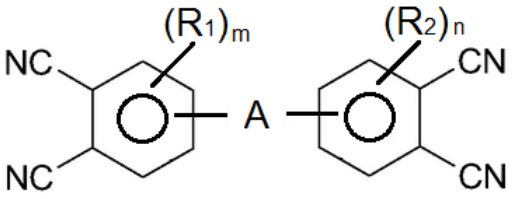
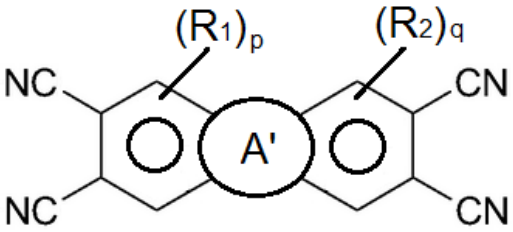
CLAIMS

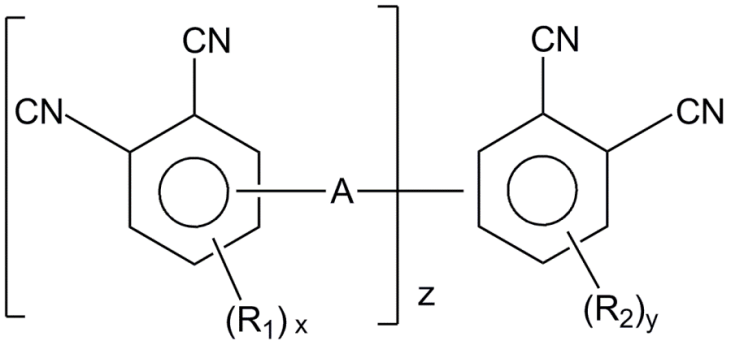
1. A method of producing a polymeric foam comprising or consisting of a polymer formed from phthalonitrile monomers having general formula (I), (II) or (III),



(I)



(II)



(III)

wherein A is a direct bond, or is a linking group selected from the group consisting of optionally substituted C_1-C_{20} alkyl, optionally substituted C_2-C_{20} alkenyl, optionally substituted C_2-C_{20} alkynyl, optionally substituted monocyclic, condensed polycyclic or bridged polycyclic C_5-C_{20} aryl, optionally substituted C_3-C_{20} mono-, or poly-cycloalkyl, optionally substituted C_3-C_{20} mono-, or poly-cycloalkenyl; optionally substituted 2-20-membered heteroalkyl, optionally substituted 2-20-membered heteroalkenyl, optionally substituted 2-20-membered heteroalkynyl, optionally substituted 5-20-membered monocyclic, condensed polycyclic or bridged polycyclic

heteroaryl, optionally substituted 3-20-membered mono-, or poly-heterocycloalkyl, and optionally substituted 3-20-membered mono-, or poly-heterocycloalkenyl; -O-, -NR-, and -S-, wherein R is selected from the group consisting of H, optionally substituted C_1-C_6 alkyl and optionally substituted C_5-C_{20} aryl;

wherein A' is nothing, or is a linking group selected from the group consisting of optionally substituted monocyclic, condensed polycyclic or bridged polycyclic C_5-C_{20} aryl and optionally substituted 5-20-membered monocyclic, condensed polycyclic or bridged polycyclic heteroaryl;

wherein each R_1 and each R_2 are independently selected from the group consisting of optionally substituted C_1-C_6 alkyl, optionally substituted C_5-C_{20} aryl, hydroxy, alkoxy, cyano, halogen group, nitro, silyl, and amino groups;

wherein m, n, x and y is independently 0, 1, 2, or 3; wherein p and q is independently 0, 1 or 2; and wherein z is an integer in the range of 1 to 20;

the method comprising

a) providing phthalonitrile monomers having general formula (I), (II), or (III) with a nanofiller;
b) mixing the monomers and nanofiller with a curing additive at a temperature sufficient to melt the monomers to form a prepolymer;
c) mixing the prepolymer with a foaming agent, and optionally a foaming stabilizer, to form a foaming mixture; and
d) simultaneously foaming and curing the foaming mixture to provide a polymeric foam.

2. The method of claim 1, wherein step d) includes heating the foaming mixture in an enclosure to a temperature which is the higher of (i) the melting temperature of the monomers, and (ii) the decomposition temperature of the foaming agent.

3. The method according to claim 1 or 2, wherein A is selected from the group consisting of Bisphenol-A, Resorcinol, and mixtures thereof.

4. The method according to any one of claims 1 to 3, wherein the nanofiller is selected from the group consisting of nanoparticles, nanorods, nanotubes, nanofibers, nanodiscs, nanoplatelets, and mixtures thereof.

