Synthesis and molecular weight determination of urethane-based anionomers

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Summary

Anionomer prepolymers based on poly(propylene oxide) (PPG), 4,4'-dicyclohexylmethane diisocyanate ($H_{12}MDI$) and dimethylol propionic acid (DMPA) were synthesized in bulk. The molecular weight of the prepolymers was determined by vapour pressure osmometry (VPO) and gel permeation chromatography (GPC).

Introduction

The continuous reduction in costs and in the control of volatile organic compound emissions are increasing the use of aqueous-based resins, motivating the development of polyurethanes dispersed in water (1-5).

Aqueous polyurethane dispersions can be tailor-made and present many of the features related to conventional solvent-born coatings. A water-born polyurethane presents chains of high molecular weight and, at the same time, low viscosity values making the coating application easier (3).

There are various ways of combining polyols and diisocyanates to produce a tailor-made polyurethane (6-7). The proper combination of these and other reagents results in very versatile polymers which can be fitted in a wide range of applications as foams, elastomers, coatings, elastomeric fibers and adhesives (8-11). Thus, the development of such polymers is of great technological importance and the production of non-toxic and non-polluting materials is an aim that must be reached.

Conventional polyurethanes are not compatible with water, so special techniques must be used to make the dispersion possible. There are two types of aqueous polyurethane dispersions: non ionic, which incorporate hydrophilic segments, and ionic, which leads to ionomers, in which the chains contain ionic hydrophilic centers. In both cases, the segments or groups act as internal surfactants making the polymer dispersable in water (12).

Ionomers are interesting precursors of commercial importance (13-15). They are often elastomers over a certain range of temperature, with ionic aggregates. There are three types of polyurethane ionomers: anionomers, cationomers and zwitterionomers (16-18).

Polyurethanes are obtained from low-molecular-weight prepolymers produced by the reaction between a diisocyanate and a diol. The later one may be an oligomer

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or a low molecular weight compound. The end groups of the chains may be NCO (isocyanate) or OH (hydroxyl), depending on the NCO/OH ratio employed in the prepolymer synthesis. The prepolymer then is chain extended with a suitable difunctional compound.

This paper presents the synthesis and characterization of polyurethane anionomer prepolymers having pendant carboxylic groups that will further be neutralized to produce anionomer-type polyurethanes.

Experimental

Monomers

Dimethylolpropionic acid (DMPA) - Aldrich; *4,4'- dicyclohexylmethane diisocyanate (H$_{12}$MDI)* (Desmodur W) - Bayer A.G.; *poly(propylene oxide)* (PPG), (Voranol 2110 (P$_1$), $\overline{M}_n$ = 1300 ^{VPO} and Voranol 2120 (P$_2$), $\overline{M}_n$ = 2450 ^{VPO}) - Dow Química S.A. The polyethers were dried under reduced pressure and N$_2$ flux, for 3 hours at 120° C (moisture contents given by the manufacturer are: P$_1$ = 0.053 % and P$_2$ = 0.040 %).

Prepolymer synthesis

Three kinds of diols were used: two high molecular weight (PPG's) and one low molecular weight (DMPA). The role of the last one was to provide the chains with ionic sites and, therefore, it was used in all anionomer prepolymer synthesis.

Prepolymers based on PPG, DMPA and H$_{12}$MDI were synthesized in bulk using dibutyltin dilaurate as catalyst, at 100° C for 2 hours, with N$_2$ flux.

Three series of prepolymers were obtained by varying the molecular weight of the polyol: P$_1$ Series ($\overline{M}_n$ = 1300), P$_2$ Series ($\overline{M}_n$ = 2450) and P$_{12}$ Series: the last Series included both polyols (50% each in equivalent-grams). The NCO/OH ratio was varied in the range from 1.5 to 3.1. The reaction was followed by the determination of the prepolymers' isocyanate end groups content (19). In order to perform prepolymer characterization, the reaction between the NCO end groups and a monofunctional compound of low molecular weight (in this case, methanol) was necessary due to the high reactivity of the NCO group. Thus, after the reaction was complete, the prepolymers were dissolved in methanol and refluxed for 2 hours. The excess of alcohol was evaporated at room temperature for five days and then at 60° C for 12 hours.

Characterization

Prepolymer characterization was performed by several techniques and the results are described as follows.

