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(54) Title: WATERSOLUBLE LINEAR COPOLYMER

(57) Abstract: The invention concerns watersoluble linear heterochain dipolymer having the general formula: $(-CH_2-CR_1R_2)n-(R_4-NHCO-R_5-NHCO-R_4)m$ where R_1 can be atom of hydrogen or alkyl CH_3, R_2 can be COOH, $CONH_2$, (CH_3)-COOH depending on the kind of vinyl monomer, R_3 is atom of hydrogen or OH group, depending on the kind of divinyl monomer, R_4 can be (CH_2-CHR_3) or $(CH_2-CHR_3-CH_2)$, R_5 can be (CH_2) or $(CH(OH))_2$, depending on the kind of divinyl monomer, m and n - interrelationships between the vinyl and divinyl monomers, herewith the correlation m/n is within 10 to 100, herewith the sections of the chain in which amide groups -CO-NH- are present, are connected with the similar sections through the H-linkages between the amide and carboxyl groups. Such a substance belongs to polymer of a new structure with different physical- chemical properties. Amide section of the molecule is unique according to its structural properties and according to peculiar intermolecular interactions. Due to the hybridization of nitrogen, carbon and hydrogen atoms in the amine group, this section is almost flat. What is also important is that the hydrogen, connected with the nitrogen atom and oxygen atom in carbon groups are able to create the strong hydrogen linkage. Besides in the mentioned substance the cross-cross-linked net of polymer is not created. Therefore the macromolecule of the substance is hydrophilic 3D matrix which arises on the account of H-linkages between the amide and carboxyl groups of polyamide, which keeps the water environment.

WATERSOLUBLE LINEAR COPOLYMER

The invention belongs to the chemistry of high molecular substances more specifically to the synthetic high molecular substances, the chain of which can be hydrophilic 3D matrix arising due to H-linkages that emerge between the amide and carboxylic groups of polyamides and provide the possibility to keep the water environment.

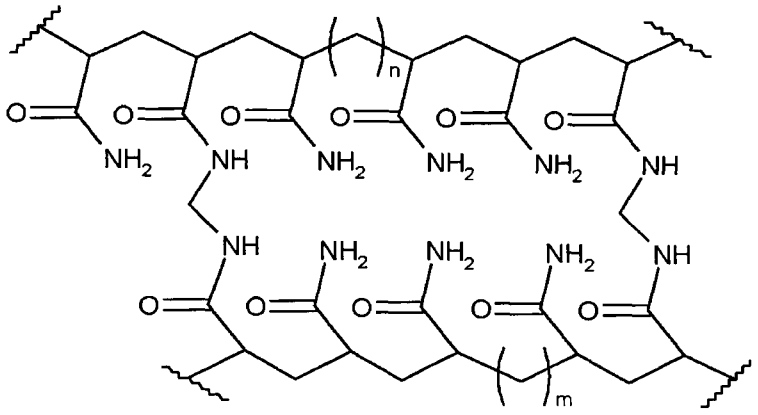
In the variety of polymer systems one can distinguish netlike or cross-linked polymers, the chains of which are connected by the covalent connections with the creation of the single space structure – polymer net. The characteristic properties of netlike polymers are the absence of viscous-flow state and little solubility in any solvent. Netlike polymers swelled in the solvent are called gels.

But the unique properties of the polymer group that provide the possibility to keep water environment and unusual sensibility to external conditions (pH, solvent content, temperature) attract the interest of the researchers. The creation of membranes with the controlled penetration, carriers of treatment preparations and their direct transport, new fillers, work at the new types of robots, plant growing in the new nutritional solutions – all these are possible due to the unique properties of such substances.

Quite a lot of substances on the basis of cross-linked polyacrylamide are developed and used nowadays. They are received usually from the following elements: acrylamide and methylene-bis-acrylamide in which the linear chains of polyacrylamide as carbochain homopolymer are connected by methylene-bis-acrylamide by the strong covalent connections, in other words cross-linked by the methylene-bis-acrylamide with the creation of 3D net, centers of which keep water. These are the chemically stable substances with the little solubility and small indexes of swelling under the normal conditions.

Because of the peculiarities of their structure these substances have the steady character (as their 3D net is based on the strong covalent connections).

For example (patent RU2301814):



As a result one can come to the conclusion that the high cross-linking by the cross-linker of 3D net of homochain polyacrylamide, restrict the swelling and fluidity in the solvent and lead to such a negative property as tixotropy. As a result these substances have the general properties: swell only during 80-100 hours at high temperatures (for example RU2301814), which points out on the cross-cross-linked polyacrylamide with branched structure.

