

(19) World Intellectual Property  
Organization  
International Bureau



(43) International Publication Date  
29 September 2005 (29.09.2005)

PCT

(10) International Publication Number  
**WO 2005/090413 A1**

- (51) International Patent Classification<sup>7</sup>: **C08F 2/18**, 291/00
- (21) International Application Number:  
PCT/NO2005/000090
- (22) International Filing Date: 14 March 2005 (14.03.2005)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:  
20041205 22 March 2004 (22.03.2004) NO
- (71) Applicant (for all designated States except US): **NORSK HYDRO ASA** [NO/NO]; N-0240 Oslo (NO).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): **PEDERSEN, Steinar** [NO/NO]; Mindåstunet 7, N-3712 Skien (NO). **LETH-OLSEN, Kari-Anne** [NO/NO]; Frognerlia 23, N-3715 Skien (NO). **PAULSEN, Øystein** [NO/NO]; Furulund Terrasse 11, N-3950 Brevik (NO).
- (74) Agent: **JOHNSEN, Venche, Høines**; Patent and Trade-mark Department, Hydro Aluminium AS, N-0240 Oslo (NO).
- (81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.
- (84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- Published:**  
— with international search report
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

(54) Title: STORAGE STABLE POLYMER-OLIGOMER PARTICLES AND THEIR USE IN SEED POLYMERISATION

(57) Abstract: Storage stable polymer-oligomer particles with a high swelling capacity are produced by means of two-stage seed polymerisation in which the mole ratio between initiator and monomer is in the range from 0.07:1 to 0.01:1. These particles are used to produce polymer particles with a narrow size distribution by seed polymerisation.

WO 2005/090413 A1

5        *"Storage stable polymer-oligomer particles and their use in seed polymerisation"*

The present invention concerns a procedure for producing storage stable, swellable polymer-oligomer particles that are used to produce polymer particles with a narrow size distribution via seed polymerisation.

10

Polymer particles today are used in several application areas such as separation, chromatography, adsorbents, ion exchangers, drug-delivery systems, solid-phase peptide synthesis, diagnostics and cosmetic preparations. Each area requires customised properties in the particles. The challenge is to control particle size, size distribution, polymer composition, porosity and functionality.

15

These applications are in continuous development and the need for particles that are uniform in terms of size, shape and functionality is growing. Uniform particles can be produced by classification of particles produced by conventional suspension polymerisation, but this is unsatisfactory as it is labour-intensive and produces a low yield of the particles required.

20

Therefore, relatively good processes have now been developed based on seed polymerisation. This method is based on uniform, relatively small particles being produced in a first stage and then being used as seed particles in one or more subsequent stages. Depending on how the seed particles are produced, they can absorb or being swelled from 0.5 to more than 1000 times their own volume with low-molecular compounds such as solvents and monomers. When monomer is incorporated in the seed particles and the monomer is subsequently polymerised, the process is

30

called seed polymerisation. US patent 5,130,343 and the literature to which reference is made in it provides a comprehensive description of prior art.

However, there are several weaknesses in the processes described. This is particularly true when relatively large polymer particles are to be produced, i.e. in the range 10 to 100 micrometers. When seed particles are swelled, their size increases proportionally to the cube root of the increase in volume. A swelling of 1000 times thus produces an increase in diameter of just 10 times. There is therefore a need for both relatively large seed particles and very swellable seed particles.

NO 31056 proposes a solution in which seed particles are produced by dispersion polymerisation. A homogeneous solution of monomer in a polar organic solvent containing initiator is subjected to polymerisation so that polymer particles are precipitated out of the solution and grow in controlled manner into free, relatively large particles. This method can produce uniform particles up to 10 micrometers in size. The particles can be swelled more than 100 times with monomer or solvent. The major known disadvantage of this technique is the use of organic solvent as the reaction medium. This requires that the particles are separated and transferred to an aqueous dispersion for use in the subsequent seed polymerisation. It is also difficult to produce cross-linked particles with this method, which prevents the synthesis of homogeneously cross-linked particles with a uniform nature. It is also known that the range of monomers that can easily be used in large-scale processes is limited.

