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Novel glycopolymers containing aminosaccharide pendant groups by chemical modification of ethylene–vinyl alcohol copolymers

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Ethylene–vinyl alcohol, EVOH, copolymers with two different vinyl alcohol compositions have been modified to incorporate different reactive functional groups by using phthalic anhydride, chloroacetyl chloride and 4-nitrophenyl chloroformate. Moreover, coupling reactions between EVOH copolymers functionalized with 4-nitrophenyl carbonate groups and three aminosaccharides (D-(+)-glucosamine, D-(+)-galactosamine and D-(+)-mannosamine) have been carried out in dimethyl sulfoxide at 70 °C. The structure of the resulting functionalized copolymers and new glycopolymers was confirmed by FTIR, ^{1}H and ^{13}C NMR. In addition, the thermal characterization of glycopolymers has been performed by DSC. A unique thermal transition, ascribed to the glass transition, is observed in both glycopolymer series. The semicrystalline character of the initial EVOH copolymers is vanished and complete amorphous polymeric materials are obtained since the resulting glycopolymers present relatively long and bulky pendant chains impossible to be included in the EVOH crystallites.

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1. Introduction

The need of polymeric materials with more complex architecture for specific applications led to the development of chemical modification of synthetic polymers. Therefore, the seeking of new chemical modifications of polymers is an interesting approach to change their properties and, accordingly, final response and applicability. In this sense, synthetic polymers containing carbohydrate pendant groups, denoted as glycopolymers, are emerging as potentially important materials for a number of applications in medicine and biotechnology mainly because of the essential role that carbohydrates play in a wide range of biomolecular recognition events. The recognition processes have been proven to be cooperative [1,2] and, consequently, strongly dependent on the spatial distribution of the carbohydrate moieties; so synthetic routes affording complex glycopolymer architectures that exhibit well-defined macromolecular structures and promising applications have been extensively investigated [3–9].

The synthesis of glycopolymers usually requires the polymerization or copolymerization of sugar-carrying monomers, although the less frequently employed chemical modification of preformed polymers using saccharide-containing reagents offers an alternative synthetic route to glycopolymers [10–14]. Using this last route a number of efforts have been made to prepare such materials, for example, poly(vinyl alcohol) [15–18], polyacrylamide [19] or hydrophilic elastomers such as poly(methylacrylamide-*g*-natural rubber) [20], poly(ethylene oxide)-*g*-poly(ethylene chlorosulfonate) [21] and poly(ethylene oxide)-*g*-butyl rubber [22–24]. In relation to this synthetic approach, ethylene–vinyl alcohol copolymers (EVOH) possess several characteristics that make them feasible carrier candidates for the preparation of macromolecular derivatives of bioactive agents [10,25–33]. However, EVOH copolymers exhibit, sometimes, the disadvantage of a low chemical reactivity with the bioactive compound at low temperature. A route to solve this problem may be the creation of more reactive functional groups in their structure that enables the coupling of the bioactive agent.

This work deals with the functionalization of EVOH copolymers through some different reactive groups (carboxylic acid, chloroacetate and *p*-nitrophenyl carbonate). Afterward and based on these results the applicability of pendant *p*-phenylcarbonate groups, linked to the initial EVOH copolymers, in the coupling reactions of some aminosaccharides is explored. The structure of the resulting polymers is determined and confirmed by FTIR, ^{1}H and ^{13}C NMR. The synthetic methodology here presented has as advantages, on one hand that the hydroxyl groups from saccharide do not need a previous protection and, on the other hand that the yield of each step is rather satisfactory. Moreover, the thermal transitions of the different synthesized polymeric derivatives, functionalized and those with saccharide moieties, are evaluated by using differential scanning calorimetry.

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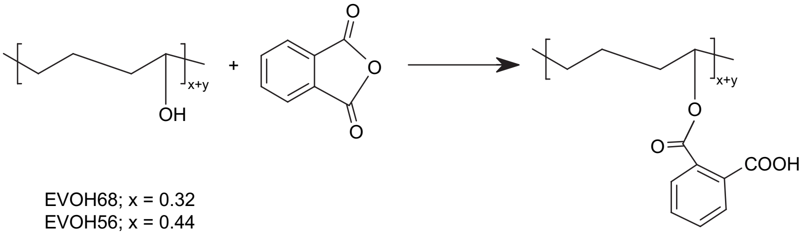


Scheme 1. Reaction of EVOH copolymers with phthalic anhydride.

2. Experimental

2.1. Materials

Two commercially available random ethylene–vinyl alcohol copolymers (EVOH, supplied by Kuraray and Dupont), were used. The nominal compositions in vinyl alcohol were 68 and 56 mol%, respectively. Therefore, these copolymers will be labeled throughout the article as EVOH68 and EVOH56, respectively. On the other hand, their melt flow indexes under ASTM D1238 norm at 210 °C are 3.1 and 16.0 g/10 min, respectively.

