out at 95°C during 24 h. The modified resin was thoroughly washed with HCl aqueous solution (0.01M), water, propanone and then dried during 24 h at 60°C (M13-M15, Table 2)

Table 2. Reaction conditions of hydrazine-hydrolysis modification

Sample	pH	t (h)	T (°C)	NH_2NH_2/CN mole ratio
M1	12	24	Reflux	1/1
M2	12	24	Reflux	2/1
M3	12	24	Reflux	3/1
M4	12	24	25	3/1
M5	12	24	65	3/1
M6	12	24	Reflux	3/1
M7	12	48	Reflux	3/1
M8	12	72	Reflux	3/1
M9	9	24	60	3/1
M10	9	72	60	3/1
M11	9	24	Reflux	3/1
M12	12	24	80	6/1[a]
M13[b]	12	24	Reflux	---
M14[c]	12	24	Reflux	---
M15[c]	9	24	Reflux	---

a: aqueous solution hydrazine
b: Hydrolysis - aqueous NaOH
c: Hydrolysis - methanolic solutions NaOH

Resin characterization

The bead size distribution was determined by different sieves. The bulk density (D_a in g/mL) was determined in a graduated cylinder [15]. The specific surface area (S_a in m^2/g), average pore diameter (D_p in Å) and pore volume in the dry state (V_p in cm^3/g) were determined by the BET and BJH methods respectively from low-temperature nitrogen adsorption isotherms (ASAP Micromeritics 2000) at 77 K using a high-vacuum volumetric apparatus. The samples were degassed at 100°C/1mPa for 3 h. Carbon, hydrogen and nitrogen contents were determined by elemental analysis (CHN Perkin-Elmer 2400). The chemical modification of nitrile groups was verified by infrared techniques (FTIR – Perkin-Elmer Spectrum One) in KBr pellets and by 75.5 MHz ^{13}C CP/MAS NMR (Brüker DRX 300 NMR spectrometer). CP-MAS probe was used, and samples were spun at 7 KHz in a 7 mm ZrO_2 rotor under a matched Hartmann-Hahn at the 1 ms of time contact. The carbon 90° pulse duration was typically 5 μ; the recycle time was 3s. Chemical shifts were relative to the methyl of hexamethylbenzene at 17.3 ppm and ambient temperature. Resin was also characterized at scanning electron microscope (Jeol JSM – 5800LV). The beads were coated with carbon film. Their external and internal parts were observed using 10 kV acceleration electron beam. The swelling degree (%S) of copolymers in methanol was calculated from the following relation $\%S = [(v_1 - v_0)/v_0].100$, where v_1 is the volume of swollen resin after 24 hours and v_0 is the volume of dry state [15].

Results and discussion

It is very common the use of modified copolymer network beads for the wastewater treatment. These materials are tailored according to their applications. This tailoring is achieved by their morphology control, porosity and chemical composition, fitting their chemical and physical properties which depend on its use. In this way, we have prepared polymeric materials with spherical morphology and controlled porous structure based on acrylonitrile/divinylbenzene (AN/DVB) crosslinked resins [1,2].

The FTIR spectra of copolymers have presented absorption bands at 2240 cm^{-1} (Figure 1) attributed to the CN stretching vibration [16]. Table 3 shows the physical and chemical characteristics of copolymers: bulk density (D_a), average pore diameter (D_p), specific surface area (D_S), swelling degree in methanol (S%) and chemical composition. The elemental analysis of both copolymers was almost 12% of the N contents, which indicated that the AN incorporation into copolymer structure was high (around 80%). It can also be observed that the obtained copolymers have presented different porous structure. The R2 resin has lower density (D_a = 0.21 g/cm^3) and smaller specific surface area (S_a = 64 m^2/g) compared to the other one (R1 resin) which presents D_a = 0.45 g/cm^3 and S_a = 98 m^2/g. These results indicate that the R1 resin has larger porous structure compared to the R2 resin.

