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Carbohydrate Polymers 42 (2000) 13–17

Carbohydrate Polymers

www.elsevier.com/locate/carbpol

Oxypropylation of sugar beet pulp. 2. Separation of the grafted pulp from the propylene oxide homopolymer

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Accepted 6 August 1999

Abstract

It is well known that the oxypropylation of polymeric substrates always gives two products, namely the expected branched macromolecules and some propylene oxide homopolymer, resulting mostly from transfer reactions. The separation of these two products was attempted using potentially selective solvents such as diethyl ether, tetrachloromethane and hexane. FTIR, ^{1}H NMR, DCS and SEC techniques showed that the latter solvent, used under reflux, was the most suitable liquid in terms of selectivity. Both fractions were thoroughly characterised and useful information was thus gathered about the actual composition of the reaction products as well as their structure, molecular weight, T_g and viscosity. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Oxypropylated sugar beet pulp; Poly(propylene oxide); Selective solvent separation; Steric exclusion chromatography

1. Introduction

In the previous study related to this investigation (Pavier & Gandini, 1999), we showed that sugar beet pulp (SBP), an intractable solid residue of the sugar industry made up of different polysaccharides, can be converted almost entirely into a liquid polyol of variable viscosity by a relatively simple oxypropylation process. The optimisation of this system was achieved by a thorough scan of the role of all the major parameters associated with the reaction. Thus, a waste product related to a renewable resource, produced in very large quantities every season, could constitute an interesting source of polyols. One of the obvious utilisations of this type of polymers is of course in the manufacture of polyurethanes and it was therefore decided to pursue this investigation.

It is well known that the oxypropylation reaction of such substrates as sugars, polysaccharides and other OH-containing structures is accompanied by the homopolymerisation of propylene oxide (PO) which arises from both concomitant initiation and chain transfer (St Pierre & Price, 1956; Steiner, Pelletier & Trucks, 1964; Wu & Glasser, 1984). In fact, when OH^- is the initiating species, e.g. from aqueous KOH, PO can be activated directly, whereas when alkoxy anions are formed from the OH moieties on the substrate to be oxypropylated, chain growth starts at those sites, but monomer transfer can provoke the detachment of the anionic active species and give rise to PO homopolymerisation.

Our experience with SBP confirmed that two products are indeed obtained upon its treatment with PO in the presence of a strong basic catalyst, namely: (i) the oxypropylated pulp and (ii) low-DP poly(propylene oxide) (PPO). Owing to the initiation and chain-breaking mechanisms leading to their formation, the latter linear oligomers bear terminal OH functions and are characterised by low viscosities and a very low glass transition temperature ($T_g = -75$°C). The oxypropylated pulp is, in contrast, a branched polymer bearing numerous OH groups per macromolecule (as many as originally contained by the substrate), with a much higher viscosity (which depends however on the extent and average length of the grafted chains) and T_g values as high as 30°C. Before dealing with the application of these mixtures of polyols as possible macromonomers for the synthesis of polyurethanes, it was deemed essential to obtain detailed information on the actual composition with respect to each component and its properties.

The present paper describes the procedures adopted to separate the oxypropylated SBP from the PO oligomers and the characterisation of both materials.

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PII: S0144-8617(99)00124-1

Table 1
Operating conditions for the synthesis of the different oxypropylated sugar beet pulps used in this study

Product	Initial pulp (g)	Initial KOH (g)	Initial propylene oxide (ml)	Reaction temperature (°C)
A	20	2	100	150
B	40	8	100	160
C	178	17.8	500	140
D	178	17.8	500	100

2. Experimental

2.1. Starting materials and reagents

The oxypropylated SBPs used in this work were obtained following the operating procedure described in detail in a previous paper (Pavier & Gandini, 1999), which consisted of mixing ground pulp with propylene oxide and a basic catalyst (here KOH) in a stainless steel reactor and heating the suspension under vigorous stirring. Reactions took place at 120–160°C and were accompanied by a pressure increase, typically to 6–8 bar, and were pursued until the pressure returned to atmospheric value. Four different batches were prepared using the specific conditions given in Table 1. These polyols were isolated after treatment of the viscous reaction product with methylene chloride, neutralisation with tartaric acid dissolved in ethanol, filtration and vacuum evaporation of all volatile materials. The percentage of CH_2Cl_2-insoluble product was very small in all instances, viz. between 0 and 14%. As already pointed out, this fraction was made up of poorly oxypropylated SBP.