In US 5,147,937, small seed particles produced by conventional emulsion polymerisation are used. Emulsion polymerisation takes place in an aqueous medium, and the particles are created in the aqueous phase and stabilised by an emulsifier. The emulsifier also ensures that the monomer is kept emulsified in the aqueous phase as relatively large drops. These drops function as a reservoir for the monomer during the process. This method

makes it possible to produce uniform particles up to approximately 1 micrometer in size. However, high-molecular weight polymer is always created in emulsion polymerisation. This greatly restricts the particles' swelling capacity, and normally it is never possible to swell a high-molecular weight polymer more than 2 to 5 times. The problem is avoided here by eliminating the need to swell the seed particles much. Instead, a controlled quantity of monomer is added to the seed particles while polymerisation takes place. The quantity of free monomer never exceeds 10 % of the polymer particle weight present. By polymerising in many repeated stages, the required particle diameter can finally be achieved. Production of particles in the range 1 to 50 micrometers is specified. The major disadvantage of this method is that the original seed particle is small and it is demanding and relatively inefficient to have such limited swelling of the seed particles. In principle, this leads to many repeated stages before large particles can be achieved.

US 4,530,956 announces a pioneering principle called the "Ugelstad process", after the inventor, or the "two-stage swelling method", which indicates the special feature of the process. The original seed particles are produced by standard emulsion polymerisation here as well. The seed particles are made very swellable by incorporating a water-insoluble, low-molecular weight compound in a first stage. This may either be an oligomer or an organic compound. In stage two of the process, the monomer is then swelled in under conditions where the oligomer or the organic compound cannot leave the seed particles. The only possible transport is of the monomer into the seed particles. Polymerisation is carried out when the swelling has been completed. The presence of oligomer or a low-molecular compound has an enormous effect on the swelling capacity, and other prior art measures such as the reduction of interfacial tension, use of solvating solvent or a slightly water-soluble organic solvent to facilitate the diffusion of monomer from the aqueous phase into the seed particles have very little effect by comparison.

The documents to which reference is made describe which common monomers, initiators and stabilisers can be used.

5 The oligomer in accordance with US 4,530,956 has a degree of polymerisation between 5 and 200, or an equivalent molecular weight between 500 and 20,000 Dalton. The monomer added in stage two has a water solubility that is more than 10 times higher than that of the oligomer, and the volume ratio between the monomer and the seed particles is greater than 20. It is claimed that it is advantageous to control the molecular weight  
10 of the oligomer created by adjusting the ratio between the initiator and the monomer. The molecular weights specified will normally require a mole ratio between monomer and initiator of from 0.25:1 to 50:1.

To create seed particles that consist of oligomer, monomer and initiator can  
15 be swelled in at the same time or in two stages. It is possible to build on the oligomer seed particles in new stages until the desired final diameter has been achieved. Therefore, it is possible to produce seed particles of virtually any size.

20 The advantage of this method is that it is possible to swell in a huge amount of monomer in stage two. This means both that a large increase in diameter can be achieved, if required, and that it is easy to customise particles by introducing mixtures of monomers and solvents. The nature of the process is such that a large range of substances can be used, and gives a great degree  
25 of freedom in the synthesis of polymer particles.

WO 00/616447 contains proposals for an optimised process of the same type as that described in US 4,530,956. When oligomer seed particles are used, the molecular weight of the oligomer is under 5000 Dalton or the degree of  
30 polymerisation is below 50.

However, here too, there are disadvantages that limit the use of the process in industrial contexts. When seed particles mainly consist of low-molecular compounds or oligomers, they are very soft and not very rigid compared to a particle that consists of high-polymer compounds. This leads to problems both during the synthesis of the seed particles and during their storage. Soft particles are often also sticky, and this combination easily leads to coalescence. The result of this will often be a broader particle size distribution, creation of aggregates and large particles as well as fouling in the reactor and storage tank. The production of polymer particles based on a large reservoir of seed particles cannot therefore be expected. This leads to a need for frequent production of small volumes of both seed particles and polymer particles. This is a major disadvantage in terms of repeatability from batch to batch and has a generally large effect on the productivity and cost of the process.

15

The storage stability will be rated good if the particles can be used with good results even after more than one month's storage. This makes it possible to produce a small number of large batches for a given production volume of the polymer particles required. This is good economically and produces the best results with regard to the reproducibility of the polymer particles.