5. The method according to any one of claims 1 to 4, wherein the nanofiller comprises a material selected from the group consisting of silica, fumed silica, metal oxide, carbon nanotubes, multiwalled carbon nanotubes, graphite, clay, and mixtures thereof.

6. The method according to any one of claims 1 to 5, wherein the nanofiller comprises or consists essentially of fumed silica, multiwalled carbon nanotubes, or graphite.

7. The method according to any one of claims 1 to 6, wherein the amount of nanofiller in the polymeric foam is in the range from about 0.1 wt % to about 30 wt %.

8. The method according to any one of claims 1 to 7, wherein the nanofiller is dispersed in a solvent.

9. The method according to claim 8, further comprising removing excess solvent from the mixture prior to step b).

10. The method according to any one of claims 1 to 9, wherein the curing additive comprises or consists of an aromatic amine selected from the group consisting of 1, 3-bis (4-aminophenoxy) benzene, 1, 4-bis (4-aminophenoxy) benzene, bis[4-(3-aminophenoxy)phenyl]sulfone, bis[4-(4-aminophenoxy)phenyl]sulfone, and mixtures thereof.

11. The method according to any one of claims 1 to 10, wherein the amount of curing additive in the prepolymer is in the range from about 1 mol % to about 7 mol %.

12. The method according to any one of claims 1 to 11, wherein the monomers having general formula (I), (II), or (III) is mixed with the curing additive at a temperature in the range from about 190 °C to about 250 °C.

13. The method according to any one of claims 1 to 12, wherein the foaming agent is selected from the group consisting of a metal carbonate, a low boiling point organic compound, an azo-compound, and mixtures thereof.

14. The method according to any one of claims 1 to 13, wherein the foaming agent comprises or consists of azodicarboxamide and/or its derivatives.

15. The method according to any one of claims 1 to 14, wherein the amount of foaming agent in the foaming mixture is in the range from about 1 wt % to about 20 wt %.

16. The method according to any one of claims 1 to 15, wherein the amount of foaming agent in the foaming mixture is in the range from about 1 wt% to about 5 wt %.

17. The method according to any one of claims 1 to 16, wherein the foaming stabilizer comprises or consists of a silicone-based compound.

18. The method according to any one of claims 1 to 17, wherein the foaming stabilizer comprises or consists of hydrophilic silica particles, hydrophilic ceramic particles, or mixtures thereof.

19. The method according to any one of claims 1 to 18, wherein the foaming mixture is heated at a temperature in the range from about 200 °C to about 300 °C.

20. The method according to any one of claims 1 to 19, wherein the foaming mixture is heated at a temperature of about 250 °C.

21. The method according to any one of claims 1 to 20, wherein the polymerization takes place at a faster rate that the rate of bubble generation.

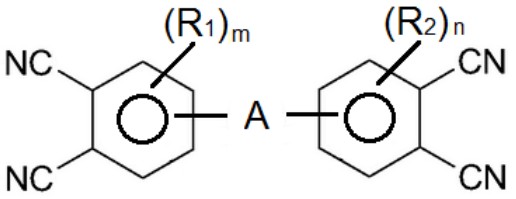
22. The method according to any one of claims 1 to 21, wherein the foam cells in the polymeric foam are essentially monodisperse.

23. The method according to any one of claims 1 to 22, wherein the foam cells in the polymeric foam have a size in the range from about 100 µm to about 2000 µm.

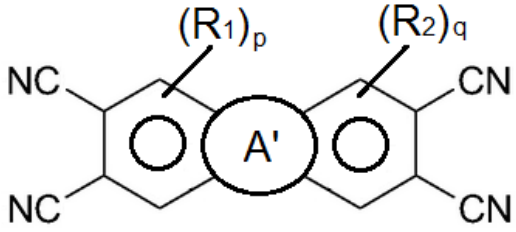
24. The method according to any one of claims 1 to 23, wherein the foam cells in the polymeric foam have a size in the range from about 100 µm to about 1500 µm.

25. The method according to any one of claims 1 to 24, wherein the foam cells in the polymeric foam are at least substantially interconnected.

