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(54) Title: METHODS OF PRODUCING AMINE-TERMINATED CAPROLACTONE POLYMERS AND USES OF THE PRODUCED POLYMERS

(57) Abstract: A method for the preparation of an amine-terminated caprolactone polymer having at least two terminal ends with a primary amine located thereon, comprising the steps of : (a) using a polycarboxylic acid as an initiator in the ring opening polymerization of epsilon-caprolactone to produce a polycaprolactone polymer having at least two terminal ends with a carboxylic acid located thereon; and then (b) reacting the product of step (a) with a polyamine at a temperature of above 50°C to produce an amine-terminated polycaprolactone polymer.

Methods of producing amine-terminated caprolactone polymers and uses of the produced polymers

FIELD OF THE INVENTION

The present invention provides a method of producing amine-terminated caprolactone polymers. The polymers produced by the method of the present invention have a number of potential applications.

BACKGROUND OF THE INVENTION

Amine-terminated polyethers are used as epoxy curing agents in the field of polymer chemistry. In addition, the reaction of amine-terminated polyethers with isocyanates to produce polyurea is an example of the commercial importance of amine-terminated polyethers.

Although amine-terminated polyethers have numerous applications, they are known to have very poor outdoor weatherability due to the ether linkages in the polymer backbone.

There is therefore a need for an alternative polymer with amine functionality which is less vulnerable to UV and/or oxidative attack that can be used as a replacement to amine-terminated polyethers.

Amine-terminated caprolactone polymers with their ester linkages provide such an alternative due to their comparatively more stable nature. However, although there are a number of known methods for producing caprolactone polymers having a single primary amine group present at a terminal end thereof, there are very few known methods of reliably producing caprolactone polymers having at least two terminal primary amine groups, and thus the use of amine-terminated polyethers is still preferred.

A reaction method to produce a lactone polymer having two terminal primary amine groups is discussed in the Abstract of Japanese Patent Number 63154735.

Such Patent Abstract discloses a three stage reaction process, wherein : 1) the raw material lactone polymer is obtained by ring opening polymerisation of epsilon-caprolactone monomer in the presence of an active hydrogen-containing initiator and a catalyst; 2) the resulting lactone polymer, having either a hydroxyl group on both of its terminals or a hydroxyl group on one terminal and a carboxyl group on the other terminal, is reacted with acid anhydride to produce a

lactone polymer with a carboxyl group on each of its terminals; 3) the lactone polymer dicarboxylic acid is then reacted with polyamine to produce the desired polymer.

The amine-terminated lactone polymer produced by the reaction method disclosed in the Japanese Patent Abstract has the following general formula:

$$H_2N\text{-}R'\text{-}NH\text{-}[C(=O)\text{-}R\text{-}C(=O)\text{-}NH\text{-}R']_n\text{-}NH_2 \quad [1]$$

and where R is a polylactone

R' is an alkyl, aryl e.g. $-(CH_2)_6$

A more specific example of an amine-terminated polylactone produced by the above referenced method is:

$$H_2N\text{-}(CH_2)_6\text{-}NH\text{-}[C(=O)\text{-}(CH_2)_2\text{-}C(=O)\text{-}O\text{-}R\text{-}O\text{-}C(=O)\text{-}(CH_2)_2\text{-}C(=O)\text{-}NH\text{-}(CH_2)_6]\text{-}NH_2 \quad [2]$$

where R is a polylactone.

Alternative methods of producing amine-terminated polylactones are discussed in earlier publications such as Degee P. et al in Macromolecules(1992, pages 4242-4248). Another prior publication is Stassen S. et al in J. Polym. Sci.: Polym. Chem. (1994, pages 2443-2455). Another publication is Tian D. et al in Macromolecules (1994, pages 4134-4144). Also, Yuan M. et al in Macromolecules (2000, pages 1613-1617); Jeong J. H. et al in Polymer(2002 pages 583-591); and Lu F.-Z et al in Bioconjugate Chemistry(2002, pages 1159-1162).

