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- (54) Process for the preparation of polymers with polyoxyalkylene chains bonded in side positions, and their use for the preparation of polyurethanes
- (57) A process for the preparation of a polymer with polyoxyalkylene chains bonded in side positions comprises free radical polymerisation of a polyoxyalkylene ether of allyl and/or methallyl alcohol with a vinyl ester of a lower carboxylic acid or with a mixture of a vinyl ester of a lower carboxylic acid and up to 50 mol % of an ester of an acrylic or methacrylic acid. The polymer thus produced is useful for the preparation of polyurethanes.

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#### **SPECIFICATION**

Process for the preparation of polymers with polyoxyalkylene chains bonded in side
positions, and their use for the preparation of polyurethanes

The invention relates to a process for the preparation of polymers with polyoxyalkylene chains bonded in side positions, by free radical polymerisation of polyoxyalkylene ethers with olefinic double bonds with other vinyl compounds capable of undergoing copolymerisation, and to their use for the preparation of polyurethanes.

Polymers with long-chain radicals bonded in side positions have proved to be very effective surface-active compounds. Polysiloxanes with polyoxyalkylene chains bonded in side positions are used as form stabilisers in the preparation of polyurethane foams. According to their hydrophilic/hydrophobic equilibrium, they can also be used as emulsifying agents or dispersing agents and for foam prevention or foam removal in aqueous or organic systems.

DE-A-3109700.6-44 describes polymers which have polyalkylene oxide chains bonded in side positions and can be prepared by reacting polyalkylene oxides with at least two free hydroxyl groups on the starting alcohol with difunctional or polyfunctional compounds which are reactive in respect of the hydroxyl groups on the starting alcohol, if appropriate in the presence of solvents and/or catalysts and/or at elevated temperatures. These compounds also are 20 distinguished by a high surface activity and are of relatively low viscosity, even at relatively high

molecular weights.

It is also known that polymers with polyalkylene oxide chains bonded in side positions can be prepared by subjecting polyoxyalkylene ethers with olefinic double bonds in the starting alcohol to free radical polymerisation. Thus, it is known from the journal "Plaste und Kautschuk", 28,

25 Volume 7, 1981, page 367, that acrylic acid can be partially esterified with alkylene glycol and alkylene oxide can be added onto the free OH groups. The compounds thus obtained can be polymerised in the presence of other monomeric compounds suitable for polymerisation, to give polymers with polyoxyalkylene chains bonded in side positions. However, these compounds have the disadvantage that they may be hydrolised in acid or alkaline media, the polyoxyalky-30 lene chains bonded in side positions being split off.

U.S. Patent Specification 2,965,615 describes the alkoxylation products of copolymers of allyl alcohol and alkenyl-aromatic compounds and their use in the preparation of lacquers and foams based on polyurethane. The disadvantages of this process are the high amounts of unreacted monomeric allyl alcohol after the polymerisation, because of the unfavourable 35 copolymerisation parameters, the requisite removal, after the alkoxylation, of the solvent necessary for carrying out the free radical polymerisation, and the high viscosity of the process

products. Japanese Preliminary Published Application 8,181,320 describes a process for the copolymerisation of polyoxyethylene ethers of allyl alcohol with acrylic acid or methacrylic acid or salts 40 thereof. However, when this process is repeated, it is found that, on polymerisation, either gelling by crosslinking via main valency bonds occurs, or polymers with only low molecular

weights are obtained.

U.S. Patent Specifications 3,383,351 and 3,652,639 describe dispersion of graft copolymers which are prepared from vinyl monomers and polyether-ols and are used for the preparation of 45 polyurethanes. According to the former patent specification, the polyols used are absolutely free from ethylenic double bonds. It is found that the presence of ethylenic double bonds promotes the formation of crosslinking bridges and undesirably increases the viscosity of the dispersions thereby formed. A substantial disadvantage of the process of U.S. Patent Specification 3,383,351 is that the stable dispersions prepared from numerous conventional vinyl monomers, 50 such as styrene, cannot be processed if these monomers are used in an amount sufficient to impart the desired mechanical strength to the polyurethanes. On the other hand, U.S. Patent Specification 3,652,639 states that graft copolymers which are homogeneous in liquid media

unsaturated polyol in the presence of a catalyst which forms free radicals. The polyols used 55 according to U.S. Patent Specification 3,652, 639 contain at least about 1 mol of unsaturated units per mol of polyol. A disadvantage of these products is their relatively high viscosity, which is to be attributed to the presence of graft copolymers of extremely small particle size and to the formation of crosslinking bridges.