Triethylamine (TEA, Scharlau), pyridine (Scharlau) were distilled as previously reported [34,35]. *p*-Dimethylamino pyridine (4DAP, Fluka), phthalic anhydride (Fluka) and *p*-nitrophenyl chloroformate (Fluka) were also used as received. Chloroacetyl chloride (Fluka), dimethyl sulfoxide (DMSO, Scharlau), *N*-methyl-2-pyrrolidone (NM2P, Scharlau) and *N*,*N*-dimethylformamide (DMF, Scharlau) were distilled prior to use.

D-(+)-Glucosamine hydrochloride (99%, Fluka), D-(+)-galactosamine hydrochloride (99%, Fluka) and D-(+)-mannosamine hydrochloride (98%, Fluka) were used as received.

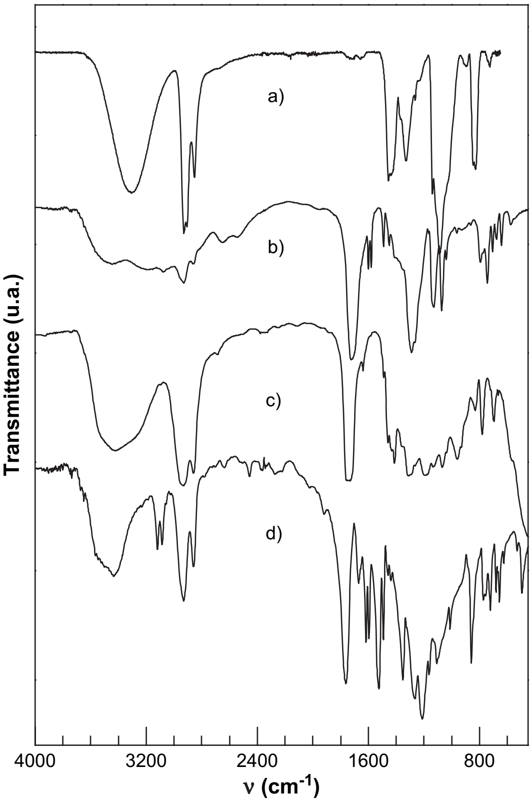


Fig. 1. FTIR of (a) EVOH68 former copolymer, and its activated copolymers with (b) phthalate (c) chloroacetate and (d) *p*-nitrophenyl carbonate groups.

2.2. Reaction of EVOH copolymers with phthalic anhydride

The reactions were performed in a Pyrex double-walled reactor that was entirely isolated from the outside to avoid any contact with humidity using DMSO as solvent and triethylamine/4DAP as catalytic system. Once the polymer is dissolved at 75 °C, the solution is maintained at 60 °C, adding the required amounts of catalyst and anhydride. After 6 h the resulting modified EVOH copolymer was isolated by precipitation in a 10-fold volume of a distilled water/chloride acid (100/1, v/v) mixture as precipitant. Posterior, all the samples were purified by reprecipitation using methanol/acetone (1/1 v/v) as solvent and distilled water/chloride acid (100/1 v/v) mixture as precipitant and then dried in vacuum at room temperature in the presence of phosphorus pentoxide until constant weight was attained.

2.3. Reaction of EVOH copolymers with chloroacetyl chloride

Each EVOH copolymer was dissolved at 80 °C in a Pyrex double-walled reactor that was entirely isolated from the outside to avoid any contact with humidity using NM2P as solvent. The solution was then cooled down up to 30 °C and the calculated amounts of pyridine and chloroacetyl chloride were added while stirring. After 4 h, the modified copolymer was isolated by precipitation in diethyl ether. The purification of polymers was performed by reprecipitation using acetone as solvent and distilled water as precipitant. The modified copolymers were dried in vacuum at room temperature in the presence of phosphorus pentoxide until constant weight was reached.

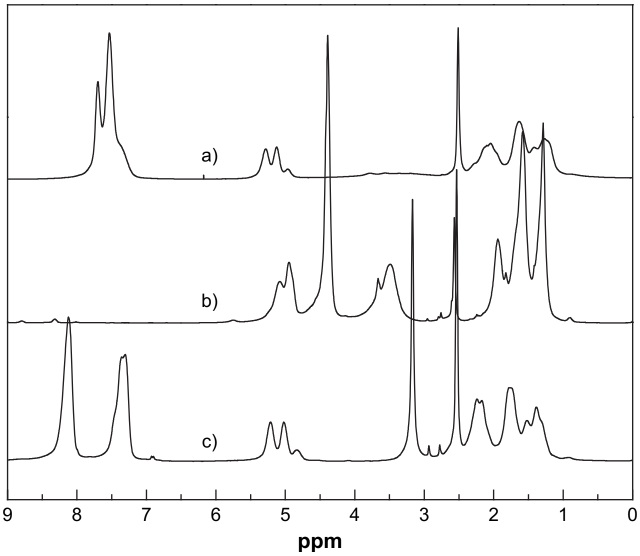


Fig. 2. ^{1}H NMR spectra of activated EVOH68 copolymers with (a) phthalate, (b) chloroacetate and (c) *p*-nitrophenyl carbonate groups.