US Patent No. 5525683A also discloses the preparation of amine-terminated polycaprolactone polymers using methane sulfonyl groups.

SUMMARY OF THE INVENTION

The present invention provides a method of producing amine-terminated caprolactone polymers that have at least two terminal ends with a primary amine group thereon.

The method comprises the steps of: firstly using a polycarboxylic acid as an initiator in the ring opening polymerisation of epsilon-caprolactone to produce a polycaprolactone polymer having at least two terminal ends with a carboxylic acid located thereon; and secondly reacting the polymer produced by the first step of the method with a polyamine, at a temperature above 50°C, to produce an amine-terminated polycaprolactone polymer.

Although the reaction between the polycaprolactone polymer, having at least two terminal carboxylic acid groups, and a polyamine can occur effectively above 100°C, the preferable temperature at which the reaction takes place is

below 80°C so as to prevent the reaction of the internal ester groups with the terminal primary amine groups.

Preferably the polyamine used in the second step of the above method is a diamine. However it is appreciated that some triamines and tetramines could also be effectively used. The polyamine used can be liquid, especially in the case of a diamine. An example of a liquid diamine is the commercial product ETHACURE® 100.

Preferably the polycarboxylic acid used in the first step of the above method is a dicarboxylic acid. However it is appreciated that some tricarboxylic acids and tetracarboxylic acids could also be effectively used.

It is appreciated that the functionality of the amine-terminated caprolactone polymer produced by the method of the present invention may be controlled by varying the type of polycarboxylic acid used to open the epsilon-caprolactone ring.

Whilst it is appreciated that the method of the present invention is primarily concerned with the production of caprolactone polymers having two terminal ends with primary amine groups thereon, it is also appreciated that branched caprolactone polymers with more than two terminal ends having primary amine groups thereon can be produced. It is understood that the presence of additional terminal ends is determined by the type of polycarboxylic acid used as an initiator in the ring opening of epsilon-caprolactone. For example, the use of a tri carboxylic acid such as citric acid may be used to introduce a branching into the polymer produced by the splitting of epsilon-caprolactone.

A second embodiment of the present invention provides an amine-terminated caprolactone polymer that has at least two primary amine groups mounted on the terminal ends of the polymer, said polymer having the generic formula :

$H_2N\text{-}(CH_2)_6\text{-}NH\text{—}CO\text{-}(CH_2)_5\text{-}O\text{-}[C(=O)\text{-}(CH_2)_5\text{-}O]_n\text{-}C(=O)\text{-}R_1\text{-}C(=O)\text{-}[O\text{-}(CH_2)_5\text{-}C(=O)]_m\text{-}O\text{-}(CH_2)_5\text{-}CO\text{-}NH\text{-}(CH_2)_6\text{-}NH_2$

where $R_1 = (CH_2)pR_2$; and

$R_2 = CH_2$ or $CH\text{-}(CH_2)_q\text{-}C(=O)\text{-}[O\text{-}(CH_2)_5\text{-}C(=O)]_s\text{-}NH\text{-}(CH_2)_6\text{-}NH_2$

[3]

A third embodiment of the present invention provides uses of the amine-terminated caprolactone polymers of the present invention. One example of a use is as an epoxy resin curative.

Another application of the amine-terminated caprolactone polymers of the present invention is in the production of polyurea, where a reaction with isocyanate can produce a polyurea polymer.