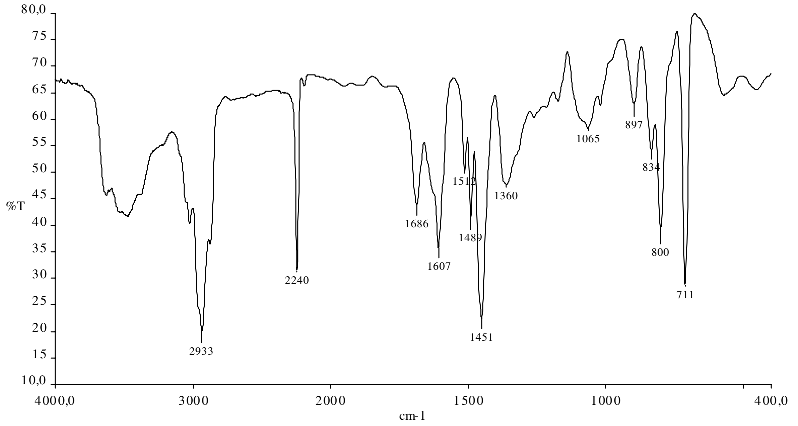


Figure 1: FTIR spectrum of R1 copolymer of AN/DVB

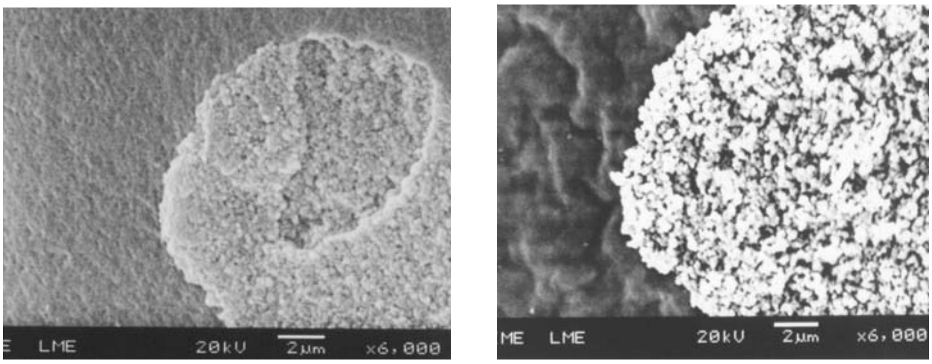
The porous structure was confirmed by the scanning electronic microscopy (SEM). Figure 2 shows the micrographs of R1 and R2 resins. The R2 resin micrograph presents rougher and more heterogeneous internal surfaces with larger porous compared to R1. These results could be explained by higher degree of phase separation, which occurred in great extension during the copolymerization process. This accentuated phase separation could be due to monomer polarity (AN), which

Table 3. Physical and chemical characteristics of copolymers networks

Sample	N Content (%)^a	AN content (%)	D_a (g/mL)^b	S_a (m^2/g)^c	V_p (cm^3/g)^d	D_p (Å)^e	S (%)^f	Yield (%)
R1	12,2	75	0.45	98	0.46	161	63	60
R2	13,0	81	0.21	64	0.32	202	20	43

[a] N_c = elemental analysis (CHN); [b] Acrylonitrile incorporation in relation to the amounts used in feed; [b] Bulk density; [c] Specific surface area determined by BET method; [d] Average pore volume determined by BJH method; [e] Average pore diameter determined by BJH method; [f] swelling degree in methanol

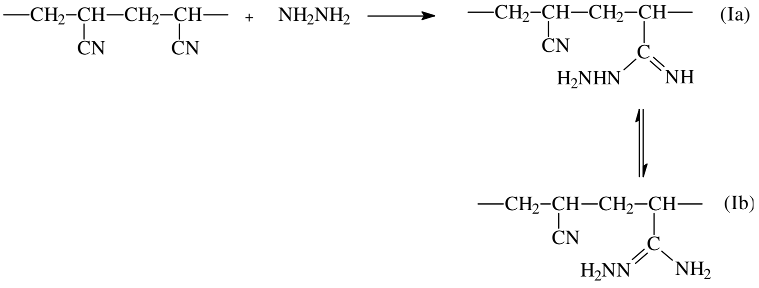
does not have affinity for employed diluent system (ANI / HEP). As it is known, macroporous resins can be easily broken [1,2]. Consequently, it is not suitable for chemical modification. Due to this aspect and high methanol swelling degree (R1 = 63% and R2 = 20%), the R1 resin was chosen for modification with hydrazine. According to the literature [4,11] the interaction mechanism of hydrazine with nitrile containing macromolecular compounds has not yet been completely established.



