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(54) **Title:** METHOD OF CONTROLLING THERMAL DEGRADATION OF ANIONICALLY TERMINATED POLYMERS AND MATERIALS OBTAINED

(57) **Abstract:** The present invention relates to a polymer having improved thermal stability and to a method for preparing said polymer that enables control of its thermal degradation and stability via chemical structure of the polymer end groups. Further the present invention relates to a blend comprising said polymer. Finally, the present invention relates to use of said polymer or blend for the preparation of polymeric materials for applications in medical, environmental, agricultural and advance materials.

METHOD OF CONTROLLING THERMAL DEGRADATION OF ANIONICALLY TERMINATED POLYMERS AND MATERIALS OBTAINED THEREOF

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BACKGROUND OF INVENTION

Field of the Invention

The present invention relates to polymers having improved thermal stability, and to a method for preparing said polymers that enables control of their thermal degradation and stability via chemical structure of the polymer end groups. Said polymers are selected from the group comprising homopolymers having repeating units as described with formula (I): -O-C(R^1R^2)-C(HR^3)-C(O)-, where R^1,R^2,R^3 are hydrogen atom, alkyl, alkenyl, aryl, alkoxyl, carboxyl substituents or copolymers that contain at least 5% of repeating units described with the above formula (I); preferably from 30% up to 99%. The sequence distribution of the copolymer comprises random, gradient, multiblock and block structures.

Said copolymers being of various topology and microstructure containing also repeating units from the group of polyesters, polycarbonates, polyamides, nucleic acids, polyacrylates, polyolefins, polyaromatics, polysiloxanes.

In a first preferred embodiment of the present invention said polymers are selected from homopolymers or copolymers that contain anionically activated moieties. Said anionically activated moieties can be present in the terminal positions in the polymer in the form of carboxylate, alkoxide or carbanionic group and/or as functional groups along the polymer chain such as a carboxylate group in salt form $(-COO^{(-)})(M^{(+)})$ where M^+ will be Li^+, Na^+, K^+, Cs^+ and their complexes with respective crown ethers as well as cryptands and $^+NR^1R^2R^3R^4$ where R^i – H, or alkyl.

In a second embodiment of the present invention said polymers are selected from homopolymers or copolymers and do not contain any anionically activated moities.

Further the present invention relates to blends with composition from 5 to 95 weight percent of each polymeric component, comprising of a first polymeric component selected from the group comprising homopolymers or copolymers as described above in the first and second embodiment and a second polymeric component selected from the group comprising polymers that require to have an anionically activated moiety.

Further, the present invention relates to the use of said polymers selected from homopolymers or copoly-

mers as described above in the first and second embodiment for the preparation of polymeric materials for medical, environmental, agricultural and advanced materials applications.

The present invention relates also to the use of said blends with composition from 5 to 95 weight percent of each polymeric component, comprising a first polymeric component selected from the group comprising homopolymers or copolymers as described above in the first and second embodiment and a second polymeric component selected from the group comprising polymers that require to have an anionically activated moiety for the preparation of polymeric materials for medical, environmental, agricultural and advanced materials applications.

Finally, the present invention relates to the use of macromers or macro initiators obtainable by a controlled thermal degradation process of said polymers or copolymers for the preparation of new polymeric materials.

Description of Prior Art

In the field of the anionic polymerization it is known that for the anionic polymerization for example of β-butyrolactone activation of the polymer carboxylate propagating species is required (Jedlinski Z.,

Kurcok P., Kowalczuk M. Macromolecules, 1985, 18, 2679). This may be achieved either by complexation of an alkali metal cation (K^+, Na^+) with suitable complexant (crown ether or cryptand) or by using a "bulky" counter ion, like for example tetra-butyl ammonium. Another solution is to use an appropriate solvent activating initiator. The polymers obtained have an anionically terminated polymeric moiety In order to obtain from an anionic polymerization process polymers with improved thermal properties suitable additives for polymer processing have to be used.

The use of additives in a process for preparing polymers involves some drawbacks.

First of all the polymers or product formulations obtained will result more expensive.

Secondly, from the industrial point of view when additives are used in mixture with polymers the processing conditions will result to be more difficult to control.

Therefore, research efforts have been directed towards a method for preparing polymers having improved thermal stability with respect to polymers known in the art without the need to add stabilizing substances during the preparation process.