DETAILED DESCRIPTION OF THE INVENTION

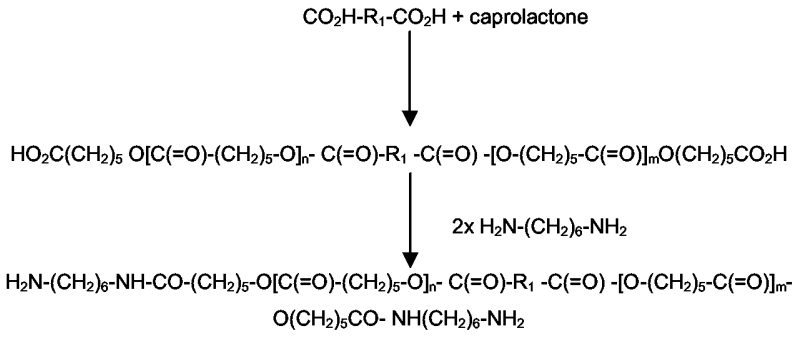
As will be appreciated from the description of the invention thus far, the provided method of producing amine-terminated caprolactone polymers comprises two main stages.

The first reaction stage being the use of a polycarboxylic acid in the splitting of epsilon-caprolactone to produce a polycaprolactone polymer having at least two terminal ends with a carboxylic acid group located thereon. It will be appreciated that a separate catalyst, in the form of an organic acid, would usually be required to promote the splitting of the epsilon-caprolactone ring. However, in some circumstances the role of the catalyst may also be satisfied by the polycarboxylic acid - this appears to be the case with citric acid.

It is appreciated that the size (i.e. Molecular weight - MWt) of the carboxylic acid-terminated caprolactone produced by the first stage reaction is determined by the ratio of the polycarboxylic acid to the monomer. Variation of the catalyst used and other reaction conditions can be used to tailor the size of polymer produced. Examples of preferred ratios of Monomer/Initiator/Catalyst are: 4269g mono/731g adipic/5g catalyst for 1000MWt; and 4126g mono/373g adipic/5g catalyst for 2000MWt.

The second reaction stage, which results in the production of the desired amine-terminated caprolactone polymer, involves the reaction of a carboxylic acid-terminated caprolactone polymer with a polyamine at a temperature of 50°C or above. It is appreciated that the carboxylic acid-terminated caprolactone polymer used in the second stage reaction would be the product of the first reaction stage. However, it will be appreciated that the second reaction stage does not necessarily have to be carried out directly after the first reaction stage.

The reactions may be considered to progress as follows :



A wide range of polycarboxylic acids may be used in the first reaction stage, and it is appreciated that the type of acid used will determine the number of potential terminals on the final amine-terminated caprolactone polymer produced by the method of the present invention.

A preferred selection of polycarboxylic acids include, but are not limited to: adipic acid; succinic acid; dodecanedioic acid; and citric acid.

It is further appreciated that a wide range of polyamines can be effectively used in the second reaction stage. In this regard a preferred selection of polyamines include: Hexamethylenediamine (HMDA); ethylenediamine; N,N'-dimethylethyenediamine; piperazine and piperazine derivatives such as 2-methylpiperazine, 2,5-dimethylpiperazine, 2,3-dimethylpiperazine, 1,4-bis(3-aminopropyl)piperazine and N-aminoethylpiperazine; isophoronediamine; polyoxypropylenediamine; bis(4-amino-3-methyldicyclohexyl)methane; diaminodicyclohexylmethane; bis(aminomethyl)cyclohexane; m-xylylenediamine; alpha-(m-aminophenyl)ethylamine; alpha-(p-aminophenyl)ethylamine; metaphenylenediamine; diaminodiphenylmethane; diaminodiphenylsulfone; norbornenediamine; inclusive of conventional aliphatic, alicyclic, and aromatic amines.

The polyamine is generally used in the second reaction stage as reactant. When the polyamine is liquid, such as the liquid diamine ETHACURE® 100, it can be used as diluent, or both as reactant and diluent.

The amount of polyamine used in the second reaction stage can vary in a wide range. It will have an effect on the viscosity of the polymer. In general, the more amine is used, the lower the viscosity of the amine.

A number of experimental examples of both the first reaction stage and the second reaction stage are provided herein after.

EXPERIMENTAL EXAMPLES

First Reaction Stage: <u>Production of carboxylic acid-terminated caprolactone polymers using a polycarboxylic acid to ring open epsilon-caprolactone monomers</u>.

