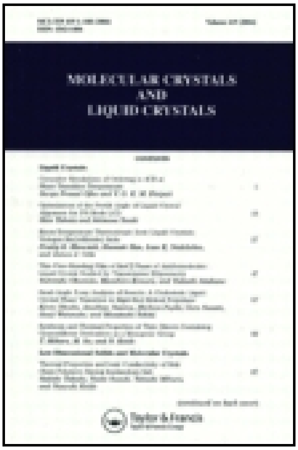

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Polymer Electrolytes Derived from Hydroxiethylcellulose/Polyether Films

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Polymer Electrolytes Derived from Hydroxiethylcellulose/Polyether Films

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Polysaccharides, like cellulose and its derivatives, can be used in polymer electrolytes because of their aptitude to generate thin films. This paper reports the reaction of hydroxyethylcellulose with oligoether-based diisocyanates. The resulting networks were investigated by differential scanning calorimetry and infrared spectroscopy.

Keywords: hydroxyethylcellulose; solid polymer electrolytes; oligoether isocyanates; polyether networks

INTRODUCTION

The development of new materials that can be applied as solid electrolytes led to the creation of modern systems of energy generation and storage [1]. Among these materials, solid polymer electrolytes, generally elastomeric materials containing ions, represent a promising alternative for the substitution of liquid electrolytes and inorganic crystals used in batteries, sensors and eletrochromic devices [2].

Materials based on poly (ethylene oxide) structures are being extensively studied [3,4], however these materials have some characteristics that limit their performance. One of these problems is the tendency to crystallization. It is known that the crystallinity of a polymeric matrix is a huge barrier to the ionic conduction phenomenon. To overcome this limitation it is possibleto prepare a modified polymer matrix through its reaction with short molecules or oligomers, in such a way that the local order is diminished and the tendency to crystallization eliminated [4]. An example of this reaction is the condensation of polymers containing OH groups with polyfunctional isocyanates making possible the generation of a great variety of networks depending on the polymer matrix structure, its molecular weight and the type of isocyanate used. After reaching a good achievement in terms of stability and conductive properties, the possibility of improving film-forming properties (in order to optimize the elaboration of thin devices) is an interesting problem to be studied. In this field, cellulose and its derivatives are very attractive because of their film-forming and mechanical properties and also because of their rich variety in nature [5]. In this context, better conduction results can be obtained with the structural modification of cellulose derivatives through graft reactions [6]. Some preliminary tests were published [3,5] reporting the good mechanical and electrical properties while improving the possibility of casting films. The systematic study of the properties of the hydroxyethylcellulose (HEC) based networks will help the optimization and understanding of the conductivity of polysaccharide networks. This work describes the procedure to obtain films of hydroxyethylcellulose cross-linked with oligoether diisocyanates in order to obtain thin films that can be used as matrix for solid polymer electrolytes.

EXPERIMENTAL

Five samples of commercial hydroxyethylcellulose (HEC) (kindly provided by UNION CARBIDE DO BRASIL), under the names QP09H, QP300H, QP4400, QP15MH and QP30MH, were used. These samples were characterized in order to determine the degree of polymerization (DP), degree of substitution (DS) and molar substitution (MS) using various techniques already reported in the literature [7-9].

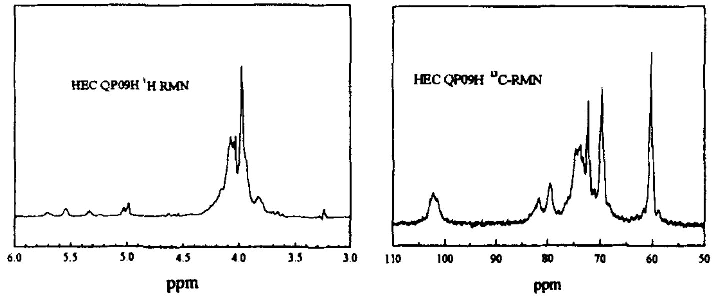
Poly (ethylene oxide) (PEO)-based and poly (propylene oxide) (PPO)-based di-isocyanates were synthesized from commercial Jeffamines ED600 and ED400 (FLUKA) following a previously developed procedure and were stored in the absence of moisture [10]. The amines and isocyanates were characterized using the spectroscopic techniques [10].