20

High swelling capacity has been achieved when the seed particles account for less than 5 percent by weight of the polymer particles. This means a degree of swelling of more than 20 times the inherent seed particle volume by a monomer or a mixture containing a monomer. A high swelling capacity means both that the seed particles have a smaller effect on the polymer particles' properties after polymerisation has ended and that the seed particles account for a lower proportion of the total costs of production of the final polymer particles.

25  
30

The particle size distribution is called narrow when the coefficient of variation (CV), defined as the standard deviation (SD) divided by the mean particle

size (dp) multiplied by 100 ( $CV = SD/dp \cdot 100 \%$ ), is less than 35 %, preferably less than 20 %.

5 The present invention attempts to remedy the disadvantages of existing processes stated above. The aim of the invention is to produce storage stable, relatively large seed particles that also have a very high swelling capacity. This will also create the basis for advantageous production of large polymer particles with a narrow size distribution for the applications stated above by means of simple, easily controllable seed polymerisation.

10

Surprisingly, it has been found that it is possible to produce polymer-oligomer particles that have both good storage stability and adequate swelling capacity to be used as seed particles for the production of large uniform polymer particles. These and other aspects of the present invention will now be  
15 described in further detail.

The starting point for the polymer-oligomer seed particles is the production of small polymer particles by means of standard emulsion polymerisation. This is a widely known technique. See, for example, "Die Angewandte  
20 Makromolekulare Chemie, 195, (1992), 151-164 (Nr. 3373)". In many cases, it is advantageous to utilise this stage of production to achieve the largest possible particles. Normally, the maximum particle size in standard emulsion polymerisation will be around 1 micrometer.

25 Polymer-oligomer seed particles are then produced from these particles. The degree of polymerisation and thus the molecular weight of the polymer-oligomer is controlled via the ratio between the initiator and monomer used. More precisely, it is the speed with which radicals are created in relation to the speed with which polymer-oligomer is created from growing radicals that  
30 determines the degree of polymerisation. As it is essential to avoid having too large a fraction of very short oligomer chains, it is usually necessary to use a mole ratio between initiator and monomer that is from 0.07:1 to 0.01:1,

preferably between 0.06:1 and 0.03:1. It is advantageous that in a first stage, the initiator is swelled into the polymer particles made by the emulsion polymerisation. As these consist of high-molecular weight polymer, it is difficult to swell in more than 5 times their volume with initiator. To facilitate  
5 the swelling as much as possible, the initiator may be added as a finely divided aqueous emulsion. It may help still further to add a solvent for the initiator that can also be mixed with water. This increases the diffusion of initiator through the aqueous phase. When the initiator has been completely swelled in, the monomer or a mixture containing the monomer can relatively  
10 easily be swelled into the particles. The monomer or the mixture containing a monomer can be added as a finely divided aqueous emulsion, it can be added dropwise or directly to the seed solution. It is preferable to add the monomer dropwise. After the polymerisation has been completed, the polymer-oligomer seed particles required are created. By repeating the  
15 process, polymer-oligomer seed particles of the sizes required can be produced.

A procedure for the production of storage stable polymer-oligomer particles with a high swelling capacity, i.e. they can absorb from 20 to 300 times their  
20 own volume of an oil-soluble compound, is characterised in that the polymerisation is carried out as two-stage seed polymerisation in which the mole ratio between initiator and monomer is in the range from 0.07:1 to 0.01:1.

25 The final seed polymerisation can then relatively easily be carried out in accordance with the prior art by swelling monomer or a mixture containing monomer into the polymer-oligomer seed particles produced in advance and carrying out polymerisation. The size and properties of the final particles can easily be controlled by the swelling ratio selected and the composition  
30 selected for the monomer mixture. The monomer mixture may consist of various types of monomer, inert solvent and polymerisation initiator. Macroporous particles can be produced if favourable mixtures of cross-



linking agents, monomers and inert solvents are selected. This is a technique familiar to an expert in the field.

The present invention will now be described in further detail in the examples given below. The results concerning swelling and storage stability are summarised in Table 1.

**Example 1: Production of polystyrene seed by emulsion polymerisation**

Deionised water (2700 g), NaCl (2.29 g), potassium persulphate (1.76 g) and styrene (267 g) were mixed and added to a 5-litre double-walled glass reactor. Oxygen was removed from the solution by bubbling nitrogen through it. The temperature was increased to 75 °C and the agitation speed was set to 200 RPM. The polymerisation was allowed to take place over night. Polystyrene particles with a diameter of 0.82  $\mu\text{m}$  and a narrow size distribution were achieved.

