Polymer Bulletin 61, 319–330 (2008)
DOI 10.1007/s00289-008-0962-2

Polymer Bulletin

Surface modification of styrene-divinylbenzene copolymers by polyacrylamide grafting via gamma irradiation

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Received: 28 March 2008 / Revised version: 10 June 2008 / Accepted: 13 June 2008

Summary

Polyacrylamide chains were grafted onto styrene-divinylbenzene (S-DVB) copolymer beads using gamma radiation from a ^{60}Co source by applying the simultaneous method. S-DVB macroporous copolymer was synthesized by aqueous suspension polymerization and characterized by determining apparent density, surface area, pore volume distribution and water uptake. Optical and electron microscopies were used in order to observe the copolymer morphology. The effect of parameters such as monomers concentration, irradiation dose and presence of inhibitor (Mohr's salt) on grafting reaction was studied. The grafting reaction was evaluated with the aid of elemental analysis, FTIR, HR-MAS NMR spectrometry, thermogravimetry (TG) and electron microscopy. Grafting yield (evaluated by nitrogen content) increased with acrylamide concentration and irradiation dose increasing. However, above determined values of those parameters it is observed a tendency of decreasing on the grafting yield. The presence of Mohr's salt inhibited the production of homopolymer as well as the progress of the grafting reaction.

Introduction

Porous styrene-divinylbenzene (S-DVB) copolymers have been extensively used as supports for chelating resins and catalysts, and as stationary phases in chromatographic processes. These materials are mainly prepared by free-radical crosslinking copolymerization of styrene (S) and divinylbenzene (DVB) in presence of an initiator and a porogen agent. It has been established that the degree of porosity and the pore size distribution of the beads are determined by the copolymer synthesis conditions such as diluent nature (solvent or nonsolvent for the polymer chains in formation or a combination of both), dilution degree of monomers and crosslinker concentration. The porous structure determines the permeability limits and the accessibility of reagents and solvents to the inner regions of the copolymers beads. Thus, the efficiency of the supported reagents and adsorbents is deeply influenced by the porous characteristics of the copolymer supports [1-4].

Chemical modifications and applications of S-DVB copolymers in aqueous systems are limited because of the hydrophobic nature of their polymer chains. Even supports with very high values of surface area present lower performance in water when compared with their behavior in thermodynamically good solvents for the copolymers. The introduction of hydrophilic polymer chains such as polyacrylamide onto styrene copolymers may promote better diffusion of aqueous solution through porous structure and offer numerous potential applications for those materials.

S-DVB copolymers grafted with polyacrylamide chains provide an efficient material for removing mercury from aqueous solutions. Most routes for functionalizing polymers with grafted polyacrylamide chains have been based on radical polymerization, using an oxidation-reduction initiation system (with ceric ion) [5] or a living radical polymerization (LRP) by copper-mediated atom transfer radical polymerization (ATRP) [6,7]. Generally, S-DVB copolymers are chlorosulfonated in order to introduce the labile chlorine atom. After that first step, subsequent substitution reactions are carried out with the objective of introducing a functional group capable of undergoing oxidation reaction forming polymer radicals to initiate acrylamide polymerization.

Although ionizing radiation, especially gamma radiation, is a common technique for polymer materials surfaces modification its use has not been evaluated for grafting of polyacrylamide chains onto S-DVB copolymers [5-9]. However, that methodology may provide materials with better properties than those produced by oxidation-reduction initiation. The use of ionizing radiation, specially by applying the methodology of simultaneous irradiation of the polymer in presence of the monomer, is a more direct route to promote the grafting reaction and may result in a reduction of synthesis steps what implies directly on the reduction of reagents consumption and residue production [10].

Therefore, the aim of this work was to promote grafting of polyacrylamide chains onto S-DVB copolymer initiated by gamma irradiation. The influence of the total irradiation dose, acrylamide concentration and homopolymerization inhibitor concentration on grafting reaction was analyzed.

