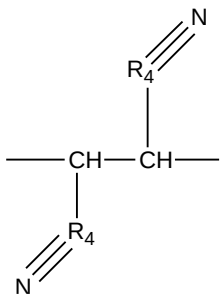
We claim:

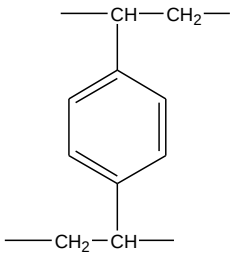
1. A porous resin for solid phase synthesis,

wherein the porous resin is a copolymer comprising repeating structural units represented by formula (I), formula (II), formula (III), and formula (IV) in its skeleton:

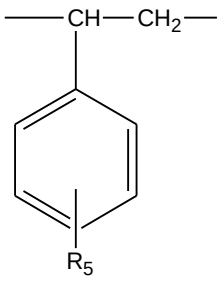


(I)

wherein, R_4=-C- or -C-CH_2-;

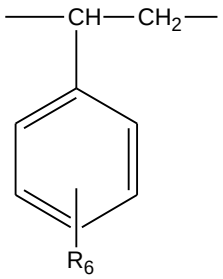


(II)



(III)

wherein, R_5 is selected from the group consisting of –OH, -CH_2OH, -NH_2, -CH_2NH_2, -CH_2OOC-C_6H_4-OH, -CH_2OOCCH_2-C_6H_4-OH, -$(CH_2)_4$OOC-C_6H_4-OH, -$(CH_2)_4$OOCCH_2-C_6H_4-OH, -CONH-C_6H_4-NH_2, -CH_2CONH-C_6H_4-NH_2, -COO-C_6H_4-OH and -CH_2COO-C_6H_4-OH;



(IV)

wherein, R_6 is –H; or $CH_3(CH_2)_n$-, n is an integer of 0-4; or $(CH_3)_2CH(CH_2)_n$-, n is an integer of 0-2; or $(CH_3)_3C$-; or $CH_3CH_2CH(CH_3)$-; or $CH_3CH_2C(CH_3)_2$-; or $CH_3CH_2CH_2CH(CH_3)$-; or $CH_3(CH_2)_n$-O-, n is an integer of 0-4.

2. The porous resin for solid phase synthesis according to claim 1, wherein the porous resin has a content of hydroxyl group or amino group of 100-1000 μmol/g.

3. The porous resin for solid phase synthesis according to claim 2, wherein the porous resin has a content of hydroxyl group or amino group of 400-700 μmol/g.

4. The porous resin for solid phase synthesis according to claim 1, wherein the porous resin has a particle size in a range of 35-200 μm.

5. The porous resin for solid phase synthesis according to claim 4, wherein the porous resin has a particle size in a range of 50-100 μm.

6. The porous resin for solid phase synthesis according to claim 1, wherein the porous resin has an average pore diameter of 10-200nm.

7. The porous resin for solid phase synthesis according to claim 6, wherein the porous resin has an average pore diameter of 40-100nm.

8. A preparation method of the porous resin for solid phase synthesis according to claim 1, comprising following steps of:

A, preparing an aqueous phase and an oil phase, respectively; the aqueous phase comprising: water, a dispersant and an inorganic salt; the oil phase comprising: a monovinyl compound, a crosslinking monomer, a functional monomer, a modified monomer, an oil-soluble surfactant, a diluent and an initiator, wherein, the monovinyl compound, the crosslinking monomer, the functional monomer and the modified monomer are monomers capable of polymerization; the oil-soluble surfactant and the diluent are incapable of polymerization but act as pore-forming agents for pore forming;

B, adding the oil phase to the aqueous phase, stirring and heating to carry out reaction, and removing the pore-forming agents after the reaction is completed, obtaining a porous polymer resin.

9. The preparation method according to claim 8, wherein the porous polymer resin is capable of undergoing a further reaction to obtain a porous resin containing a hydroxyl group or an amino group as functional groups.