and are based on acrylonitrile can be prepared by polymerisation of acrylonitrile in situ with an

German Patent Specification 2,359,617 relates to dispersions of graft copolymers which are 60 prepared by polymerising a vinyl monomer in situ in a polyether-ol containing 0.1 to 0.7 mol of unsaturated units per mol of polyether-ol in the presence of a catalyst which forms free radicals. A substantial disadvantage of this process is that an upper limit may not be exceeded in respect of the ratio of unsaturated to saturated polyether-ols if high viscosity or crosslinking of the process product are not accepted. The reason for this is that the unsaturated polyether-ols 65 described can also carry several unsaturated double bonds in one molecule on the basis of the

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random distribution. In the upper range of the stated ratio of unsaturated to saturated polyetherols, it is therefore entirely possible that highly viscous, cloudy and even gelled products form during the free radical grafting copolymerisation.

The present invention provides a process for the preparation of a polymer with polyoxyalky-lene chains bonded in side positions, which process comprises free radical polymerisation of a polyoxyalkylene ether of allyl and/or methallyl alcohol with a vinyl ester of a lower carboxylic acid or with a mixture of a vinyl ester of a lower carboxylic acid and up to 50 mol % of an ester of acrylic or methacrylic acid.

It is thus possible to prepare polymers with polyoxyalkylene chains bonded in side positions, which contain a large number of polyoxyalkylene chains bonded in side positions in the micromolecule, have a relatively low viscosity, in spite of their high molecular weight, and are suitable as raw materials for the preparation of polyurethanes.

Since the unsaturated double bond is an integral constituent of the starting alcohol, it is possible in each case to introduce only one double bond into a polyether chain and thus to avoid the danger of crosslinking.

It was surprising that the polyoxyalkylene ethers of allyl and/or methallyl alcohol can be polymerised with the abovementioned monomers to give copolymers of relatively high molecular weight, since it is known, on the one hand, that allyl and methallyl compounds form relatively stable allyl radicals on free radical polymerisation by transfer of a growing chain, so that only oligomers of relatively low molecular weight are obtained, and, on the other hand, linear copolymers of relatively high molecular weight are hardly obtained with acrylic acid by itself. In addition, the free radical polymerisation of macromolecules which have, on one chain end, a double bond capable of undergoing polymerisation is hindered for steric reasons. However, in the process according to the invention, it is possible to prepare copolymers with molecular weights of 10,000 or far higher.

Polyoxyalkylene ethers of allyl and/or methallyl alcohol of the following general formula are particularly employed for the process according to the invention

$$30^{-R^2-O-\left[CH_2-CH-O-\atop l_1l_1\right]_{R}^{H}}$$

In this formula, R¹ denotes a hydrogen radical or an optionally halogenated hydrocarbon group with 1 to 30 carbon atoms. Ethylene oxide, propylene oxide, butylene oxide or α-olefin oxides of long-chain hydrocarbons with up to 30 C atoms are thus used as the alkylene oxides. The polyoxyalkylene chains can be built up from identical or different alkylene oxides. The hydrophobic properties or hydrophilic properties of the copolymers can be controlled within the desired limits by appropriate balancing of the oxyethylene and oxypropylene units or units of longer hydrocarbon chains, so that either readily water-soluble products or water-insoluble product, or products of which the turbidity point in aqueous solution can be adjusted as desired can be prepared.

Also in the formula above,  $R^2$  is an allyl or methallyl radical and n is an integer > 1, in particular  $\geq 5$ .

The vinyl esters capable of undergoing copolymerisation which are used are, in particular, esters of a carboxylic acid of formula RCOOH in which R is an alkyl group containing 1 to 4 carbon atoms, such as vinul acetate, vinyl propionate and vinyl butyrate. Where a mixture of a vinyl ester with up to 50 mol % of an alkyl ester of acrylic acid or methacrylic acid is used, the alkyl group has 1 to 20 carbon atoms and the alkyl esters are compounds such as methyl acrylate, methyl methacrylate, butyl acrylate, butyl methacrylate, lauryl methacrylate or stearyl methacrylate.