These properties of polymers as solubility, ability to thick flow, stability, high sensibility to the creation of covalent chemical connections between the macromolecules (the so called cross-linking).

Solubility of polymers and their chemical stability depend on the peculiarities of the structure, presence of branching, cross-linkages, length of macromolecule and other factors.

Cellulose is a known watersoluble cross-linked dipolymer. It has three dimensional structure formed with the help of acrylamide or acrylamide and acrylate linked through the divinyl monomer that is used in the composition and has water and group of salts (see, patent US4051086).

Upper boarder line of the swelling of known watersoluble cross-linked dipolymer is restricted by the low values, besides strictly linked and three dimensional structure restricts its fluidity. Copolymer is characterized by the long termed chemical stability, which is undesirable in some practical cases.

Watersoluble cross linked dipolymer which has the three dimensional structure (see, patent JP6227328) formed on the basis of ammonium acrylate and linking agent is also known.

Upper boarder line of the swelling of known watersoluble cross-linked dipolymer is restricted by the low values, besides strictly linked and three dimensional

structure restricts its fluidity. Copolymer is characterized by the long termed chemical stability, which is undesirable in some practical cases.

The aim of the development work is the creation of watersoluble linear heterochain dipolymer on account of low-energetic connections of monomers, that create it, which is hydrophilic 3D matrix that keeps water environment and gives it watersolubility, increases fluidity and reduces its chemical stability.

To fulfill this aim watersoluble linear heterochain dipolymer has the general formula:

$$(-CH_2-CR_1R_2)_n-(R_4-NHCO-R_5-NHCO-R_4)_m$$

in which

R_1 can be atom of hydrogen or alkyl CH_3,

R_2 can be COOH, $CONH_2$, (CH_3)-COOH depending on the kind of vinyl monomer,

R_3 is atom of hydrogen or OH group, depending on the kind of divinyl monomer,

R_4 can be (CH_2-CHR_3) or $(CH_2-CHR_3-CH_2)$,

R_5 can be (CH_2) or $(CH(OH))_2$, depending on the kind of divinyl monomer.

m and n – interrelationships between the vinyl and divinyl monomers,

herewith the correlation m/n is within 10 to 100,

herewith the sections of the chain in which amide groups -CO-NH- are present, are connected with the similar sections through the H-linkages between the amide and carboxyl groups.

Such a substance belongs to the polymer of new structure, that can be referred to the watersoluble dipolymers, that can be received in a way of copolymerization of vinyl monomers of group of ethylene carboxylic acid $CH_2=CH-COOH$ and its derivatives (methyl-acrylic acid (2-methylpropene acid) $CH_2=C(CH_3)-COOH$, acrylamide $(CH_2=CH-CO-NH_2)$, methylmethacrylate $(CH_2=C(CH_3)-COOCH_3$, and divinyl monomers that have in their content amide groups (-CO-NH-) N,N'-diallyltartardiamide (DATD) $-CH_2=CH-CH_2-NH-CO-CH(OH)-CH(OH)-CO-NH-CH_2-CH=CH_2$, BISAM $(C_2H_3-CO-NH-CH_2-CO-NH-C_2H_3)$ into the linear dipolymer. After the copolymerization as a consequence of the receiving the amide groups -CO-NH- by the main chain, the homopolymer gets the structure of heteropolymer (polyamide) with the different physical-chemical properties.

Polyamides are the heterochain polymers, in which in the main chain of macromolecule the amide groups -CO-NH- are present. Carbon-chain polymers with the side amide groups -CO-NH_2, for example polyacrylamide, do not belong to the polyamides.

Amide section of the molecule is unique according to its structure properties and according to the peculiar intermolecular interactions. Due to the hybridization of nitrogen, carbon and hydrogen atoms in the amine group, this section is almost flat. What is also important is that the hydrogen, connected with the nitrogen atom and oxygen atom in carbon groups are able to create the strong hydrogen linkage.

Besides in the mentioned substance the cross-cross-linked net of polymer is not created. Therefore the macromolecule of the substance is hydrophilic 3D matrix which arises on the account of H-linkages between the amide and carboxyl groups of polyamide, which keeps water environment.

H-linkages are approximately 20 times less strong than covalent. Unlike the usual chemical linkages, H-linkage arises not as a result of single-stage synthesis using the radical linking agent but is created under the correspondent artificial circumstances.

