

Synthesis of polymer polyols in unsaturated polyols, polymer polyols and their use

Description

The present invention relates to the synthesis of polymer polyols in unsaturated polyols as liquid phase and their use.

- 5 WO2013039907 and US20100160469 (BASF SE, Bayer) describe the production of polymer polyol dispersions from natural oils for the manufacture of polymer polyols by using macromere polyols, polymerizable monomers, chain transfer agents and radical initiators by free radical polymerization.

- 10 JP 2011207943 A (Sanyo) discloses the production of polymer polyol dispersions based on castor oil and castor oil derivatives. The obtained products allegedly have excellent dispersion stabilities. JP2011098310 describes the use of such polyols for the manufacture of polyurethane (PU) sealing materials.

JP2010177066 discloses the use of such polyols in PU resins, and

WO2010055631 in sealing materials for membrane modules.

- 15 JP61200116 (Sanyo) discloses polymer polyols made from polyether polyols, polyester polyols and low-molecular polyols as liquid phase and from ethylenically unsaturated monomers forming the dispersed phase.

- 20 EP755953 mentions the manufacture of polymer polyols from modified castor oil polyols by free radical polymerization. The modified castor oil polyols were obtained by transesterification of castor oil with polyols based on propylene oxide (PO), ethylene oxide (EO) and dimeric fatty acids. The products allegedly are stable, agglomerate free and low-viscous graft co-polymer dispersions. The use of modified castor oil suggests that unmodified castor oil was not suitable.

WO 2009/138379 A2 describes dispersions containing at least one liquid polymer and at least one polymer particle mixture comprising at least one meltable solid and at least one copolymer.

- 25 WO 2008/055952 A1 discloses polyol dispersions, comprising at least one polyol and at least one polymer particle mixture comprising at least a thermoplastic polymer and at least a block copolymer.

EP 14166515.8 discloses a process for the production of polymer polyols by using an extruder and a rotor-stator.

- 30 EP 14166528.1 describes a stabilizer for melt emulsification processes to produce polymer polyols.

- 35 Polymer polyols, also known as filled polyols, are viscous fluids comprising fine particles dispersed in polyols. Examples of solids used include styrene-acrylonitrile co-polymers and polyureas. The solids are typically prepared by *in situ* polymerization of monomers in the base polyol. Polymer polyols are commonly used for the production of polyurethane foams.

In some cases, it is desirable to use compounds containing C-C unsaturation as liquid phase referred to as carrier polyols or carriers for polymer polyols. For example, it may be preferable to employ compounds from naturally occurring renewable sources, like vegetable oils, as raw material, due to the limited supply of fossil resources. These compounds usually contain C-C unsaturation.

However, a problem that is frequently encountered when using C-C-unsaturated alcohol compounds as carriers for polymer polyols is that several side reactions can take place during radical polymerization. This often leads to high viscosity of the product. It is often almost impossible to process these polymer polyols, at least for standard applications.

Besides, filtration of these polymer polyol product obtained via radical polymerization is usually necessary, but when using C-C-unsaturated alcohol compounds as carriers, the filtration step is most often very difficult and time consuming due to formation of undesired larger particles. In addition, the polymer polyol product obtained via radical polymerization in some cases is not quite homogeneous.

Thus, there was a need in the art to avoid the above-mentioned problems. Furthermore, there was a desire in the art to provide hydrophobic polymer polyols, for example for the use in the production of polyurethanes for coating applications.

Surprisingly, the mentioned problems could be overcome by using a purely mechanical process for the production of polymer polyols in unsaturated polyols, a so-called "melt emulsification" process.

The melt emulsification process is very different from the standard process for the synthesis of polymer polyols by radical polymerization. Since there is no chemical polymerization reaction in the melt emulsification process, the dispersion is created through a physical (i. e. mechanical) process. Therefore, the melt emulsification method also requires different stabilizers (as defined below).

The term melt emulsification is defined in WO2009/155427 as follows:

Another way of dispersion the previously-formed polymer is to melt it, and then blend the molten polymer with the polyol under shear. The shearing action breaks the molten polymer into small droplets which become dispersed in the polyol phase. This process is described in US patent No. 6,623,827. That patent describes a process wherein a previously-formed polymer is melted in an extruder, mixed with a stabilizer and a polyether polyol, and subsequently mixed with more of with the polyether polyol. The mixture is then cooled to solidify the particles.

Usually it is necessary to use stabilizers, as defined below, to maintain the dispersion stable (i. e. to avoid phase separation).