The influence of the chemical structure of the

polymer end groups plays a fundamental role on the thermal degradation of a specific class of polymers such as polyesters and copolymer thereof for example poly(3-hydroxybutyrate) - PHB.

It is well known from the former literature, that natural PHB (derived by biotechnological approach) degrades by random scission of polymer chains with the formation of crotonate end groups and crotonic acid release (Grassie N, Murray EJ, Holmes PA. Polym Degrad Stab 1984, 6, 127-34; Grassie N, Murray EJ, Holmes PA. Polym Degrad Stab 1984, 6, 95-103).

It is also known that in the case of synthetic poly(3-hydroxybutyrate), derived by ring-opening polymerization of β-butyrolactone, crotonic acid is also released during the thermal decomposition (Kurcok P., Kowalczuk M., Adamus G., Jedlinski Z. J.M.S.-Pure Appl. Chem., 1995, A32, 875-880).

Attempts have been made to prepare polymeric compositions (blends) containing polyesters and copolymers, especially obtained by the way of anionic polymerization or copolymerization of for example racemic β-butyrolactone.

For example, PL320208 relates to a method of production of a biodegradable and biodisintegrable polymeric composition, containing synthetic poly(3-

hydroxybutyrate) or its copolymers, characterized with content of 10-95% of synthetic poly(3-hydroxybutyrate) and/or its copolymers.

However said polymeric compositions show unsatisfactory thermal stability in high temperature processing conditions.

SUMMARY OF THE INVENTION

Applicants felt the need to improve thermal stability and/or control thermal degradation of said polymers selected from the group comprising homopolymers having:

(i) repeating units as described with formula (I): $-O-C(R^1R^2)-C(HR^3)-C(O)-$, where R^1, R^2, R^3 are hydrogen atom, alkyl, alkenyl, aryl, alkoxyl, carboxyl substituents; and

(ii) anionically activated moieties that may be present in the terminal positions in the polymer chain in the form of carboxylate, alkoxide or carbanionic group and/or as functional groups along the polymer chain such as a carboxylate group in salt form $(-COO^{(-)})(M^{(+)})$ where M^+ will be Li^+, Na^+, K^+, Cs^+ and their complexes with respective crown ethers as well as cryptands and $^+NR^1R^2R^3R^4$ where R^i – H, or alkyl.

Applicants felt the need to improve thermal stability and/or control thermal degradation of said copolymers that contain:

(i)at least 5% of repeating unit described with the above formula (I): $-O-C(R^1R^2)-C(HR^3)-C(O)-$, where R^1, R^2, R^3 are hydrogen atom, alkyl, alkenyl, aryl, alkoxyl, carboxyl substituents; and

(ii) anionically activated moieties that may be present in the terminal positions in the polymer chain in the form of carboxylate, alkoxide or carbanionic group and/or as functional groups along the polymer chain such as a carboxylate group in salt form $(-COO^{(-)})(M^{(+)})$ where M^+ will be Li^+, Na^+, K^+, Cs^+ and their complexes with respective crown ethers as well as cryptands and $^+NR^1R^2R^3R^4$ where R^i - H, or alkyl.

Applicants felt the need to improve thermal stability and/or control thermal degradation of said blends comprising of a first polymeric component selected from the group comprising homopolymers or copolymers as described above in the first and second embodiment and a second polymeric component selected from the group comprising polymers that require to have an anionically activated moiety.

Applicants perceived that the conversion of anionically terminated polymers to the polymers containing the desired inactive end groups protects said polymers from thermal degradation.

Applicants perceived that it is possible to improve, at the molecular level, thermal stability of polymers having anionically terminated polymeric moieties due to the control of the chemical structure of the polymer end groups.

According to a first object, the present invention relates to polymers having improved thermal stability as claimed in the independent claim.

According to a second object, the present invention relates to a method for preparing said polymers that enables control of their thermal degradation and stability via chemical structure of the polymer anionically activated moieties as claimed in the independent claim.

According to another object, the present invention relates to a method for preparing a blend having a controlled thermal stability as claimed in the independent claim.

According to another object, the present invention relates to the use of polymers, blends or macromers for the preparation of polymeric materials for

applications in medical, environmental, agricultural and advanced materials as claimed in the independent claim.