The condensation reactions were performed inside a glove box under nitrogen atmosphere from dimethylacetamide (DMAc) solutions at room temperature using traces of dibutyltin dilaurate as catalyst (Aldrich). DMAc was previously distilled and stored over molecular sieves. The transparent films were obtained by pouring the viscous solutions in a mould, immediately after mixing the reagents. After 48h the films were dried at 40°C for 24h. The obtained materials were characterized by differential scanning calorimetry (DSC) with SHIMADZU DSC-50 equipment, to determine their Tg. These analyses were performed in duplicate on the temperature range from −100 to 200°C in a nitrogen atmosphere (20 ml/min). The first run was recorded at a heating rate of 20°C/min and the second, used for the Tg determination, at a heating rate of 10°C/min. The films were also characterized by FTIR with Perkin-Elmer PARAGON 1000 equipment. To determine the amount of soluble materials, the films were extracted with carbon tetrachloride in soxhlet apparatus for 24 hours.

RESULTS AND DISCUSSION

HEC characterization

The molar substitution (MS) of the HEC samples were determined from the ^{1}H-NMR spectra quantifying the peak areas from 3.5 to 4.4 ppm and from 4.3 to 5.8 ppm (figure 1a) [8]. The degrees of substitution (DS) were obtained from MS results and the peak areas at 69.7 and 60.0 ppm in the correspondent ^{13}C-NMR spectra (figure 1b) [9]. The degrees of polymerization (DP) were determined through the Mark-Houwick-Sakurada equation ($K=1.1 \cdot 10^{-2}$ and $\alpha=0.87$[11]) using intrinsic viscosity values determined with a capillary viscometer. The values of DS, MS and DP are shown in table I. All the samples have DS values equal or lower than 1 and are linearly related with the corresponding values of MS (figure 2). The linearity observed in this plot is that expected, taking into account the industrial procedure employed in HEC production. This procedure involves, in a first step, the activation of cellulose hydroxyl groups with sodium hydroxide followed by the reaction with ethylene oxide [12]. The linearity is limited to lower MS and DS values once DS grows asymptotically until 3 and MS values reach higher values. The values of DP, although somewhat high for some samples, are in accordance with the literature [9] and, as expected, do not show any relation with MS or DS. This indicates that the cellulosic chain lengths are not affected by the oxylation reaction or by substituent distribution.



(a) (b)

FIGURE 1 NMR spectra of hydroxyethylcellulose QP09H. (a) ^{1}H-NMR, (b) ^{13}C-NMR

TABLE I Characteristics of hydroxyethylcellulose samples

HEC	MS	DS	DP
QP09H	1.22	0.75	260
QP300H	0.58	0.34	850
QP4400	1.35	0.88	1840
QP15MH	1.72	1.01	2450
QP30MH	0.91	0.54	2480

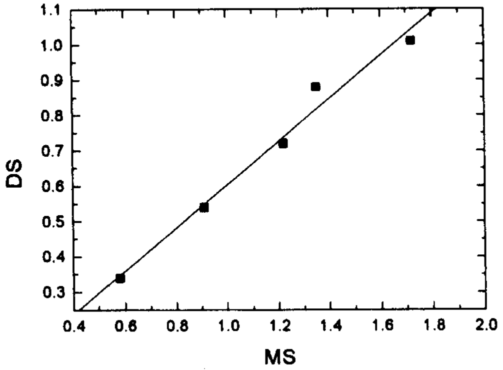


FIGURE 2 Molar substitution (MS) versus degree of substitution (DS) for the hydroxyethylcellulose samples

Jeffamine and isocyanate characterization

The isocyanates prepared from Jeffamines showed the typical signal at 125 ppm on the ^{13}C-NMR spectra and the characteristic absorption of NCO groups at 2250 cm^{-1} on FTIR spectra. The molar masses of the Jeffamines and the percentage of NCO functions present in the correspondent isocyanates are shown in table II. The obtained dosages of 8.4% and 11.6% NCO groups correspond to a conversion of NH_2 to NCO groups, of 61.3% and 66.7%, respectively.

