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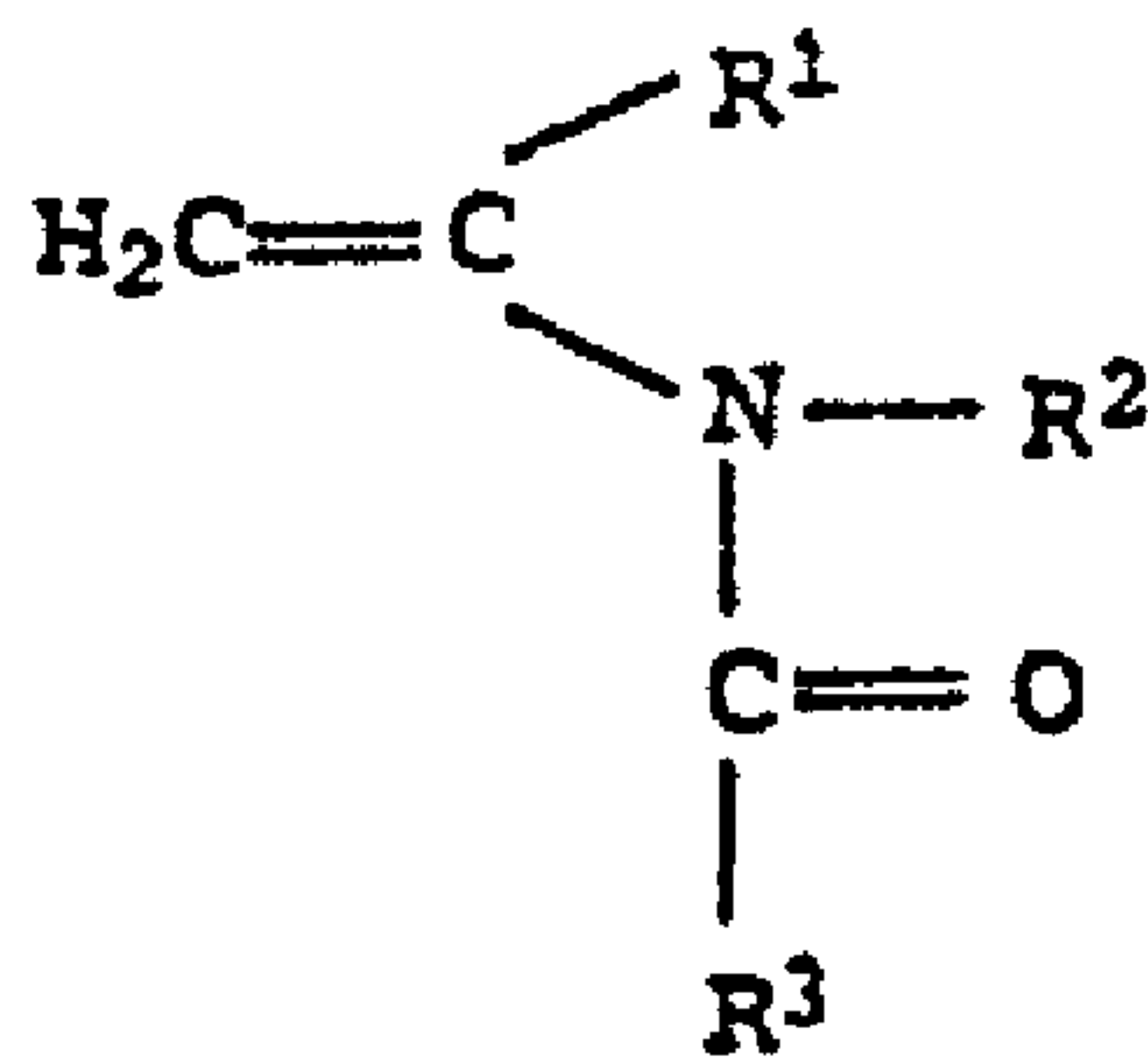
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