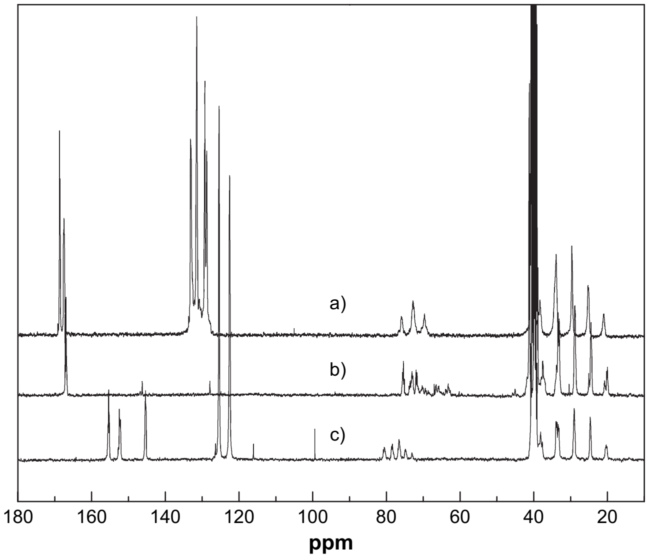


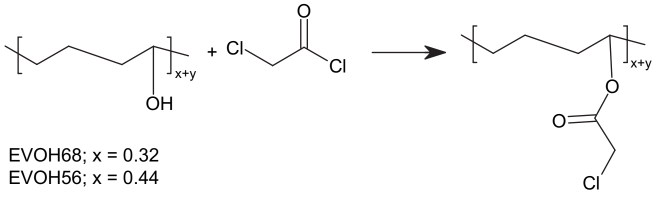
Fig. 3. ^{13}C NMR spectra of activated EVOH56 copolymers with (a) phthalate, (b) chloroacetate and (c) *p*-nitrophenyl carbonate groups.

2.4. Reaction of EVOH copolymers with 4-nitrophenyl chloroformate

EVOH copolymers were dissolved in NM2P at 80 °C, using a Pyrex double-walled reactor, which was entirely isolated from the outside to avoid any contact with humidity. Once the polymer is solved the temperature is equilibrated at 0 °C. Pyridine and *p*-nitrophenyl chloroformate in equimolecular ratio were successively added while stirring. The reaction was performed at 0 °C for 24 h. The modified copolymers were isolated by precipitation in ethanol. The samples were purified by reprecipitation from tetrahydrofurane in ethanol. Then, the polymer was dried in vacuum at room temperature in the presence of phosphorus pentoxide until constant weight was reached.

2.5. Reaction of aminosaccharides with carbonate activated EVOH copolymers

The modified EVOH copolymers with *p*-nitrophenyl carbonate groups were dissolved in DMSO at 70 °C using a Pyrex double-walled reactor through which thermostated water at the reaction temperature was circulated. Equimolar concentrations of triethylamine and aminosaccharide were added while stirring. The polymer remained soluble throughout the process. After 24 h, the glycopolymers were isolated by precipitation using isopropanol. All samples were purified by reprecipitation from DMSO in water. The resulting glycopolymers were dried in vacuum at room temperature in the presence of phosphorus pentoxide until constant weight was reached.



Scheme 2. Reaction of EVOH copolymers with chloroacetyl chloride.

2.6. Polymer characterization

The ^{1}H and ^{13}C NMR spectra were recorded at 70 °C in DMSO-d_6 with a Bruker Advance spectrometer operating at 300 MHz. The proton spectra were used to determine the modification extent of EVOH copolymers. The relative signal intensities of the spectra were measured from the integrated peak area, which was calculated with an electronic integrator. Fourier transform infrared spectroscopy (FTIR) measurements were performed on a FT-IR 1720X from Perkin–Elmer using KBr pellets.

Differential scanning calorimetry measurements were performed in a Perkin Elmer DSC/TA7DX, PC series with an Intra-cooler for low temperatures. The temperature scale was calibrated from the melting point of high purity chemicals (lauric and stearic acids and indium). Samples ($\sim$20 mg) weighed to $\pm$0.002 mg with an electronic autobalance (Perkin–Elmer AD4) were scanned at 10 °C/min under dry nitrogen (20 cm^3/min). The first heating scan was performed after decreasing the temperature from room temperature to -45 °C, then the sample was heated up to 110 °C. Consecutively to this heating process, the sample was cooled down at the same rate and after that a new successive heating run was performed.