Experimental

Chemicals

Commercial styrene (S) and divinylbenzene (DVB) were donated by Nitriflex Indústria e Comércio S.A. (Rio de Janeiro/Brazil) and used after washing with 5% w/v NaOH aqueous solution, to remove inhibitor, and water until neutral pH. Acrylamide (P.A) and poly(vinyl alcohol) were purchased from Aldrich Chemical Co. (St Louis/ USA) and Kurary Company (Umeda/Japan) respectively, and used without further purification. Other reagents and solvents were purchased from Vetec Química Fina Ltda. (Rio de Janeiro/Brazil) and used as received.

Synthesis of S-DVB support

S-DVB copolymer was synthesized by aqueous suspension polymerization in a 1 L three-necked round bottomed reactor flask equipped with a mechanical stirrer and a reflux condenser containing a silicon oil seal at its top. The organic phase composed of 0.12 mol of styrene (S), 0.18 mol of divinylbenzene (DVB), $3x10^{-3}$ mol of benzoyl peroxide and a diluent mixture constituted of 20% of toluene and 80% of n-heptane (1:1.5 v/v in relation to monomers mixture) was prepared and transferred to the flask which already contained the aqueous phase constituted of PVA and NaCl solutions (both 0.5% w/v in relation to water). The volumetric ratio between the aqueous and organic phases was 4:1. The system was maintained under stirring (500 rpm) at 90°C during 30 h. The beads obtained were washed several times with hot water and sieved. The 50-106 μm fraction was collected and washed with hot ethanol and methanol and finally dried for 48 h at 60°C. That fraction was used for further modification reactions.

Grafting procedure

The S-DVB copolymers were weighed into glass tubes and imbibed in an acrylamide methanol solution of known concentration. The tubes were sealed with rubber septa and nitrogen was bubbled through the solution for 10 min in order to create an inert atmosphere. The samples were irradiated by a ^{60}Co-γ source (MDS Nordion, Gammacell 220 Excel, 56 Gy min^{-1}) at room temperature using different irradiation doses and acrylamide concentrations. The influence of Mohr's salt concentration $[(NH_4)_2Fe(SO_4)_2.6H_2O]$, a known homopolymerization inhibitor, on grafting reaction was also evaluated. Afterwards, the copolymers were washed several times with hot water to remove polyacrylamide (homopolymer) prior to drying for 48 h at 60°C.

Characterization of supports and modified resins

The porosity of S-DVB copolymer was characterized by determining apparent density by the graduated cylinder method [11], surface area and pore volume by nitrogen adsorption measurements following the BET and BJH methods respectively (Micromeritcs ASAP 2010 apparatus) and fixed pore volume by water uptake [12].

The appearance of copolymer beads was observed in an optical microscope (Olympus SZ10) and morphology in a scanning electron microscope (JEOL_JSM 6460LV).

FTIR spectra of polymers as KBr discs were taken in a Perkin-Elmer (Spectrum One) spectrometer (4 scans and 4 cm^{-1} resolution).

The samples were swelled in $CDCl_3$ by 12 h before NMR evaluation. The analyses were recorded in a BRUKER, AVANCE, 9.4 Tesla equipment using a 4 mm HR/MAS probe head at a constant temperature (298K). The spectra were obtained with acquisition time of 2.93s, relaxation delay of 2.0 s, sweep width (SWH) 5593 Hz, using a pulse sequence with CPMG before the 90° pulse and using a drop of D_2O with sodium-3-trimethylsilylpropionate (TMSP-2,2,3,3-d4) for the lock and internal reference respectively.

Termogravimetric (TG) and derivative thermogravimetric (DTG) curves of polymers were obtained by using a TA Q50 instrument in a temperature range of 30-650°C at constant heating rate of $20°C min^{-1}$ under nitrogen atmosphere at a flow rate of $60\ mL\ min^{-1}$.
Elemental analyses of polymers were carried out using GE instruments (EA 1110 CHN-O) applying the Dynamic Flash Combustion for sample analysis.