(a) (b)

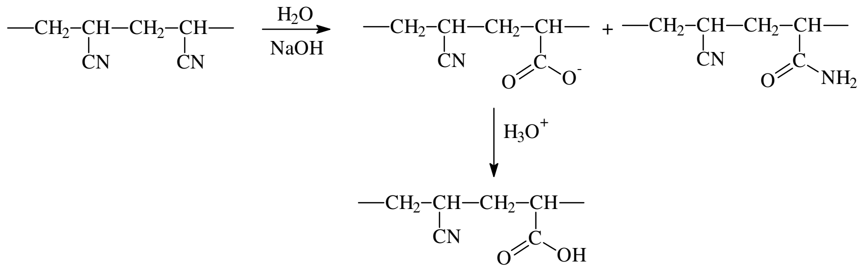
Figure 2. Scanning electron micrographs (SEM) of the external and internal parts (a) R1 and (b) R2

The hypothetical structure can be illustrated by Scheme 1. The modification with hydrazine were carried out at pH=12 during 24 hours at reflux temperature only varying the NH_2NH_2 / CN mole ratio (M1-M3, Table 2).



Scheme 1. Hypothetical structures of amydrazones (Ia and Ib)

Figure 3 shows the FTIR spectra of modified copolymers with hydrazine. In all reactions, it was observed the presence of the absorption at 1671 cm^{-1} and 1636 cm^{-1}. Compounds with nitrile groups can be hydrolyzed in alkaline conditions, producing amide and/or carboxylate groups (Scheme 2). These groups present an intense absorption at 1670 cm^{-1} in the FTIR spectrum [17]. Hence, it may be concluded that in lower hydrazine / nitrile mole ratios (1/1 or 2/1), the hydrolyzed reaction predominately occurs. On the other hand, the reaction carried out with 3/1 mole ratio has produced the absorption bands more intense in 1636 cm^{-1} corresponding at C=N stretching absorptions [12,14].



Scheme 2. Hydrolysis of the nitrile groups in alkaline conditions

The Figure 4 shows the ^{13}C CP/MAS NMR typical spectra of modified copolymers with different spinning speeds. The copolymer spectra present four peak groups: 20-50 ppm (-CH_2- and -CHPh-), 120-150 ppm (CN and aromatic carbon atoms); 180 ppm (C=O of the carboxyl group) and 200-240 ppm (side bands related to aromatic carbon atoms). These side bands (see asterisk) were confirmed by increasing the spinning speed from 5 (Figure 4a) to 7 kHz (Figure 4b).

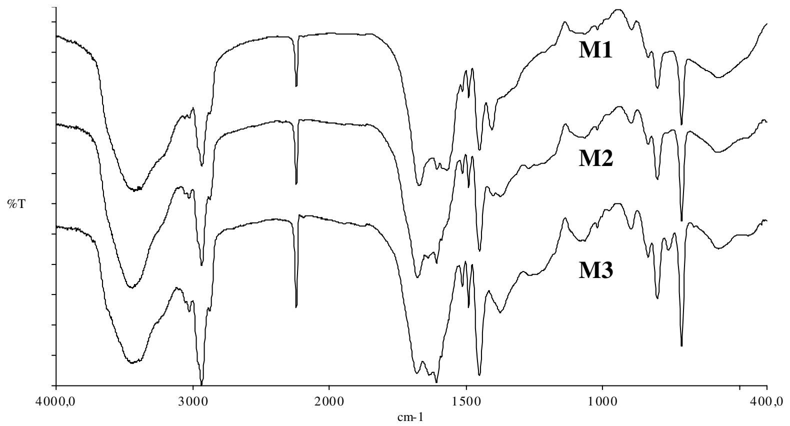


Figure 3. FTIR spectra of modified copolymers with hydrazine. Reaction conditions: hydrazine/nitrile mole ratio - M1 = 1/1; M2 = 2/1; M3 = 3/1