The actual value for the glass transition temperature, T_g, was estimated as the temperature at the midpoint of the line drawn between the temperature of intersection of the initial tangent with the tangent drawn through the point of inflection of the trace and the temperature of intersection of the tangent drawn through the point of inflection with the final tangent. The quoted value is the average of several measurements on each sample.

3. Results and discussion

3.1. Reactions of EVOH copolymers with phthalic anhydride

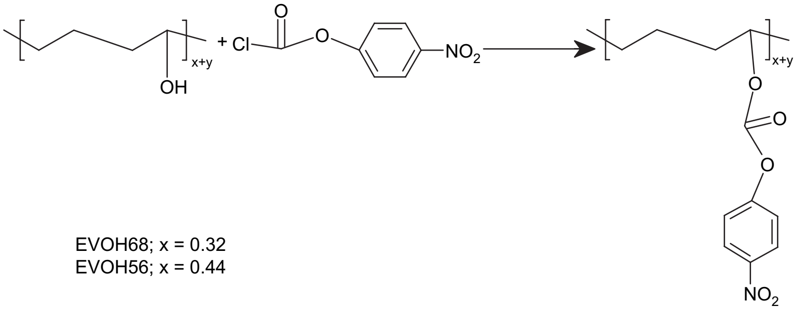
EVOH copolymers modified with carboxylic acid groups are synthesized in a homogeneous medium by using DMSO as solvent according to Scheme 1.

The resulting copolymers are characterized by FTIR, ^{1}H and ^{13}C NMR. Fig. 1 shows the FTIR spectrum of activated EVOH68 and the characteristic band at 1722 cm^{-1} of C=O groups corresponding to the carboxylic acid and ester groups can be observed. The specific absorptions of aromatic ring appear at 1600 and 1580 cm^{-1}. The

Table 1
Experimental conditions used in the modification reactions in homogeneous medium phase of EVOH copolymers

Copolymer	[EVOH] g/100 ml	[OH] mol/L	Solvent	Reactive compound	[Reactive compound] mol/L	Catalyst	[Catalyst] mol/L	Modification extent mol%[a]
EVOH68	6.00	1.05	DMSO	Phthalic anhydride	1.37	TEA-4DAP	0.93–0.026	92
EVOH68	2.60	0.45	NM2P	Chloroacetyl chloride	0.45	Pyridine	0.45	90
EVOH68	2.60	0.45	NM2P	*p*-Nitrophenyl chloroformate	0.45	Pyridine	0.45	78
EVOH68	2.60	0.45	NM2P	*p*-Nitrophenyl chloroformate	0.68	Pyridine	0.68	95
EVOH56	6.00	0.89	DMSO	Phthalic anhydride	1.37	TEA-4DAP	0.80–0.022	99
EVOH56	3.00	0.45	NM2P	Chloroacetyl chloride	0.45	Pyridine	0.45	89
EVOH56	3.00	0.45	NM2P	*p*-Nitrophenyl chloroformate	0.45	Pyridine	0.45	71
EVOH56	3.00	0.45	NM2P	*p*-Nitrophenyl chloroformate	0.68	Pyridine	0.68	99

[a] Modification extent related to the initial hydroxyl groups in the copolymer.



Scheme 3. Reaction of EVOH copolymers with 4-nitrophenyl chloroformate.

former EVOH68 copolymer is also presented for comparative purposes. Fig. 2 depicts the ^{1}H NMR spectrum of the activated EVOH68. The peaks between 7.0 and 8.0 ppm correspond to protons of the phthalic ring, those between 1.0 and 2.4 ppm allow identifying the presence of methylene protons in the main chain. In addition, it can be observed that the protons of OH groups are shifted to lower field [25]. In Fig. 3, the ^{13}C NMR spectrum of EVOH56 modified with carboxylic acid groups is depicted. Several peaks appear in the region of 38.2–20.9 ppm that correspond to the methylene carbons of the main chain. The peaks between 65.0 and 76.0 ppm are ascribed to the methynic carbons. The carbons associated with the aromatic ring are shown in the interval of 133.0–128.0 ppm; the peak at 167.0 ppm corresponds to the carboxylic group of the acid group, while the peak at 169.0 ppm is related to the C═O of the ester group.