10. The preparation method according to claim 8, wherein the monovinyl compound is an aromatic monovinyl compound.

11. The preparation method according to claim 10, wherein the monovinyl compound is styrene, unsubstituted or substituted with C1-C5 alkyl or alkoxy on its benzene ring.

12. The preparation method according to claim 8, wherein the crosslinking monomer is a multifunctional monomer having two or more non conjugated vinyl groups.

13. The preparation method according to claim 12, wherein the crosslinking monomer is divinylbenzene.

14. The preparation method according to claim 8, wherein the functional monomer has a double bond capable of free radical polymerization, and also has a hydroxyl group, an amino group, a halogenated group or other group capable of converting into a hydroxyl group and an amino group via reaction.

15. The preparation method according to claim 14, wherein the functional monomer is selected from the group consisting of hydroxystyrene and derivatives thereof, such as 4-hydroxystyrene; hydroxyalkyl styrene and derivatives thereof, such as 4-hydroxymethyl styrene; acyloxy styrene and derivatives thereof, such as 4-acetoxystyrene and benzoyloxy styrene; amino styrene and derivatives thereof, such as 4-amino styrene; aminoalkyl styrene and derivatives thereof, such as 4-aminomethyl styrene; haloalkyl styrene monomers, such as 4-(4-bromobutyl) styrene and p-chloromethyl styrene; 4-vinylphenyl ester monomers, such as methyl 4-vinylbenzoate and 4-ethenylbenzeneacetic acid ethyl ester.

16. The preparation method of the porous resin for solid phase synthesis according to claim 8, wherein the modified monomer has a double bond capable of free radical polymerization and two cyano groups.

17. The preparation method according to claim 16, wherein the modified monomer is selected from the group consisting of fumaronitrile and 1,4-dicyano-2-butene.

18. The preparation method according to claim 8, wherein the initiator is selected from the group consisting of organic peroxides and azo compounds.

19. The preparation method according to claim 18, wherein the initiator is selected from the group consisting of benzoyl peroxide, lauroyl peroxide, tert butyl peroxy-2-

ethylhexanoate, 2,2'-azobis(2-methylpropionitrile), 2,2'-azobis(2-methylbutyronitrile) and 2,2'-azobis(2,4-dimethyl)valeronitrile.

20. The preparation method according to claim 8, wherein the oil-soluble surfactant is not polymerizable but is insoluble or slightly soluble in water.

21. The preparation method according to claim 20, wherein the oil-soluble surfactant is selected from the group consisting of sorbitan trioleate, polyoxyethylene sorbitol beeswax derivative, sorbitan tristearate, polyoxyethylene sorbitol hexastearate, ethylene glycol fatty acid ester, propylene glycol fatty acid ester, propylene glycol monostearate, sorbitan sesquioleate, polyoxyethylene sorbitol oleate, monostearin, lanolin hydroxylated, sorbitol monooleate, propylene glycol laurate, and any combinations thereof.

22. The preparation method according to claim 8, wherein, the diluent is an organic solvent which is not polymerizable but is insoluble or slightly soluble in water.

23. The preparation method according to claim 22, wherein the diluent is selected from the group consisting of aromatic hydrocarbons such as benzene, toluene and ethylbenzene; aliphatic hydrocarbons, such as C6-C12 linear or branched alkanes or C6-C12 cycloalkanes, such as hexane, heptane, octane, dodecane, isooctane, isododecane and cyclohexane, etc; halogenated hydrocarbons such as chloroform and chlorobenzene; esters containing 4 or more carbon atoms, such as ethyl acetate, butyl acetate, dibutyl phthalate, etc; alcohols, such as C4-C12 linear or branched alkane alcohol or C4-C12 cycloalkane alcohol, such as hexanol, cyclohexanol, octanol, isooctanol, decanol and dodecanol.