The solvents used in this study were high-purity commercial products.

2.2. Operating procedure and characterisation

The difficulty associated with the separation of the two products was related to their great chemical similarity, which made them hard to differentiate. From an analytical standpoint, a separation based on macromolecular size seemed reasonable, but on a preparative scale, the best approach was provided by the use of selective solvent extraction.

The choice of solvents capable of separating the oxypropylated pulp from PPO was dictated by previous work in our laboratory and elsewhere. Indeed, in a similar study on the oxypropylation of chitosan (Velazquez-Morales, 1997), diethyl ether was shown to be a good selective solvent for the separation of the homopolymer of PO from oxypropylated chitosan. In other studies, hexane was used to eliminate PPO from oxypropylated lignosulfonates (Hornof & Hombek, 1990), and from oxypropylated lignins (Glasser, Wu & Selin, 1983; Wu & Glasser, 1984).

In the procedures adopted here, the isolated polyol mixture was either stirred with an excess of diethyl ether (or carbon tetrachloride, see below), or extracted three times with refluxing hexane. In both instances, two fractions were obtained, which were separated by filtration and dried in an oven to constant weight after vacuum-removal of most of the solvent.

The analysis of each fraction involved FTIR (KBr pellets) and ^1H NMR (300 MHz, solvent $CDCl_3$) spectroscopy, DSC (in a helium stream with a heating rate of 10°C min^{-1}) and SEC (THF, three columns in series, calibration with low-dispersity polystyrene standards).

3. Results and discussion

3.1. Separation with diethyl ether or carbon tetrachloride

In the process of finding the best experimental conditions for the correct separation of the two reaction products, we found that carbon tetrachloride, a solvent of modest polarity, gave results entirely comparable to those obtained with diethyl ether, thus providing a possible additional way of dissolving PPO selectively.

The two fractions arising from these separations were analysed by DSC and their glass transition temperatures measured. The soluble fractions showed two glass transitions at −73 (run A) or −69°C (run B) and 23 (run A) or 31°C (run B), respectively, which indicated that they contained both the oxypropylated pulp, with a glass transition around room temperature, and the PO oligomers, with a T_g close to −70°C. The insoluble fractions displayed a single T_g at 27 (run A) or 24°C (run B). The same results were obtained with CCl_4 as a selective solvent. It was concluded that, although the two solvents had removed all the PPO homopolymer, they were too strong in that they also removed a small, but significant amount of the oxypropylated SBP. It was therefore decided to try hexane as an alternative. Its use at room temperature did not achieve total dissolution of the PO oligomers and, as a consequence, we decided to use hot hexane as the selective solvent as described below.

3.2. Extraction with refluxing hexane

When hot hexane was used as separating solvent, the soluble fraction showed a glass transition of −72°C, which corresponds to that of PO oligomers. The very low viscosity of this fraction confirmed that it did indeed consist of a low-DP PPO, in contrast with the insoluble fraction which displayed a glass transition close to −40°C and a very high viscosity. These results suggested that there was practically no PO homopolymer left in the latter fraction. Table 2 summarises the quantitative characterisation of both fractions obtained from runs C and D.

3.3. ^{1}H-NMR and FTIR spectroscopy

The ^{1}H-NMR spectra confirmed the quality of the hot-hexane-based separation of the two products, based on the assessment of the ratio of the integrals between protons from CH_3–C moieties and those from CH_2–O and CH–O groups. Indeed, in the case of the PO homopolymer, this ratio must be equal to unity, whereas for the oxypropylated materials, it becomes lower; in fact the lower it is the smaller the extent of grafting. Fig. 1 shows the spectra corresponding to each fraction of product C. For the soluble fraction, the integration ratio of the signals

Table 2
Characterisation of the fractions obtained using hot hexane as solvent

	C, soluble	C, insoluble	D, soluble	D, insoluble
% extracted	41.6	–	47	–
Viscosity (Pa s)	0.098	40,000	0.073	> 40,000
T_g (°C)	−72	−45	−74	−32