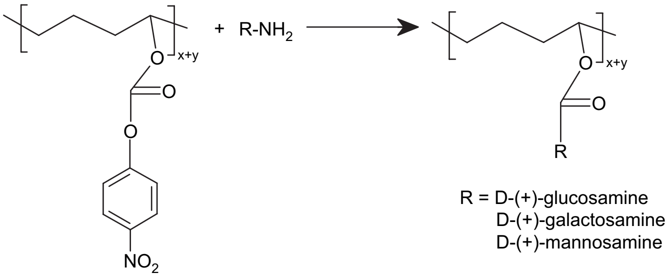
The quantitative determination of the content in carboxylic acid groups is obtained for the different modified EVOH by comparison of the peaks in the interval 8.0–7.0 ppm, ascribed to the aromatic protons, and the peaks in the region of 2.4–1.0 ppm, corresponding to the methylene protons of the main chain. The yielding is almost quantitative for both the EVOH copolymers (see Table 1).

3.2. Reactions of EVOH copolymers with chloroacetyl chloride

EVOH copolymers functionalized with chloroacetate groups are synthesized in a homogeneous medium by using the method followed in the bromoacetylation of poly(vinyl alcohol) [36] according to Scheme 2.

The FTIR spectrum of a modified EVOH copolymer with chloroacetate groups, depicted in Fig. 1, shows the characteristic bands of the pendant groups at 1740 cm^{-1} corresponding to the carbonyl group and at 690 cm^{-1} associated with the C–Cl bond [37].

On the other hand, ^{1}H–NMR of the same copolymer (Fig. 2) presents a peak at 4.2 ppm characteristic of methylene protons of chloroacetate groups [38]. In the range between 1.9 and 1.2 ppm, the peaks of methylene protons of main chain appear and the peak at 4.9 ppm is attributed to the methyne protons of modified units. In the ^{13}C NMR spectrum represented in Fig. 3, the methylene carbons of the main chain appear in the region of 38.2–20.0 ppm. Likewise to the previous activated copolymers, the peaks between 60.0 and 76.0 ppm are ascribed to the methynic carbons. In this case, the peak at 167.0 ppm corresponds to C═O of the chloroacetate group.



Scheme 4. Chemical incorporation of different aminosaccharides to activated EVOH derivatives with *p*-nitrophenyl carbonate groups.

Similar to the aforementioned modified copolymers, the quantitative determination of the content in chloroacetate groups of the different modified EVOH is estimated by comparison of methylene protons peaks, with those corresponding to the chloroacetate pendant groups with respect to those of the main chain. The yield reached in this functionalization is also very high for both copolymers, as listed in Table 1.

3.3. Reactions of EVOH copolymers with 4-nitrophenyl chloroformate

The reaction of EVOH copolymers with *p*-nitrophenyl chloroformate, using NM2P as solvent and pyridine as catalyst, leads to derivatives containing *p*-nitrophenyl carbonate groups according to Scheme 3. The use of an equimolecular ratio makes affordable a high reaction yield that can be further increased up to almost a quantitative yield if the amount of *p*-nitrophenyl chloroformate is raised in the reaction medium.

Fig. 1 also shows the FTIR spectrum of EVOH68 modified with *p*-nitrophenyl carbonate groups. The characteristic band of acyclic carbonate groups at 1765 cm^{-1} becomes now visible. Confirming the structure, two peaks at 7.3 and 8.1 ppm appear in the ^{1}H NMR spectrum of modified copolymer also represented in Fig. 2, attributed to aromatic protons of *p*-nitrophenyl carbonate groups. The peak at 5.2 ppm is assigned to the methyne of modified vinyl alcohol units and the corresponding one at 2.2 ppm is ascribed to the methylene protons of these units. As well, several peaks at 155.7, 145.7, 125.8 and 122.7 ppm are observed in the ^{13}C NMR spectrum (Fig. 3) corresponding to the aromatic carbons within side group. The peak at 152.6 ppm is associated with the carboxylic carbon of the incorporated group. The peaks observed in the range of 82.3–72.3 ppm and 39.6–20.9 ppm are attributed to the methyne and methylene carbons of main chain, respectively.

At this point, it is important to mention that the three approaches here proposed are effective for modification of EVOH copolymers, opening up new possibilities to change their functionality. The challenge for glycopolymer preparation deals with the EVOH activation with *p*-nitrophenyl carbonate in this present investigation. Nevertheless, glycosylation will also be tested in the near future using the other successful approaches of EVOH functionalization.