For the purpose of the present description and of the claims which follow, except where otherwise indicated, all numbers expressing amounts, quantities, percentages, and so forth, are to be understood as being modified in all instances by the term "about". Also, all ranges include any combination of the maximum and minimum points disclosed and include any intermediate ranges therein, which may or may not be specifically enumerated herein.

DETAILED DESCRIPTION OF INVENTION AND PREFERRED EMBODIMENTS

Applicants have found a method for preparing polymers having improved thermal stability said method enabling to control the thermal degradation and stability via chemical structure of the anionically activated moieties.

Moreover Applicants have found a method for preparing blends with composition from 5 to 95 weight percent of each polymeric component, comprising of a first polymeric component selected from the group comprising of homopolymers or copolymers as described above in the first and second embodiment and a second

polymeric component selected from the group comprising of polymers that require to have an anionically activated moiety.

Advantageously polymers or blends according to the present invention are useful for the preparation of polymeric materials for medical, enviromental, agricultural and advanced materials applications.

According to the present invention the method for preparing polymers with improved thermal stability comprises at least one reaction step in which polymers selected from homopolymers or copolymers that contain anionically activated moieties are reacted with a protonating agent or with a compound of formula (II) R-X.

Further, the present invention relates to the method of the improvement of thermal stability of anionically terminated polymers by conversion of their end groups to inactivated ones, preferably carboxylic, hydroxyl and/or their anionically inactive derivatives, by protonation, alkylation, esteryfication or etheryfication, acylation and amidation.

The anionically activated moieties can be present in the terminal positions in the polymer in the form of carboxylate, alkoxide or carbanionic group and/or as functional groups along the polymer chain such as a carboxylate group in salt form $(-COO^{(-)})(M^{(+)})$ where M^{+}

will be Li^+, Na^+, K^+, Cs^+ and their complexes with respective crown ethers as well as cryptands and $^+NR^1R^2R^3R^4$ where R^i – H, or alkyl.

The compound of general formula (II) is: R-X. In R-X: X represents a leaving group, and R is selected from the groups with general formula selected from the group comprising: C_nH_{2n+1}, PhC_nH_{2n}, $C_nH_{2n+1}C(O)$ or $PhC_nH_{2n}C(O)$ where n is preferably in the range 1 to 10; preferably 1 to 5 .

Preferably, R is selected from methyl or benzyl.

Advantageously, X is an halogen.

The protonating agent is selected from the group comprising acid substances.

Advantageously, said acid substances are selected from the group comprising mineral acids such as hydrochloric acid or sulfuric acid, organic acids e.g. acetic acid, as well as ion-exchange resins in acid form: sulfonated polystyrene/divinylbenzene (DVB) matrix, for example Dowex 50Wx2.

The present invention is also related with controlled thermal degradation of polymers which are selected from homopolymers or copolymers that contain anionically activated moieties by adjusting the appropriate concentration of anionically activated moie-

ties, type of counterion, temperature and time of degradation.

The anionically activated moieties can be present in the terminal positions in the polymer in the form of carboxylate, alkoxide or carbanionic group and/or as functional groups along the polymer chain such as a carboxylate group in salt form $(-COO^{(-)})(M^{(+)})$ where M^+ will be Li^+, Na^+, K^+, Cs^+ and their complexes with respective crown ethers as well as cryptands and $^+NR^1R^2R^3R^4$ where R^i - H, or alkyl.

The present invention is also related with controlled thermal degradation of blends.

Schematically, the anionically activated moieties can be represented by the following formula as an example $-COO^{(-)}\ M^{(+)}$, where $-COO^{(-)}$ is the activated carboxylate polymer end group, and $M^{(+)}$ comes from the activator used in the anionic polymerization. The activator can be for example an alkali metal cation (Li^+, Na^+, K^+, Cs^+) preferably with suitable complexant (crown ether or cryptand) or a "bulky" counter ion, like for example tetra-butyl ammonium.

Figure 1 illustrates the degradation mechanism by which the carboxylate end group attacks the hydrogen at C2 carbon of the polymer (homopolymer or

copolymer of formula (I)), exemplified in Figure 1 by poly(2-unsubstituted-3-hydroxyalkanoate).