1) Preparation of 1000MWt carboxylic acid-terminated caprolactone polymer from ε-caprolactone monomer using succinic acid as an initiator and p-TsOH as the reaction catalyst.
   a) 15,874.38g of ε-caprolactone monomer mixed with 2,125.62g of succinic acid and the vacuum sparged at 80°C for an hour to remove water from the mix.

b) The mixture was then heated to 160°C.

c) Then over a period of 30 minutes 90g of catalyst was added to the mixture.

d) 2 hours after the beginning of the reaction the mixture is vacuum sparged at 160°C to remove water from the mixture.

Analysis of the produced carboxylic acid-terminated caprolactone polymer by Acid Value showed the MWt of the product to be 970.

2) Preparation of 2000MWt carboxylic acid-terminated caprolactone polymer from ε-caprolactone monomer using citric acid as an initiator and as the reaction catalyst.

a) 1,891.26g of citric acid added to 16,108.74g of ε-caprolactone monomer at 80°C.

b) The mixture was heated to 120°C for 4 hours.

Analysis of the produced carboxylic acid-terminated caprolactone polymer by Acid Value showed the MWt of the product to be 1795.

3) Preparation of 2000MWt carboxylic acid-terminated caprolactone polymer from ε-caprolactone monomer using adipic acid as an initiator and p-TsOH as the reaction catalyst.

a) 4,126g of ε-caprolactone monomer mixed with 372.7g of adipic acid at 80°C under vacuum for 1.5 hours to remove water.

b) Mixture heated to 180°C (at atmospheric pressure) and the catalyst was added.

c) After 68 hours only 1.04% of the original monomer remained unreacted.

Analysis of the produced carboxylic acid-terminated caprolactone polymer by Acid Value showed the MWt of the product to be 1778.

Second Reaction Stage: Production of primary amine-terminated caprolactone polymers by reacting a polyamine with a carboxylic acid-terminated caprolactone polymer.

1) Production of 2000MWt amine-terminated caprolactone polymer by mixing a carboxylic acid-terminated caprolactone polymer - as produced by the first reaction stage shown in example 3) – with HMDA (a diamine).

a) 117.5g of HMDA (1.013 mole) melted at 50°C.

b) 882.5g of carboxylic acid-terminated caprolactone polymer is heated to 80°C and then added to the HMDA in 4 batches of about 220g over a period of 1 hour. Heated polyol is added periodically to prevent the temperature of the HMDA being increased over 80°C.

c) The reaction mix was then vacuum sparged at 60°C for 1 hour and then at 80°C for a further 1.5 hours to remove water.

The total amine content of the resultant reaction mix was analysed by titrating against 0.1M perchloric acid until the methyl violet turns from violet to blue. Results of the analysis showed that the actual primary amine content of the reaction mix was greater that the calculated theoretical primary amine content which suggested the presence of unreacted diamine in the reaction mix.

2) Production of 1000MWt amine-terminated caprolactone polymer by mixing carboxylic acid-terminated caprolactone polymer with HMDA (a diamine).
   a) 191.75g of HMDA melted at 50°C to make it molten.
   b) 819.6g of carboxylic acid-terminated caprolactone polymer heated to 80°C and then gradually mixed into HMDA over a period of 1.5 hours.
   c) The reaction mix was then vacuum sparged at120°C for 1 hour to remove water.

The total primary amine content of the reaction mix, as measured by titration against perchloric acid, was found to by less than half that of the theoretical amine content. This suggests the occurrence of a reaction between the internal esters groups and the terminal primary amine groups, which was probably due to the temperature increases during the process of the reaction.