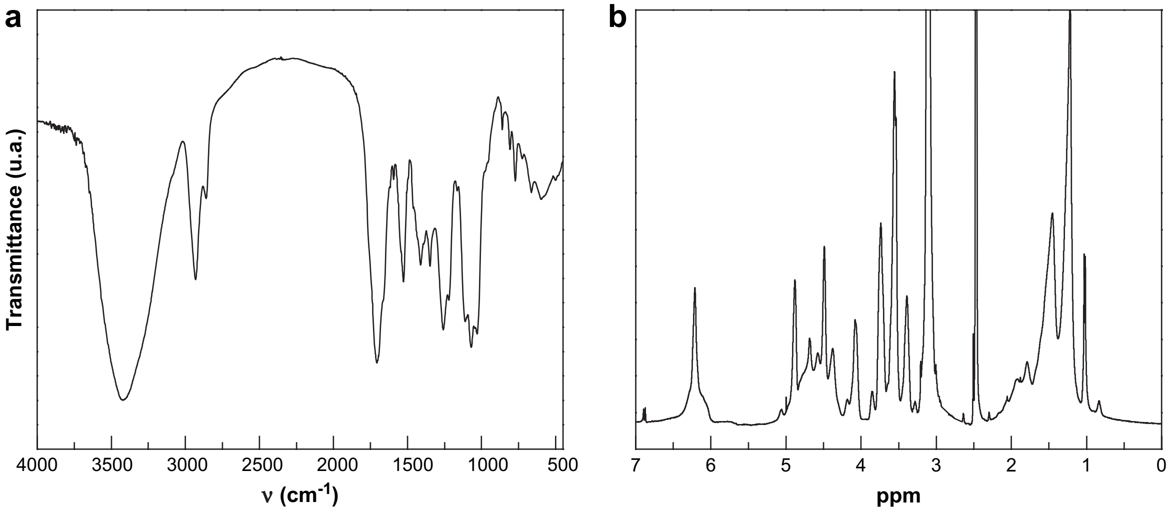


Fig. 4. (a) FTIR and (b) ^{1}H NMR spectra of EVOH56-Ma.

3.4. Reaction of aminosaccharides with carbonate activated EVOH copolymers: glycopolymer preparation

New glycopolymers are obtained by the chemical incorporation of different aminosaccharides (D-(+)-glucosamine, D-(+)-galactosamine and D-(+)-mannosamine) to activated EVOH derivatives with *p*-nitrophenyl carbonate groups. This incorporation was carried out in a homogeneous phase at 70 °C using DMSO as solvent and TEA as catalyst according to Scheme 4.

The structure of these new glycopolymers is determined and confirmed by FTIR and ^{1}H and ^{13}C NMR. In the FTIR spectra, the disappearance of the band at 1765 cm^{-1} attributed to the *p*-nitrophenyl carbonate groups is observed as well as the presence of new bands at 1690 cm^{-1} (C═O carbamate groups) and 1530 cm^{-1} (–NH– carbamate groups) [39,40]. The corresponding FTIR and ^{1}H NMR spectra of EVOH56-Ma, taken as representative example of glycopolymers, are illustrated in Fig. 4. The ^{1}H NMR spectra of the ensuing glycopolymers show peaks between 2.0 and 0.9 ppm, assigned to methylene protons of main chain, and those located in the range of 5.3–3.0 ppm corresponding to protons of the incorporated carbohydrate and also to the methyne ones of the main chain. The modification extent is calculated by the ratio between the methylene protons and those appearing within the range of 5.3–4, being assigned to the methyne protons of the main chain and C1 and C5 of carbohydrate and the carbohydrate methylene of C6. The choice of this assignment allows avoiding in the final composition a possible contribution of water absorption by the glycopolymer. The values obtained are collected in Table 2, being noticeable that the modification extent is rather analogous independently of the monosaccharide incorporated.

Fig. 5 shows ^{13}C NMR spectra of the three glycopolymers obtained from EVOH68. The peaks in the region between 37.0 and 21.0 ppm are assigned to the methylene carbon of the main chain. The peaks located between 95.0 and 55.0 ppm are attributed to the saccharide carbons, while the peak at 156.5 ppm is ascribed to the carbonyl carbon. Table 3 collects the assignation of carbons for the different aminosaccharides that has been made on the basis of the data reported by Houdier and Vottero [41] and Grothus et al. [42].

These glycopolymers are soluble in DMSO, DMF and 2NMP but insoluble in water at room temperature probably due to their intermediate modification extent. Water-soluble glycopolymers could be synthesized either by the incorporation of di or trisaccharides, leading to a higher overall hydrophilicity within the macromolecular chain, or by the use of another of the synthetic routes commented for changing functionality within the EVOH copolymers. These approaches are being currently explored.

3.5. Thermal characterization of the glycopolymers

Fig. 6a exhibits the DSC curves for the initial EVOH68 copolymer as well as for the activated EVOH68 with *p*-nitrophenyl carbonate groups (EVOH68-N) and the D-(+)-glucosamine glycopolymer derivative EVOH68-Gl obtained from the activated copolymer. Both EVOH68 and EVOH56 copolymers are semicrystalline, exhibiting, therefore, on heating two thermal transitions: one related to the amorphous regions, i.e., the glass transition, and another associated with the melting of crystalline entities, T_m. However, either the different activated EVOH derivatives or the subsequent glycopolymers present a unique thermal transition, the one ascribed to the