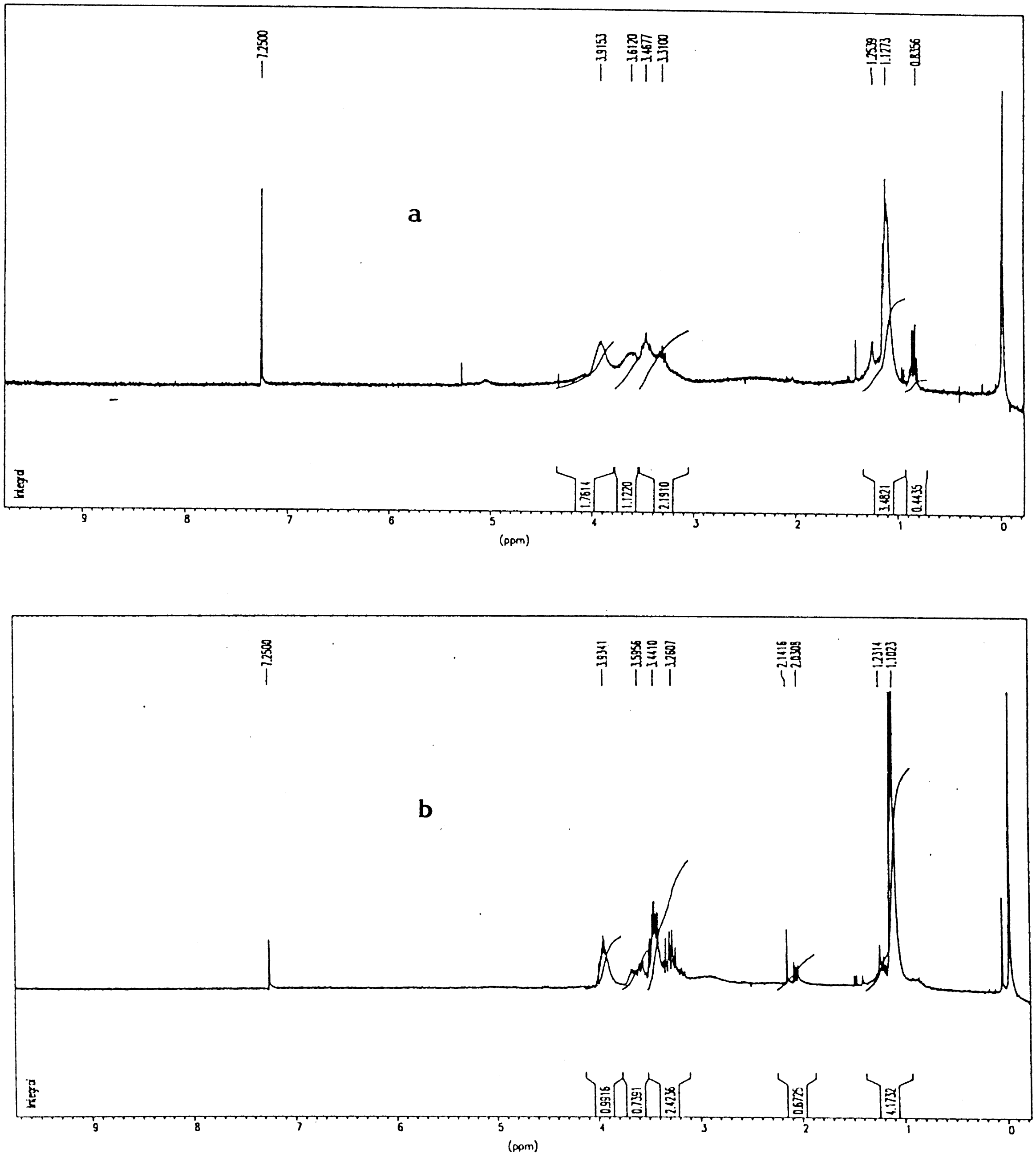

Fig. 1. ^{1}H NMR spectra of the fractions obtained by the extraction of product C with hot hexane: (a) Insoluble fraction; (b) soluble fraction.