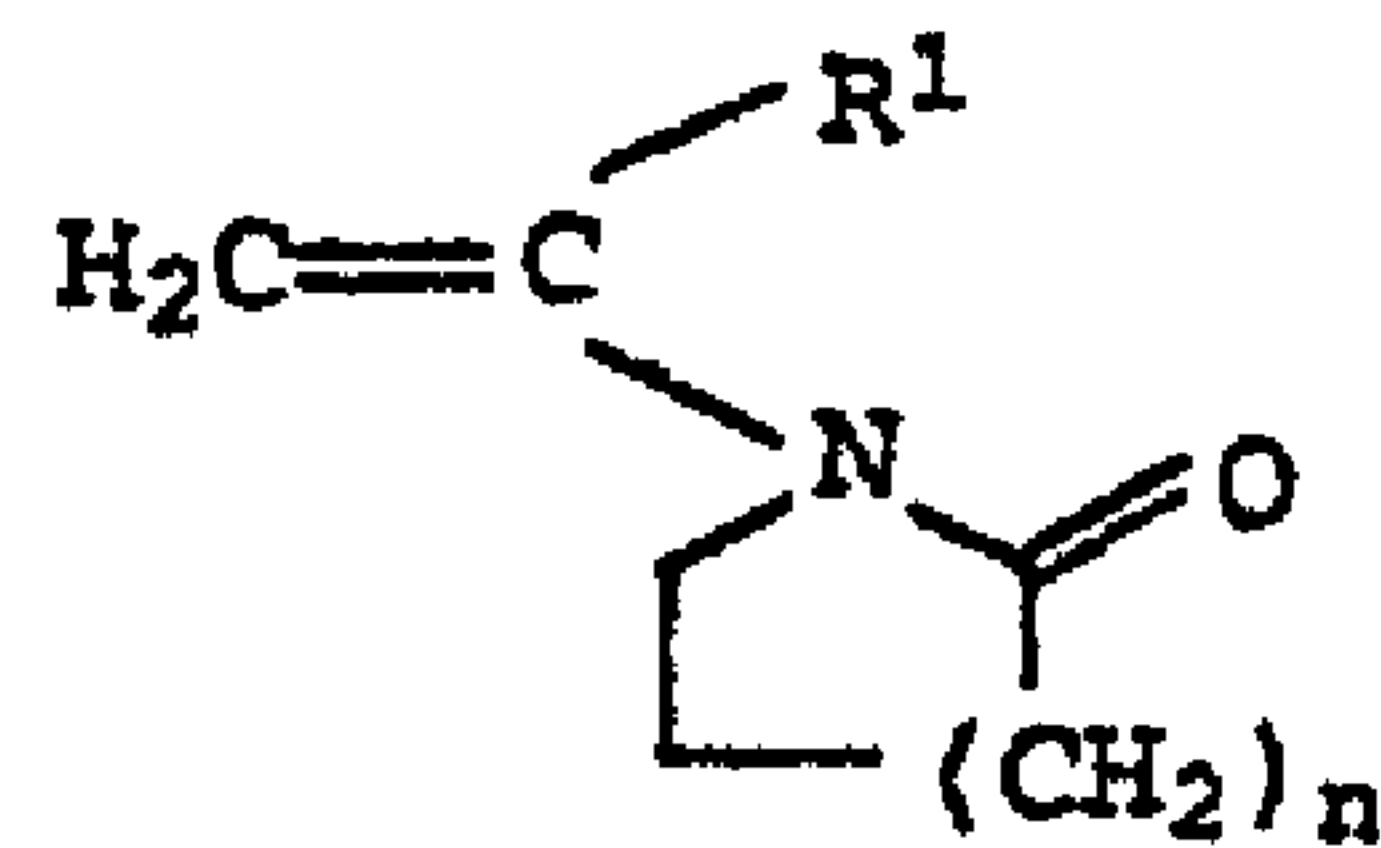
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(54) **PROCEDE DE PRODUCTION DE COPOLYMERES PAR
POLYMERISATION RADICALE**