3) Preparation of 1kg of 1000MWt amine-terminated caprolactone polymer using the method as above but with more strictly controlled conditions.
   a) 191.75g of HMDA melted at 50°C to make it molten.
   b) 819.6g of carboxylic acid-terminated caprolactone polymer heated to 80°C and then admixed to HMDA in 4 batches of about 200g over a period of 2 hours.
   c) Then the mixture was heated to 70°C for a further hour to ensure complete amine addition.
   d) The reaction mix was then vacuum sparged with N2 at 70°C for 1.75 hours, although the vacuum pressure was reduced from an initial pressure of 130mBar to 30mBar and then to 16mBar in an attempt to reduce the occurrence of frothing in the reaction mix.

Analysis of the reaction product using infra-red spectroscopy revealed presence of peaks relating to primary amines but an absence of peaks relating to diamines.

Analysis of the melting range of the reaction product was noted to be similar to that of other caprolactone polymers.

Analysis of the amine content using the above mentioned titration method suggested that majority of diamine had reacted during experiment.

4) Preparation of 2.5kg of 1000MWt amine-terminated caprolactone polymer repeating the conditions of the previous method, but on a slightly larger scale.
   a) 500g of HMDA heated to 50°C.
   b) 2107g of carboxylic acid-terminated caprolactone polymer heated to 80°C and then admixed to HMDA sequentially over a period of 4 hours.
   c) The reaction mix then vacuum sparged at 84°C for 1.5 hours.

   Analysis of the product of the above experiment provided similar results to those collected from the previous method.

5) Preparation of 1kg of 2000MWt amine-terminated caprolactone polymer by mixing a carboxylic acid-terminated caprolactone polymer - as produced by the first reaction stage shown in example 2) – with HMDA (a diamine).
   a) 154.6g of HDMA heated to 50°C.
   b) 845.4g of carboxylic acid-terminated caprolactone polymer is heated to 80°C and then added to HMDA in 3 batches of about 280g over a period of about an hour.
   c) The reaction mix was then vacuum sparged at 72°C.

   Analysis of the product indicated a completed reaction, although difficulties with the sparging equipment left residual moisture in the mix.

CLAIMS

1. - A method for the preparation of an amine-terminated caprolactone polymer having at least two terminal ends with a primary amine located thereon, comprising the steps of :

a) using a polycarboxylic acid as an initiator in the ring opening polymerisation of epsilon-caprolactone to produce a polycaprolactone polymer having at least two terminal ends with a carboxylic acid located thereon; and then

b) reacting the product of step a) with a polyamine at a temperature above 50°C to produce an amine-terminated polycaprolactone polymer.

2. - The method of claim 1, wherein the reaction of step b) is carried out at temperature below 80°C.

3. - The method of claim 1 or 2, wherein the polyamine used in step b) is a diamine.

4. - The method of claim 1, 2 or 3, wherein the polycarboxylic acid used in step a) is a dicarboxylic acid.

5. - The method of any of the preceding claims, wherein the polyamine used in step b) is selected from the group consisting of: Hexamethylenediamine (HMDA); ethylenediamine; N,N'-dimethylethyenediamine; piperazine and piperazine derivatives such as 2-methylpiperazine, 2,5-dimethylpiperazine, 2,3-dimethylpiperazine, 1,4-bis(3-aminopropyl)piperazine and N-aminoethylpiperazine; isophoronediamine; polyoxypropylenediamine; bis(4-amino-3-methyldicyclohexyl)methane; diaminodicyclohexylmethane; bis(aminomethyl)cyclohexane; m-xylylenediamine; alpha-(m-aminophenyl)ethylamine; alpha-(p-aminophenyl)ethylamine; metaphenylenediamine; diaminodiphenylmethane; diaminodiphenylsulfone; norbornenediamine; and also including conventional aliphatic, alicyclic, and aromatic amines.

6. - The method of any of the preceding claims, wherein the polycarboxylic acid used in step a) is selected from the group consisting of: adipic acid; succinic acid; dodecanedioic acid; and citric acid.

7. - The method of any of the preceding claims, wherein step a) further involves an acid catalyst.

8. - The method of claim 7, wherein the acid catalyst is an organic acid such as p-Tolunesulphonic acid.