**Example 2: Production of polystyrene seed by emulsion polymerisation**

Deionised water (2700 g), NaCl (2.29 g), Aerosol MA (0.40 g), potassium persulphate (1.76 g) and styrene (267 g) were added to a 5-litre double-walled steel autoclave. Oxygen was removed by repeated pressurisation of the reactor with nitrogen with intermediate evacuation. The temperature was increased to 75 °C and the agitation speed was set to 400 RPM. The polymerisation was allowed to take place over night. Polystyrene particles with a diameter of 1.2  $\mu\text{m}$  and a narrow size distribution were achieved.

**Example 3: Production of styrene-based polymer-oligomer seed (1.7  $\mu\text{m}$ )**

Deionised water (720 g), sodium lauryl sulphate (NaLS, 4.3 g)(emulsifier), dioctanoyl peroxide (Perkadox SE-8, 40.0 g)(initiator) and acetone (133 g) were emulsified using an ultrasonic probe for 10 minutes. Polystyrene seed produced according to Example 1 (48.0 g seed, 578 g latex) was added to the emulsion together with NaLS (0.8 g) and acetone (29.6 g). The mixture was transferred to a flask, which was left to agitate at approximately 25 °C for

approximately 48 hours. Acetone was then removed and the solution was added to a 5-litre double-walled glass reactor. The temperature was increased to 40 °C while styrene (336 g) and divinyl benzene (DVB80, 0.88 g)(cross-linking agent) were added dropwise over approximately 60 minutes.

5 After 4 hours from the start of adding styrene and DVB, deionised water (1200 g), potassium iodide (KI, 1.28 g) and polyvinyl pyrrolidone (PVP K-30, 18.48 g) were added and the temperature was increased to 70 °C. The polymerisation was allowed to take place for 6 hours at 70 °C and 1 hour at 90 °C. Styrene-based oligomer particles with a diameter of 1.7  $\mu\text{m}$  and a

10 narrow size distribution were achieved.

**Example 4: Production of styrene-based polymer-oligomer seed (3.5  $\mu\text{m}$ )**

Deionised water (720 g), NaLS (4.3 g), Perkadox SE-8 (40.0 g) and acetone (133 g) were emulsified using an ultrasonic probe for 10 minutes. Styrene-

15 based polymer-oligomer seed produced according to Example 3 (48.0 g seed, 331 g latex) was added to the emulsion together with NaLS (0.33 g) and acetone (34.8 g). The mixture was transferred to a flask, which was left to agitate at approximately 25 °C for approximately 48 hours. Acetone was then removed and the solution was added to a 5-litre double-walled glass

20 reactor. The temperature was increased to 40 °C while styrene (336 g) and DVB80 (0.88 g) were added dropwise over approximately 60 minutes. After 4 hours from the start of adding styrene and DVB80, deionised water (1200 g), KI (1.28 g) and PVP K-30 (18.48 g) were added and the temperature was increased to 70 °C. The polymerisation was allowed to take place for 6 hours

25 at 70 °C and 1 hour at 90 °C. Styrene-based oligomer particles with a diameter of 3.5  $\mu\text{m}$  and a narrow size distribution were achieved.

**Example 5: Production of styrene-based polymer-oligomer seed (2.3  $\mu\text{m}$ )**

Deionised water (720 g), NaLS (4.3 g), Perkadox SE-8 (40.0 g) and acetone (133 g) were emulsified using an ultrasonic probe for 10 minutes. Polystyrene

30 seed produced according to Example 1 (16.0 g seed, 193 g latex) was added to the emulsion. The mixture was transferred to a flask, which was left to

agitate at approximately 25 °C for approximately 48 hours. Acetone was then removed and the solution was added to a 5-litre double-walled glass reactor. The temperature was increased to 40 °C while styrene (336 g) and DVB80 (0.88 g) were added dropwise over approximately 60 minutes. After 4 hours  
5 from the start of adding styrene and DVB80, deionised water (1200 g), KI (1.28 g) and PVP K-30 (18.48 g) were added and the temperature was increased to 70 °C. The polymerisation was allowed to take place for 6 hours at 70 °C and 1 hour at 90 °C. Styrene-based oligomer particles with a diameter of 2.3 µm and a narrow size distribution were achieved.

