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Declarations under Rule 4.17:

— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*

— *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*

Published:

— *with international search report (Art. 21(3))*

— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*

WO 2016/160187 A1

(54) **Title**: METHODS OF MANUFACTURING POLY(HEXAHYDROTRIAZINE)S VIA SUSPENSION OR EMULSION POLYMERIZATION

(57) **Abstract**: A method of manufacturing a hemiaminal dynamic covalent network (HDCN) comprises reacting a diamine and formaldehyde in the presence of a reaction medium comprising a polar solvent and a nonpolar solvent at a temperature of about 15 °C to about 100°C to form the HDCN. A composition comprising the produced HDCN can be molded to form various articles comprising poly(hexahydrotriazine)s.

METHODS OF MANUFACTURING POLY(HEXAHYDROTRIAZINE)S VIA SUSPENSION OR EMULSION POLYMERIZATION

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Application No. 14/674213, filed on March 31, 2015, which is incorporated herein by reference in its entirety.

BACKGROUND

[0002] Poly(hexahydrotriazine)s are thermosetting polymers having good Young's moduli, solvent resistance, and resistance to environmental stress cracking as disclosed by Garcia et al. in Science Vol. 344, pages 732-735. However, their applications have been limited because of the challenges encountered in making the polymers as well as forming large molded parts from the polymers. The current methods of making poly(hexahydrotriazine)s involve mixing reactants in one homogeneous phase. The reaction is not readily scalable. In addition, a gel can be formed trapping solvents inside. Therefore, poly(hexahydrotriazine)s are typically made into films to facilitate solvent evaporation. Accordingly, the industry is always receptive to improved methods of making poly(hexahydrotriazine)s that is readily scalable. It would be a further advantage if poly(hexahydrotriazine)s can be readily molded to articles having various forms.

BRIEF DESCRIPTION

[0003] The above and other deficiencies in the prior art are overcome by, in an embodiment, a method of manufacturing a hemiaminal dynamic covalent network (HDCN), the method comprising reacting a diamine and formaldehyde in the presence of a reaction medium comprising a first solvent and an immiscible second solvent at a temperature of about 15°C to about 100°C to form the hemiaminal dynamic covalent network.

[0004] In another embodiment, a method of manufacturing a hemiaminal dynamic covalent network comprises combining a polar phase with a nonpolar phase; the polar phase comprising a diamine, formaldehyde, and a polar solvent; and the nonpolar phase comprising a nonpolar solvent to form an emulsion or suspension; and reacting the diamine with formaldehyde in the emulsion or suspension to form the hemiaminal dynamic covalent network.

[0005] A method of manufacturing an article comprising a poly(hexahydrotriazine) comprises providing a composition comprising a hemiaminal dynamic covalent network

manufactured according to the methods described herein, and molding the hemiaminal dynamic covalent network to form the article comprising a poly(hexahydrotriazine).

DETAILED DESCRIPTION

[0006] The disclosure provides readily scalable methods to produce hemiaminal dynamic covalent networks. The methods use emulsion polymerization or suspension polymerization and provide HDCNs in dry powder form having controlled particle sizes. HDCNs are precursors of poly(hexahydrotriazine)s. As a further advantageous feature, the inventors have found that HDCN powders can be readily converted to poly(hexahydrotriazine)s during a molding process providing articles having various shapes and dimensions.

[0007] As used herein, a hemiaminal refers to a compound that has a hydroxyl group and an amine attached to the same carbon atom. To produce a hemiaminal, a diamine and a formaldehyde are reacted in the presence of a reaction medium comprising a first solvent and an immiscible second solvent. The reaction produces a hemiaminal dynamic covalent network (HDCN).

[0008] The first solvent is a polar solvent comprising 1-methyl-2-pyrrolidone (DMP), N,N-dimethyl formamide (DMF), N,N-dimethyl acetamide (DMAc), N-methyl-2-pyrrolidone (NMP), dimethyl sulfoxide (DMSO), hexamethylphosphoramide (HMPA), diphenyl sulfone, tetramethylene sulfone, or a combination comprising at least one of the foregoing.