High polymerisation yields and at the same time copolymers of high molecular weight are preferentially obtained in the copolymerisation of the polyoxyalkylene esters of allyl and/or methallyl alcohol with the vinyl esters of lower carboxylic acids or mixtures thereof with acrylates or methacrylates if the amount of the vinyl ester of a lower carboxylic acid to be copolymerised is matched to the molecular weight of the polyoxyalkylene ether to be employed. In a particularly preferred embodiment of the process according to the invention, the quotient of the molecular weight of the polyoxyalkylene ether and the molar number of the vinyl ester of a lower carboxylic acid to be copolymerised is 100 to 300; i.e.

molar quantity of vinyl ester to be copolymerised

This means that, for example, if a polyoxyalkylene ether with a molecular weight of 1,000 is used, about three to ten times the molar amount of vinyl monomers to be copolymerised should 65

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be employed. The yield of the copolymerisation is then greater than 90%, and products of molecular weight >10,000, in particular ≥20,000, are obtained.

Whilst the copolymerisation of polyoxyalkylene ethers of allyl and/or methallyl alcohol with esters of acrylic acid or methacrylic acid alone gives only unsatisfactory yields, since a large proportion of the polyoxyalkylene ether remains unreacted, it is found that on combined use of vinyl esters and methacryl esters, the polyoxyalkylene ether is substantially incorporated, during the reaction, into the polymer formed. Because the copolymerisation may be carried out in a manner known to the expert, it can be carried out in bulk or in dilution or solution. Since the polymers have a relatively low viscosity, it is generally sufficient to carry out the reaction without 10 using a diluent or solvent. Suitable solvents are aromatic hydrocarbons, such as benzene and 10 toluene, chlorinated hydrocarbons, such as chloroform and carbon tetrachloride, lower alcohols. such as methanol and ethanol, ketones, such as acetone and methyl ethyl ketone, and mixtures thereof. The polymerisation is carried out at temperatures from 50 to 130°C. Polymerisation initiators which can be used are azo compounds or peroxides, such as, for example, azodiisobu-15 tyronitrile, benzoyl peroxide, cumene or dicumene peroxide, in amounts of 0.1 to 2 % by 15 weight, based on the monomers. For the polymerisation, it is advisable to take the allyl polyether and slowly to add the low-molecular comonomer, in which case the initator can be dissolved in the latter.

The copolymers obtained according to the invention are in most cases liquid substances of 20 low viscosity. According to a further subject of the present invention, they are particularly suitable as reactants, containing hydroxyl groups, in the preparation of polyurethanes. The polyurethane foams are distinguished by outstanding mechanical properties, in particular by a high compressive strength.

The polymers prepared according to the invention with polyoxyalkylene chains bonded in side 25 positions can also be reacted with other compounds of higher molecular weight which are known per se and contain groups which are reactive towards isocyanates, and/or with chain lengthening agents with polyisocyanates to give homogeneous or foam-like polyurethane plastics.

The process according to the invention may be illustrated in still more detail with the aid of 30 30 the following examples.

#### Example 1

A) Preparation of an allyl polyether-monool (not claimed)

116 g (about 2 mol) of allyl alcohol and 21 g (about 0.3 mol) of potassium methylate are 35 introduced into a reactor with an automatically conveying circulatory system. After careful flushing with pure nitrogen, the reactor is heated to 110°C, and 1,276 g (about 22 mol) of propylene oxide are added at a rate such that the internal temperature of the reactor does not exceed 120°C and the pressure does not exceed 6 bar. After all of the alkylene oxide has been introduced, the temperature is kept at 115°C until constant pressure indicates the end of the 40 after-reaction. The residual monomers are then removed at 80 to 90°C in vacuo.

The resulting product is neutralised with the aid of phosphoric acid, the water is removed by distillation and the sodium phosphate formed is removed by filtration with a filtration auxiliary. The hydroxyl number of the process product is 92.7, which corresponds to a molecular weight of 605, assuming the functionality is 1. The iodine number is 36.5 and thus corresponds to a 45 double bond content of 87.0 mol %.

B) Copolymerisation of the allyl polyether-monool with vinyl acetate (according to the invention) 605 g (about 1 mol) of the allyl polypropylene oxide monool obtained under A) are heated to 80°C in a three-necked flask under a stream of nitrogen. 430 g (about 5 mol) of vinyl acetate, 50 50 in which 8.4 g of azodiisobutyronitrile have been dissolved, are then added uniformly over a period of 2 hours. Four portions, divided over 2 hours, of 1 g of azodiisobutyronitrile are then added, the temperature being kept at 80°C; finally, an after-reaction is carried out at this temperature for a further 2 hours.