Aiming to maximize the chemical modification of nitrile groups to amidrazone groups reactions were carried out taking into account higher NH_2NH_2/CN ratio (3/1) and also reducing the temperature reaction (M4 and M5, Table 2). It was observed that, in higher temperature (65°C), the hydrolysis reaction was preferred (1670 cm^{-1} – C=O) if we compare to the amidrazone modification (1636 cm^{-1} - Figure 5). The reactions conducted in lower temperature presented both situations, but with low extension reaction considering the decreasing of the CN absorption (2240 cm^{-1}).

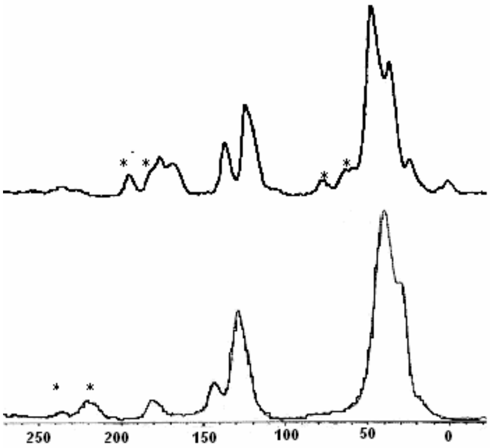


Figure 4. ^{13}C CP/MAS NMR spectra of M3 modified copolymers with hydrazine (*: side bands)

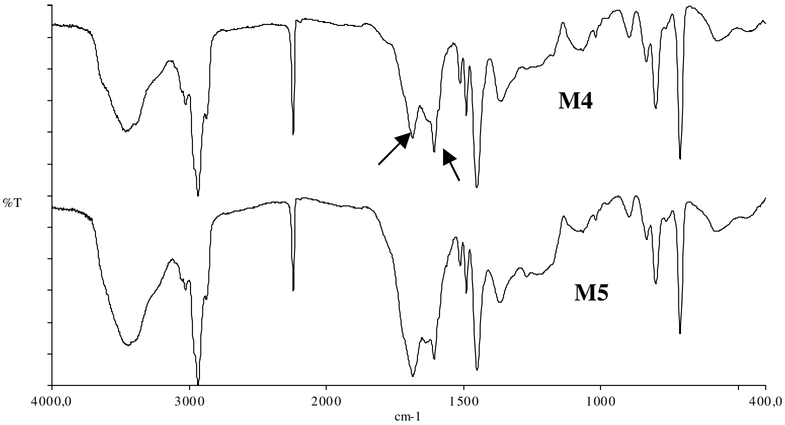


Figure 5. FTIR spectra of modified copolymers with hydrazine varying temperature (M4 = 25°C; M5 = 65°C)

Therefore, the new experiments were carried out, in reflux, only varying reaction time (M6, M7 and M8, Table 2). In the longer time reactions, it was observed in the FTIR spectra (Figure 6) an increasing of bands in the 1685-1606 cm^{-1} region attributed to the carboxyl group. This way, higher pH conditions (pH=12) were expected to be the responsible for the production of hydrolyzed material.

Thus, the set of reactions in lower pH (pH = 9) were made (M9 - M11, Table 2). No modification was observed when the reaction was conducted at the 60°C during 24 h (M9). On the other hand, when the reaction time was raised and temperature at reflux was employed (M11), the absorptions at 1631 and 1679 cm^{-1} were detected in the FTIR (Figure 7). These absorptions at 1631 and 1679 cm^{-1} were attributed to C=N (amidrazone) and carboxyl group (amide or carboxylate ion).