Results and Discussion

Porous characteristics of S-DVB copolymer support

The extraction capacity of chelating resins prepared by the immobilizing active functional groups on S-DVB supports is dependent on the matrix structure characteristics and that dependence is observed even in the copolymer functionalization step. The type of porous structure directly influences the process of reagent diffusion through the internal structure of the copolymer and consequently, the extent of modification reaction and the distribution of chelating groups. A gel type support only swells in a thermodynamically good solvent for polystyrene chains. Thus, a reagent solution constituted of a nonsolvent for polystyrene cannot access the internal structure of a gel type copolymer. As a consequence, this material is functionalized in a very low extension in such medium, probably only on the external surface. On the other hand, the reactivity of macroporous supports is not accentuately dependent on the polymer swelling ability in the reagent solution and then high functionalization degrees can be reached even in the presence of nonsolvents for polystyrene chains [4]. In this study, the irradiation of S-DVB copolymer was carried out in presence of an acrylamide methanol solution (simultaneous method). Water is an excellent solvent for acrylamide, however S-DVB copolymers are hydrophobic materials and do not permit the access of acrylamide aqueous solutions into the beads. Thus, the grafting reaction of polyacrylamide should not be performed in that solvent. The choice of methanol was based on its thermodynamic affinity for acrylamide as well as on its better capacity to diffuse into the macroporous copolymer. Methanol is not considered a solvent for polystyrene chains, but it can permeate through the copolymer matrix solvating the internuclear chains and favoring the access of monomer molecules to polymer radicals on the inner regions of that matrix. In order to favor the diffusion of acrylamide methanol solution through the interior of the polymer matrix a macroporous S-DVB copolymer with high surface area and pore volume for grafting polyacrylamide chains via gamma irradiation was prepared. The porous characteristics of that material are presented in Table 1.

Table 1: Porous characteristics of S-DVB copolymer

Material	DD (%)	S/DVB (%)	d_{ap} ($g\ cm^{-3}$)	A ($m^2\ g^{-1}$)	Vfp_a ($cm^3\ g^{-1}$)	Vfp_b ($cm^3\ g^{-1}$)
S-DVB copolymer	150	40/60	0.20	278	0.6	0.35

DD=dilution degree of monomers in toluene (20%) and n-heptane (80%) mixture, S/DVB= percentage of styrene/divinylbenzene in monomers mixture, d_{ap}=apparent density, A= surface area (BET method), Vfp_a= fixed pore volume determined by BJH method, Vfp_b= fixed pore volume determined by water uptake

The mechanisms proposed for explaining the porous structure formation of divinylbenzene copolymers are based on a phase separation process between the growing polymer chains and the diluent mixture during the conversion of the system from liquid to solid-like stage (the gel point). This process can occur in different stages of the polymerization reaction, depending on the synthesis conditions (type and amount of diluent, crosslinker concentration, etc), and determines the type of porous structure as well as the pore distribution of copolymer beads [13]. When synthesis parameters are varied in the copolymerization reaction, the porous characteristics of the copolymers are a result of the combination of each parameter effect on the phase separation proccess [2].

It has been demonstrated that the synthesis parameters adopted in this work promoted the formation of macroporous copolymers with high porosity degree [2-4,13]. The presence of a nonsolvent for polystyrene chains (as the diluent mixture used in this work) induced the phase separation of the growing polymer chains before the gel point. The insoluble polymer tends to agglomerate rapidly resulting in the formation of a porous structure. When a higher dilution degree (as 150%) is used, the collapse of these internuclear chains produces larger microspheres and thus a more porous structure containing larger pores. If the monomers mixture is also composed of a higher DVB concentration, a highly crosslinked network is formed promoting the phase separation in an earlier stage of the polymerization and thus the formation of a more porous structure. In opposition to the effect of dilution degree, high DVB contents generate high intramoleculary crosslinked nuclei favoring the reduction of pore sizes and thus contributing to the formation of a structure with high amount of pores of small diameters. Thus, the porous characteristics of the synthesized copolymer (average pore size and pore size distribution) are a consequence of the combination of those three synthesis parameters, a diluent mixture with a high proportion of nonsolvent, a high dilution degree (150%) and a high DVB content (60%).