Thermal degradation may take place through E1cB elimination reaction involving an anionically activated moiety and (i) another macromolecule of poly(2-unsubstituted-3-hydroxyalkanoate) susceptible of abstraction of hydrogen atom at C2 leading to reaction (intermolecularly) or (ii) the polymer chain itself (intramolecularly) according to the so-called back-biting and/or unzipping reactions, leading to formation of unsaturated end groups: HRC=CH-COO ---(polymer chain).

Both inter- and intra-molecular reactions lead to molar mass decrease.

In the blends, the anionically activated moieties (a) in figure 1 can be present either in both polymeric components, i.e. homopolymer or copolymer as described above in the first embodiment and second polymeric component, or only in the second polymer component of the blend.

In the blends the activated carboxylate polymer end groups additionally enable intermolecular attack on the hydrogen at C2 carbon of the first blend component with general formula given above and containing at least one hydrogen at C2 carbon in repeat

unit. Precise control of thermal degradation of homo- and copolyesters as well as of the respective polymer blends is achieved.

The end group $-COO^{(-)}M^{(+)}$ is reacted with a suitable protonating agent to obtain a deactivated carboxylic end group -COOH or is reacted with a suitable compound of general formula R-X (defined above) to obtain a deactivated ester group -COOR.

Contrary to activated carboxylate group $-COO^{(-)}M^{(+)}$, both deactivated end groups -COOH and -COOR are unable to induce the intra- and intermolecular attack on the hydrogen at C2 carbon thus the thermal properties of the polymer and/or copolymer are improved.

The present invention is based on experimental evidence that activated carboxylate polymer end groups play an important role on polymer thermal stability and may be the driving force of a new polymer degradation mechanism, as described above.

The invention will be further illustrated hereinafter with reference to the following experimental results.

a) Influence of the presence of an activated polymer end-group on thermal decomposition temperature of synthetic atactic poly(3-hydroxybutyrate), a-PHB.

The polymer containing activated end groups shows thermal degradation by thermogravimetric analysis (TGA) at 228 °C, whereas the same a-PHB where the end groups have been deactivated (protonated) shows thermal degradation at 292°C. Thus, the polymer with activated end-group degrades about 65°C lower than the deactivated one.

Moreover, the thermal decomposition temperature may be controlled between the above mentioned extremes depending on the ratio of activated to deactivated end groups.

b) Influence of activated polymer end-groups on molecular weight of synthetic a-PHB at moderate-to-elevated temperatures.

Two different a-PHB samples, one with activated carboxylate end groups, the other with deactivated (protonated) end groups, were subjected to thermal treatment at 80°C for 12 h. Gel permeation chromatography (GPC) measurements showed that the molar mass of the polymer sample containing activated end-groups markedly decreases during heat treatment at 80°C (i.e. at a moderate temperature where no weight loss is observed by TGA) whereas no significant molecular weight changes are shown by the deactivated sample.

c) Blends containing synthetic a-PHB bearing activated polymer end-groups. Effect of the activated end-groups on the blend thermal stability.

Blends prepared by solvent casting technique (composition: 50/50 by weight) of a-PHB possessing activated carboxylate end groups with (1) natural n-PHB and with (2) poly(L-lactide), PLL, , were subjected to TGA analysis.

The thermal decomposition temperature (T_{max}) of individual (pure) blend components was as follows:

a-PHB(with activated end groups)	Tmax = 228 °C
n-PHB (no active end groups)	Tmax = 292 °C
poly(L-lactide) (PLL)	Tmax = 363 °C

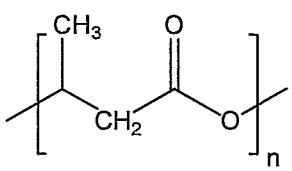
Blend a-PHB(A)/n-PHB (50/50) expresses only one thermal degradation event with maximum weight loss rate at 241 °C , i.e. located between T_{max} of individual components. It demonstrates the intermolecular reaction between activated a-PHB and non activated natural n-PHB.