The distinctive feature of the H-linkages is comparatively low strength, its energy is almost one order less than the energy of covalent chemical linkage for example.

These exactly linkages provide the big swelling and watersolubility of the mentioned substance.

In some variants of realization of watersoluble linear heterochain dipolymer the vinyl monomers are chosen from the group of ethylene carboxylic acid CH_2=CH-COOH and its derivatives (methylacrylic acid (2-methylpropene acid) CH_2=C(CH_3)-COOH,

and acrylamide (CH_2=CH-CO-NH_2)

or methylmethacrylate (CH_2=C(CH_3)-$COOCH_3$

The usage of the mentioned peculiarities in dipolymer additionally increases the swelling of the target substance.

In some variants of realization of watersoluble linear heterochain dipolymer the vinyl monomers are chosen from the group of N,N'-diallyltartardiamide (DATD)-CH_2 = CH-CH_2-NH -CO-CH(OH)-CH(OH)-CO-NH-CH_2-CH=CH_2, BISAM (C_2H_3-CO-NH-CH_2-CO-NH-C_2H_3).

The usage of the mentioned peculiarities in dipolymer additionally increases the solubility of the target substance.

Watersoluble linear heterochain dipolymer is illustrated by the examples. On the figure 1 the structure of watersoluble linear heterochain dipolymer with the mentioning of the H-linkages between the amide and carboxyl groups is graphically represented in general view.

The substances in the general view are received by two step polymerization in water environment with the initiating agents of polymerization. The following substances can be used as the initiating agents of the first grade of polymerization:

Tetramethylethylenediamine (TEMED) $C_6H_{16}N_2$ - $(CH_3)_2N\text{-}CH_2\text{-}CH_2\text{-}N(CH_3)_2$,

Dimethylaminopropionitrile (DMAPN) $C_5H_{10}N_2$ - $(CH_3)_2N\text{-}CH_2\text{-}CH_2\text{-}CN$,

Ammonium persulphate (APS) $(NH_4)_2S_2O_8$

6,7-Dimethyl-9-(D-1-ribitil) – isoalloxazine (riboflavin) $C_{17}H_{20}N_4O_6$

Example 1

Target dipolymer on the basis of methyl-acrylic acid and BISAM was received by two step polymerization in water environment with the initiating agents of polymerization.

Polymerization was performed according to the following scheme.

To receive 100 ml of solution which contains 5 weight percent of polymethyl-acrylic acid, 5 ml of methyl-acrylic acid (MAA) were used, BISAM 0,009 g was taken as a divinyl monomer in an amount of 1 section for 100 sections of polymethyl-acrylic acid. Water solution of ammonium persulphate (APS) (0,5 g) and small quantity of dimethylaminopropionitrile (DMAPN) were added. The received solution was mixed and left for 45 minutes. After that primarily synthesized preproduct was taken out of the glass and comminuted.

The preproduct was scoured with distilled water, after that the homogenization was performed mechanically (under the ultraviolet lamp) adding drop by drop water solution of riboflavin – this way the second step of polymerization was performed.

Example 2.

Target dipolymer on the basis of methyl-acrylic acid and (DATD) was received by two step polymerization in water environment with the initiating agents of polymerization.

To receive 100 ml of solution which contains 5 weight percent of acrylic acid, 5 ml of acrylic acid (AA) were used, N,N'-diallyltartardiamide (DATD) 0,65 g was taken

as a divinyl monomer in an amount of 1 section for 80 sections of acrylic acid. Water solution of ammonium persulphate (APS) (0,5 g) and small quantity of dimethylaminopropionitrile (DMAPN) were added. The received solution was mixed and left for 45 minutes at room temperature. After that primarily synthesized preproduct was taken out of the bottle and comminuted.

The preproduct was scoured with distilled water, after that the homogenization was performed mechanically (under the ultraviolet lamp) adding drop by drop water solution of riboflavin – under these circumstances the second step of polymerization was performed.

Example 3.

Target dipolymer on the basis of acrylamide and BISAM was received by two step polymerization in water environment with the initiating agents of polymerization.

To receive 100 ml of solution which contains 4 weight percent of acrylamide, 4 g of acrylamide (AA) were used, BISAM 0,08 g was taken as a divinyl monomer in an amount of 1 section for 50 sections of acrylamide. Water solution of ammonium persulphate (APS) (0,5 g) and small quantity of dimethylaminopropionitrile (DMAPN) were added. The received solution was mixed and left for 45 minutes. After that primarily synthesized preproduct was taken out of the bottle and comminuted.