The free vinyl acetate which still remains is distilled off in vacuo. From the amount of 55 monomers collected in a cold trap, a polymerisation yield, based on the vinyl acetate, of 92% of 55 theory results. From the determination of the iodine number (3.0), it can be concluded that about 86.5% of the allyl polypropylene oxide monool is consumed in the copolymerisation. Investigation by gel chromatography shows a numerical molecular weight of about 20,000. From this, it can be concluded that a comb-like polymer in which the macromolecules most 60 60 frequently present have a number of about 20 side branches has been obtained.

#### Examples 2 to 18

A number of allyl polyether-monools with different contents of ethylene oxide and propylene oxide and adjusted to different molecular weights were prepared by the process according to 65 Example 1 A) and were copolymerised with vinyl acetate, in some cases in different molar ratios. 65

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The amount of ethylene oxide and propylene oxide employed in the polyether used, the molecular weight, calculated from the hydroxyl number and assuming a functionality of 1, and the molar content of double bonds, that is to say the content of allyl polyether-monools, are given in Table 1. The amount of allyl alcohol used in the alkylene oxide polymerisation is always 30.5 g, that is to say 0.87 mol, and the amount of potassium methylate used as the catalyst is 9.1 g (about 0.13 mol). The table also shows the molar ratio of vinyl acetate to allyl polyether, the yield of copolymer by determination of the iodine number and the most frequent molecular weight from the investigation by gel chromatography. The initiator azodiisobutyronitrile is used in the concentration and time sequence described in Example 1 B).

It can be seen that as the molecular weight of the allyl polyether increases, the molar ratio of vinyl acetate to polyether must be increased in order to obtain high polymerisation yields. The molecular weight of the copolymer likewise increases as the vinyl acetate content increases.

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Example No.	Ethylene oxide/ propylene oxide (g/g)	Molecular weight from OH no.	Double bond content (mol %)	Molar ratio vinyl acetate allyl polyether	Yield from iodine no. (% of theory)	Molecular weight from GPC*
0	133/ 111	296	87.3	2.0	71.3	18,000
3	133/ 111	296	87.3	3.0	89.5	19,000
4	279/ 187	510	94.5	2.5	84.0	20,000
5	0/ 570	605	87.0	2.5	82.0	18,000
5 6	0/ 570	605	87.0	5.0	86.5	19,500
7	0/ 570	605	87.0	9.0	90.2	21,000
8	0/ 570	605	87.0	12.0	93.4	25,000
9**	0/ 779	800	86.2	9.0	88.2	23,000
10	114/ 653	808	79.2	3.0	65.0	14,000
O 11	114/ 653	808	79.2	6.0	79.3	17,000
12	39/ 754	820	75.6	4.5	78.2	12,500
13	81/ 754	855	78.5	4.5	76.3	11,000
14	146/1,090	1,247	86.0	6.0	72.0	14,000
15	820/1,050	1,839	83.4	9.0	78.0	27,000
5 16	1,069/1,335	2,367	86.5	9.0	79.2	40,000
17	1,069/1,335	2,367	86.5	15.0	89.5	46,000
18	1,069/1,335	2,367	86.5	21.0	93.7	49,500

<sup>\*</sup> most frequent molecular weight from the 40 gel phase chromatogram

In the following comparison examples, it will be shown that copolymerisation of polyoxyalkylene ethers of allyl and/or methallyl alcohol with vinyl ethers, styrenes, methyl methacrylates or acrylic acid is impossible or gives only unsatisfactory yields. On the other hand, this shows that 45 the expert was not able to predict the course of the process according to the invention.

## Comparison Example 1

605 g (about 1 mol) of the propylene oxide monool obtained in Example 1 A) are copolymerised with 500 g (about 5 mol) of n-butyl vinyl ether according to Example 1B), with a 50 total amount of 29.2 g of azodiisobutyronitrile as the initiator. The time of the after-reaction in this case is 4 hours.

The free butyl vinyl ether which still remains is removed by distillation in vacuo. Determination of the iodine number shows that only 39.8 % of the allyl polyether has been consumed.

### 55 Comparison Example 2

605 g (about 1 mol) of the polypropylene oxide monool obtained in Example 1 A) are heated with 520 g (about 5 mol) of styrene according to Example 1 B), a total of 29.2 g of azodiisobutyronitrile being added. After a reaction time of 6 hours at 80°C, a two-phase system of polystyrene and, as can be seen from the iodine number, unreacted allyl polyether is formed.