Table 2
Experimental conditions used in the incorporation reactions of aminosaccharides (0.12 mol/L) into activated EVOH with *p*-nitrophenyl carbonate groups (EVOH-N) in DMSO at 70 °C using triethylamine (TEA) as catalyst (0.18 mol/L)

Activated EVOH	[Activated EVOH] g/100 ml	[*p*-Nitrophenyl carbonate] mol/L	Aminosaccharide	Modification extent mol%[a]
EVOH68-N	2.59	0.12	D-(+)-Glucosamine, Gl	56
EVOH68-N	2.21	0.10	D-(+)-Galactosamine, Ga	54
EVOH68-N	2.21	0.10	D-(+)-Mannosamine, Ma	53
EVOH56-N	2.88	0.12	D-(+)-Glucosamine, Gl	56
EVOH56-N	2.32	0.10	D-(+)-Galactosamine, Ga	57
EVOH56-N	2.32	0.10	D-(+)-Mannosamine, Ma	50

[a] Modification extent related to the initial hydroxyl groups in the copolymer.

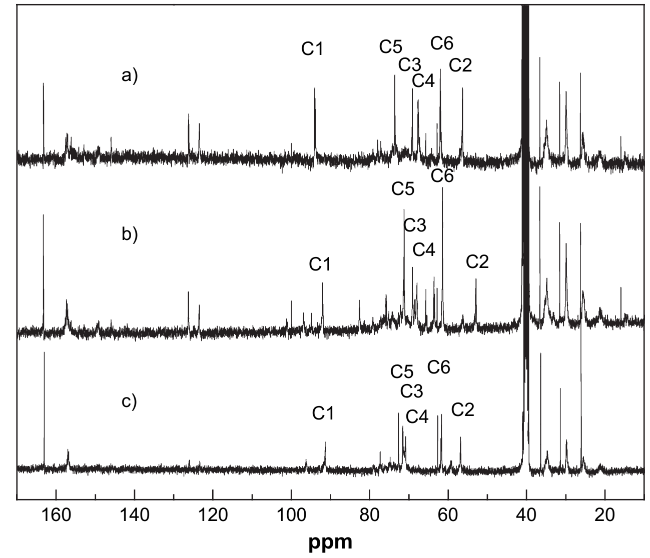


Fig. 5. ^{13}C NMR spectra of EVOH68 derivatives glycopolymers in DMSO-d_6: (a) D-(+)-mannosamine, (b) D-(+)-galactosamine and (c) D-(+)-glucosamine.

Table 3
Assignation of ^{13}C NMR (ppm) signals corresponding to the carbon atoms of monosaccharides incorporated to the carbonate activated EVOH68 and EVOH56

	EVOH68-Gl	EVOH68-Ga	EVOH68-Ma	EVOH56-Gl	EVOH56-Ga	EVOH56-Ma
C1	91.3	91.3	93.2	91.6	91.6	94.0
C2	56.7	52.2	55.6	56.9	53.0	56.4
C3	71.5	68.4	68.3	71.5	68.7	69.1
C4	70.9	67.2	66.9	70.6	67.8	67.3
C5	72.9	70.6	72.8	72.0	71.1	73.0
C6	61.5	60.8	61.2	61.3	60.8	61.8

glass transition. In the EVOH68 and EVOH56 copolymers, the ethylene units can be incorporated as defects into the poly(vinyl alcohol) crystal lattice developed whereas the exchange of functionality from the former hydroxyl groups to the different activated derivatives and subsequent glycopolymers leads to the complete damage of crystalline ordering and, therefore, the disappearance of the melting process. The glass transition temperatures, T_g, for the different compounds are reported in Table 4. The comparison between the two initial EVOH copolymers shows that EVOH68 presents temperature values for both thermal transitions higher than those found in EVOH56. These facts are associated with the lower distortion of crystalline structure and, consequently, higher crystallinity values and larger crystallites in EVOH68 [43] because of its higher vinyl alcohol content. The obtained data are similar to those found in the literature [44–46].

This figure also points out that the T_g in the activated copolymer with *p*-nitrophenyl groups, EVOH68-N, is moved toward superior temperatures and that no melting endothermic peak is observed. The capability of tridimensional order and, accordingly, crystallite development is completely vanished in the activated copolymers because of incorporation of these bulky functional groups. The increment of the T_g with regard to the former EVOH68 copolymer is also ascribed to the inclusion of these rigid and voluminous groups that considerably reduce the overall mobility. These results are concordant with others described [25,27,30].