Besides the significant values of surface area and pore volume determined by nitrogen adsorption, the copolymer also presented a lower value of apparent density confirming its high porosity. The value of pore volume determined by water uptake for this copolymer demonstrates that an acrylamide methanol solution can permeate through its macroporous structure. The determination of pore volume in S-DVB copolymers by water uptake needs a pretreatment with methanol in order to reduce the hydrophobicity of that material. That treatment makes possible the water diffusion through the copolymer beads because methanol diminishes its hydrophobicity. The same argument can be applied to explain the choice for using methanol as solvent for

Figure 1: Optical micrography of the unmodified S-DVB copolymer (magnification: x50)

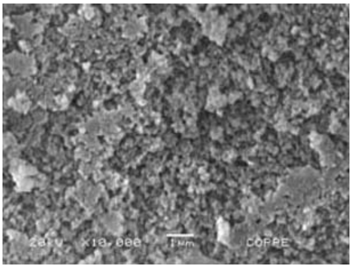


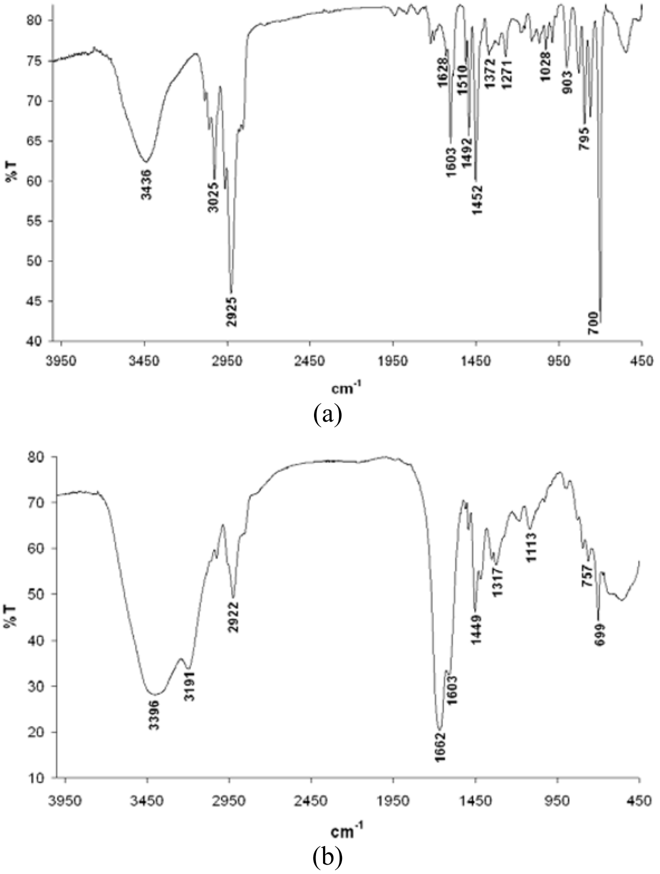
Figure 2: Electron micrography of the internal structure of the unmodified S-DVB copolymer (magnification: x10000)

acrylamide: methanol can access the inner regions of the copolymer beads and swell the internuclear chains, favoring the reaction with acrylamide [12].

Optical appearance and electron microscopy of the internal structure of that copolymer also confirm that its structure presents a high porosity (Figures 1 and 2). The presence of pores on polymer matrix provokes an accentuated light scattering resulting in an opaque appearance [4]. Electron microscopy of the internal surface of that copolymer reveals the existence of channels between the aggregates of microspheres, characterizing the presence of fixed pores.

Characterization of grafted S-DVB copolymer

S-DVB copolymer was submitted to the reaction with acrylamide initiated by gamma radiation. The presence of polyacrylamide chains is indicated by the FT-IR spectra of unmodified and irradiated copolymers (Figure 3). The spectrum of the modified copolymer shows a strong absorption near 1660 cm^{-1} involving C=O stretching and NH_2 deformation (amide I and amide II bands) and a broad absorption band around 3400 cm^{-1}, which is a doublet, attributed to asymmetric and symmetric NH_2 stretching [14].