(54) **METHOD FOR PRODUCING COPOLYMERS BY RADICAL
POLYMERISATION**



(I)



(II)

(57) The invention relates to a method for producing copolymers by radical polymerisation of a) 5 to 95 wt. % of a monomer of formula (I), b) 95 to 5 wt. % of a monomer of formula (II), wherein R¹ and R² represent H, C₁-C₃-alkyl, R³ = H, C₁-C₆-alkyl and n = 1 to 3 respectively and c) 0 to 40 wt. % of another fully or partially water-soluble monomer. The inventive method is characterised in that the polymerisation is carried out in an aqueous medium.



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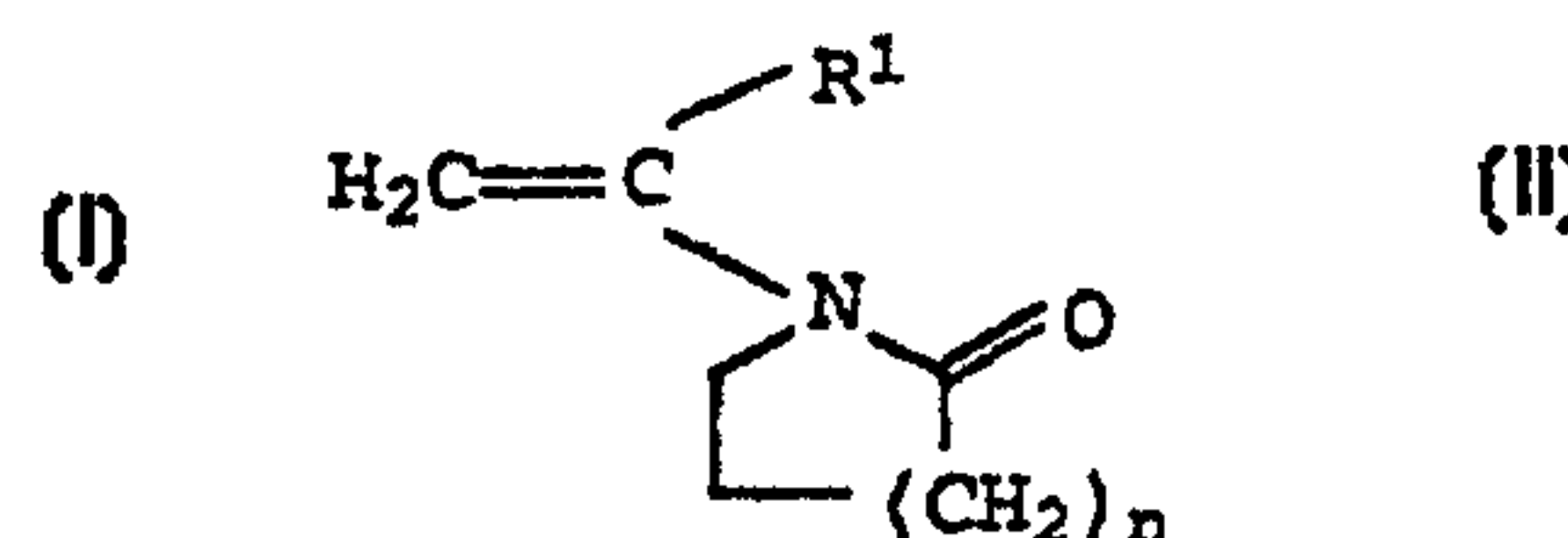
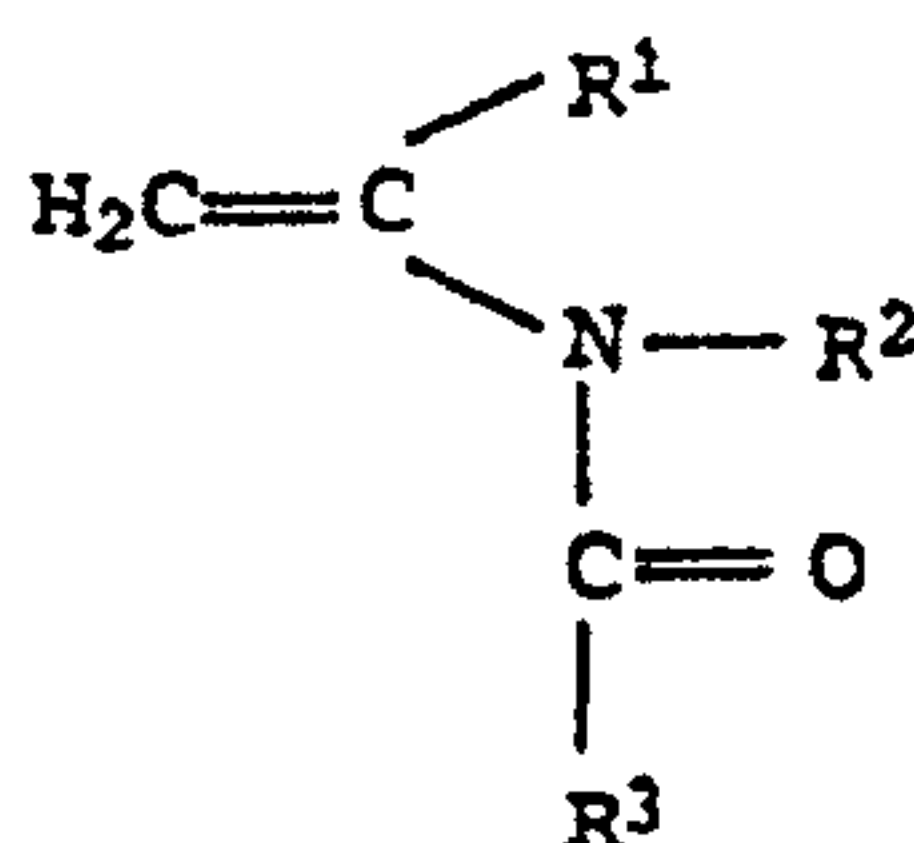
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(54) Title: METHOD FOR PRODUCING COPOLYMERS BY RADICAL POLYMERISATION