[0009] The second solvent is a nonpolar solvent including aromatic hydrocarbons comprising 6 to 20 carbon atoms and aliphatic hydrocarbons. Examples of nonpolar solvent include one or more of the following: benzene; toluene; xylenes; diethyl benzene; C5-C20 alkanes; or diethyl ether. In an embodiment, the nonpolar solvent comprises an isoparaffinic hydrocarbon having less than about 5 wt.%, less than about 2 wt.%, or less than about 1 wt.% of aromatics. Isoparaffinic hydrocarbons are mixtures of hydrocarbons having carbon numbers in the range of 5-20, 7-18, 10-18, or 11-16. The isoparaffinic hydrocarbons include greater than 50 wt.%, greater than 60 wt.%, greater than 70 wt.%, or greater than 80 wt.% of isoparaffins. Branched hydrocarbons and linear hydrocarbons can also be present. Isoparaffinic hydrocarbons are commercially available, for example, as Isopar® from ExxonMobil Chemical Company.

[0010] The volume ratio of the first solvent and the second solvent is 1:1 to 1:5, 1:1 to 1:3, or 1:1 to 1:1.5.

[0011] The first solvent and the second solvent are immiscible, which means that they do not form a homogeneous mixture when added together. Thus, the polymerization can be carried out in a suspension or an emulsion.

[0012] The reaction medium can also contain water, which is either produced from the reaction of diamine and formaldehyde or carried over from the formaldehyde starting material. In an embodiment, no additional water is added to the reaction medium.

[0013] The reaction medium can comprise a surfactant, a stabilizer, or a combination comprising at least one of the foregoing. The surfactant is anionic, cationic, zwitterionic, or non-ionic. In an embodiment, the surfactant is non-ionic. Exemplary surfactant includes sorbitan esters, such as sorbitane trioleate, polyoxyethylene sorbitans, and polyoxyethylene sorbitane monooleate. Sorbitan esters are commercially available. SPAN™ 85 (sorbitane trioleate) and SPAN™ 80 (sorbitane monooleate) are specifically mentioned. The surfactant can be used alone or in combination with other surfactants known in the art. The surfactant can be present in an amount of about 0.1 to about 15 parts, about 0.5 to about 15 parts, or about 1 to about 15 parts, based on 100 total parts of the nonpolar solvent.

[0014] Any stabilizers that can lead to an improved stability of an emulsion or suspension can be used. In an embodiment, the stabilizer includes amphiphilic copolymers which have a polar unit and an apolar unit. The stabilizer can be present in an amount of about 0.01 to about 15 parts, about 0.1 to about 10 parts, or about 0.5 to about 10 parts, based on 100 total parts of the nonpolar solvent.

[0015] Exemplary diamines include 4,4'-oxydianiline,4,4′-diaminodiphenylmethane, 3,3′-methylenedianiline, and 4-aminophenyl sulfone. As used herein, formaldehyde includes paraformaldehyde, which is the polymerization production of formaldehyde with a typical degree of polymerization of about 8 to about 100 units. The molar ratio between the diamine and the formaldehyde is about 1:5 to about 3:10, or 2:5 to about 1:2.

[0016] The monomers diamine and formaldehyde, the first and second solvents, and surfactants, and stabilizers, if present, can be mixed in any order to make a reaction mixture. In an embodiment, a first phase and a second phase are separately prepared then mixed with each other to provide a reaction mixture. The first phase is a polar phase comprising the diamine, the formaldehyde, and the polar solvent. The second phase is a nonpolar phase comprising the nonpolar solvent. The nonpolar phase can also contain a surfactant, a stabilizer, or a combination comprising at least one of the foregoing. The first phase and the second phase are made by mixing the components either at room temperature or at an elevated temperature. In an embodiment, both the first phase and the second phase are