(a)

(b)

Figure 3: FT-IR spectra of the unmodified (a) and modified (grafted) copolymers (b)

Figure 4 shows the NMR spectra of unmodified and grafted copolymers. Compared with the one of S-DVB copolymer, the spectrum of modified copolymer shows a change at 2.2 ppm that can be attributed to the presence of methylene protons attached to acrylamide group. However, it is possible to observe a peak less intense in the same region on S-DVB copolymer spectrum due the benzylic hidrogen. Moreover, it is possible to observe a new line at 1.6 ppm relative to the protons of methylene groups $(CH_2)_n$ of the polyacrylamide chains [15]. Those changes can be an indication of the presence of polyacrylamide chains onto S-DVB copolymers.

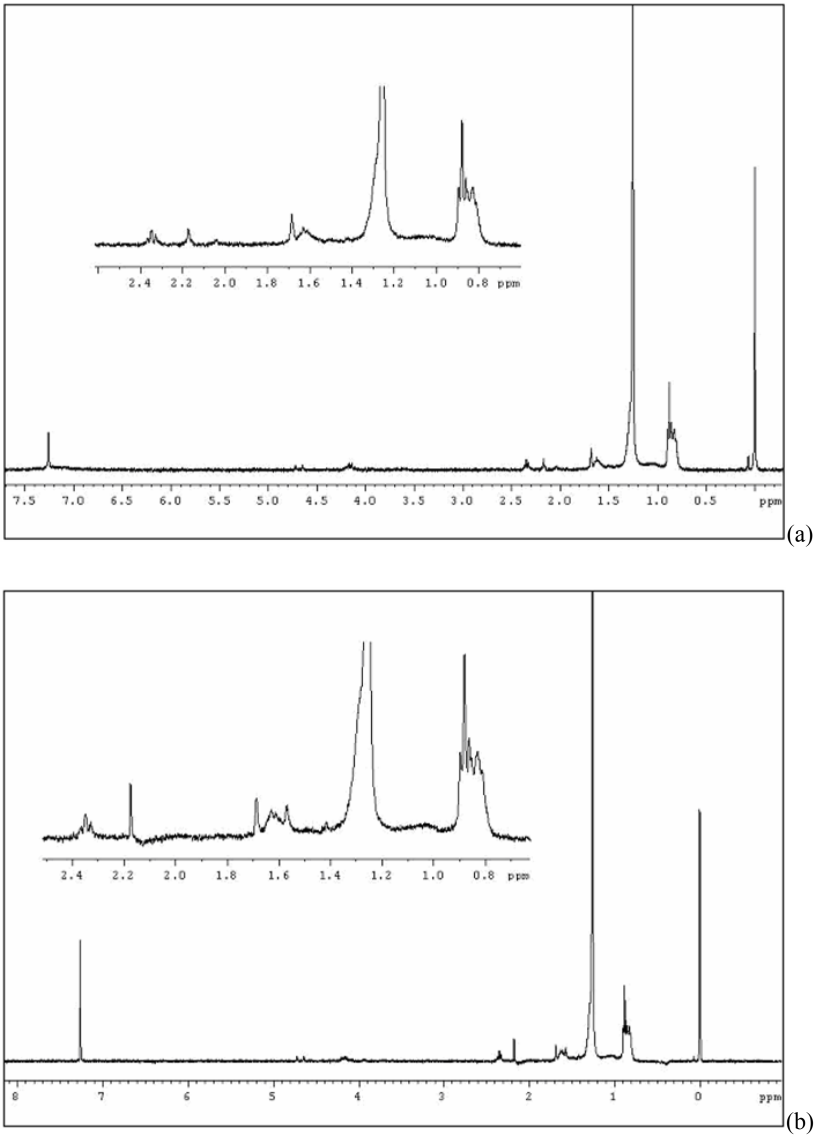
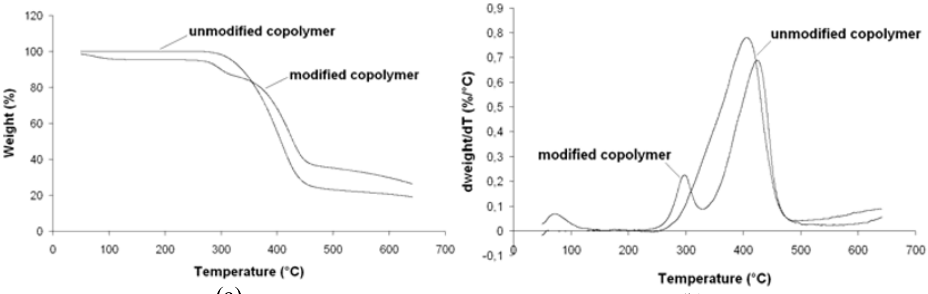