(54) Bezeichnung: VERFAHREN ZUR HERSTELLUNG VON COPOLYMERISATEN DURCH RADIKALISCHE POLYMERISATION

(57) Abstract

The invention relates to a method for producing copolymers by radical polymerisation of
 a) 5 to 95 wt. % of a monomer of formula (I),
 b) 95 to 5 wt. % of a monomer of formula (II),
 wherein R¹ and R² represent H, C₁-C₃-alkyl, R³ = H, C₁-C₆-alkyl and n = 1 to 3 respectively and
 c) 0 to 40 wt. % of another fully or partially water-soluble monomer. The inventive method is characterised in that the polymerisation is carried out in an aqueous medium.



(57) Zusammenfassung

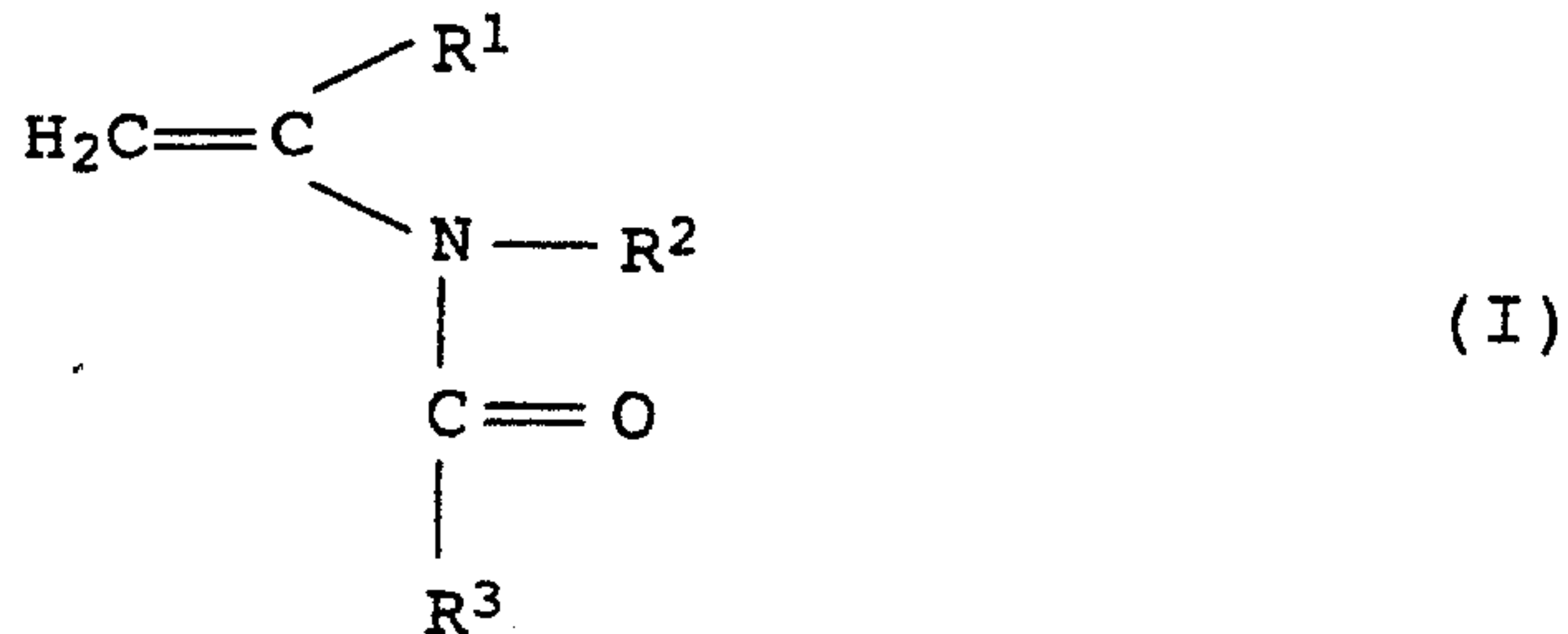
Verfahren zur Herstellung von Copolymerisaten durch radikalische Polymerisation von a) 5 bis 95 Gew.-% eines Monomeren der Formel (I), b) 95 bis 5 Gew.-% eines Monomeren der Formel (II), in denen jeweils R¹ und R² H, C₁-C₃-Alkyl, R³ = H, C₁-C₆-Alkyl und n = 1 bis 3, bedeuten, und c) 0 bis 40 Gew.-% eines weiteren vollständig oder eingeschränkt wasserlöslichen Monomeren, dadurch gekennzeichnet, daß die Polymerisation in einem wäßrigen Medium durchgeführt wird.