Thus, one object of the present invention is a process for making a polymer polyol, comprising mixing at least one melted thermoplastic styrene-acrylonitrile-copolymer (TP) with at least one polyol (P) in the presence of at least one stabilizer (S), comprising from 10 to 70% by weight,

- preferably 30 to 60% by weight, more preferably 40 to 55% by weight, based on the sum of all components, at least one polyol P2, and at least one polyol CSP which comprises the reaction product of at least one macromer M, styrene and acrylonitrile in polyol P2, optionally with an initiator and/ or a chain transfer agent, wherein the content of macromer M of the stabilizer (S) is
- 5 between 30-70 wt%, preferably 35 to 54 wt%, based on the sum of all components, and/or wherein the polyol CSP is preferably comb-structured, wherein the polyol (P) comprises at least one unsaturated carbon-carbon bond per molecule.

The mixing can be done with a stirrer, in one embodiment. The mixing may also be done by a stirrer, with vigorous stirring.

- 10 In another embodiment of the inventive process, in a first step (1), TP, P and S are fed into an extruder (E) to form an initial dispersion, and the initial dispersion obtained from the extruder is then fed, in a second step (2), into at least one rotor-stator device (RS) comprising at least one rotor-stator combination, and subsequently (3) the dispersion is cooled below the T_g of the thermoplastic styrene-acrylonitrile-copolymer (TP) to obtain the final polymer polyol, .
- 15 In a preferred embodiment of the present invention, the polyol (P) on average has at least two, preferably at least 2.5, double bonds per molecule.

The average number of double bonds per molecule may be determined by measuring the iodine number according to DIN 53241-1:1995-05 (based on the addition of iodine monochloride to olefinic double bonds).

- 20 In another embodiment of the present invention, polyol (P) comprises at least one polybutadiene diol.

In another embodiment of the present invention, polyol (P) consists of a polybutadiene diol.

- The term polybutadiene diol, in the context of this invention, refers to low molecular weight, hydroxyl-terminated diols based on homopolymers of butadiene with molecular weights (M_n) lower
- 25 than 10000 g/mol.

The polybutadiene diols, as used in this invention, may be selected from the group consisting of Krasol® resins and Poly bd® resins, manufactured by Cray Valley.

- In particular, the following Krasol® resins and Poly bd® resins may be used, separately or in combination: LBH-2000, LBSH-3000, LBH P-2000, LBH P-3000, Poly bd R45HTLO, Poly bd
- 30 R45V, Poly bd R20LM.

The following table gives a summary of polybutadiene resins that may be used for the inventive process.

Krasol®						
Polybutadiene Resins						
Product	OH Functionality	1,2 vinyl (weight%, relative to the total compound)	Mn (g/mol)	OH value (meg/g)	Viscosity Pa.s @ 30C	Functionality
LBH 2000	1.9	65	2100	0.91	9	secondary OH
LBH 3000	1.9	65	3000	0.64	13	secondary OH
LBH 5000	1.9	65	5000	0.38	19	secondary OH
LBH - P 2000	1.9	65	2100	0.91	9	primary OH
LBH - P 3000	1.9	65	3000	0.64	13	primary OH
LBH - P 5000	1.9	65	5000	0.38	19	primary OH
Polyolefin Resins						
						Hydrogeneated
HLBH - P 2000	1.9	-	2100	0.91	62.6	primary OH
HLBH - P 3000	1.9	-	3000	0.64	40	primary OH

• Poly bd grades

Commercial Name	Mn (g/mol)	T _g (°C)	Vinyl (%)	Viscosity (cps @ 30°C)	Functionality
R45HTLO	2700	-75	20	5000	
R20LM	1230	-70	20	1400	

• Krasol grades

Commercial Name	Mn (g/mol)	T _g (°C)	Vinyl (%)	Viscosity (cps @ 25°C)	Functionality
LBH 2000	2100	-33	65	13,000	Secondary 
LBH 3000	3000	-40	65	20,000	
LBH 5000	5000	-45	65	29,000	
LBH 10000	10000	-50	65	35,000*	
LBH-P 2000	2100	-30	65	13,000	Primary 
LBH-P 3000	3000	-41	65	20,000	
LBH-P 5000	5000	-42	65	29,000	

OH-Functionality of R45HTLO: OH value 0,85 meq/g, and of R20 LM: OH value 1,8 meq/g.

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In a preferred embodiment of the inventive process, the polyol (P) comprises at least one polybutadiene diol.

Advantageously, the polybutadiene diols used for this invention have an OH functionality in the range of 1.5 to 2.5, preferably 1.7 to 2.1, and/ or an 1,2-vinyl content of 55 to 75 %, preferably 60 to 70 %, and/ or a molecular weight (Mn) of 1000 to 6000 g/mol, preferably 1200 to 5500 g/mol, more preferably 2000 to 5200 g/mol, and/ or an OH value of 0.2 to 1.2 mg KOH/g, preferably 0.3 to 1.0 mg KOH/g, and/ or a viscosity at 30 °C of 8 to 25 Pa.s, preferably 9 to 20 Pa.s.