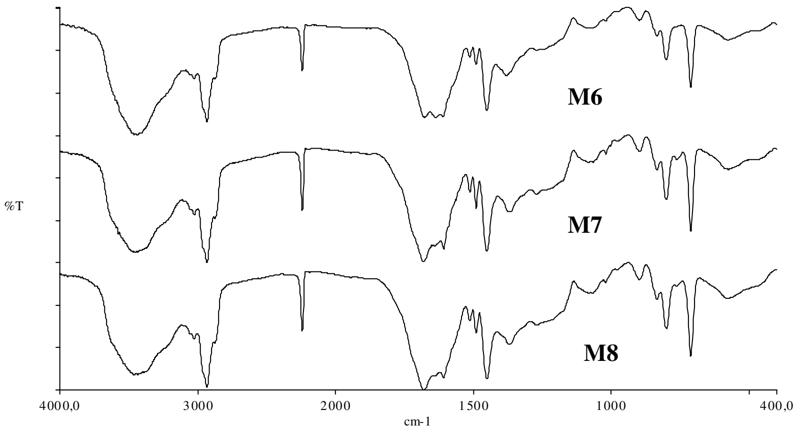


Figure 6. FTIR spectra of modified copolymers with hydrazine varying reaction time - M6: 24 h; M7: 48 h and M8: 72 h

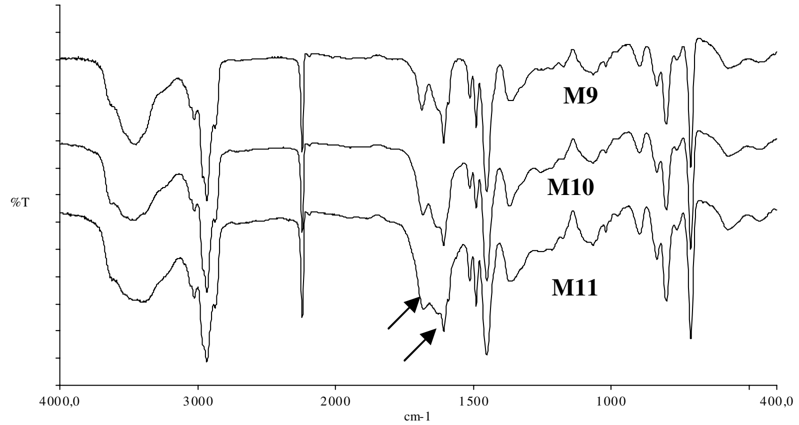


Figure 7. FTIR spectra of modified copolymers with hydrazine. Reaction conditions: M9 - pH = 9; t= 24 h; T = 60°C; M10 - pH = 9; t= 72 h; T = 60°C; M11 - pH = 9; t= 24 h; T = reflux

Taking into consideration that it was not possible to avoid the hydrolysis reaction using the $NH_2NH_2.2HCl$ due to the higher content of water necessary for the salt solubilization, a reaction was carried out (M12, Table 2) employing hydrazine aqueous solution (wt 65%) without pH correction. The FTIR spectrum of modified resins shows an intense band at ~1635 cm^{-1}, which was attributed to C=N of the amidrazone group (Figure 8). The broad absorption near 3330 cm^{-1} was attributed to O-H groups of absorption of water by modified copolymer.

Some reactions were developed without hydrazine to confirm the hydrolysis reaction. Hence, this reaction was studied in alkaline conditions (pH =12) and temperature at reflux. During alkaline hydrolysis reaction the beads have gradually become yellow. The FTIR spectra before and after hydrolysis reaction are shown in Figure 9. As it can be seen, after the hydrolysis with sodium hydroxide in aqueous solution, the hydrolyzed resin spectrum (M13) has greatly changed. Two new bands

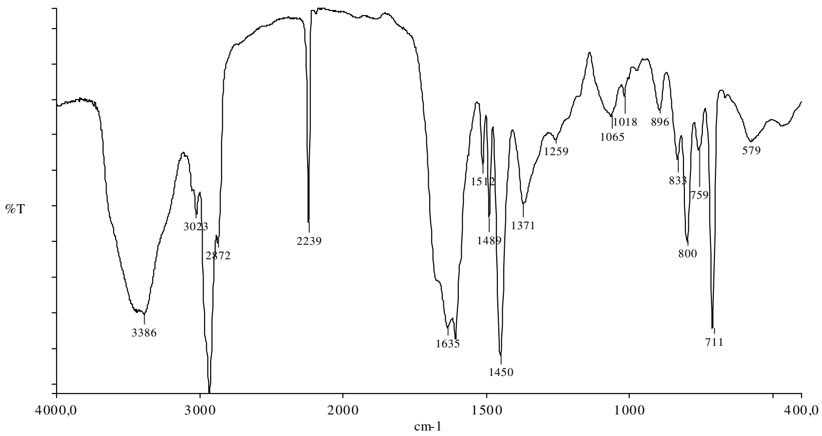


Figure 8. FTIR spectrum of M12 modified copolymer with aqueous solution hydrazine