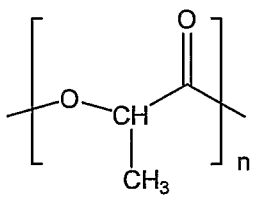
The observed behavior is due to the newly proposed abstraction of hydrogen atom at C2 thermal degradation mechanism of polyesters containing activated carboxylate end groups, which is the core of the present invention and comes into play in the blends containing e.g nonactivated natural poly-3-

hydroxyalkanoate (n-PHA). The results clearly demonstrate that the presence of the activated end-groups in synthetic a-PHB promotes the intermolecular thermal decomposition of the natural polymeric counterpart, leading to a single degradation event at a much lower temperature than in the pure natural counterpart polymer (n-PHB).

The above conclusion is substantiated by evidence of the absence of thermal stability changes when in the blend with natural n-PHB a protonated (deactivated) a-PHB is used instead of the active a-PHB used in the former blend. Deactivation of end groups in a-PHB prevents the occurrence of intermolecular abstraction of proton at C2 from the natural n-PHB that TGA curve is coincident with that of the plain natural polymer (degradation temperature 292°C).

Natural n-PHB (see scheme 1) contains an easily abstractable labile proton at C2, and is susceptible to subsequent E1cB elimination reaction which leads to C3-O chain scission favored by the presence of the aliphatic beta substituent.





scheme 1 scheme 2

If the proton at C2 carbon is much less easily abstractable and such E1cB elimination reaction is not possible, like in polylactic acid (PLL, scheme 2), the illustrated intermolecular degradation mechanism is unlikely to occur and indeed does not occur, as found when a blend of activated a-PHB with PLL is subjected to thermal degradation. In this case two separate degradation events are observed at the same temperatures as in the pure components (i.e. 228°C for a-PHB and 363°C for PLL).

Advantageously the blends according to the present invention have an important value because, on the one hand, the thermal degradation of polyesters possessing α-hydrogen atoms in their structures (including all family of poly(3-hydroxyalcanoates)) may be adjusted by blending with a-PHB containing activated carboxylate end groups.

On the other hand, the invention will improve the polymer materials processing, by deactivation of the active carboxylate end group, and will reduce the costs of the respective product formulations.

This invention is of particular importance for application of anionically terminated polymers in medicine.

The invention will be further illustrated hereinafter with reference to the following examples.

Example 1 (Method 1): Protonation of activated carboxylate centers of a-PHB with elimination of tetrabutylammonium (TBA) counter-ion, using ion-exchange resin.

Atactic poly(3-hydroxybutyrate), was obtained from the reaction of 0.38352g (1.272mmol) TBA acetate initiator with 50g (613.3mmol) of β-butyrolactone in bulk. When polymerization was completed (no residual monomer by FT-IR spectrometry was found) the polymer molecular mass was M_n= 33 200 (by GPC) and thermal degradation temperature T_{max}=253°C as measured by TGA. The sample of 3.586g of the polymer was dissolved in 15ml chloroform, stirred intensively with 0.083g of ion exchange resin in acid form (Dowex 50Wx2, from Fluka) for 10 minutes; the resin was filtered off and polymer was precipitated in hexane. Its thermal decomposition temperature was T_{max}= 265°C. Then the recovered polymer (3.340g) was again dissolved in 20ml of chloroform and stirred intensively with 0.1g of Dowex 50Wx2 for 3 hours. After Dowex filtration and polymer precipitation in hexane the degradation temperature was T_{max}= 281°C. Finally, when a sample of 0.28g of the polymer thus obtained was dissolved in 15 ml of $CHCl_3$;

stirred with 0.09g of Dowex 50Wx2 for 2 hours and precipitated in hexane its thermal decomposition temperature was T_{max}= 291°C as measured by TGA. The further protonation procedure reflected no influence on the T_{max}.

Example 2 (Method 2): Protonation of activated carboxylate centers of a-PHB with elimination of tetrabutylammonium (TBA) counter-ion, using acidic solution. Atactic poly(3-hydroxybutyrate) was obtained by the solution polymerization of 2.957g (34.34mmol) of β-butyrolactone in 8ml of dry THF, using TBA acetate (0.09075g; 0.300mmol) as initiator. When polymerization was completed (no residual monomer by FT-IR spectrometry was found) the crude polymer was precipitated in hexane (yield 100%) and its molecular weight determined by GPC method was M_n= 9700 while its degradation temperature was T_{max}=225°C (as measured by TGA). Then, 2.5g of polymer was dissolved in 15ml of chloroform and 0.05ml of concentrated $HCl_{(aq)}$ in 10ml of distilled water was added. The two-phase system was vigorously stirred for 10 minutes and after phase separation the chloroform phase was washed five times with 10 ml of distilled water for 10 minutes each. After phase separation the polymer was precipitated in hexane from the chloroform solution. The polymer degradation tempera-

ture was T_{max}=275°C. After repetition of this purification procedure for 3 times, the polymer molar mass was M_n=10 000 and degradation temperature was T_{max}=292°C. The further protonation procedure reflected no influence on the T_{max}.