In a different embodiment of the inventive process, polyol (P) comprises at least one unsaturated natural oil with at least one an OH functional group per molecule, preferably castor oil.

15 In a preferred embodiment, polyol (P) consists of castor oil.

The inventive process may be a continuous process or a semi-batch process.

The term stabilizer may be defined as a compound obtained by reacting a macromer containing reactive unsaturation with styrene and acrylonitrile in a polyether polyol (usually a saturated pol-

yl), optionally a chain transfer agent can be used. The inventive stabilizers are used for preparing polymer polyols containing small particles with D50 of below 25 μm , preferably below 10 μm , most preferably below 5 μm , via melt emulsification process and should be able to stabilize the polymer polyol dispersion for a prolonged period of time (prevention of phase separation).

- 5 The stabilizing effect is determined by storing samples for a prolonged time and visually inspecting them before and after the storage period of, usually, six months. When no precipitation has been formed at the bottom of the sample container (i. e. no phase separation), the sample is considered to be stable and thus, the stabilizer works.

10 The inventive stabilizers (S) are inherently different from preformed stabilizers used for standard graft process via free radical polymerization described in EO1675885, US6013731, 5990185 or EP0786480. Requirements and challenges for the process to form and stabilizer polymer polyol dispersions via radical polymerization are fundamentally different.

The stabilizer (S) is a compound that is assumed to stabilize dispersions of styrene acrylonitrile copolymers in a polyether phase, and thus is assumed to stabilize polymer polyol dispersions.
15 In particular, the stabilizer (S) is assumed to stabilize polymer polyol dispersions obtained by melt emulsification processes.

In a preferred embodiment the polyols CSP contained in the stabilizers (S) are comb-structured.

20 In this preferred comb-structure, the typical distance between two macromers is between 16 units styrene and acrylonitrile up to 500 units of styrene and acrylonitrile, preferentially 30 units styrene and acrylonitrile up to 200 units of styrene and acrylonitrile.

These polyols CSP are assumed to have a backbone formed of styrene/acrylonitrile (SAN) polymer which interacts with the SAN contained in the polymer polyol product to be stabilized. Moreover, the macromers used for synthesizing the inventive stabilizer usually have functional groups that are assumed to interact with the polyols of the polymer polyol product to be stabilized and can reaction with the isocyanate during the PU reaction. This process improves the
25 integration of graft particles in the PU network.

The stabilisers (S) usually have a viscosity in the range between 1000 to 100000 mPas, preferably 5000 to 80000 mPas, more preferably 8000 to 60000 mPas at 25 °C.

30 The stabilisers (S) usually have an OH number of 1 to 100, preferably 1 to 50 mg KOH/g, more preferentially 10 to 40 mg KOH/g.

The hydroxyl number is determined in accordance with DIN 53240 from 2012 (DIN = "Deutsche Industrienorm", i. e. German industry standard).

35 The viscosity of the polyols is, unless indicated otherwise, determined at 25°C in accordance with DIN EN ISO 3219 from 1994 by means of a Rheotec RC20 rotational viscometer using the spindle CC 25 DIN (spindle diameter: 12.5 mm; internal diameter of measuring cylinder: 13.56 mm), however at a shear rate of 100 /1s (instead of 50/1s).

In a preferred embodiment of the stabilizer (S), the ratio of styrene to acrylonitrile is greater than 1:1, preferentially greater 1.5:1, most preferred greater 2:1.

The synthesis of the stabilizers (S) described herein is usually carried out by reacting a macromere or a mixture of macromeres with styrene and acrylonitrile in a carrier polyol (P2), usually a saturated polyol, in the presence of a radical initiator and optionally a chain transfer agent in a free radical polymerization. This reaction is usually carried out in a semi-batch process; however a batch procedure or a continuous process is also possible. The monomers, the macromere or the macromere mixture, the carrier polyol, the initiator or the chain transfer agent can be added to the reactor before, during or after the reaction, continuously or stepwise.

Different radical initiators can be used, for example azoderivatives, such as AIBN, peroxides such as tert-amyl peroxides, hydroperoxides and percarbonates. Most preferred are azoderivatives, in particular AIBN (azoisobutyronitrile) and/or Dimethyl 2,2'-azobis(2-methylpropionate).

The stabilizers (S) preferably have a particle size D50 smaller than 0,5 µm, more preferentially smaller than 0,3 µm (as determined by static laser diffraction using a Mastersizer 2000 (Malvern Instruments Ltd) after dilution of the sample with isopropanol in order to obtain an optical concentration suitable for the measurement. For the dispersion of the sample a dispersing module Hydro SM was used with a stirrer speed of 2500 rpm. The calculation of the particle size distribution may be performed by the Mastersizer 2000 using Fraunhofer theory.)