## Comparison Example 3

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605 g (about 1 mol) of the polypropylene oxide monool obtained in Example 1 A) are heated with 500 g (about 5 mol) of methyl methacrylate according to Example 1 B), a total of 29.2 g azodiisobutyronitrile being added. After a reaction time of 6 hours at 80°C, a two-phase system 65 of polymethyl methacrylate and, as can be seen from the iodine number, unreacted allyl

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prepared using 72 g (about 1 mol) of methallyl lalcohol as the starting alcohol

polyether is formed.

Determination of the iodine number shows that only 31.4% of the allyl polyether has been consumed.

5 Comparison Example 4

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53 g (about 0.1 mol) of an allyl ethylene oxide monool with on average 10 monomer units are dissolved in 600 g of water. The solution is heated to 95°C under pure nitrogen and a solution of 216 g (about 3 mol) of acrylic acid and 3.5 g of (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> in 400 g of water is added in the course of 120 minutes, the temperature being kept constant at 95°C. Gelling 10 occurs after addition of only 2.5 mol of acrylic acid. The dehydrated product is no longer soluble.

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Comparison Example 5

1.3 g of azodiisobutyronitrile are dissolved in 121 g (about 0.2 mol) of an allyl polypropylene 15 oxide monool with on average 10 monomer units, the solution is warmed to 80°C under pure nitrogen and 72 g (about 1 mol) of acrylic acid are added dropwise. Gelling occurs after only half a mol of acrylic acid has been introduced. The resulting product is no longer soluble.

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Comparison Example 6

121 g (about 0.2 mol) of an allyl polypropylene oxide monool with on average 10 monomer units are mixed with 121 g of a mixture of toluene and ethanol in a volume ratio of 1:1. 1.6 a of azodiisobutyronitrile are added, the mixture is heated to 80°C under pure nitrogen and 72 g (about 1 mol) of acrylic acid are added dropwise. Three portions of 1.6 g of azodiisobutyronitrile are further added at intervals of 1 hour. The reaction is discontinued after a total of 6 hours.

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The volatile constituents are completely removed by distillation. From the iodine number of the resulting product, it can be concluded that 75% of theory of the allyl polyether has been reacted. From analysis of the product by gel chromatography, it follows that only an average molecular weight of 910 has been achieved.

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30 Example 19

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A polyether was prepared from 58 g (about 1 mol) of allyl alcohol and 572 g (about 13 mol) of ethylene oxide by the process according to Example 1 A). The resulting product has a hydroxyl number of 92.2, which corresponds to a molecular weight of 608, assuming a functionality of 1. The iodine number is 36.6 and thus corresponds to a double bond content of 35 88 mol %.

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162 g (about 0.27 mol) of the resulting polyether are copolymerised with a mixture of 100.6 g (about 1.2 mol) of vinyl acetate and 59.3 g (about 0.23 mol) of lauryl methacrylate by the process according to Example 1 B), 1.6 g of azodiisobutyronitrile being added at the start of the reaction, and the same amount of the initiator in each case being added after 1, 2 and 3 hours. 40 The free volatile monomer which still remains is distilled off in vacuo. From the determination of

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the iodine number of 3.1, it can be concluded that 84.0% of the allyl polyethylene oxide monool has been consumed in the copolymerisation. Investigation by gel chromatography shows a very broad molecular weight distribution with a molecular weight range between 1,000 and 100,000 without a clear maximum.

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Examples 20 to 23

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A number of allyl polyether-monools with different contents of ethylene oxide and propylene oxide and with different molecular weights established were prepared by the process according to Example 1 A) and were copolymerised with mixtures of vinyl acetate and lauryl or stearyl 50 methacrylate in different molar ratios. Table 2 shows the amount of ethylene oxide and propylene oxide employed in the polyether used, the molecular weight calculated from the hydroxyl number, assuming a functionality of 1, and the molar content of double bonds, that is to say the content of ally polether-monools. The amount of allyl alcohol employed in the alkylene oxide polymerisation is in each case 58 g, that is to say 1 mol, and the amount of

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55 potassium methylate used as the catalyst is 7 g (about 0.1 mol). Table 2 also shows the amounts of allyl polyether, vinyl acetate and lauryl or stearyl methacrylate used in mol, the yield of copolymer for the determination of the iodine number and the most frequent molecular weight or the molecular weight range from investigation by gel chromatography.