Properties of the networks

The influence of the HEC parameters (DS, MS and DP) on the network properties the grafted derivatives were studied using the same NCO/OH ratio of 0.6 NCO, to produce tridimensional structures, as illustrated in figure 3.

TABLE II Molar masses of Jeffamines and percentage of NCO groups in the corresponding isocyanates

Jeffamine	MM (g/mol)
O,O'-bis(2-aminopropyl) polyethylene glycol 500 (JEFFAMINE ED 600)	660
O,O'-bis(2-aminopropyl) polypropylene glycol 300 (JEFFAMINE D400)	450
Isocyanate	% NCO
O,O'-bis(2-isocyanopropyl) polyethylene glycol 500 (DPEO)	8.4
O,O'-bis(2-isocyanopropyl) polypropylene glycol 300 (DPPO)	11.6

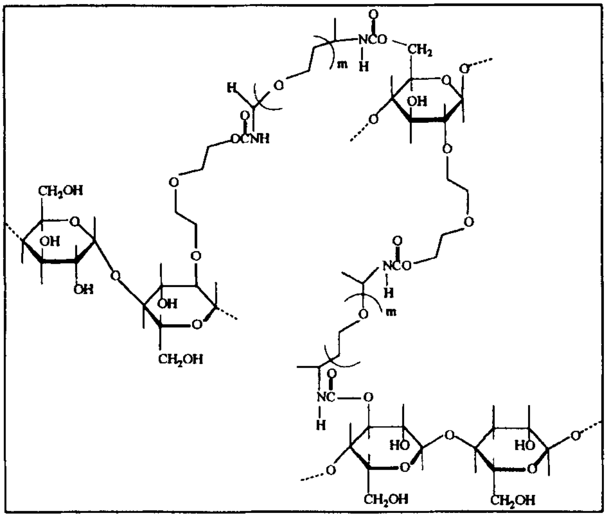


FIGURE 3 Schematic representation of a network based on hydroxyethylcellulose cross-linked with poly (ethylene oxide) diisocyanate (DPEO).

The FTIR analysis of the films obtained in the reaction of HEC with DPEO (figure 4) allows the identification of some characteristic bands (table III). The absorption corresponding to the urethane carbonyl can be observed at 1720 cm^{-1} and the small shoulder observed at 1650 cm^{-1} is due to the urea carbonyl. The presence of this group indicates that some amine groups (from Jeffamine) have reacted with the synthesized isocyanate.

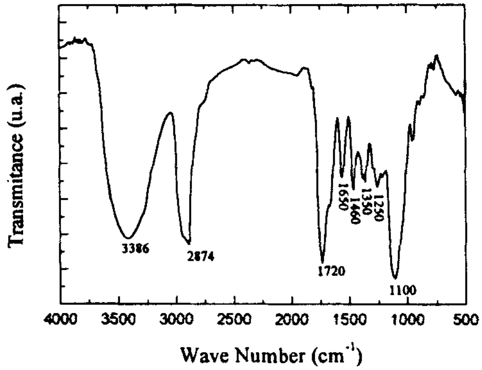


FIGURE 4 FT-IR spectra of hydroxyethylcellulose (QP09H) crosslinked with diisocyanate (DPEO).

TABLE III Assignments of the main bands observed on the FTIR spectra of hydroxyethylcellulose cross-linked with isocyanates

Assignment	Wave Number (cm^{-1})
Axial deformation NH + OH	3350
Axial deformation CH_2	2860, 2920
Axial deformation C=O urethane	1720
Axial deformation C=O urea	1650
Angular deformation de CH_2	1460
Axial deformation CN	1250
Axial deformation C-O-C	1100

The glass transition temperature (Tg) was determined from the DSC curves as showed in figure 5 for the sample of HEC grafted with DPEO. No other transitions, such as melting or crystallization, were observed in these thermograms. The comparison of Tg values for the two series of HEC grafted with different types of isocyanate (table IV) indicates lower temperatures for the films obtained from the grafting and cross-linking with DPEO. The DPEO derivatives had Tg around –50° C, while the DPPO-grafted series had values close to –35° C. The glass transition temperatures represent an important property in the context of ionic conduction of polymer electrolytes. It can be concluded that the Tg values are affected by the type of oligomeric isocyanate used to for the reaction with the polysaccharide chains. The poly (propylene oxide) containing the methyl side group, leads to an increase of 15 degrees in the glass transition temperature. This tendency was already observed with networks prepared from polyisocyanate oligoethers[2].