Example 3 (Method 3): Protonation of carboxylate activated centers of a-PHB with removal of alkali metal 18-Crown-6 counter-ion complex, using acidic solution. Atactic poly(3-hydroxybutyrate) was prepared with the aid of equimolar complex of potassium acetate with 18-Crown-6 ether as initiator. β-Butyrolactone in the amount of 4.910g (57.0mmol) was added into a reactor containing 0.19796g (0.546mmol) of initiator complex in 3ml of dry THF under dry nitrogen atmosphere. When polymerization was completed (as determined by FT-IR spectrometry) the polymer was precipitated in hexane (yield 99.0%). Its molecular weight determined by GPC was M_n= 9400 and thermal degradation temperature was T_{max}=228°C (as measured by TGA). Then, 2.947g of recovered polymer were dissolved in 15ml of chloroform and 0.05 ml of concentrated $HCl_{(aq)}$ in 10ml of distilled water were added. The two phase system was vigorously stirred for 10 minutes and after phase separation the chloroform fraction was washed five times with 10 ml of distilled water. The polymer was precipitated in

hexane from the chloroform phase. The thermal degradation temperature was T_{max}= 269°C. After repetition of this purification procedure for 3 times, the polymer molar mass was M_n= 8400 and degradation temperature was T_{max}=285°C.

Example 4 (Method 4): Benzylation of carboxylate activated centers of a-PHB with removal of alkali metal 18-Crown-6 counter-ion complex, using benzylbromide. Atactic poly(3-hydroxybutyrate) was prepared with the aid of equimolar complex of potassium acetate with 18-Crown-6 ether as initiator. β-Butyrolactone in the amount of 6.58g (76.5 mmol) was added into a reactor containing 0.09212g (0.94mmol) of initiator complex and 0.248g of 18-Crown-6 in 10ml of dry THF under dry nitrogen atmosphere. When polymerization was completed (as determined by FT-IR spectrometry) the polymer was precipitated in hexane (yield 99.0%). Its molecular weight determined by GPC was M_n= 7000 and thermal degradation temperature was T_{max}=227°C (as measured by TGA). Then, 6.5g of recovered polymer were dissolved in 30ml of THF and 0.241g (1.41 mmol) of benzylbromide was added. After 10h of stirring the polymer was precipitated in 150ml of cold hexane. Then after separation of the liquid phase, the precipitate was redissolved in 30ml chloroform. The polymer solution was

washed 10 times with 30ml distilled water 10 min. each. Then the polymer was precipitated and dried under the vacuum to the constant weight. The T_{max} of such prepared sample was 284°C.

Example 5 (Method 5): Methylation of carboxylate activated centers of a-PHB with removal of alkali metal 15-Crown-5 counter-ion complex, using methyliodide. Atactic poly(3-hydroxybutyrate) was prepared with the aid of equimolar complex of potassium acetate with 18-Crown-6 ether as initiator. β-Butyrolactone in the amount of 5.0g (58.13mmol) was added into a reactor containing 0.0672g (0.8199mmol) of initiator (sodium acetate) and 0.1804g of 15-Crown-5 in 10ml of dry THF under dry nitrogen atmosphere. When polymerization was completed (as determined by FT-IR spectrometry) the polymer was precipitated in hexane (yield 99.8%). Its molecular weight determined by GPC was M_n= 6100 and thermal degradation temperature was T_{max}=230°C (as measured by TGA). Then, 5.9g of recovered polymer were dissolved in 30ml of THF and 0.5822g (4.1mmol) of methyliodide was added. After 16h of stirring the polymer was precipitated in 150 cm^3 of cold hexane. Then after liquid phase separation, the precipitate was redissolved in 30 cm^3 chloroform. The polymer solution was washed 10 times with 30 cm^3 distilled water 10

min. each. Then the polymer was precipitated and dried under the vacuum to the constant weight. The T_{max} of such prepared sample was 279°C.