On the other hand, the incorporation of D-(+)-glucosamine in the polymeric chain leads to a decrease of the T_g compared with the value exhibited by the activated copolymer, as observed in the Fig. 6a. However, the comparison between the glycopolymer T_gs and that found in the initial copolymer shows a shift to higher temperature when monosaccharide moieties are incorporated. This feature seems to be related to the large amount of inter and intramolecular interactions through hydrogen bonds between the carbohydrate hydroxyl groups within themselves or with the unreacted hydroxyl groups. These physical interactions seem to impose similar mobility restrictions than those derived from the existence of crystallites in EVOH68. An analogous behavior is observed in the different derivatives from the EVOH56 copolymer. In the case of the activated copolymer, EVOH56-N, it has to be said that it presents a T_g lower than that found by EVOH68-N because of its higher ethylene content and, accordingly, higher mobility.

Fig. 6b shows the DSC curves of the three different glycopolymers obtained from EVOH68. The T_g does not differ significantly from each other, i.e., its value is rather independent of the saccharide used since the modification extent is comparable. Moreover, similar T_g values are also found in the distinct EVOH56 glycopolymer derivatives. Accordingly, the T_g in both glycopolymer sets, those derived from EVOH68 and from EVOH56, is essentially analogous. As aforementioned, the balance between the loss of crystallization capability and the establishment of hydrogen inter/intramolecular interactions seems to compensate the mobility hindrance and, consequently, be responsible for reaching those similar T_g values.

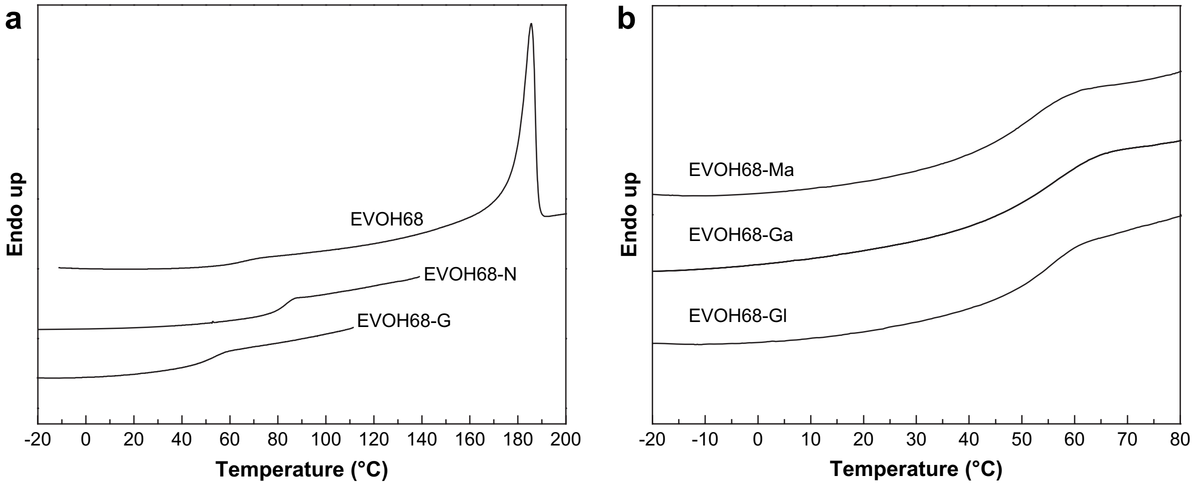


Fig. 6. (a) DSC curves of EVOH68 copolymer, activated copolymer with *p*-nitrophenyl carbonate groups EVOH68-N and the D-(+)-glucosamine derivative of copolymer, EVOH68-Gl; (b) DSC curves of the different glycopolymers.

Table 4
Glass transition temperature, T_g, melting temperature, T_m, and modification degree of former EVOH68 and EVOH56 copolymers, as well as the corresponding activated EVOH with *p*-nitrophenyl carbonate groups and glycopolymers

Copolymer	Modification extent mol%[a]	T_g (°C)	T_m (°C)
EVOH68	–	50.0	185.5
EVOH68-N	95	83.0	–
EVOH68-Gl	56	53.5	–
EVOH68-Ga	54	55.5	–
EVOH68-Ma	53	51.0	–
EVOH56	–	42.0	167.0
EVOH56-N	99–100	61.0	–
EVOH56-Gl	56	55.0	–
EVOH56-Ga	57	57.5	–
EVOH56-Ma	50	54.5	–

[a] Modification extent related to the initial hydroxyl groups in the copolymer.

4. Conclusions

Several methods have been explored and described for changing functionality in ethylene–vinyl alcohol copolymers, transforming hydroxyl groups in other ones considerably more active. The high yielding obtained in all of the different routes proposed makes them successful approaches for activation of EVOH copolymers, the possibility of tailoring different properties being opened. Moreover, the preparation of different glycopolymers with distinct saccharides from carbonate activated EVOH derivatives has also been checked. Differences in their thermal response have been described by comparison with the characteristics found in the neat EVOH copolymers. The main features are related to the loss of the initial semicrystalline character and the similar T_g values shown by the different glycopolymers.

Acknowledgment

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