Preferably, the amount of stabilizer in the inventive process, relative to the total amount of all components, is between 5 to 30 weight%, particularly preferably 8 to 20 weight%.

Synthesis of macromers M

A macromere is defined as a molecule which comprises one or more polymerizable double bonds able to copolymerize with vinylic monomers such as styrene and acrylonitrile and which comprises one or more hydroxyl-terminated polyether chains. Typical macromers comprise polyether polyols having an unsaturated group, which are commonly manufactured by reacting a standard polyether polyol with an organic compound containing an unsaturated group and a carboxyl, anhydride, isocyanate, epoxy or other functional group able to react with active hydrogen-containing groups. The group of useful isocyanates comprises isocyanato ethyl methacrylate (IEM) and 1,1-dimethyl meta isopropenyl benzyl isocyanate (TMI).

In a preferred embodiment of this invention, TMI is used for manufacturing the macromere (M).

Usually, macromers are synthesized in the presence of Lewis acid catalysts.

The suitable Lewis acid catalysts generally comprise tin-based, boron-based, aluminum-based, gallium-based, rare earth-based, zinc-based, or titanium-based compounds.

Representative tin-based compounds include: Dibutyltin diacetate, Dibutyltin

dibromide, Dibutyltin dichloride, Dibutyltin dilaurate, Dibutyltin dimethoxide, Dibutyltin oxide, Dimethyltin diacetate, Dimethyltin dibromide, Diphenyltin dichloride, Diphenyltin oxide, Methyltin trichloride, Phenyltin trichloride, Tin(IV) acetate, Tin(IV) bromide, Tin(IV) chloride, Tin(IV) iodide, Tin(II) oxide, Tin(II) acetate, Tin(II) bromide, Tin(II) chloride, 5 Tin(II) iodide, and Tin(II) 2-ethylhexanoate (stannous octoate). Representative boron-based compounds include: Boron tribromide, Boron trichloride, Boron trifluoride, and tris(pentafluorophenyl)borane. Representative aluminum-based compounds include: Aluminum chloride and Aluminum bromide. Representative gallium-based compounds include: Gallium chloride, Gallium bromide, and Gallium(III) acetylacetonate.

10 Representative rare earth catalysts are generally salts of Scandium, Yttrium, Lanthanum, Praseodymium, Neodymium, Erbium, Thulium, Ytterbium, Neodymium or Lutetium. Examples include: Ytterbium triflate, Ytterbium(III) acetylacetonate, Erbium(III) trifluorosulfonate (erbium triflate), Erbium(III) acetylacetonate, Holmium triflate, Terbium triflate, Europium triflate, Europium(III) trifluoroacetate, Samarium triflate, Neodymium 15 triflate, Neodymium(III) acetylacetonate, Praseodymium triflate, Lanthanum triflate, and Dysprosium triflate. Representative zinc-based compounds include Zinc chloride and Zinc bromide. Representative titanium compounds include Titanium(IV) bromide and Titanium(IV) chloride.

A number of methods for inducing reactive unsaturation into a polyol are known in the art. The 20 synthesis of useful macromers is described in WO2005/003200. Macromer A is a product obtained by reaction of a three-functional polyether polyol with 1,1-Dimethyl meta-isopropenyl benzyl isocyanate (TMI). Macromer B is a product obtained by reaction of a six-functional polyether polyol with 1,1-Dimethyl meta-isopropenyl benzyl isocyanate (TMI).

In a preferred embodiment of this invention, the macromere (M) has a functionality of 2 to 8.

25 Preferably, the macromere (M) is based on glycerine and/or sorbitol, and/or has a molecular weight of more than 4000 g/mol.

Usually, according to this invention, the amount of the macromere in relation to the total stabilizer is 30 to 70 weight%, preferably 35 to 54 weight%.

In a preferred embodiment of the inventive process, the amount of the sum of the monomers 30 styrene and acrylonitrile, relative to the total stabilizer, is 5 to 30 weight%, preferably 7 to 25 weight%.

General procedure for synthesizing a stabilizer

A glass reactor was charged with an additional polyol (P2, so-called "carrier polyol"), optionally already in the beginning a macromer or a mixture of macromers, optionally acrylonitrile, option- 35 ally styrene, optionally a chain transfer agent and heated to 125°C. A mixture of carrier polyol, initiator, styrene, acrylonitrile and macromer or a mixture of macromers were added over 100 minutes. The reaction mixture was stirred for another 20 minutes at 125 °C. The mixture was

subsequently evacuated under reduced pressure for 120 minutes at 125 °C to remove residual monomers. The obtained stabilizers were characterized and used without further purification.