10

**Example 6: Production of styrene-based polymer-oligomer seed (5.2 µm)**

Deionised water (720 g), NaLS (4.3 g), Perkadox SE-8 (40.0 g) and acetone (133 g) were emulsified using an ultrasonic probe for 10 minutes. Styrene-based polymer-oligomer seed produced according to Example 5 (29.0 g  
15 seed, 182 g latex) was added to the emulsion together with NaLS (2.5 g) and acetone (15.4 g). The mixture was transferred to a flask, which was left to agitate at approximately 25 °C for approximately 48 hours. Acetone was then removed and the solution was added to a 5-litre double-walled glass reactor. The temperature was increased to 40 °C while styrene (336 g) and DVB80  
20 (0.88 g) were added dropwise over approximately 60 minutes. After 4 hours from the start of adding styrene and DVB80, deionised water (3600 g), KI (2.60 g) and PVP K-90 (37.5 g) were added and the temperature was increased to 70 °C. The polymerisation was allowed to take place for 6 hours at 70 °C and 1 hour at 90 °C. Styrene-based oligomer particles with a  
25 diameter of 5.2 µm and a narrow size distribution were achieved.

**Example 7: Use of styrene-based polymer-oligomer seed for the production of porous particles**

Deionised water (110 g), methyl hydroxypropyl cellulose (Methocel K-100,  
30 0.22 g), NaLS (0.31 g), styrene (23.0 g), ethylene glycol dimethacrylate (EGDMA, 23.0 g), pentyl acetate (50.7 g) and azo bis methyl butyronitrile (AMBN, 0.16 g) were mixed and emulsified using an ultrasonic probe for 5

minutes. Styrene-based polymer-oligomer seed produced according to Example 6 (3.13 g seed, 38 g latex) was added to the emulsion. The mixture was transferred to a 0.5-litre double-walled glass reactor with agitators and the temperature was increased to 40 °C. After 2.5 hours, deionised water  
5 (279 g), KI (0.04 g) and Methocel K-100 (1.89 g) were added to the reactor before the temperature was increased to 80 °C. The polymerisation was allowed to take place over night. Porous poly(styrene-ko-EGDMA) particles with a diameter of 17 µm and a narrow size distribution were achieved.

10 **Comparative example 1: Production of oligomer seed (2.2 µm)**

Deionised water (90 g), NaLS (0.54 g), Perkadox SE-8 (4.55 g) and acetone (16.64 g) were emulsified using an ultrasonic probe for 10 minutes. Polystyrene seed produced according to Example 2 (2.0 g seed, 27.3 g latex) was added to the emulsion. The mixture was transferred to a flask, which  
15 was left to agitate at approximately 25 °C for approximately 48 hours. Acetone was then removed and the solution was added to a 0.5-litre double-walled glass reactor. The temperature was increased to 40 °C while styrene (19.21 g) and DVB80 (0.05 g) were added dropwise over approximately 60 minutes. After 4 hours from the start of adding styrene and DVB80, deionised  
20 water (400 g) and KI (0.16 g) were added and the temperature was increased to 70 °C. The polymerisation was allowed to take place for 6 hours at 70 °C and 1 hour at 90 °C. Styrene-based oligomer particles with a diameter of 2.2 µm and a narrow size distribution were achieved.

25 **Comparative example 2: Production of oligomer seed (4.2 µm)**

Deionised water (90 g), NaLS (0.54 g), Perkadox SE-8 (4.55 g) and acetone (16.64 g) were emulsified using an ultrasonic probe for 10 minutes. Styrene-based oligomer seed produced according to Comparative example 1 (4.0 g seed, 138 g latex) was added to the emulsion. The mixture was transferred to  
30 a flask, which was left to agitate at approximately 25 °C for approximately 48 hours. Acetone was then removed and the solution was added to a 0.5-litre double-walled glass reactor together with deionised water (100 g). The

temperature was increased to 40 °C while styrene (19.21 g) and DVB80 (0.05 g) were added dropwise over approximately 60 minutes. After 4 hours from the start of adding styrene and DVB80, deionised water (400 g), KI (0.16 g) and PVP K-30 (2.31 g) were added and the temperature was  
5 increased to 70 °C. The polymerisation was allowed to take place for 6 hours at 70 °C and 1 hour at 90 °C. Styrene-based oligomer particles with a diameter of 4.2 µm and a narrow size distribution were achieved.