Bch

METHOD FOR PRODUCING COPOLYMERS BY RADICAL POLYMERISATION

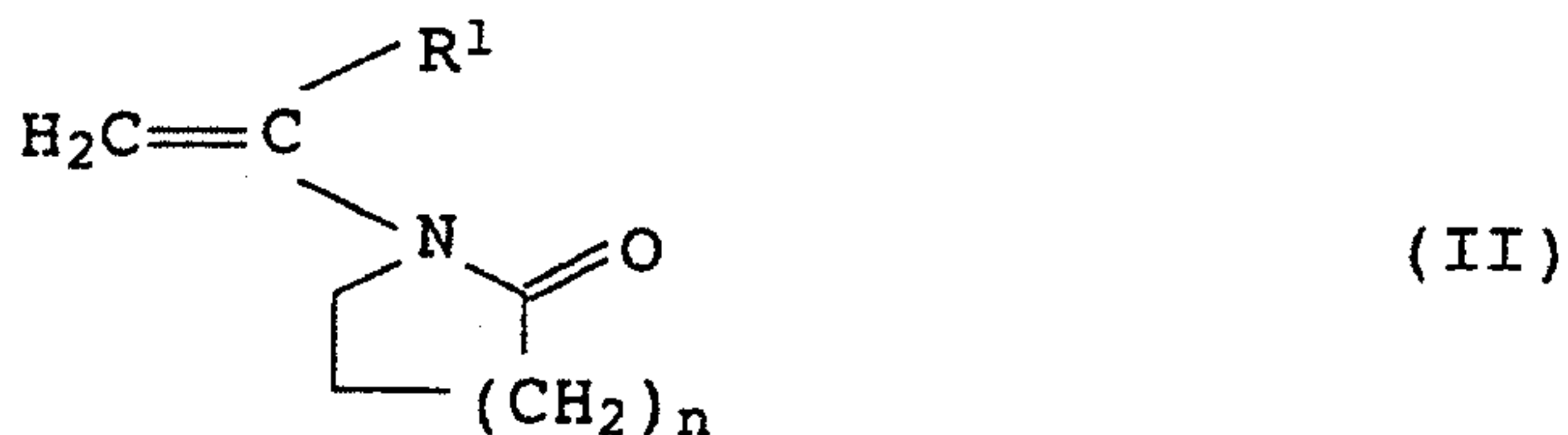
The present invention relates to a process for the preparation of copolymers by free radical polymerization of

- a) from 5 to 95% by weight of a monomer of the formula I



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- b) from 95 to 5% by weight of a monomer of the formula II



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where in each case R^1 and R^2 are H or C_1 - C_3 -alkyl,
 R^3 is H or C_1 - C_6 -alkyl
 and n is from 1 to 3,

and

- c) from 0 to 40% by weight of a further monomer which is
 30 completely water-soluble or has limited water solubility,

wherein the polymerization is carried out in an aqueous medium,

and copolymers prepared by this process and their use as gas hydrate inhibitors.

WO 96/41785 discloses a process for inhibiting hydrate formation, i.e. a process by means of which the formation of gas hydrates in media which contain gas molecules and water is prevented.