CLAIMS

1. A method for preparing polymers having improved thermal stability that comprises:

- supplying polymers selected from homopolymers or co-polymers containing anionically activated moieties, and

- reacting said polymers with a protonating agent or with a compound of formula (II) R-X wherein X is a leaving group and R is selected from the group comprising: C_nH_{2n+1}, PhC_nH_{2n}, $C_nH_{2n+1}C(O)$, or $PhC_nH_{2n}C(O)$ wherein n is comprised from 1 to 10.

2. The method according to claim 1, wherein said homopolymers are selected from the group comprising homopolymers having repeating units as described with formula (I): $-O-C(R^1R^2)-C(HR^3)-C(O)-$, where R^1,R^2,R^3 are hydrogen atom, alkyl, alkenyl, aryl, alkoxyl, carboxyl substituents.

3. The method according to claim 1, wherein said copolymers are selected from the group comprising copolymers containing at least 5% of repeating units described with the above formula (I): $-O-C(R^1R^2)-C(HR^3)-C(O)-$, where R^1,R^2,R^3 are hydrogen atom, alkyl, alkenyl, aryl, alkoxyl, carboxyl substituents.

4. The method according to claim 3, wherein said copolymers contain from 30 to 99% of repeating units described with the above formula (I)

5. The method according to claim 3 or 4, wherein the sequence distribution of the repeating units of formula (I) is random, gradient, multiblock or block structures.

6. The method according to claim 3, wherein said copolymers further contain repeating units selected from the group of: polyesters, polycarbonates, polyamides, nucleic acids, polyacrylates, polyolefins, polyaromatics, polysiloxanes.

7. The method according to claim 1, wherein said anionically activated moieties are present in the terminal positions in the polymer in the form of carboxylate, alkoxide or carbanionic group and/or as functional groups along the polymer chain such as a carboxylate group in salt form $(-COO^{(-)})(M^{(+)})$ where M^+ will be Li^+, Na^+, K^+, Cs^+ and their complexes with respective crown ethers as well as cryptands and $^+NR^1R^2R^3R^4$ where R^i – H, or alkyl.

8. The method according to claim 1, wherein said protonating agent is selected from acid substances.

9. The method according to claim 8, wherein said acid substances are selected from the group comprising min-

eral acids, organic acids and ion-exchange resins in acid form.

10. The method according to claim 9, wherein said mineral acids are selected from hydrochloric acid, sulfuric acid.

11. The method according to claim 9, wherein said organic acid is acetic acid.

12. The method according to claim 9, wherein said ion-exchange resins in acid form are selected from sulfonated polystyrene/divinylbenzene (DVB) matrix, for example Dowex 50Wx2.

13. The method according to claim 1, wherein n is comprised from 1 to 5.

14. The method according to claim 1, wherein R is selected from methyl and benzyl.

15. The method according to claim 1, wherein X is a halogen atom.

16. Polymers obtainable by the method according to anyone claims 1-15.

17. Use of polymers according to claim 16 for the preparation of polymeric materials for medical, environmental, agricultural and advanced materials applications.

18. A method for preparing a blend having a controlled thermal stability, said method comprising:

- supplying a first polymeric component selected from the group comprising homopolymers as claimed in claim 2 or copolymers as claimed in anyone of claims 3 to 6; and

- blending said first polymeric component with a second polymeric component selected from the group comprising polymers having an anionically activated moiety.

19. The method according to claim 18, wherein the blend composition comprises from 5 to 95 weight percent of each polymeric component.

20. The method according to claim 18, wherein said first polymeric component contains anionically activated moieties which can be present in the terminal positions in the polymer in the form of carboxylate, alkoxide or carbanionic group and/or as functional groups along the polymer chain such as a carboxylate group in salt form $(-COO^{(-)})(M^{(+)})$ where M^+ will be Li^+, Na^+, K^+, Cs^+ and their complexes with respective crown ethers as well as cryptands and $^+NR^1R^2R^3R^4$ where R^i – H, or alkyl.