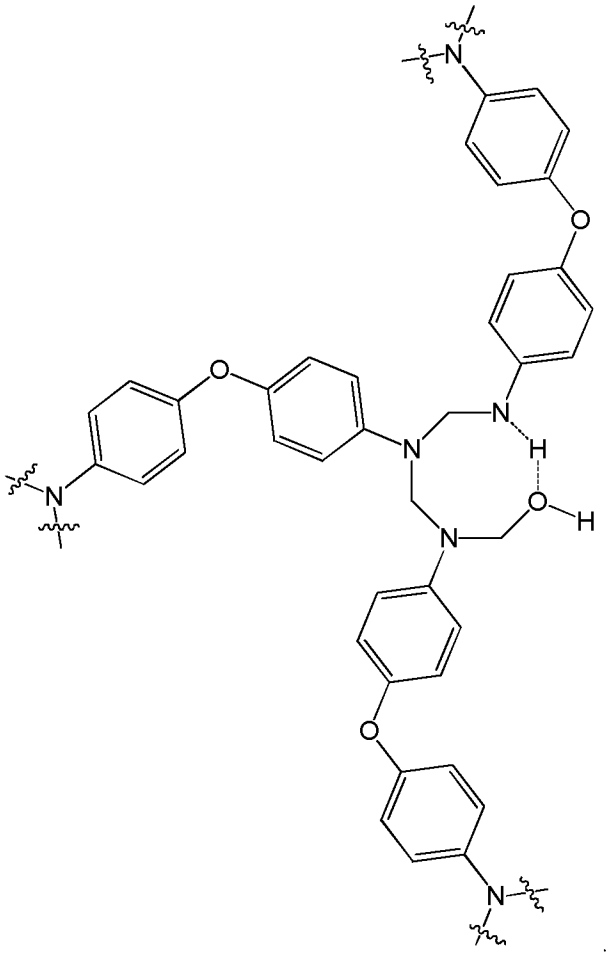
homogeneous solutions. The volume ratio of the first phase relative to the second phase is about 1:1 to about 1:5, about 1:1 to about 1: 3, or about 1:1 to about 1:1.5. Once prepared, the first phase and the second phase are combined and homogenized forming a suspension or an emulsion.

[0017] The polymerization reaction is conducted at a temperature of about 15°C to about 100°C or about 20°C to about 80°C for about 10 minutes to about 10 hours or about 1 hour to about 5 hours depending on the reaction temperature and the specific diamine used. The reaction can be conducted at atmospheric pressure.

[0018] The crude product comprising HDCN and the first and second solvents can be contacted with a polar protic solvent to precipitate the HDCN. In various embodiments, the crude product can be poured, sprayed, or fed in drop-wise into a polar protic solvent. Exemplary polar protic solvent includes methanol, ethanol, isopropanol, and the like. The precipitated HDCN is then filtered and optionally dried.

[0019] The crude product can also be extracted via spray drying. The dried HDCN powders can be obtained from the emulsion by rapidly drying with a hot gas.

[0020] When the diamine is 4,4'-oxydianiline, the produced HDCN has a structure represented by the following formula:



[0021] The process for making HDCNs described herein can be performed in batch mode, continuous mode or semi-continuous mode. The produced HDCNs can be used in one or more subsequent reactions to form materials such as poly(hexahydrotriazine)s.

[0022] Advantageously, the HDCNs can be molded into articles having different shapes. During the molding process, the HDCNs are converted to poly(hexahydrotriazine)s. The shapes and the types of the articles are not particularly limited and can vary depending on the particular applications. Accordingly, articles comprising poly(hexahydrotriazine)s having different shapes and dimensions can be provided.

[0023] The molding process is not particularly limited. The HDCNs are placed in a mold and heated to a temperature that is, for example, about 100°C to about 400°C, specifically about 150°C to about 350°C, and more specifically about 150°C to about 300°C, and held at this temperature for about 2 hours to about 10 hours. While the HDCNs are at the elevated temperature, a compressive force is applied. The force is, for example, about 10,000 pounds per square inch (psi) to about 25,000 psi, specifically about 12,000 to about 20,000

psi, and more specifically about 15,000 psi to about 20,000 psi. The formed article is then cooled and de-molded to obtain the article comprising poly(hexahydrotriazine)s.