9. - The method of claim 7, wherein the role of acid catalyst is provided by the polycarboxylic acid initiator.

10. - The method of any of the preceding claims, wherein the ratio of monomer/initiator/catalyst used in step a) is 4269:731:5.

11. - The method of any one of claims 1 to 9, wherein the ratio of monomer/initiator/catalyst used in step a) is 4126:373:5

12. - The use of an amine-terminated caprolactone polymer produced by the method of any of claims 1 to 11 as a epoxy resin curative.

13. - The use of an amine-terminated caprolactone polymer produced by the method of any of claims 1 to 11 in the production of polyurea.

14. - The use of claim 13, wherein the caprolactone polymer is reacted with isocyanate to produce a polyurea polymer.

15. - An amine-terminated caprolactone polymer having the general formula :

H_2N-$(CH_2)_6$-NH-CO-$(CH_2)_5$O-[C(=O)-$(CH_2)_5$-O]$_n$- C(=O)-R_1-C(=O) -[O-$(CH_2)_5$-C(=O)]$_m$-O-$(CH_2)_5$ CO-NH-$(CH_2)_6$-NH_2

Wherein $R_1 = (CH_2)_pR_2$;

$R_2 = CH_2$ or CH-$(CH_2)_q$-C(=O)-[O-$(CH_2)_5$-C(=O)]$_s$-NH-$(CH_2)_6$-NH_2

m is a whole number between 0 and 500;

n is a whole number between 0 and 500;

wherein m + n is >/= 3;

s is a whole number between 0 and 500;

p is a whole number between 0 and 100; and

q is a whole number between 0 and 100.

16. - The caprolactone polymer of claim 15, wherein p is 3.

17. - The caprolactone polymer of claim 15 or 16, wherein n is </= 20.

18. - The caprolactone polymer of any of claims 15 to 17, wherein m is </= 20.

19. - The caprolactone polymer of any of claims 15 to 18, wherein m + n is </= 20.

20. - The use of an amine-terminated caprolactone polymer according to any of claims 15 to 19 as an epoxy resin curative.

21. - The use of an amine-terminated caprolactone polymer according to any of claims 15 to 19 in the production of polyureas.

22. - The use of claim 19, wherein the caprolactone polymer is reacted with isocyanate to produce a polyurea polymer.

INTERNATIONAL SEARCH REPORT

International Application No
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A. CLASSIFICATION OF SUBJECT MATTER
C08G63/08 C08G63/664 C08G63/685 C08G63/91 C08G63/78

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

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, PAJ, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 525 683 A (ADKINS ET AL) 11 June 1996 (1996-06-11) the whole document -----	1-22
A	PATENT ABSTRACTS OF JAPAN vol. 012, no. 426 (C-542), 10 November 1988 (1988-11-10) & JP 63 154735 A (DAICEL CHEM IND LTD), 28 June 1988 (1988-06-28) abstract -----	1-22
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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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Date of the actual completion of the international search	Date of mailing of the international search report
25 November 2005	02/12/2005

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Marquis, D

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP2005/055306

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	S. STASSEN, S. ARCHAMBEAU, PH. DUBOIS,* R. JEROME, AND PH. TEYSSIE: "Macromolecular Engineering of Polylactones and Polylactides. XVI. On the Way to the Synthesis of w-Aliphatic Primary Amine Poly (c-caprolactone) and Polylactides" JOURNAL OF POLYMER SCIENCE PART A POLYMER CHEMISTRY, vol. 32, 1994, pages 2443-2455, XP002321541 the whole document	1-22
A	YING SONG, LIJIAN LIU, XIAOCHENG WENG AND RENXI ZHUO: "Acid-initiated polymerization of epsilon-caprolactone under microwave irradiation and its application in the preparation of drug controlled release system" JOURNAL OF BIOMATERIAL SCIENCE POLYMER EDITION, vol. 14, no. 3, 2003, pages 241-253, XP009045394 the whole document	1-22

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/EP2005/055306

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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