The composition of representative stabilizers obtained by this procedure are shown in table x. All amounts are given in weight%. All experiment were carried out by using 0,5 weight% of azo initiator (Dimethyl 2,2'-azobis(2-methylpropionate) and 0,4% of a thiol containing chain transfer agent. The weight percentages given in this section refer to the final product (i. e. the stabilizer).

Stabilizer No.	styrene in weight%	acrylonitrile in weight%.	macro-mer A in weight%	macro-mer B in weight%	carrier Polyol, in weight %I	OH-value in mg KOH/g	viscosity in mPas
1	7,8	4,2	50	0	37	25,3	14990
2	5,5	4	0	41	48,5	25,1	9913

The additional polyol ("carrier polyol") P2 contained in the stabilizer S may be selected from polyether polyols (PEOLs), preferably from the group consisting of PEOLs with a molecular weight between 1000 and 6000 g/mol, more preferably selected from the group consisting of PEOLs with a molecular weight between 2000 and 5000 g/mol.

As the additional polyol P2 ("carrier polyol"), for example the BASF product Lupranol® 2095 may be used.

Lupranol® 2095 is a trifunctional polyether polyol with primary hydroxyl end groups and an OH no. of 35 mg KOH/g (as measured according to DIN53240) and a viscosity of 850 mPas at 25 °C (as measured according to DIN EN 12092). Lupranol® 2095 is mainly used for the production of highly elastic soft polyurethane formed foams. Furthermore, Lupranol® 2095 is used for the manufacture of semi-rigid formed parts. Other fields of use are flexible integral foams and RIM parts for the automotive sector.

In the following examples, some aspects of the present invention are illustrated.

The following dispersions were obtained by using commercially available styrene-acrylonitrile copolymer types with different compositions of styrene and acrylonitrile. For example Starex®

types from Samsung, Luran® types from Styrolution, Tyril® types from Dow Chemical, Lustran® types from Ineos can be used. The relative composition is typically between 65 and 85% by weight styrene and 15 to 35% acrylonitrile.

Comparative Example 1: Radical polymerization using castor oil as carrier polyol

- 5 714,9 g castor oil, 4,5 g macromer B (6-functional polyetherol having a hydroxyl number of 18.4 mg KOH/g, reacted with meta TMI (1-2-isocyanatopropan-2-yl)-3-(prop-1-en-2-yl)benzene)) were charged in a stirred reactor and purged with nitrogen. The mixture was heated to 125 °C. A mixture of 333,3 g acrylonitrile, 10,5 g 1-dodecanthiol, 666,7 g styrene as well as 4.7 g Vazo 64 dissolved in 714,9 g castor oil were added to the reaction mixture in 2 separate streams over
10 150 min. At the end of this reaction the mixture was allowed to react for another 15 min. The resulting product was stripped under vacuum and finally cooled to room temperature.

Viscosity: 4500 mPas measured at RT with a shear rate of 100 1/s

OH-value: 96.8 mg KOH/g

The sample was not phase stable and contained particles that precipitated overnight.

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Example 1: Use of stabilizer 2 with castor oil

- A round bottom-flasked equipped with a stirrer and a nitrogen inlet was charged with 280 g of Luran® VLR and 70 g of the stabilizer 1 and heated to 240 °C under nitrogen atmosphere. The mixture was stirred for 20 minutes at this temperature. 350 g castor oil was heated to 240 °C
20 and added with vigorous stirring. The mixture was stirred for additional 60 minutes after addition and then cooled to RT. The particle size was determined by light scattering as described before. The particle size is used as an indicator for the efficiency of the stabilizer system.

Viscosity: 5680 mPas

OH-value: 84.55 mg KOH/g

- 25 Particle size D10: 0,95 µm

Particle size D50: 2.54 µm

Particle size D90: 5.21 µm

Example 2: Use of stabilizer 1 with castor oil

- 30 A round bottom-flasked equipped with a stirrer and a nitrogen inlet was charged with 280 g of Luran® VLR and 70 g of the stabilizer 2 and heated to 240 °C under nitrogen atmosphere. The mixture was stirred for 20 minutes at this temperature. 350 g castor oil was heated to 240 °C

and added with vigorous stirring. The mixture was stirred for additional 60 minutes after addition and then cooled to RT. The particle size was determined by light scattering as described before. The particle size is used as an indicator for the efficiency of the stabilizer system.