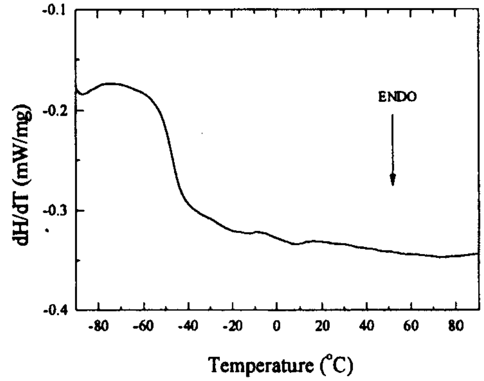


FIGURE 5 DSC curve for hydroxyethylcellulose QP4400 cropss-linked with poly (ethylene oxide) diisocyanate (DPEO).

TABLE IV Glass transition temperatures (Tg) for the films of hydroxyethylcellulose cross-linked with diisocyanates

Sample	Tg (°C)	
	DPEO	DPPO
QP09H	-54	-36
QP300H	-47	-35
QP4400	-48	-35
QP15MH	-52	-33
QP30MH	-52	-34

The degree of crosslinking in the networks was verified by submitting the films to an extraction procedure with CCl_4. The amounts of extractives were of the order of 60% (table V). This high percentage of soluble materials leads to the hypothesis of soluble products formed from the self condensation of isocyanate molecules. The films change their physical properties after the extractions losing its transparency and becoming less flexible. The glass transitions of the extracted films were spread over a wider temperature range (figure 6) which included higher values than those recorded for the unextracted samples. The extracted molecules acted therefore as plasticizers.

TABLE V Percentage of soluble materials in the films of hydroxyethylcellulose crosslinked with isocyanates

Network	% Soluble Material in CCl_4
QP09H/DPEO	71
QP300H/DPEO	67
QP4400/DPEO	61
QP15MH/DPEO	64
QP30MH/DPEO	78
QP09H/DPPO	65
QP300H/DPPO	77
QP4400/DPPO	60
QP15MH/DPPO	56
QP30MH/DPPO	59

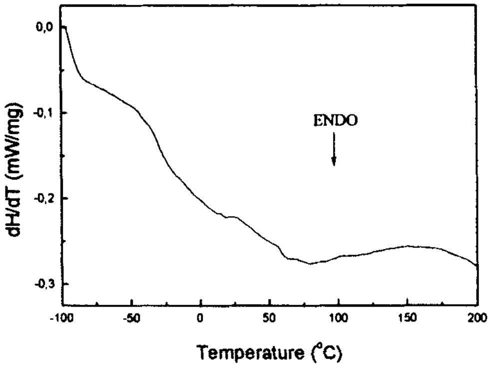


FIGURE 6 DSC curve an extracted film of hydroxyethylcellulose QP4400 crosslinked with poly (ethylene oxide) diisocyanate (DPEO).

CONCLUSION

The systematic study of the properties of the films synthesized with hydroxyethylcellulose cross-linked with diisocyanates of poly (ethylene oxide) and poly (propylene oxide) contributes to the search of new solid polymer electrolyte. These materials combine the good mechanical and film-forming properties of the polysaccharide with the solvation and ionic conduction properties of the oligoether, making possible their use in electochromic devices.

It was demonstrated that the transition temperatures of the synthesized materials were lower than room temperature. This characteristic is important in terms of ionic transport, which is insured by the segmental motions of the network polyether chains. The Tg values depend on the type of isocyanate used to cross-link HEC. This value is about -50°C for poly (ethylene oxide) and about -35°C for poly (propylene oxide) networks. Removal of the soluble products, probably made up of branched structures and self-condensation polymers of the diisocyanates, produced a increase in the Tg of the residual insoluble films.

Acknowledgements

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