Example

[0024] Paraformaldehyde (3.04 g) and 4,4'-oxydianiline (8.00 g) were added into N-methyl-2-pyrrolidone (60 ml). The mixture was stirred at 50°C for 0.5 h. Another oil phase was prepared from ISOPAR™ H, surfactant and stabilizer. For example, SPAN™ 85 (3.6 g) and HYPEMER™ 1599 (1.2 g) were added into ISOPAR™ H (120 mL), and allowed to form a clear solution by stirring for 5 minutes. Then the two oil phases were mixed and homogenized at 15000 rpm for 2 min. The as-formed emulsion was then transferred to a flask and stirred for 3 h. Then the emulsion was poured into ethanol (1 liter) for extraction. HDCNs powders were precipitated from ethanol and filtered out. The HDCNs powders were dried in vacuum oven at 50°C overnight. Finally, the powders were compression molded at 200°C to form the molded part.

[0025] All ranges disclosed herein are inclusive of the endpoints, and the endpoints are independently combinable with each other. "Or" means "and/or." As used herein, "combination" is inclusive of blends, mixtures, alloys, reaction products, and the like. "A combination thereof" means "a combination comprising one or more of the listed items and optionally a like item not listed." All references are incorporated herein by reference.

[0026] The use of the terms "a" and "an" and "the" and similar referents in the context of describing the invention (especially in the context of the following claims) are to be construed to cover both the singular and the plural, unless otherwise indicated herein or clearly contradicted by context. Further, it should further be noted that the terms "first," "second," and the like herein do not denote any order, quantity, or importance, but rather are used to distinguish one element from another. The modifier "about" used in connection with a quantity is inclusive of the stated value and has the meaning dictated by the context (e.g., it includes the degree of error associated with measurement of the particular quantity).

[0027] While typical embodiments have been set forth for the purpose of illustration, the foregoing descriptions should not be deemed to be a limitation on the scope herein. Accordingly, various modifications, adaptations, and alternatives can occur to one skilled in the art without departing from the spirit and scope herein.

CLAIMS

What is claimed:

1. A method of manufacturing a hemiaminal dynamic covalent network, the method comprising:

reacting a diamine and formaldehyde in the presence of a reaction medium comprising a first solvent and an immiscible second solvent at a temperature of about 15°C to about 100°C to form the hemiaminal dynamic covalent network.

2. The method of claim 1, wherein the first solvent is a polar solvent comprising one or more of the following: 1-methyl-2-pyrrolidone; N,N-dimethyl formamide; N,N-dimethyl acetamide; N-methyl-2-pyrrolidone; dimethyl sulfoxide; hexamethylphosphoramide; diphenyl sulfone; or tetramethylene sulfone.

3. The method of claim 1 or claim 2, wherein the immiscible second solvent is a nonpolar solvent comprising one or more of the following: benzene; toluene; xylenes; diethyl benzene; C5-C20 alkanes; or diethyl ether; preferably the immiscible second solvent is a paraffinic hydrocarbon.

4. The method of any one of claims 1 to 3, wherein the volume ratio of the first solvent relative to the immiscible second solvent is about 1:1 to about 1:5.

5. The method of any one of claims 1 to 4, wherein the reaction medium further comprises water.

6. The method of any one of claims 1 to 5, wherein the reaction medium further comprises one or more of a surfactant; or a stabilizer.

7. The method of claim 6, wherein the surfactant comprises sorbitan esters; and the stabilizer comprises amphiphilic copolymers.

8. The method of any one of claims 1 to 7, wherein the reaction is conducted in an emulsion or a suspension.

9. The method of any one of claims 1 to 8, wherein the diamine is 4,4'-oxydianiline,4,4′-diaminodiphenylmethane, 3,3′-methylenedianiline, or 4-aminophenyl sulfone.

10. The method of any one of claims 1 to 9, further comprising obtaining a powder of the hemiaminal dynamic covalent network by spray drying.

11. The method of any one of claims 1 to 10, further comprising contacting a reaction product comprising the hemiaminal dynamic covalent network, the first solvent, and the second solvent with a polar protic solvent to precipitate the hemiaminal dynamic covalent network; and filtering the precipitated hemiaminal dynamic covalent network.