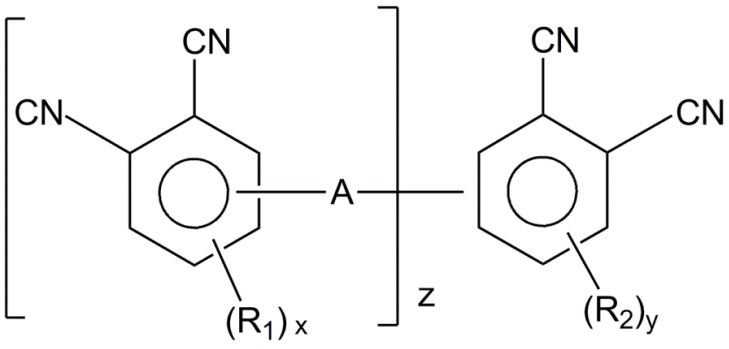
26. A polymeric foam comprising or consisting of a polymer formed from phthalonitrile monomers having general formula (I), (II) or (III),



(I)



(II)



(III)

wherein A is a direct bond, or is a linking group selected from the group consisting of optionally substituted C_1-C_{20} alkyl, optionally substituted C_2-C_{20} alkenyl, optionally substituted C_2-C_{20} alkynyl, optionally substituted monocyclic, condensed polycyclic or bridged polycyclic C_5-C_{20} aryl, optionally substituted C_3-C_{20} mono-, or poly-

cycloalkyl, optionally substituted C_3-C_{20} mono-, or poly-cycloalkenyl; optionally substituted 2-20-membered heteroalkyl, optionally substituted 2-20-membered heteroalkenyl, optionally substituted 2-20-membered heteroalkynyl, optionally substituted 5-20-membered monocyclic, condensed polycyclic or bridged polycyclic heteroaryl, optionally substituted 3-20-membered mono-, or poly-heterocycloalkyl, and optionally substituted 3-20-membered mono-, or poly-heterocycloalkenyl; -O-, -NR-, and -S-, wherein R is selected from the group consisting of H, optionally substituted C_1-C_6 alkyl and optionally substituted C_5-C_{20} aryl;

wherein A' is nothing, or is a linking group selected from the group consisting of optionally substituted monocyclic, condensed polycyclic or bridged polycyclic C_5-C_{20} aryl and optionally substituted 5-20-membered monocyclic, condensed polycyclic or bridged polycyclic heteroaryl;

wherein each R_1 and each R_2 are independently selected from the group consisting of optionally substituted C_1-C_6 alkyl, optionally substituted C_5-C_{20} aryl, hydroxy, alkoxy, cyano, halogen group, nitro, silyl, and amino groups;

wherein m, n, x and y is independently 0, 1, 2, or 3; wherein p and q is independently 0, 1 or 2; and wherein z is an integer in the range of 1 to 20, and

a nanofiller.

27. The polymeric foam according to claim 26, wherein A is selected from the group consisting of imides, bisphenols, dihydroxy benzene, ether, diether, aromatic ether, thioether, phosphine oxide, benzoxaine, and mixtures thereof.

28. The polymeric foam according to claim 26 or 27, wherein A is selected from the group consisting of Bisphenol-A, Resorcinol, and mixtures thereof.

29. The polymeric foam according to any one of claims 26 to 28, wherein the nanofiller is selected from the group consisting of nanoparticles, nanorods, nanotubes, nanofibers, nanodiscs, nanoplatelets, and mixtures thereof.

30. The polymeric foam according to any one of claims 26 to 29, wherein the nanofiller comprises a material selected from the group consisting of silica, fumed silica, metal

oxide, carbon nanotubes, multiwalled carbon nanotubes, graphite, clay, and mixtures thereof.

31. The polymeric foam according to any one of claims 26 to 30, wherein the nanofiller comprises or consists essentially of fumed silica, multiwalled carbon nanotubes, or graphite.

32. The polymeric foam according to any one of claims 26 to 31, wherein the amount of nanofiller in the polymeric foam is in the range from about 0.1 wt % to about 30 wt %.

33. The polymeric foam according to any one of claims 26 to 32, wherein the foam cells in the polymeric foam are essentially monodisperse.

34. The polymeric foam according to any one of claims 26 to 33, wherein the foam cells in the polymeric foam have a size in the range from about 100 µm to about 2000 µm.

35. The polymeric foam according to any one of claims 26 to 34, wherein the foam cells in the polymeric foam have a size in the range from about 100 µm to about 1500 µm.

36. The polymeric foam according to any one of claims 26 to 35, wherein the foam cells in the polymeric foam are at least substantially interconnected to one another.

37. The polymeric foam according to any one of claims 26 to 36, wherein the polymeric foam is sandwiched between a first skin layer and a second skin layer, the first skin layer and second skin layer being arranged on opposing sides of the polymeric foam.

38. The polymeric foam according to claim 37, wherein the first skin layer and the second skin layer are independently selected from the group consisting of metal, ceramic, glass fiber mesh, carbon fiber mesh, and mixtures thereof.

39. The polymeric foam according to claim 37 or 38, wherein at least a portion of the first skin layer and/or the second skin layer that is in contact with the polymeric foam is porous.

40. Use of a polymeric foam according to any one of claims 26 to 39 for thermal insulation, acoustic insulation, padding purposes, structural materials, flotation devices, automobile, or filtration.