Viscosity: 5340 mPas

5 OH-value: 84.7 mg KOH/g

Particle size D10: 0.91 μm

Particle size D50: 1.91 μm

Particle size D90: 3.82 μm

Comparative example 2 : Radical polymerization using PolyBD R20 as carrier polyol

- 10 714,9 g PolyBD R20, 4,5 g macromere B (6-functional polyetherol having a hydroxyl number of 18.4 mg KOH/g, reacted with meta TMI (1-2-isocyanatopropan-2-yl)-3-(prop-1-en-2-yl)benzene)) were charged in a stirred reactor and purged with nitrogen. The mixture was heated to 125 °C. A mixture of 333,3 g acrylonitrile, 10,5 g 1-dodecanthiol, 666,7 g styrene as well as 4.7 g Vazo 64 dissolved in 714,9 g PolyBD R20 were added to the reaction mixture in 2 separate
- 15 streams over 150 min. Stirring could not be continued due to an significant increase of viscosity. At the end of this reaction the mixture was allowed to react for another 15 min. The resulting product was stripped under vacuum and finally cooled to room temperature. Instead of a dispersion a solid, rubber like material was formed.

20 Example 3: Use of stabilizer 1 with PolyBD R20 as carrier polyol

- A round bottom-flasked equipped with a stirrer and a nitrogen inlet was charged with 200 g of Luran® VLR and 50 g of the stabilizer 1 and heated to 240 °C under nitrogen atmosphere. The mixture was stirred for 20 minutes at this temperature. 300 g PolyBD R20 was heated to 240 °C and added with vigorous stirring. The mixture was stirred for additional 60 minutes after addition
- 25 and then cooled to RT. The particle size was determined by light scattering as described before. The particle size is used as an indicator for the efficiency of the stabilizer system.

Viscosity: 17300 mPas

OH-value: 48.64 mg KOH/g

Particle size D10: 1.11 μm

30 Particle size D50: 2.61 μm

Particle size D90: 34.91 μm

Example 4: Use of stabilizer 2 with PolyBD R20 as carrier polyol

A round bottom-flasked equipped with a stirrer and a nitrogen inlet was charged with 200 g of Luran® VLR and 50 g of the stabilizer 1 and heated to 240 °C under nitrogen atmosphere. The mixture was stirred for 20 minutes at this temperature. 300 g PolyBD R20 was heated to 240 °C and added with vigorous stirring. The mixture was stirred for additional 60 minutes after addition and then cooled to RT. The particle size was determined by light scattering as described before. The particle size is used as an indicator for the efficiency of the stabilizer system.

Viscosity: 17800 mPas

OH-value: 48.42 mg KOH/g

Particle size D10: 1.12 µm

Particle size D50: 5.07 µm

Particle size D90: 40.10 µm

The experimental data show that the inventive process leads, on average, to smaller particles compared to the standard radical polymerization process. In addition, it can be seen that the polymer polyol dispersions produced by the inventive process are, on average, more homogeneous than the products obtained by the standard process.

The polymer polyol products obtainable by the inventive process usually have OH numbers of less than 300 mg KOH/g, preferably less than 200 mg KOH/g.

The polymer polyols produced by the inventive process may be used to manufacture polyurethanes. In addition, elastomers (for example cast elastomers) may be produced.

The resultant cast elastomers are suitable for industrial applications that require durable physical and mechanical properties in the final elastomers. Industrial rolls such as paper mill rolls, industrial wheels for example.

Possible applications include roller coatings, electrical encapsulation, pipeline pigs, knives, wheels, rollers, screens. Furthermore, the cast elastomers may be used for the production of formed parts as adhesives or sealants.

Line segments coated with polyurethane in the sense of this invention do not only include classically coated tube coatings, but also welding areas of tubes coated with polyurethane (so-called „field joints“) and objects coated with polyurethane connected with tubes, for example muffles, drill hole connexions, Xmas trees („Eruptionskreuze“), tube collectors, pumps and buoys.

In a preferred embodiment of this invention, the inventive line segment coated with polyurethane is a tube of an off-shore pipeline coated with polyurethane, for example for the extraction of crude oil.

- 5 Examples of embodiments of the present invention also include specific elastomer coating and sealing applications, like wheels and tires, drum coatings, spring elements and absorbers, sieves, sealing elements, for example gasket rings, doctor blades, and isolators and switches in anticorrosive coatings.