Figure 4: H NMR characterization of unmodified copolymer (a) and grafted copolymer (b)

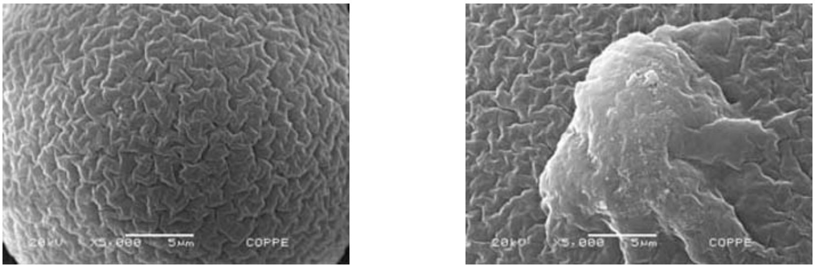
Thermogravimetric data of unmodified and modified copolymers (Figure 5) also confirm the grafting occurrence. A comparison among those data shows that the unmodified copolymer possesses only one significant weight loss step (11.58%) at 250-450°C relative to the decomposition of the polymer main chain. The irradiated copolymer presents two degradation steps. The first one around 290°C (6%) is attributed to the decomposition of amide groups and the second one at 420°C (24.1 %), to the degradation of carbon chains of the polyacrylamide and S-DVB copolymer [16].



(a) (b)

Figure 5: TG (a) and DTG (b) curves of the unmodified and grafted copolymers

The presence of polyacrylamide is observed on the electron micrography of the modified copolymer surface shown in Figure 6 (b).



(a) (b)

Figure 6: Electron micrographies of external surfaces of the unmodified copolymer (a) and grafted copolymer (b). (Magnifications of 5000 x)

Relationship between the grafting conditions and grafting yield

Influence of acrylamide concentration on grafting yield

The influence of monomer concentration on grafting reaction was studied at a constant dose of 33 kGy. As can be seen in Figure 7, the nitrogen content increased with the increase of acrylamide concentration until 7.5 mol L^{-1}. Above this point, it is observed a tendency of decreasing of nitrogen content. The initial increase in the grafting yield is due to the higher probability of association between the monomers and polymer macroradicals when higher amounts of acrylamide are present. Thus, more concentrated solutions lead to an increase in the propagation reaction. The tendency of decreasing of the grafting yield in presence of higher acrylamide concentrations can be attributed to the formation of large amounts of homopolymer. This can make the reaction mixture more viscous, hindering the diffusion of unreacted acrylamide molecules through the polymer matrix. The same behavior has been observed by other researchers in the grafting of vinyl monomers on different polymers [17,18].