24. The preparation method according to claim 8, wherein,

the dispersant is present in the aqueous phase in an amount of 0.1-5% by weight, and the inorganic salt is present in the aqueous phase in an amount of 20% by weight or

lower;

a weight ratio of the oil phase to the aqueous phase is 1:3-1:20;

the monovinyl compound in the oil phase accounts for 40-95.9% by weight based on a total weight of the monomers;

the crosslinking monomer in the oil phase accounts for 2-20% by weight based on a total weight of the monomers;

the functional monomer in the oil phase accounts for 2-20% by weight based on a total weight of the monomers;

the modified monomer in the oil phase accounts for 0.1-20% by weight based on a total weight of the monomers;

the pore-forming agents in the oil phase account for 15-70% by weight based on a total weight of the monomers;

the oil-soluble surfactant in the pore-forming agents accounts for 0.1-15% by weight based on a total weight of the pore-forming agents; and

the diluent in the pore-forming agents accounts for 85-99.9% by weight based on a total weight of the pore-forming agents.

25. The preparation method according to claim 24, wherein,

the monovinyl compound in the oil phase accounts for 60-88% by weight based on a total weight of the monomers;

the crosslinking monomer in the oil phase accounts for 5-15% by weight based on a total weight of the monomers;

the functional monomer in the oil phase accounts for 5-15% by weight based on a total weight of the monomers;

the modified monomer in the oil phase accounts for 2-10% by weight based on a total weight of the monomers; and

the pore-forming agents in the oil phase account for 25-50% by weight based on a total weight of the monomers.

26. The preparation method according to claim 8, wherein the polymerization is carried out at a temperature of 50-90 ℃.

27. The preparation method according to claim 26, wherein the polymerization is carried out at a temperature of 60-85 ℃.

28. The preparation method according to any one of claims 8-27, comprising following steps of:

adding a certain amount of purified water to a reactor, adding the dispersant in an amount which is 0.1-5% by weight of the aqueous phase and the inorganic salt in an amount which is not more than 20% by weight of the aqueous phase, and dissolving to obtain the aqueous phase;

weighing out the monovinyl compound, crosslinking monomer, functional monomer, modified monomer, pore-forming agents and initiator according to a weight ratio of the oil phase to the aqueous phase being1:3-1:20; wherein, the monovinyl compound accounts for 40-95.9% of the total weight of the monomers, the crosslinking monomer accounts for 2-20% of the total weight of the monomers, the functional monomer accounts for 2-20% of the total weight of the monomers, and the modified monomer accounts for 0.1-20% of the total weight of the monomers, the pore-forming agents account for 15-70% of the total weight of the monomers; the oil-soluble surfactant in the pore-forming agents accounts for 0.1-15% of the weight of the pore-forming agents; and the diluent accounts for 85-99.9% of the weight of the pore-forming agents, and mixing well to obtain the oil phase;

adding the oil phase to the reactor, stirring and heating to 50-90 ℃ to carry out reaction; removing the pore-forming agents after the reaction is completed, screening and collecting the resin with appropriate particle size, and vacuum drying to obtain a porous polymer resin;

carrying out a further reaction with the resin to obtain a porous resin having amino group or carboxyl group.

29. The preparation method according to claim 28, comprising following steps of:

adding a certain amount of purified water to a reactor, adding the dispersant in an amount which is 0.1-5% by weight of the aqueous phase and the inorganic salt in an amount which is not more than 20% by weight of the aqueous phase, and dissolving to obtain the aqueous phase;

weighing out the monovinyl compound, crosslinking monomer, functional monomer, modified monomer, pore-forming agents and initiator according to a weight ratio of the oil phase to the aqueous phase being1:3-1:20; wherein, the monovinyl compound accounts for 60-88% of the total weight of the monomers, the crosslinking monomer accounts for 5-15% of the total weight of the monomers, the functional monomer accounts for 5-15% of the total weight of the monomers, and the modified monomer accounts for 2-10% of the total weight of the monomers, the pore-forming agents account for 25-50% of the total weight of the monomers; the oil-soluble surfactant in the pore-forming agents accounts for 0.1-15% of the weight of the pore-forming agents; and the diluent accounts for 85-99.9% of the weight of the pore-forming agents, and mixing well to obtain the oil phase;

adding the oil phase to the reactor, stirring and heating to 60-85 ℃ to carry out reaction; removing the pore-forming agents after the reaction is completed, screening and collecting the resin with appropriate particle size, and vacuum drying to obtain a porous polymer resin;

carrying out a further reaction with the resin to obtain a porous resin having amino group or carboxyl group.