(Figure 9 - M13) at 1569 and 1407 cm^{-1} are respectively related to unsymmetric and symmetric stretching of carboxylate group vibrations. To confirm the carboxylate produced by hydrolysis of nitrile groups, the hydrolyzed beads (M13) were thoroughly washed with acid aqueous solution (0.1M HCl). This resin spectrum (Figure 9 - M13a) displayed a band at 1718 cm^{-1} related to the carboxyl acid (C=O) stretching vibration. The alkaline hydrolysis extent was more significant when methanol was employed as a solvent (M14) in comparison to the other one (M13) in which the reaction was conducted with NaOH aqueous. This result can be attributed to the better wetting capacity of the methanol compared to the water and the higher strength base of the metoxide ion than the hydroxide ion. Finally, a reaction was performed at reflux during 24 hours at pH=9; furthermore, the hydrolysis were not verified (M15). This result confirmed that hydrazine reactions employed $NH_2NH_2.2HCl$ were more efficient when pH=9 was used.

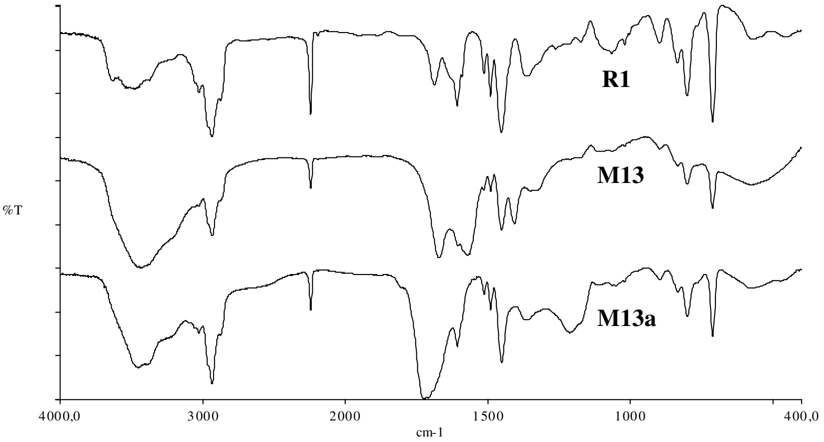


Figure 9. FTIR spectra of unmodified and hydrolysis modification of copolymers. Reaction conditions: M13 – pH = 12, t = 24h; T = reflux. M13a - neutralized M13 with acid aqueous solution (0.1M HCl)

The conversion increase of the nitrile groups and subsequent losses or gains of nitrogen respectively in the saponification reaction and / or amidrazone formation can be evaluated by the nitrogen content analysis of the polymer at different chemical treatment.

The Table 4 shows that while the relative nitrogen content of hydrolyzed resins decrease (M14), the nitrogen content of the modified polymers with hydrazine increase (M12). In addition, the oxygen content of modified polymers with hydrazine also increase compared to the unmodified copolymers, which indicates that some extent of hydrolysis reaction can occur.

Table 4. Elemental analyses results of hydrazine-hydrolysis modifications

Resin	N (%)	O (%)
R1	12,9	0,2
M14	9,0	10,3
M12	14,1	3,5

Conclusion

The results presented in this paper show that the porous structure of crosslinked copolymers (based on AN and DVB) depends on the diluent system employed in their synthesis. The best conditions to modify the copolymer (based on AN), which produce amidrazone, with $NH_2NH_2.2HCl$ was pH = 9 and high temperature. On the other hand, pH=12 favors the hydrolysis reaction in the presence of methanol as solvent. Finally, the better modification to amidrazone was obtained when the hydrazine aqueous was employed.

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