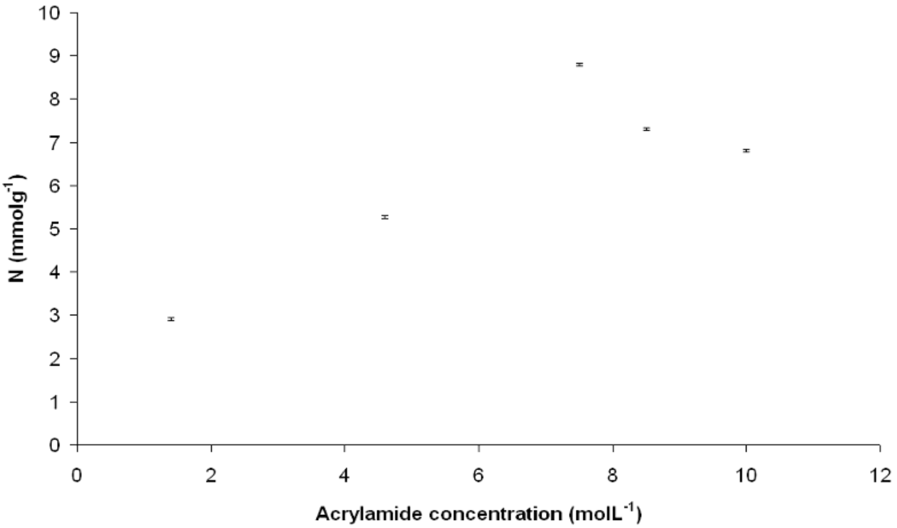


Figure 7: Relationship between the nitrogen content of grafted copolymer and monomer concentration (irradiation dose: 33 kGy, dose rate: 56 Gy min^{-1})

Influence of irradiation dose on grafting yield

The influence of irradiation dose on grafting yield (nitrogen content) is presented on Figure 8. The increase of the irradiation dose from 5 to 50 kGy caused an increase on

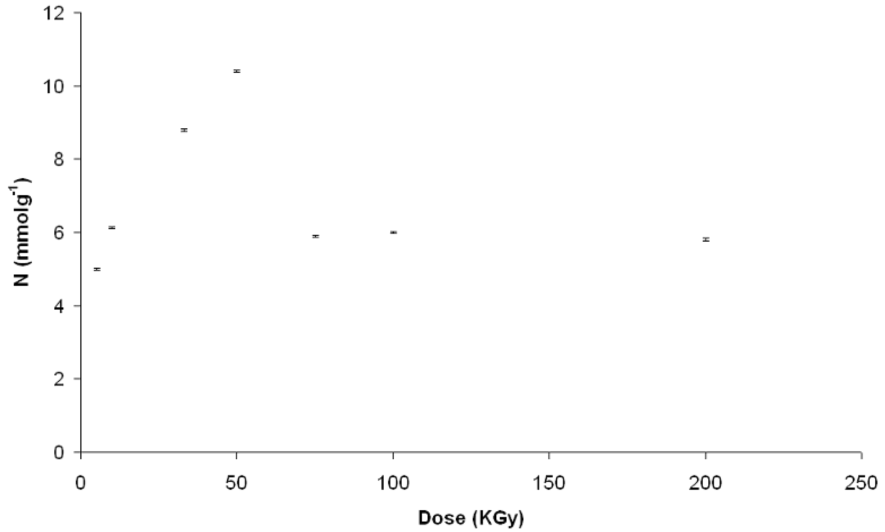


Figure 8: Relationship between the nitrogen content of grafted copolymer and irradiation dose (acrylamide concentration: 7.5 mol L^{-1}, dose rate: 56 Gy min^{-1})

nitrogen content of modified copolymers due the enhancement of the number of free-radical sites on polymer substrate. Probably, above that point the number of free-radicals from monomer molecules increased significantly favoring the termination reaction. Moreover, polyacrylamide chains already grafted onto the copolymer can be broken with the excess of irradiation dose.

Influence of the addition of homopolymerization inibihitor on grafting yield

The grafting reaction is usually accompanied by the undesirable homopolymerization reaction. The excess of homopolymer turns the reaction medium more viscous and limits the mobility of unreacted monomer molecules towards polymer radicals, making the grafting reaction unfavored. In addition, the removal of the homopolymer is generally a tedious process. Literature presents some papers about the use of Fe^{2+} in the form of Mohr's salt to suppress the homopolymerization [19-23]. According to Huglin and Johnson [24] that reaction can be explained by considering that Fe^{2+} ions undergo oxidation in the presence of H^+ and the resultant radical formed in this process ($H^\cdot$) combine with monomer radical resulting on the homopolymerization termination.