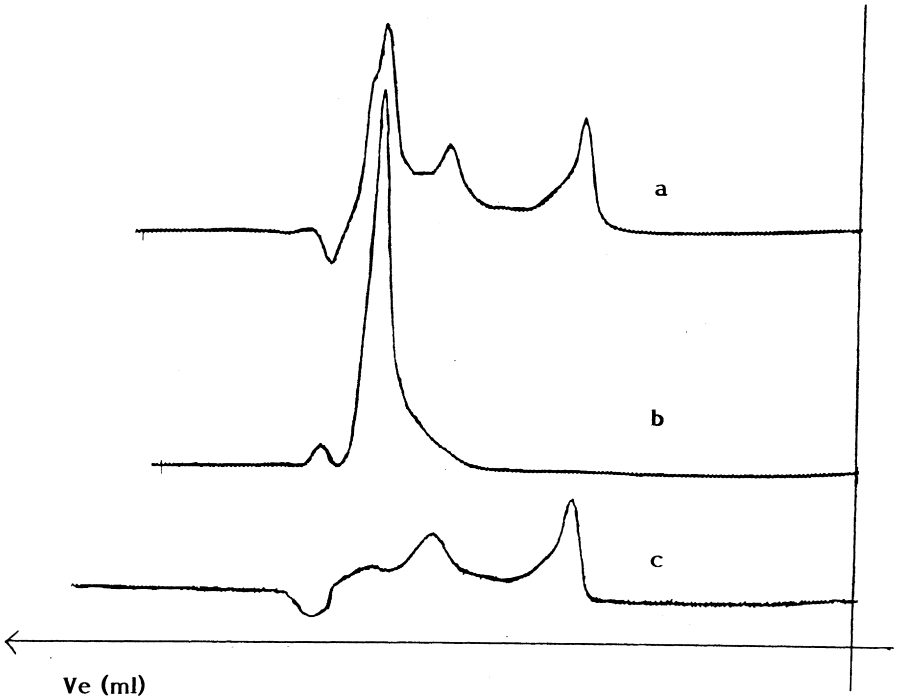

Fig. 2. SEC tracings of the pristine oxypropylated pulp C (a) and of the fractions obtained by extracting it with hot hexane: (b) soluble fraction; (c) insoluble fraction.

$[CH_3]/[CH_2O + CH\text{–}O]$ was unity, whereas for the insoluble fraction it decreased to 0.7. The most relevant feature here is of course the fact that the soluble material only contained PO oligomers, as suggested by the expected integration ratio.

From the spectrum of the hexane-insoluble fraction (Fig. 1(a)) corresponding to the oxypropylated SBP, we calculated a total extent of branching in product C which was close to nine PO units per saccharide unit (considered as a mixture of pentosans and hexoses). This does not mean necessarily that the average graft length amounted to three PO units, based on three OH groups per sugar element, because steric factors and the different reactivities of primary and secondary OH groups would certainly introduce an uneven pattern of branching and branch lengths. Unfortunately, these structural details could not be discerned and the lack of solubility of the starting SBP made it impossible to characterise it quantitatively by NMR.

The FTIR spectra of the soluble and insoluble fractions obtained from each oxypropylated sample differed essentially in the region related to the methyl stretching vibrations. The spectra of the soluble portions were virtually identical to that of a commercial PPO diol sample with $M_n = 425\ \mathrm{g\ mol^{-1}}$. The spectra of the residues had a weaker peak at $2970\ \mathrm{cm^{-1}}$, in tune with a lower proportion of CH_3 groups, because of the presence of the polysaccharide chains which did not bear any methyl group, as verified in the FTIR spectrum of the starting SBP, by the absence of the characteristic peak mentioned above. The other features of all these spectra were very similar, as expected from the close similarity of the structures involved, viz. the presence of CH_2 and CH groups, linkage among themselves and to oxygen atoms, and the presence of OH groups.

3.4. SEC

Fig. 2 shows typical chromatograms related to the hot-hexane-based fractionation. The tracing related to the crude product, shows three peaks corresponding to molecular weights of $220\ \mathrm{g\ mol^{-1}}$, which represents the PO homopolymer, and 725 and $10{,}000\ \mathrm{g\ mol^{-1}}$, both representing the oxypropylated sugar beet pulp. The tracings of the two fractions clearly confirm the quality of the fractionation procedure. The presence of two widely different DPs for the oxypropylated pulp arose from the fact that both high molecular weight and oligomeric polysaccharides are present in this agricultural waste.

4. Conclusion

Despite the close similarity of macromolecular structure, it was possible to separate efficiently the product of the oxypropylation of sugar beet pulp from the concomitant homopolymer by using hot hexane as a selective solvent. This enabled us to determine the proportion of each product as well as its molecular weight. The grafted polysaccharides were also characterised in terms of extent of branching.

Acknowledgements

The authors wish to thank the Eridania Beghin-Say Company for financial support and sugar beet pulp samples.

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