**Comparative example 3: Production of oligomer seed (7.5 µm)**

10 Deionised water (90 g), NaLS (0.54 g), Perkadox SE-8 (4.55 g) and acetone (16.64 g) were emulsified using an ultrasonic probe for 10 minutes. Styrene-based oligomer seed produced according to Comparative example 2 (5.0 g seed, 147 g latex) was added to the emulsion. The mixture was transferred to a flask, which was left to agitate at approximately 25 °C for approximately  
15 hours. Acetone was then removed and the solution was added to a 0.5-litre double-walled glass reactor together with deionised water (100 g). The temperature was increased to 40 °C while styrene (19.21 g) and DVB80 (0.05 g) were added dropwise over approximately 60 minutes. After 4 hours from the start of adding styrene and DVB80, deionised water (400 g), KI  
20 (0.16 g) and PVP K-90 (2.31 g) were added and the temperature was increased to 70 °C. The polymerisation was allowed to take place for 6 hours at 70 °C and 1 hour at 90 °C. Styrene-based oligomer particles with a diameter of 7.5 µm and a narrow size distribution were achieved.

25 The swelling capacity was determined by making an emulsion of styrene in water using NaLS as the emulsifier. The styrene emulsion was added to seed particles in a volume ratio of styrene:seed = 100:1. The diameter of the swelled particles in relation to that of the seed particles was determined using a light microscope.

30

The storage stability was determined by storing produced seed particles on a shaking machine under equal, very mild conditions. The coalescence of seed

particles was determined by observing the seed particles daily in a light microscope. The results are shown in Table 1.

5 **Table 1: Results concerning storage stability and swelling capacity**

	Diameter ( $\mu\text{m}$ )	Initiator/ monomer (mole/mole)	Degree of polymerisation (mon. units)	Swelling capacity (volume)	Storage stability (days)
Example 3	1.7	0.04	71	> 100	> 40
Example 4	3.5	0.04	71	> 100	> 40
Example 5	2.3	0.04	73	> 100	> 40
Example 6	5.2	0.04	72	> 100	> 40
Comparative example 1	2.2	0.09	49	> 100	36
example 2	4.2	0.08	49	> 100	13
example 3	7.5	0.09	46	> 100	7

10 Table 1 shows that the storage stability increases considerably while an acceptable swelling capacity is maintained if the initiator/monomer ratio is reduced below 0.07.

**Claims:**

1. A procedure for the production of storage stable polymer-oligomer particles with a high swelling capacity, i.e. the polymer-oligomer particles can absorb 20-300 times and preferably 30-100 times their own volume of an oil-soluble compound, by a polymerisation process,  
5 **characterised in that**  
the polymerisation is carried out as two-stage seed polymerisation in which the mole ratio between initiator and monomer is in the range from  
10 0.07:1 to 0.01:1.
2. A procedure in accordance with claim 1,  
**characterised in that**  
the mole ratio between initiator and monomer is in the range from 0.06:1  
15 to 0.03:1.
3. A procedure in accordance with claim 1,  
**characterised in that**  
initiator is swelled into the seed particles as a finely divided emulsion  
20 before monomer or a mixture containing monomer is added.
4. A procedure in accordance with claims 1-3,  
**characterised in that**  
monomer is added dropwise to the seed particles.  
25
5. The use of polymer-oligomer particles produced in accordance with claim 1 as seed particles for the production of polymer particles with a narrow size distribution.  
30

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/NO 2005/000090

## A. CLASSIFICATION OF SUBJECT MATTER

IPC7: C08F 2/18, C08F 291/00

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)

IPC7: C08F

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

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-INTERNAL, WPI DATA, CHEM. ABS. 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 20030109657 A1 (FONNUM ET AL), 12 June 2003 (12.06.2003), figure 1, abstract, paragraph (0011), (0029), examples --	1-5
A	US 5496897 A (YOSHIMATSU ET AL), 5 March 1996 (05.03.1996), abstract --	1-5
A	EP 0448391 A2 (ROHM AND HAAS COMPANY), 25 Sept 1991 (25.09.1991), column 4, line 18 - line 20, abstract --	1-5
A	US 5677407 A (SOJKA), 14 October 1997 (14.10.1997), abstract --	1-5

 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

11 July 2005

Date of mailing of the international search report

13-07-2005

Name and mailing address of the ISA/

Swedish Patent Office  
Box 5055, S-102 42 STOCKHOLM  
Facsimile No. +46 8 666 02 86

Authorized officer

Monika Bohlin / JA A  
Telephone No. +46 8 782 25 00



## INTERNATIONAL SEARCH REPORT

International application No.