The preproduct was scoured with distilled water, after that the homogenization was performed mechanically (under the ultraviolet lamp) adding drop by drop water solution of riboflavin – under these circumstances the second step of polymerization was performed.

CLAIMS

1. Watersoluble linear heterochain dipolymer of general formula:

$(-CH_2-CR_1R_2)_n-(R_4-NHCO-R_5-NHCO-R_4)_m$

where

R_1 can be atom of hydrogen or alkyl CH_3,

R_2 can be COOH, $CONH_2$, (CH_3)-COOH depending on the kind of vinyl monomer,

R_3 is atom of hydrogen or OH group, depending on the kind of divinyl monomer,

R_4 can be (CH_2-CHR_3) or $(CH_2-CHR_3-CH_2)$,

R_5 can be (CH_2) or $(CH(OH))_2$, depending on the kind of divinyl monomer.

m and n – interrelationships between the vinyl and divinyl monomers,

herewith the correlation m/n is within 10 to 100,

herewith the sections of the chain in which amide groups -CO-NH- are present, are connected with the similar sections through the H-linkages between the amide and carboxyl groups.

2. Watersoluble linear heterochain dipolymer according to claim 1, where the vinyl monomers were chosen from the group of ethylene carboxylic acid CH_2=CH-COOH or its derivatives (methyl-acrylic acid (2-methylpropane acid) $CH_2=C(CH_3)$-COOH, and acrylamide (CH_2= CH-CO-NH_2) or methylmethacrylate $CH_2=C(CH_3)$-$COOCH_3$.

3. Watersoluble linear heterochain dipolymer according to claim 1, where the vinyl monomers were chosen from the group of N,N'-diallyltartardiamide (DATD) - CH_2=CH-CH_2-NH-CO-CH(OH)-CH(OH)-CO-NH-CH_2-CH=CH_2, BISAM (C_2H_3-CO-NH-CH_2-CO-NH-C_2H_3).

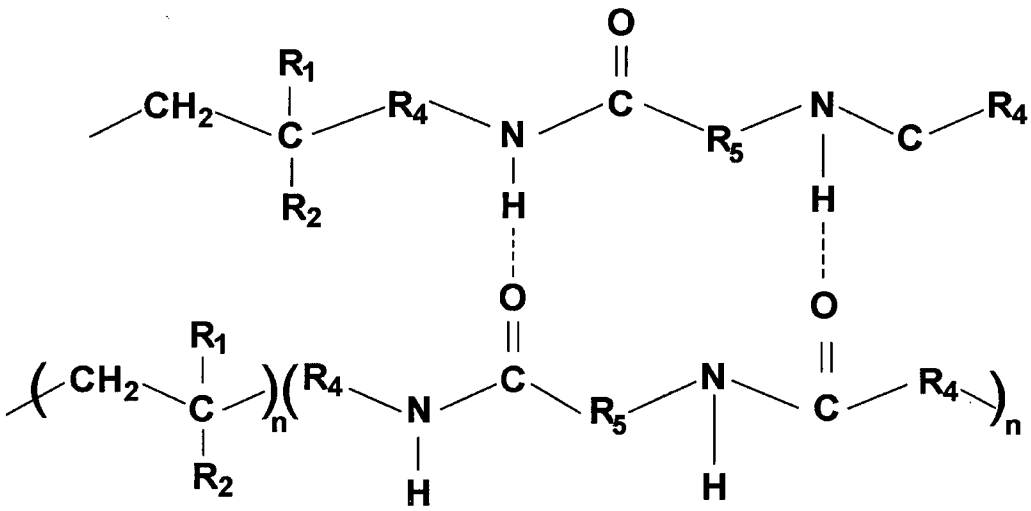


Fig. 1

INTERNATIONAL SEARCH REPORT

International application No
PCT/UA2012/000052

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08G81/02 C08F222/38 C08F220/56 C08F2/10 C08F220/06 C08F226/02
ADD.
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 C08F

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 practicable, search terms used)
EPO-Internal, 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 4 658 000 A (TYIHAK ERNO [HU] ET AL) 14 April 1987 (1987-04-14) example 9	1-3
A	US 5 055 521 A (PARSY ROLAND [FR] ET AL) 8 October 1991 (1991-10-08) example 3	1-3
A	US 2004/068071 A1 (HOFF HEINZ [CH] ET AL) 8 April 2004 (2004-04-08) example 15	1-3

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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"O" document referring to an oral disclosure, use, exhibition or other means

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
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INTERNATIONAL SEARCH REPORT

Information on patent family members

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