Claims

1. Process for making a polymer polyol, comprising mixing at least one melted thermoplastic styrene-acrylonitrile-copolymer (TP) with at least one polyol (P) in the presence of at least one stabilizer (S), comprising from 10 to 70% by weight, preferably 30 to 60% by weight,
5 more preferably 40 to 55% by weight, based on the sum of all components, at least one polyol P2, and at least one polyol CSP which comprises the reaction product of at least one macromer M, styrene and acrylonitrile in polyol P2, optionally with an initiator and/ or a chain transfer agent, wherein the content of macromer M of the stabilizer (S) is between 30-70 wt%, preferably 35 to 54 wt%, based on the sum of all components, and/or wherein
10 the polyol CSP is preferably comb-structured, wherein the polyol (P) comprises at least one unsaturated carbon-carbon bond per molecule, and wherein the macromer M is defined as a molecule which comprises one or more polymerizable double bonds able to co-polymerize with vinylic monomers and which comprises one or more hydroxyl-terminated polyether chains.
- 15 2. Process for making a polymer polyol according to claim 1, wherein the process is a continuous process.
3. Process for making a polymer polyol according to claim 1, wherein the process is a semi-batch process.
4. Process for making a polymer polyol according to any of claims 1 to 3, wherein polyol (P)
20 comprises at least one polybutadiene diol.
5. Process for making a polymer polyol according to claim any of claims 1 to 4, wherein polyol (P) comprises at least one natural oil with an at least one OH functional group per molecule, preferably castor oil.
6. Process for making a polymer polyol according to any of claims 1 to 3, wherein the polyol-
25 (P) consists of castor oil.
7. Process for making a polymer polyol according to any of claims 1 to 6, wherein the polyol- (P) on average has at least two, preferably 3.5, double bonds per molecule.
8. Process for making a polymer polyol according to any of claims 1 to 3 and 7, wherein the polyol (P) consists of a polybutadiene polyol.
- 30 9. Process for making a polymer polyol according to any of claims 1 to 3, wherein the polyol- (P) consists of a polybutadiene polyol and wherein the polyol (P) on average has at least 2, preferably at least 3.5, particularly preferably at least 5 double bonds per molecule.
10. Process for making a polymer polyol according to any of claims 1 to 9, wherein the stabilizer S consists of one or two polyols P2 and one or two polyols CSP which comprise the
35 reaction product of at least one macromer M, styrene and acrylonitrile in P2, optionally with an initiator selected from the group consisting of azo initiators and peroxide initiators,

and/ or a chain transfer agent selected from the group consisting of dodecane thiol, isopropanol and 2-butanol.

11. Process for making a polymer polyol according to any of claims 1 to 10, wherein the stabilizer S consists of one or two polyols P2 one or two polyols CSP which consist of the reaction product of a macromer M, styrene and acrylonitrile in P2.
12. Process for making a polymer polyol according to any of claims 1 to 11, wherein the macromer M has an average molecular weight M_w of from 1000 to 50000 g/mol, preferably 2000 to 30000 g/mol, more preferably 3000 to 20,000 g/mol.
13. Process for making a polymer polyol according to any of claims 1 to 12, wherein the macromer M has from 0.2 to 1.2 polymerizable ethylenically unsaturated groups per molecule in average and/or from 2 to 8 hydroxyl groups per molecule.
14. Process for making a polymer polyol according to any of claims 1 to 13, wherein the macromer M is obtained by reacting TMI with a polyether polyol PM, optionally in the presence of a Lewis acid catalyst.
15. Process for making a polymer polyol according to claim 14, wherein the polyether polyol PM used in the production of the macromer M is selected from the group consisting of three- and sixfunctional polyether polyols, preferably from the group consisting of glycerine, sorbitol and 1,1,1-trimethylol propane (TMP).
16. Process for making a polymer polyol according to any of claims 1 to 15, wherein the ratio of styrene to acrylonitrile in the stabilizer (S) is greater than 1:1, preferentially greater 1.5:1, most preferred greater 2:1.
17. Process for making a polymer polyol according to any of claims 1 to 16, wherein the viscosity of the stabilizer is between 1000 and 100000 mPas, preferably 5000 to 80000 mPas at 25 °C, determined according to DIN EN ISO 3219 and a shear rate of 100 1/s.
18. Process for making a polymer polyol according to any of claims 1 to 17, wherein the overall content of styrene of the stabilizer (S) is between 0,5-20 wt%, preferably 4 to 15 wt%, and/or the overall content of acrylonitrile of the stabilizer (S) is between 0,5-15 wt%, preferably 2 to 7 wt%, and/or the overall content of polyol P2 of the stabilizer (S) is between 20-70 wt%, preferably 32 to 55 wt%.
19. Process for making a polymer polyol according to any of claims 1 to 18, wherein no additional solvent is used in the stabilizer (S).
20. Process for making a polymer polyol according to any of claims 1 to 19, wherein the stabilizer (S) is produced by free radical polymerization of styrene, acrylonitrile and at least one macromer M in the presence of at least one polyol P2.