30. The preparation method according to any one of claims 8-29, comprising the following steps of:

adding 2L purified water, 20g polyvinyl alcohol and 60g sodium chloride to a 3L reactor equipped with a condenser, an agitator and a thermometer, and dissolving to obtain an aqueous phase;

weighing out 110g styrene, 10g divinylbenzene (80% by weight), 12g p-chloromethyl styrene, 8g fumaronitrile, 5g sorbitol monooleate, 45g isooctanol and 2.5g benzoyl peroxide, and mixing well to obtain an oil phase;

adding the oil phase to the reactor, stirring, and heating to 80 ℃ to carry out polymerization for 4h; washing with hot water after the polymerization is completed, removing the pore-forming agents by ethanol reflux extraction, screening and collecting resin with a particle size of 50-100 μm and vacuum drying to obtain a polymer porous resin with a chlorine content of 550 μmol/g;

adding 50g of the polymer porous resin and 500ml N,N-dimethylformamide to a 1L reactor equipped with a condenser, an agitator and a thermometer, and stirring; then adding 30g potassium phthalimide and raising the temperature to 95 ℃ to carry out reaction for 16 hours; cooling to room temperature after reaction is completed, washing twice with N,N-dimethylformamide, washing to neutral with purified water, washing three times with absolute ethanol, and filtering and drying the resin; adding 200g absolute ethanol and 50g hydrazine hydrate to the reactor, raising the temperature to 75 ℃ and reacting for 16 hours; thereafter washing three times with ethanol/purified water solution with a volume ratio of 50:50, washing with purified water to neutral, washing three times with absolute ethanol, and filtering and drying, adding 200g absolute ethanol and 50g concentrated hydrochloric acid to the reactor, raising the temperature to 60 ℃ and reacting for 6h, thereafter cooling to room temperature, washing to neutral with water, and then vacuum drying to obtain a solid phase synthesis carrier with an amino content of 543 μmol/g and an average pore diameter of 48nm measured by mercury intrusion method.

31. The preparation method according to any one of claims 8-29, comprising the following steps of:

adding 2L purified water, 20g polyvinyl alcohol and 60g sodium chloride to a 3L reactor equipped with a condenser, an agitator and a thermometer and dissolving to obtain an aqueous phase;

weighing out 111g styrene, 11g divinylbenzene (80% by weight), 13g 4-acetoxystyrene, 5g fumaronitrile, 8g sorbitol monooleate, 40g isooctanol, 20g isododecane and 2.5g benzoyl peroxide, and mixing well to obtain an oil phase;

adding the oil phase to the reactor, stirring, and raising the temperature to 78 ℃ to carry out polymerization for 6h; thereafter washing the resin with hot water,

removing the pore-forming agents by ethanol reflux extraction, screening and collecting the resin with a particle size of 50-100 μm and vacuum drying to obtain a polymer porous resin;

adding 50g of the polymer porous resin and 300ml acetonitrile to a 1L reactor equipped with a condenser, an agitator and a thermometer, and stirring; adding 7.5ml hydrazine hydrate slowly and reacting for 3h at room temperature; thereafter washing to neutral with water, and then vacuum drying to obtain a solid phase synthesis carrier having a hydroxyl group content of 550 μmol/g and an average pore diameter of 64nm measured by mercury intrusion method.

32. Use of the porous resin for solid phase synthesis of claim 1 prepared via the method according to any one of claims 8-31 in the solid phase synthesis of oligonucleotides.