

[0056] 2. Production of Polymeric 1-hydroxymethylene-1,1-bisphosphonic Acids from Carboxylated Polymers

[0057] As already mentioned in part 1, it is known, that 1-hydroxymethylene-1,1-bisphosphonic acids can be made from acid chlorides $R-COCl$ or acid anhydrides with tris(trimethylsilyl)phosphite and following hydrolysis of the silyl compound or by reaction of carbonic acids with phosphorous trichloride in phosphorous acid. Surprisingly it has been found that this reaction is successful also with polymeric carbonic acids/polymeric carbonic acid halides. Polymers modified with the 1-hydroxymethylene-1,1-bisphosphonic acid groups are also part of this invention. In FIG. 12 is shown the production of polysulfone Udel® modified with 1-hydroxymethylene-1,1-bisphosphonic acid groups from PSU-carbonic acid chloride. In principal with this synthetic method all carboxylated polymers can be reacted to polymers containing the 1-hydroxymethylene-1,1-bisphosphonic acid group.

[0058] Semi empirical calculation with the Software ACD Laboratories (pK_A module) have shown surprisingly, that the acidity of 1-hydroxymethylene-1,1-bisphosphonic acids of the type $R-C(PO_3H_2)_x(OH)_y$, (here $x=2$ and $y=1$) as in FIG. 13 and FIG. 14 have a high acidity for phosphonic acids of pK_A=0 up to even pK_A=-1. Semi empirical calculation with the Software ACD Laboratories (pK_A module) on polymeric model compounds containing the 1-hydroxymethylene-1,1-bisphosphonic acid groups have shown surprisingly that also the phosphonic acid groups of the corresponding polymers show a high acidity for phosphonic acids of about pK_A=0 (FIG. 15).

[0059] 3. Production of Polymeric 1-hydroxymethylene-1,1-bisphosphonic Acids from Polymers Containing Carbonyl Groups (Aldehyde or Ceio Groups)

[0060] In the literature there is one publication describing the production of 1-hydroxymethylene-1,1-bisphosphonic acids from aldehyds⁴⁴. It has been found surprisingly, that this reaction can be carried out with polymers carrying aldehyd groups. The reaction is shown exemplarily in FIG. 16 for an aldehyd-modified polythioethersulfone made from lithiated polythioethersulfone by reaction of N,N-dimethylformamide (DMF)⁴⁵. Also surprisingly was that polymers carrying ceto groups (made for example as in⁴⁶) can be modified with this method with 1-hydroxymethylene-1,1-bisphosphonic acid groups. An example of such a reaction is shown in FIG. 17.

⁴⁴ Y. L. Xie, Q. Zhu, X. R. Qin, Y. Y. Xie, *Chinese Chemical Letters* 2003, 14(1), 25-28

⁴⁵ M. D. Guiver, H. Zhang, G. P. Robertson, Y. Dai, *Journal of Polymer Science, Part A. Polymer Chemistry* 2001, 39, 675-682

⁴⁶ J. Keres, A. Ullrich, T. Haring, U.S. Pat. No. 6,590,067; granted at Aug. 7, 2003; European Patent EP1 105 433 B1; granted at 27 Oct. 2004

[0061] In principal all common polymers containing the functional groups as mentioned in part 1 can be used.

[0062] The following polymers are preferred:

[0063] polyolefines like polyethylene, polypropylene, polyisobutylene, polynorbornene, polymethylpentene, polyisoprene, poly(1,4-butadiene), poly(1,2-butadiene)

[0064] styrene(co)polymers like polystyrene, poly(methylstyrene), poly(α,β,β -trifluorostyrene), poly(pentafluorostyrene)

[0065] polyvinylalkohols and their copolymers

[0066] polyvinylphenols and their copolymers

[0067] poly(4-vinylpyridine), poly(2-vinylpyridine) and their copolymers

[0068] perfluorinated ionomers like Nafion® or their SO_2Hal precursor of Nafion® (Hal=F, Cl, Br, I), Dow®-membrane, GoreSelect®-membrane

[0069] sulfonated PVDF and/or the SO_2Hal -precursor, whereby Hal represents fluorine, chlorine, bromine or iodine

[0070] (het)aryl main chain polymers like:

[0071] polyetherketones like polyetherketone PEK Victrex®, polyetheretherke one PEEK Victrex®, polyetherketoneketone PEKK, polyetheretherketoneketone

[0072] PEEKK, polyetherketoneetherketoneketone PEKEKK Ultrapek®

[0073] polyethersulfone like polysulfone Udel®, polyphenylsulfone Radel R®, polyetherethersulfone Radel A®, polyethersulfone PES Victrex®

[0074] poly(benz)imidazole like PBI Celazol® and other oligomers and polymers containing the (benz)imidazole building block whereby the (benz)imidazole group can be in the main chain or in the polymer side chain polyphenyleneether like e.g. poly(2,6-dimethyloxyphenylene), poly(2,6-diphenyloxyphe-nylene)

[0075] polyphenylensulfide and copolymers

[0076] poly(1,4-phenylene) or poly(1,3-phenylene), which can be modified in the side chain if necessary in with benzoyl-, naphthoyl- or o-phenyloxy-1,4-benzoyl groups, m-phenyloxy-1,4-benzoylgroups or p-phenyloxy-1,4-benzoyl groups.

[0077] poly(benzoxazole) and copolymers

[0078] poly(benzthiazole) and copolymers

[0079] poly(phtalazinone) and copolymers

[0080] polyaniline and copolymers

[0081] In principle all polymers especially all aryl main chain polymers are possible as base polymers for the polymers and polymer mixtures according to the invention. Also all possible block copolymers from these polymers, especially from aryl main chain polymers are possible, whereby the following types of block copolymers are preferred:

[0082] block copolymers made from cation exchange group modified blocks ($-COX$, POX_2 , SO_2X with $X=OH$, $OMet$, NR_2 , $Met=metal$ cation, ammonium ion, OR with $R=alkyl$ or $aryl$) and from unmodified blocks;

[0083] block copolymers made from OH group modified blocks and from unmodified block;

[0084] block copolymers made from blocks containing basic groups and from unmodified block; thereby the choice of basic groups is not limited, however preferred are heterocyclic or heteroaromatic, e.g. pyridyl-, imidazolyl-, benzimidazolyl- or pyrazolyl groups;

[0085] block copolymers, made from blocks modified with hydrophobic groups (e.g. trimethylsilyl $-Si(CH_3)_3$, trifluormethyl $-CF_3$, fluoride $-F$) and from blocks modified with cation exhcange groups ($-COX$, $-POX_2$, $-SO_2X$ with $X=OH$, $OMet$, NR_2 , $Met=metal$ cation, ammonium ion, OR with $R=alkyl$ or $aryl$);

[0086] block copolymers from acidic blocks containing cation exchange groups and blocks containing basics groups;

[0087] block copolymers with OH groups containing blocks and acidic groups containing blocks;

[0088] block copolymers with OH groups containing blocks and basic groups containing blocks.