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In this known process, the gas hydrate inhibitors used are copolymers which consist of N-methyl-N-vinylacetamide and an N-vinyl lactam. The copolymers are prepared by free radical polymerization in benzene or in alcohols. However, these organic solvents present problems in the preparation and handling of the resulting copolymer solution. They must be removed in certain cases prior to use as gas hydrate inhibitors, which requires energy and time.

10 Polymer Journal, 17, No. 1 (1985), 143-152 discloses that vinylpyrrolidone can be prepared by free radical polymerization in organic solvents or in H₂O, the polymers prepared in H₂O being sensitive to oxidation.

15 It is an object of the present invention to avoid the abovementioned disadvantages during handling.

We have found that this object is achieved by carrying out the polymerization in an aqueous medium.

The monomers of the formula I are preferably used in amounts of from 20 to 80% by weight and the monomers of the formula II preferably in amounts of from 80 to 20% by weight. In the formula I, R² and R³ are each preferably methyl and R¹ in both monomers I and II is hydrogen. The preferred monomer of the formula I is N-methyl-N-vinylacetamide, and the preferred monomer of the formula II is vinylcaprolactam.

30 A comonomer which is completely water-soluble or has limited water solubility may be used as further copolymerizable comonomers c).

35 Preferably used comonomers c) are, for example, carboxylic acids and their esters, anhydrides, amides, nitriles, vinyl esters or vinyl ethers. Particular examples are: acrylic acid, methacrylic acid, methyl acrylate, ethyl acrylate, methyl methacrylate, ethyl methacrylate, hydroxyethyl acrylate, hydroxypropyl acrylate, hydroxybutyl acrylate, hydroxyethyl methacrylate, hydroxypropyl methacrylate, hydroxyisobutyl acrylate, hydroxyisobutyl methacrylate, monomethyl maleate, dimethyl maleate, monoethylene maleate, diethyl maleate, monoethyl maleate, diethylene maleate, maleimides, ethylhexyl acrylate, 2-ethylhexyl methacrylate, acrylamide, methacrylamide, N-dimethylacrylamide [sic],
 45 N-tert-butylacrylamide: [sic] N-isopropylmethacrylamide, methacryloylpyrrolidine, acrylonitrile, methacrylonitrile, dimethylaminoethyl acrylate, dimethylaminoethyl methacrylate,

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diethylaminoethyl acrylate, diethylaminoethyl methacrylate and the salts of the last-mentioned monomers with carboxylic acids or mineral acids and the quaternized products. Examples of vinyl esters are vinyl acetate, vinyl propionate and vinyl esters of a synthetic fatty acid of 10 carbon atoms (versatic-10 acid) or of 9 carbon atoms (versatic-9 acid), both commercially available (e.g. from Shell). Examples of vinyl ethers are vinyl C₁-C₄-alkyl ethers, in particular vinyl isobutyl ether. Suitable as monomers are, in addition, acrylamidoglycolic acid, vinylsulfonic acid, allylsulfonic acid, methallylsulfonic acid, styrenesulfonic acid, 3-sulfopropyl acrylate, 3-sulfopropyl methacrylate and acrylamidomethylpropanesulfonic acid and monomers containing phosphonic acid groups, such as vinyl phosphate, allyl phosphate and acrylamidomethylpropanephosphonic acid. It is of course also possible to use mixtures of said monomers, for example mixtures of acrylates and vinyl acetate, mixtures of different acrylates, mixtures of acrylates and acrylamide or mixtures of acrylamide and hydroxyethyl acrylate.

20 Acrylamide and acrylates are particularly preferred.

The aqueous medium may consist exclusively of H₂O or may be a mixture of H₂O and alcohol, in particular CH₃OH or C₂H₅OH.

25 The initiation is effected with water-soluble initiators in amounts of from 0.1 to 5, particularly preferably from 0.2 to 2, % by weight, based on monomer.

30 Hydrogen peroxide is particularly preferred as water-soluble initiator, with simultaneous introduction of traces of Cu(II) salts into the reaction mixture comprising monomer and water.

35 The pH during the polymerization is from 4 to 9, particularly preferably from 6 to 8. The pH during the (total) polymerization is controlled by adding aqueous acids and alkalis. In general, the addition of an alkali is sufficient, an aqueous ammonia solution, e.g. 10% strength, being particularly preferably used.

40 The K values of the polymers prepared according to the invention (determined according to Fikentscher, Cellulose Chemie, 13 (1932), 58-64 and 71-74, 1% strength aqueous solution, 20°C, K = k·10³) are from 10 to 100, preferably from 15 to 45. The molecular weights of the polymers (M_w) are from 2000 to 800,000, preferably
45 from 5000 to 100,000.