21. Process for making a polymer polyol according to any claim 20, wherein at least one chain transfer agent is used in the production of stabilizer (S), preferably selected from the group consisting of thiols and low molecular weight alcohols with MW lower than 200 g/mol.
- 5 22. Process for making a polymer polyol according to claim 21, wherein at least one, preferably all chain transfer agents are selected from the group consisting of dodecane thiol, iso propanol and 2-butanol.
23. Process for making a polymer polyol according to any of claims 21 and 22, wherein less than 5 % by weight, preferably less than 2 % by weight of the chain transfer agents are
10 used in sum, relating to the weight of the entire reaction mixture.
24. Process for making a polymer polyol according to any of claims 20 to 23, wherein the reaction temperature during the production of the stabilizer (S) is between 80° and 150 °C, preferably between 90° to 130 °C, and/ or the reaction takes between 10 min and 300 min, preferably 50 min to 200 min.
- 15 25. Process for making a polymer polyol according to any of claims 20 to 24, wherein at least one initiator is used in the production of the stabilizer (S), preferably selected from the group consisting of azo initiators or peroxides, especially preferably azoisobutyronitrile (AIBN) and/ or Dimethyl 2,2'-azobis(2-methylpropionate).
26. Process for making a polymer polyol according to any of claims 20 to 25, wherein less
20 than 1 % by weight of the initiators are used in sum in the production of the stabilizer (S), relating to the weight of the entire reaction mixture.
27. Process for making a polymer polyol according to any of claims 1 to 26, wherein the polyol P2 contained in the stabilizer S is selected from polyether polyols (PEOLs), preferably from the group consisting of PEOLs with a molecular weight M_w between 1000 and 6000
25 g/mol, more preferably selected from the group consisting of PEOLs with a molecular weight between 2000 and 5000 g/mol.
28. Process for making a polymer polyol according to any of claims 1 to 27, wherein, in a first step (1), TP, P and S are fed into an extruder (E) to form an initial dispersion, and the initial dispersion obtained from the extruder is then fed, in a second step (2), into at least
30 one rotor-stator device (RS) comprising at least one rotor-stator combination, and subsequently (3) the dispersion is cooled below the T_g of the thermoplastic styrene-acrylonitrile-copolymer (TP) to obtain the final polymer polyol.
29. Process for making a polymer polyol according to any of claims 1 to 28, wherein the extruder (E) is divided into at least two, preferably at least three separate process zones,
35 more preferably at least four separate process zones and an extruder head.

30. Process for making a polymer polyol according to any of claims 1 to 29, wherein TP is fed into the first process zone Z1 of the extruder E, S is fed into the second process zone Z2 or a later process zone, and P is fed into one of the process zones following the process zone of addition of S, wherein the terms "first" and "second" refer to the flow direction of the reaction mixture in the extruder E.
31. Process for making a polymer polyol according to any of claims 1 to 30, wherein there is at least one process zone of the extruder E with no addition of components between the addition of the stabilizer S and the addition of the polyol P.
32. Process for making a polymer polyol according to any of claims 1 to 31, wherein P is fed into at least two different process zones of the extruder E.
33. Process for making a polymer polyol according to any of claims 1 to 32, wherein the extruder (E) is operated at a barrel temperature in the range of between 160° to 250 °C, preferably 180° to 210 °C in at least one of the process zones, preferably in all of the process zones but the first.
34. Process for making a polymer polyol according to any of claims 1 to 33, wherein the extruder (E) has a rotation speed in the range of 400 to 1200 rpm, preferably 500 to 900 rpm.
35. Process for making a polymer polyol according to any of claims 1 to 34, wherein a stripping column or stripping-vessel is used after the rotor-stator device to remove volatile material.
36. Process for making a polymer polyol according to any of claims 1 to 35, wherein at least one, preferably all of the at least one-level rotor-stator devices (RS) are operated at a set temperature in the range of between 160° to 250 °C, preferably 180 °C to 220 °C.
37. Process for making a polymer polyol according to any of claims 1 to 36, wherein at least one, preferably all of the rotor-stator devices (RS) have a circumferential speed in the range of 10 to 60 s⁻¹, preferably 20 to 50 s⁻¹.
38. Process for making a polymer polyol according to any of claims 1 to 37 wherein at least one, preferably all of the rotor-stator devices comprise at least two, preferably at least three rotor-stator combinations.
39. Process for making a polymer polyol according to any of claims 1 to 38, wherein the single rotor-stator combinations have differing teeth, wherein preferably, the first rotor-stator combination has coarse teeth, and the next rotor-stator combination in the flow direction has medium fine teeth, and the third rotor-stator combination in the flow direction has fine teeth.

40. Process for making a polymer polyol according to any of claims 1 to 39, wherein the polyol (P) is added to the extruder (E) at a temperature of above 100 °C, preferably above 150 °C.
- 5 41. Process for making a polymer polyol according to any of claims 1 to 40, wherein the stabilizer (S) is added to the extruder (E) at a temperature of above 100 °C, preferably above 150 °C.
42. Polymer polyols, obtainable by the process of any of claims 1 to 41.
- 10 43. Use of a polymer polyol, obtainable by the process of any of claims 1 to 41, for the production of polyurethanes by reaction with at least one di- or polyisocyanate and optionally at least one blowing agent.
44. Use of a polymer polyol, according to claim 43, wherein the polyurethane serves as a coating.