12. A method of manufacturing a hemiaminal dynamic covalent network, the method comprising:

combining a polar phase with a nonpolar phase; the polar phase comprising a diamine, formaldehyde, and a polar solvent; and the nonpolar phase comprising a nonpolar solvent to form an emulsion or a suspension; and

reacting the diamine with formaldehyde in the emulsion or suspension to form the hemiaminal dynamic covalent network.

13. The method of claim 12, wherein the nonpolar phase further comprises one or more of a surfactant or a stabilizer.

14. The method of claim 12 or 13, wherein the volume ratio of the polar phase relative to the nonpolar phase is about 1:1 to about 1:5.

15. A method of manufacturing an article comprising a poly(hexahydrotriazine), the method comprising:

providing a composition comprising a hemiaminal dynamic covalent network manufactured according to the method of any one of claims 1 to 14, and

molding the composition to form an article comprising a poly(hexahydrotriazine).

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2016/019545

A. CLASSIFICATION OF SUBJECT MATTER

C08G 73/06(2006.01)i, C08J 5/00(2006.01)i, C08L 79/04(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C08G 73/06; C10L 1/22; C10L 1/18; C08G 8/32; C08J 5/00; C08L 79/04

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & keywords: hemiaminal dynamic covalent network, diamine, formaldehyde, polar solvent, non-polar solvent, emulsion, suspension, poly(hexahydrotriazines)s, particle

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GARCIA, J. M. et al., `Recyclable, strong thermosets and organogels via paraformaldehyde condensation with diamines`, SCIENCE, 16 May 2014, vol. 344, no. 6185, pp. 732-735 See page 732, second column, lines 5-23; figure 1, (B).	1-3,12-14
A	GHANDI, M. et al., `Novel reaction of N,N`-bisarylmethanediamines with formaldehyde. Synthesis of some new 1,3,5-triaryl-1,3,5-hexahydrotriazines`, Molecules a journal of synthetic chemistry and natural product chemistry, 2006, vol. 11, no. 7, pp. 556-563 See abstract; schemes 1, 5, 6.	1-3,12-14
A	JONES, G. O. et al., `Computational and experimental studies on the mechanism of formation of poly(hexahydrotriazine)s and poly(hemiaminal)s from the reactions of amines with formaldehyde`, Organic letters, 2014, vol. 16, no. 2 , pp. 5502-5505 See abstract; schemes 1-3; table 1.	1-3,12-14
A	US 7384434 B2 (MALFER, D. J. et al.) 10 June 2008 See column 2, line 58-column 3, line 30; claim 1.	1-3,12-14
A	US 2010-0107476 A1 (COSIMBESCU, L.) 06 May 2010 See paragraph [0047]; claims 5, 8, 9.	1-3,12-14

☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents,such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
21 July 2016 (21.07.2016)	**25 July 2016 (25.07.2016)**

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2016/019545

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2014-0148560 A1 (GEORGIA-PACIFIC CHEMICALS LLC.) 29 May 2014 See paragraphs [0121], [0122]; claims 1, 7, 8, 10.	1-3,12-14

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2016/019545

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.: 7
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
Claim 7 is unclear because it refers to multiple dependent claim 6 which does not comply with PCT Rule 6.4(a).

3. ☒ Claims Nos.: 4-6, 8-11, 15
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required addtional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of any additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2016/019545

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 7384434 B2	10/06/2008	CN 1704407 A	07/12/2005
		EP 1602707 A1	07/12/2005
		RU 2005116968 A	20/11/2006
		US 2005-0268538 A1	08/12/2005
US 2010-0107476 A1	06/05/2010	None	
US 2014-0148560 A1	29/05/2014	CN 104884488 A	02/09/2015
		EP 2925800 A1	07/10/2015
		JP 2015-537091 A	24/12/2015
		KR 10-2015-0091135 A	07/08/2015
		US 9133295 B2	15/09/2015
		WO 2014-085603 A1	05/06/2014