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 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.

In an aspect, there is provided 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, 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, wherein the content of macromer M of the stabilizer (S) is between 30-70 wt%, based on the sum of all components, 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 copolymerize with vinylic monomers and which comprises one or more hydroxyl-terminated polyether chains.

In another aspect, there is provided polymer polyols, obtainable by the process as defined above.

In another aspect, there is provided the use of a polymer polyol, obtainable by the process as defined above, for the production of polyurethanes by reaction with at least one di- or polyisocyanate and optionally at least one blowing agent.

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

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, .

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).

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

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, 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, wherein the content of macromer M of the stabilizer (S) is between 30-70 wt%, based on the sum of all components, 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 copolymerize with vinylic monomers and which comprises one or more hydroxyl-terminated polyether chains.

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 the reaction product of the at least one macromer M, styrene and acrylonitrile in polyol P2 is obtained in the presence of an initiator.

5. Process for making a polymer polyol according to any of claims 1 to 4, wherein the reaction product of the at least one macromer M, styrene and acrylonitrile in polyol P2 is obtained in the presence of a chain transfer agent.

6. Process for making a polymer polyol according to any of claims 1 to 5, wherein the polyol CSP is comb-structured.7. Process for making a polymer polyol according to any of claims 1 to 6, wherein polyol (P) comprises at least one polybutadiene diol.

8. Process for making a polymer polyol according to claim any of claims 1 to 7, wherein polyol (P) comprises at least one natural oil with an at least one OH functional group per molecule, preferably castor oil.

9. Process for making a polymer polyol according to any of claims 1 to 6, wherein the polyol-(P) consists of castor oil.

10. Process for making a polymer polyol according to any of claims 1 to 9, wherein the polyol-(P) on average has at least two, preferably 3.5, double bonds per molecule.

11. Process for making a polymer polyol according to any of claims 1 to 7 and 10, wherein the polyol (P) consists of a polybutadiene polyol.

12. Process for making a polymer polyol according to any of claims 1 to 6, 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.

13. Process for making a polymer polyol according to any of claims 1 to 12, wherein the stabilizer S consists of one or two polyols P2 and one or two polyols CSP which comprise the 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, iso-propanol and 2-butanol.

14. Process for making a polymer polyol according to any of claims 1 to 13, wherein the stabilizer S consists of 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.

15. Process for making a polymer polyol according to any of claims 1 to 14, 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.

16. Process for making a polymer polyol according to any of claims 1 to 15, 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.

17. Process for making a polymer polyol according to any of claims 1 to 16, wherein the macromer M is obtained by reacting TMI with a polyether polyol PM, optionally in the presence of a Lewis acid catalyst.

18. Process for making a polymer polyol according to claim 17, 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).

19. Process for making a polymer polyol according to any of claims 1 to 18, 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.

20. Process for making a polymer polyol according to any of claims 1 to 19, 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.

21. Process for making a polymer polyol according to any of claims 1 to 20, wherein the over-all 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%.

22. Process for making a polymer polyol according to any of claims 1 to 21, wherein no additional solvent is used in the stabilizer (S).

23. Process for making a polymer polyol according to any of claims 1 to 22, 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.

24. Process for making a polymer polyol according to any claim 23, 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.

25. Process for making a polymer polyol according to claim 24, wherein at least one, preferably all chain transfer agents are selected from the group consisting of dodecane thiol, iso propanol and 2-butanol.

26. Process for making a polymer polyol according to any of claims 24 and 25, wherein less than 5 % by weight, preferably less than 2 % by weight of the chain transfer agents are used in sum, relating to the weight of the entire reaction mixture.

27. Process for making a polymer polyol according to any of claims 23 to 26, 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.

28. Process for making a polymer polyol according to any of claims 23 to 27, 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 azoisobutyro nitrile (AIBN) and/ or Dimethyl 2,2`-azobis(2-methylpropionate).

29. Process for making a polymer polyol according to any of claims 23 to 28, wherein less 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.

30. Process for making a polymer polyol according to any of claims 1 to 29, 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 g/mol, more preferably selected from the group consisting of PEOLs with a molecular weight between 2000 and 5000 g/mol.

31. Process for making a polymer polyol according to any of claims 1 to 30, 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 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.

32. Process for making a polymer polyol according to any of claims 1 to 31, wherein the extruder (E) is divided into at least two, preferably at least three separate process zones, more preferably at least four separate process zones and an extruder head.

33. Process for making a polymer polyol according to any of claims 1 to 32, 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.

34. Process for making a polymer polyol according to any of claims 1 to 33, 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.

35. Process for making a polymer polyol according to any of claims 1 to 34, wherein P is fed into to at least two different process zones of the extruder E.

36. Process for making a polymer polyol according to any of claims 1 to 35, 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.

37. Process for making a polymer polyol according to any of claims 1 to 36, wherein the extruder (E) has a rotation speed in the range of 400 to 1200 rpm, preferably 500 to 900 rpm.

38. Process for making a polymer polyol according to any of claims 1 to 37, wherein a stripping column or stripping-vessel is used after the rotor-stator device to remove volatile material.

39. Process for making a polymer polyol according to any of claims 1 to 38, 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.

40. Process for making a polymer polyol according to any of claims 1 to 39, 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}.

41. Process for making a polymer polyol according to any of claims 1 to 40 wherein at least one, preferably all of the rotor-stator devices comprise at least two, preferably at least three rotor-stator combinations.

42. Process for making a polymer polyol according to any of claims 1 to 41, 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.

43. Process for making a polymer polyol according to any of claims 1 to 42, wherein the polyol (P) is added to the extruder (E) at a temperature of above 100 °C, preferably above 150 °C.

44. Process for making a polymer polyol according to any of claims 1 to 43, wherein the stabilizer (S) is added to the extruder (E) at a temperature of above 100 °C, preferably above 150 °C.

45. Polymer polyols, obtainable by the process of any of claims 1 to 44.

46. Use of a polymer polyol, obtainable by the process of any of claims 1 to 44, for the production of polyurethanes by reaction with at least one di- or polyisocyanate and optionally at least one blowing agent.

47. Use of a polymer polyol, according to claim 46, wherein the polyurethane serves as a coating.