PCT/NO 2005/000090

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 6346592 B1 (SAETHRE ET AL), 12 February 2002 (12.02.2002), abstract  --	1-5
P,A	US 20040097656 A1 (NYHUS ET AL), 20 May 2004 (20.05.2004), abstract  -- -----	1-5

## INTERNATIONAL SEARCH REPORT

Information on patent family members

28/05/2005

International application No.

PCT/NO 2005/000090

US	20030109657	A1	12/06/2003	AU	3942201	A	03/10/2001
				EP	1268563	A	02/01/2003
				GB	0007005	D	00/00/0000
				JP	2003528179	T	24/09/2003
				NO	20024517	A	22/11/2002
				WO	0170825	A	27/09/2001
				GB	0023070	D	00/00/0000
				GB	0023673	D	00/00/0000
				GB	0101278	D	00/00/0000

US	5496897	A	05/03/1996	DE	3886860	D,T	30/06/1994
				EP	0308864	A,B	29/03/1989
				SE	0308864	T3	
				JP	1081810	A	28/03/1989
				JP	2108581	C	21/11/1996
				JP	5064964	B	16/09/1993
				NO	177598	B,C	10/07/1995
				NO	884162	A	28/03/1989

EP	0448391	A2	25/09/1991	SE	0448391	T3	
				AT	138400	T	15/06/1996
				AU	648293	B	21/04/1994
				AU	7361491	A	03/10/1991
				BR	9101115	A	05/11/1991
				CA	2038502	A,C	23/09/1991
				CN	1038756	B,C	17/06/1998
				CN	1059913	A	01/04/1992
				CZ	280984	B	15/05/1996
				CZ	9300778	A	19/01/1994
				DE	69119633	D,T	23/01/1997
				FI	911386	A	23/09/1991
				HU	61781	A	01/03/1993
				HU	910973	D	00/00/0000
				IE	910947	A	25/09/1991
				IL	97610	A	26/05/1995
				JP	3055071	B	19/06/2000
				JP	5093075	A	16/04/1993
				KR	171604	B	30/03/1999
				MX	173510	B	10/03/1994
				NO	911076	A	23/09/1991
				NZ	237483	A	27/07/1993
				PL	289528	A	16/12/1991
				PT	97102	A	29/11/1991
				US	5147937	A	15/09/1992
				ZA	9102111	A	25/03/1992

## INTERNATIONAL SEARCH REPORT

Information on patent family members

28/05/2005

International application No.

PCT/NO 2005/000090

US	5677407	A	14/10/1997	DE	69623012	D,T	12/12/2002
				EP	0830398	A,B	25/03/1998
				ES	2181891	T	01/03/2003
				US	5712358	A	27/01/1998
				US	5777054	A	07/07/1998
				US	5830960	A	03/11/1998
				US	5830967	A	03/11/1998
				US	5834577	A	10/11/1998
				US	5837790	A	17/11/1998
				US	5955552	A	21/09/1999
				US	6107429	A	22/08/2000
				US	6248849	B	19/06/2001
				US	6387995	B	14/05/2002
				WO	9640809	A	19/12/1996
-----							
US	6346592	B1	12/02/2002	AU	5886198	A	07/08/1998
				DE	69809885	D,T	11/09/2003
				EP	0954538	A,B	10/11/1999
				SE	0954538	T3	
				ES	2189129	T	01/07/2003
				JP	2001518125	T	09/10/2001
				NO	310360	B	25/06/2001
				NO	970247	A	21/07/1998
				PT	954538	T	30/04/2003
				WO	9831714	A	23/07/1998
-----							
US	20040097656	A1	20/05/2004	NONE			
-----							