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60 Use Example 1

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210 g of the copolymer obtained according to Example 7, having a hydroxyl number of 26.7, 7.2 g of water, 0.45 g of bis-(2-N,N'-dimethylaminoethyl) ether, 4 g of a stabiliser based on a polysiloxane/polyether block copolymer and 0.8 g of tin-II octoate are mixed for 2 minutes in a stirred container. After about 1 minute, 82.0 g of a mixture of 80% by weight of toluylene 2,4-65 diisocyanate and 20% by weight of 2,6-toluylene diisocyanate having a TDI index of 105 are

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added and the mixture is stirred with a high-speed stirrer for a few seconds. A yellowish polyurethane foam with a weight per unit volume of 31 kg/m³, a tensile strength of 1.40 kg/cm², an elongation of 105% and a compressive strength at 25% compression of 0.072 kg/cm² is obtained.

Use Example 2

The procedure followed is as in Use Example 1, 262 g of the copolymer obtained according to Example 15, of hydroxyl number 21.4, 7.2 g of water, 0.5 g of bis-(2-N,N-dimethylaminoethyl) ether, 4.5 g of a stabiliser based on a polysiloxane/polyether block copolymer and 0.8 g of tin-II octoate being mixed with one another and 82.0 g of the toluylene diisocyanate mixture then being added. A slightly yellowish polurethane foam with a weight per unit volume of 30.5 kg/m³, a tensile strength of 1.31 kg/cm², an elongation of 115% and a compressive strength at 25% compression of 0.061 kg/cm² is obtained.

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Table 2									-
Example No.	Ethylene oxide/ Molecular Amount or propylene oxide weight polyether (% by wt/% by wt) from OH No. (mol)	Molecular weight t) from OH No.	Amount of polyether (mol)	Amount of vinyl acetate (mol)	Amount of lauryl metha- crylate (mol)	Amount of stearyl metha- crylate (mol)	Amount** of ADBN (g)	Yield from iodine No. (%)	Molecular weight from GPC
20 21 22	100/ 0 100/ 0 100/ 0	608 270 270	0.23 0.50 0.50	1.2 2.0 2.0	0.5	0.23 0.50	7.2 12.0 13.2	85 90 90	10 <sup>3</sup> -10 <sup>5</sup> 10 <sup>3</sup> -5·10 <sup>4</sup> 10 <sup>3</sup> -5·10 <sup>4</sup> Max. 12,000
23*	30/70 100/ 0 100/ 0	1,753 608 270	0.20 0.40 0.40	4.0	0.4	0.40	30.0	79	10³–6·10⁴ Max. 13,000

\* The copolymer contains three different allyl polyethers. \*\* Equal parts of the initiator are added at the start of the reaction and three times after in each case one hour.

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**CLAIMS** 

- 1. A process for the preparation of a polymer with polyoxyalkylene chains bonded in side positions, which process comprises free radical polymerisation of a polyoxyalkylene ether of allyl and/or methallyl alcohol with a vinyl ester of a lower carboxylic acid or with a mixture of a vinyl ester of a lower carboxylic acid and up to 50 mol % of an ester of acrylic or methacrylic acid.
- 2. A process according to claim 1, in which the polyoxyalkylene ether of allyl and/or methallyl alcohol is a compound of the general formula

$$10^{-R^2-O-\left[CH_2-CH-O-\atop R^1\right]_{R}^{H}}$$

wherein R<sup>1</sup> is a hydrogen radical or an optionally halogenated hydrocarbon group with 1 to 30 carbon atoms,

- carbon atoms,

  15 R<sup>2</sup> is an allyl or methallyl radical, and

  n is an integer >1.
  - 3. A process according to claim 1 or 2, in which the quotient of the molecular weight of the polyoxyalkylene ether and the molar quantity of the vinyl ester to be copolymerised is 100 to 300.
- 20 4. A process for the preparation of a polymer with polyoxyalkylene chains bonded in side positions, said process being substantially as hereinbefore described in Example 1 (B) or any one of Examples 2 to 23.
- 5. A process for the preparation of a polyurethane, which process comprises preparing the polyurethane using a polymer with polyoxyalkylene chains bonded in side positions as one of the reactants.
  - A process for the preparation of a polyurethane, said process being substantially as hereinbefore described in either of the Use Examples.

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