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The novel copolymers can be used as gas hydrate inhibitors, as described in WO 96/41785. For this purpose, the polymers are added to the liquid systems, for example the mineral oil or natural gas mixtures, in the usual amounts which a person skilled
5 in the art adapts to the respective conditions.

The polymers used according to the invention can be used together with other compositions for the purpose of gas hydrate inhibition. These other compositions may be other polymers, such
10 as hydroxyalkylcelluloses, polyvinylpyrrolidone or polyvinylcaprolactam, preferably in an amount of from 1 to 3.5% by weight, based on the weight of the total liquid system, but also alcohols, such as methanol, ethanol or ethylene glycol, or water-soluble salts, preferably in an amount of from 10 to 30% by
15 weight, based on the weight of the total liquid system.

Examples

20 Preparation example

Initially taken mixture: 1125.00 g of demineralized water
 300.00 g of vinylcaprolactam
 200.00 g of N-vinylmethacetamide

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Feed 1: 8.30 g of hydrogen peroxide (30% strength)

Feed 2: 0.50 g of copper(II) chloride (0.01% strength)

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Feed 3: xx g of ammonia water (5% strength)

Feed 4: 0.50 g of copper(II) chloride (0.1% strength)

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Feed 5: 5.00 g of hydrogen peroxide (30% strength)

Procedure

40 The initially taken mixture is flushed with nitrogen and heated to an internal temperature of about 80°C.

At an internal temperature of about 78°C, feed 1 is added, followed by feed 2.

With feed 3, the pH is kept at 7.0 during the entire
45 polymerization time.

After a polymerization time of 3.5 hours, feeds 4 and 5 are added.

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After the addition of feeds 4 and 5, polymerization is continued for a further 4 hours at an internal temperature of about 80°C. The experimental batch is then cooled to room temperature.

Characterization

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Solids content	30% by weight
K value	34 (1% strength in water)
pH	6

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Table

Example	Composition	K value 1% strength in H ₂ O	"Freezing point"							
			4°C	3.5°C	3°C	2.5°C	2°C	1.5°C	1°C	
Comparison 1			-	X						
Comparison 2	VIMA/VCap, 40:60 % by weight, polymerized in C ₂ H ₅ OG [sic]	35	-	-	-	-	-	-	X	
1	VIMA/VCap, 40:60 % by weight, polymerized in H ₂ O	34	-	-	-	-	-	-	-	X

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- corresponds to liquid state
- x corresponds to the freezing point

In comparison 1, no polymer was added
All polymers in water

VIMA: N-methyl-N-vinylacetamide;

VCap: vinylcaprolactam

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The "freezing point" was measured by the ball-stop method, analogously to the test method described in Example 1 of W095/32356.

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This method relates to freezing points to be tested for water/THF mixtures by adding various polymers (detection of hydrate formation), which are frozen in a concentration of 0.5% in a water/THF (81/19% by weight) mixture.

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The following apparatuses and reagents are required for determining the freezing point of various polymer/(water/THF) mixtures:

- 15 - Water/THF mixture (81/19% by weight)
- Julabo F 18 thermostat bath with water/ethylene glycol (5:1) refrigerant mixture
- Multifix Constant stirrer
- Holder for test tubes (5 ml)
- 20 - Small stainless steel balls for better mixing in the test tube

A 0.5% strength solution of the polymer to be investigated in water/THF (81/19) is prepared. The test tube is 2/3 filled, provided with a small stainless steel ball, closed and fixed in the test tube holder. The measurement is started at a bath temperature of 4°C and a speed of 20 rpm and the temperature is decreased by 0.5°C per hour until the sample has frozen or the steel ball in the test tube no longer moves or the temperature of 30 0°C has been reached. A blank test runs simultaneously with each measurement.