Molecular weight determination by vapour pressure osmometry (VPO)

The measurements were performed in chloroform at 40° C. Two standards were used: benzyl was the primary standard and eicosane the secondary one. The analysis error was around 1 %.

Table 1 shows number-average molecular weights ($\overline{M}_n$), and free NCO contents before the reaction with methanol. An increase in NCO/OH ratio caused an

increase in the amount of free NCO groups and a consequent decrease in the molecular weight of the prepolymer. The length of the flexible segment also influenced prepolymer molecular weight. An increase in the former led to an increase in the latter.

However, an unexpected behaviour related to the $\overline{M}_n$ values of the prepolymers synthesized at higher NCO/OH ratios was observed: the $\overline{M}_n$'s were smaller than those measured for the polyols (PPG's) employed as monomers in the respective Series. Those results can be attributed to the occurrence of the reaction between the diisocyanate and the low molecular weight diol (DMPA) in a high degree when high NCO/OH ratios were employed. In that case, the large amount of diisocyanate acted as a diluent for the bulk and its reaction with DMPA (more polar than PPG's) was favoured due to the higher affinity between them.

Table 1. Free NCO groups and $\overline{M}_n$ values of prepolymers

NCO/OH	P₁ Series			P₁₂ Series			P₂ Series		
	NCO (%)		$\overline{M}_n$	NCO (%)		$\overline{M}_n$	NCO (%)		$\overline{M}_n$
	Calc.	Exp.		Calc.	Exp.		Calc.	Exp.	
1.5	4.0	3.7	3450	3.2	3.2	2360	2.7	2.2	5850
1.7	5.3	4.8	2520	4.3	4.2	3150	3.6	3.3	4580
1.9	6.5	6.2	2750	5.3	5.1	2270	4.5	4.3	3040
2.1	7.7	7.1	1910	6.3	5.5	1980	5.3	5.0	2530
2.3	8.7	7.9	1580	7.2	6.9	1990	6.1	5.6	2300
2.5	9.6	9.3	1330	8.0	7.7	1700	6.9	6.5	2030
3.1	12.0	11.5	1230	10.2	10.1	1290	8.9	8.3	1390
3.5	13.3	11.7	800	11.5	10.6	940	10.0	8.8	890

P₁: $\overline{M}_n$ = 1300 and P₂: $\overline{M}_n$ = 2450
Calc.: Calculated values of free NCO groups content
Exp.: Free NCO groups content experimentally determined (19) before reaction with methanol

Molecular weight determination by gel permeation chromatography (GPC)

The measurements were performed in N-methyl-2-pyrrolidone at 50° C, using a Waters 510 gel permeation chromatograph equipped with two Ultrastyragel columns (7×10^4 Å pore size). The calibration curve was obtained with polystyrene standards in the molecular weight range of 450,000 to 8,500. Table 2 shows number-average molecular weights, weight-average molecular weights ($\overline{M}_w$) and polydispersities for some prepolymer samples.

It can be observed that the samples prepared with NCO/OH = 3.5 had molecular weight values below the resolution power of the chromatographic columns. The GPC results are in agreement with those obtained by VPO. For higher NCO/OH ratios, the polydispersity was higher and the molecular weight was lower, which is an indication of the heterogeneity of the chain length of the prepolymers.

Table 2. $\bar{M}n$, $\bar{M}w$ and polydispersity ($\bar{M}w$/ $\bar{M}n$) values of the prepolymers

NCO/OH	P₁			P₁₂			P₂		
	$\bar{M}_n$	$\bar{M}_w$	M_w/M_n	$\bar{M}_n$	$\bar{M}_w$	M_w/M_n	$\bar{M}_n$	$\bar{M}_w$	M_w/M_n
1.5	5580	7930	1.4	3530	5280	1.4	7320	10830	1.4
3.1	1210	2240	1.9	1680	2660	1.6	740	1660	2.2
3.5	(a)			(a)			(a)		

(a) It was not possible to analyse these samples because of the low efficiency of the columns in the range of low molecular weight.

Conclusions

An increase in the length of the flexible segment caused an increase in the molecular weight of prepolymer chains. An increase in NCO/OH ratio caused a decrease in those values and for higher ratios the values of molecular weight were smaller than the ones obtained for the polyols. The values of polydispersity showed that for higher NCO/OH ratios there was an increase in the heterogeneity of the prepolymer chain length.

Acknowledgements

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