The effect of Mohr's salt on the grafting yield has been controversy [19-23]. Some studies demonstrate that when the pre-irradiation technique in air is used to promote the grafting reaction of acrylic acid (AAc) and sodium styrenesulfonate (SSS) onto nonwoven polypropylene fabric, the addition of Mohr's salt on the reaction mixture may conduct to an increase in grafting degree. The ferrous ions can cause the decomposition of hydroperoxide groups formed on polymer matrix during the irradiation in air leading to an increase on the number of radicals on that matrix. However, that reagent may also cause the deactivation of the grafting reaction when used in excess [22,23]. In other works [19-21] when pre-irradiation technique or simultaneous method (when polymer is irradiated in the presence of monomers) to promote the grafting reaction are used it is possible to observe that the presence of

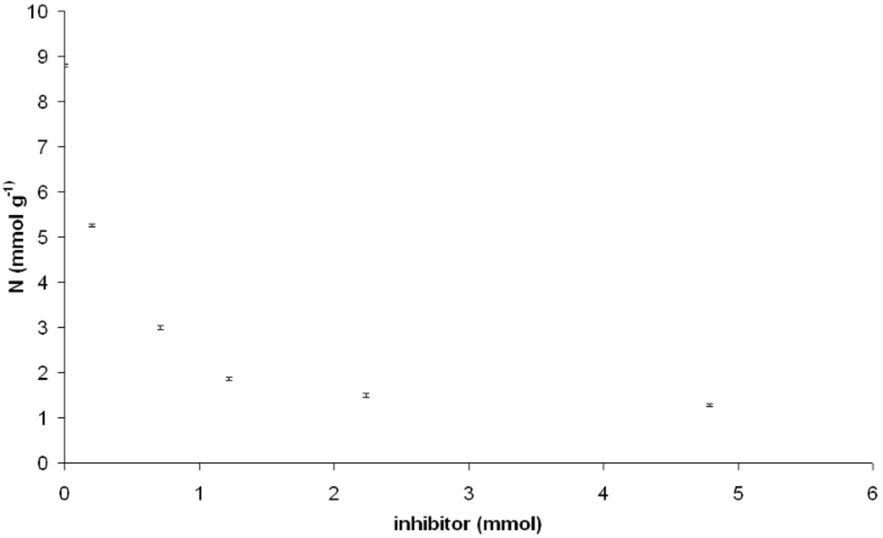


Figure 9: Relationship between the nitrogen content of grafted copolymer and inhibitor concentration, acrylamide concentration (7.5 molL^{-1}, total dose: 33 kGy, dose rate: 56 Gy min^{-1})

Mohr's salt on the reaction mixture, in any amount, suppresses the homopolymer formation and also results in a decrease of the grafting yield. A similar behavior was also observed in this work (Figure 9). In absence of Mohr's salt the grafting yield (nitrogen content) of the modified copolymer is maximum (8.8 mmolg^{-1}). Variations on the inhibitor concentration in the range from 0.204 to 4.79 mmol provoked a reduction of nitrogen content from 5.26 to 1.28 mmol g^{-1} indicating that probably a fraction of the free radicals on the polymer matrix was extinguished by the action of the inhibitor.

Our results show that the addition of 0.204 mmol of Mohr's salt into reaction mixture provoked a decrease around 40% on the nitrogen content of the modified copolymer. However, in this work variations on Mohr's salt concentration below that value were not studied. Probably, there is an inhibitor concentration smaller than 0.204 mmol that suppress the homopolymerization, making easier the purification step of the modified copolymer, without reducing drastically the grafting reaction.

Conclusions

It was verified that macroporous S-DVB copolymers may be functionalized with polyacrylamide chains using gamma-ray (^{60}Co source) by applying the simultaneous method (irradiation of polymer imbibed in an acrylamide metanol solution). The grafting reaction evaluated by determining nitrogen content of modified copolymers is influenced by the concentration of monomer, irradiation dose and inhibitor concentration (Mohr's salt). It was observed that the grafting yield (evaluated by nitrogen content) increased with acrylamide concentration and irradiation dose increasing. However, a tendency of grafting yield decreasing at higher acrylamide concentrations and dose irradiations was also observed. In a general way, the presence of Mohr's salt in the reaction mixture inhibited the homopolymerization as well as the grafting reaction.

Acknowledgements. The authors thank the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), Fundação Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES) and Fundação de Amparo à Pesquisa do Estado do Rio de Janeiro (FAPERJ) for financial support and to the professor Antônio Gilberto Ferreira, Universidade Federal de São Carlos (São Paulo/Brazil) for H NMR characterizations.

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