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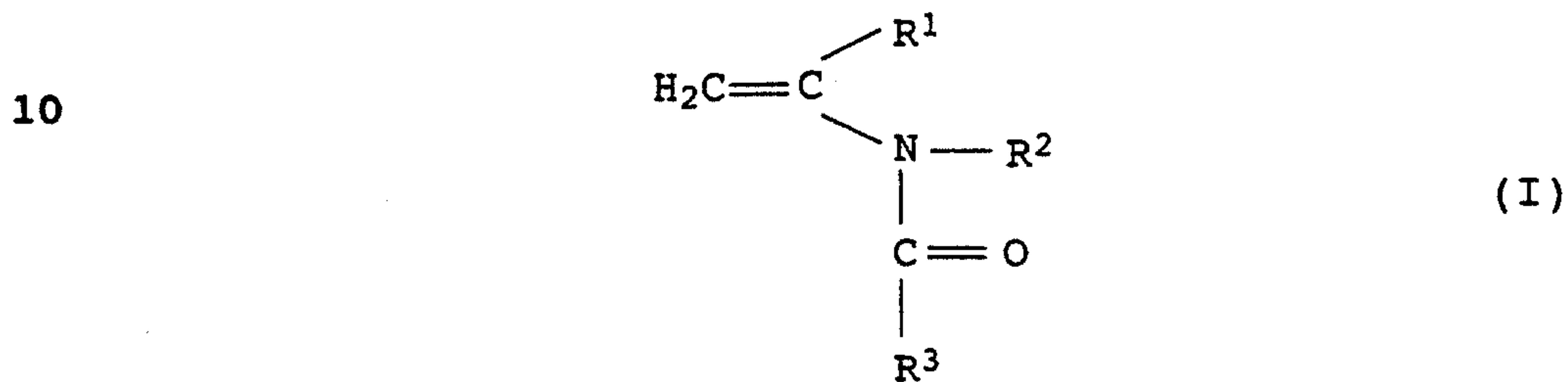
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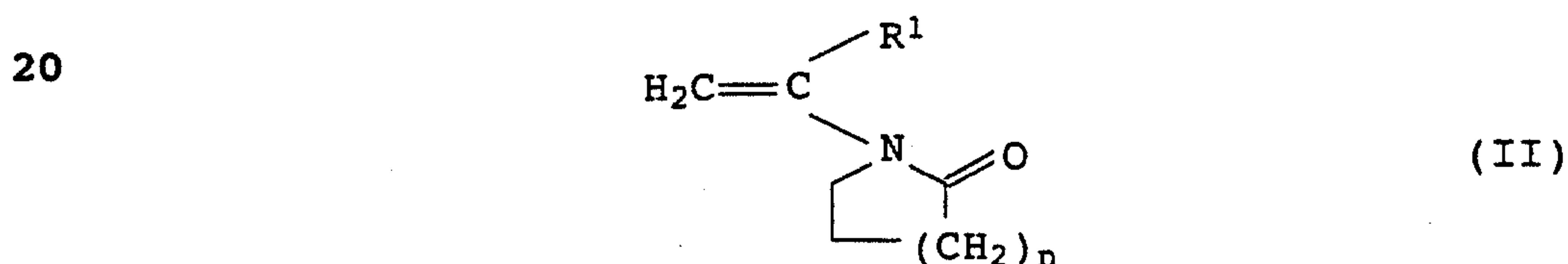
We claim:

1. A process for the preparation of copolymers by free radical polymerization of

a) from 5 to 95% by weight of a monomer of the formula I



b) from 95 to 5% by weight of a monomer of the formula II



where in each case R^1 and R^2 are H or C_1 - C_3 -alkyl
 R^3 is H or C_1 - C_6 -alkyl
 and n is from 1 to 3,

30 and

c) from 0 to 40% by weight of a further monomer which is completely water-soluble or has limited water solubility,

35 wherein the polymerization is carried out in an aqueous medium.

2. A process as claimed in claim 1, wherein from 20 to 80% by weight of the monomer a) and from 80 to 20% by weight of the monomer b) are used.

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3. A process as claimed in claim 1, wherein the monomer b) is vinylcaprolactam.

4. A process as claimed in claim 1, wherein R^2 and R^3 in the monomer a) are each methyl.

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5. A process as claimed in claim 1, wherein R¹ in the monomers a) and/or b) is hydrogen.
6. A process as claimed in claim 1, wherein the aqueous medium is water.
7. A process as claimed in claim 1, wherein a polymerization initiator system which contains H₂O₂ is used.
8. A copolymer prepared by a process as claimed in claim 1.
9. A copolymer as claimed in claim 8, which has terminal hydroxyl groups.
10. A copolymer as claimed in claim 8, which has a K value of from 10 to 100.
11. The use of a copolymer as claimed in claim 8 as a gas hydrate inhibitor.

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