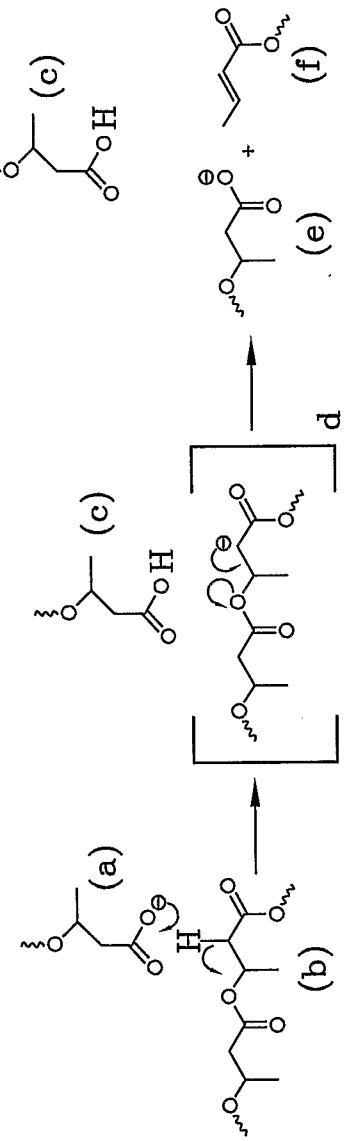
21. The method according to claim 18, wherein said first polymeric component does not contain any anionically activated moieties.

22. The method according to claim 18, wherein said second polymeric component is any polymer or copolymer containing anionically activated moieties which can be present in the terminal positions in the polymer in the form of carboxylate, alkoxide or carbanionic group and/or as functional groups along the polymer chain such as a carboxylate group in salt form $(-COO^{(-)})(M^{(+)})$ where M^+ will be Li^+, Na^+, K^+, Cs^+ and their complexes with respective crown ethers as well as cryptands and $^+NR^1R^2R^3R^4$ where R^i - H, or alkyl.

23. A blend obtainable by the method according to any-one claims 18-22.

24. Use of a blend according to claim 23 for the preparation of polymeric materials for medical, environmental, agricultural and advanced materials applications.

FIG. 1/1



INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2006/000898

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08G85/00 C08L67/04

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 C08L

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, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 3 824 197 A (SMITH S ET AL) 16 July 1974 (1974-07-16) column 2, line 11 - column 2, line 14	1
Y	ABATE R ET AL: "Thermal-degradation of microbial poly(4-hydroxybutyrate)" MACROMOLECULES, ACS, WASHINGTON, DC, US, vol. 27, no. 2, 1994, pages 332-336, XP002906005 ISSN: 0024-9297 the whole document	1
A	US 3 824 198 A (SMITH S ET AL) 16 July 1974 (1974-07-16) the whole document	1-17

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[X] Further documents are listed in the continuation of Box C.

[X] 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 document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

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

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
25 January 2007	02/02/2007

Name and mailing address of the ISA/	Authorized officer
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INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2006/000898

C(Continuation). . DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2002/143116 A1 (NODA ISAO [US] ET AL) 3 October 2002 (2002-10-03) claims 1-20	18-24
X	WO 96/08535 A (PROCTER & GAMBLE [US]) 21 March 1996 (1996-03-21) claims 1-10	18-24
X	IANNACE S ET AL: "POLY(3-HYDROXYBUTYRATE)-CO-(3-HYDROXYVALE RATE)/POLY-L-LACTIDE BLENDS: THERMAL AND MECHANICAL PROPERTIES" JOURNAL OF APPLIED POLYMER SCIENCE, JOHN WILEY AND SONS INC. NEW YORK, US, vol. 54, no. 10, 5 December 1994 (1994-12-05), pages 1525-1535, XP000514124 ISSN: 0021-8995 abstract	18-24

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IB2006/000898

Box II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

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

2. ☐ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

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

see additional sheet

1. ☒ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

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

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

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

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☒ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-17

   Method for improving thermal stability of polymers containing anionically activated moieties by reacting the polymers with a protonating agent or with a compound of formula R-X (see claim 1), the polymers themselves and the use of the polymers.

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2. claims: 18-24

   Method for preparing a blend by mixing a first polymer containing or not containing anionically activated moieties with a second polymer having anionically activated moieties, the blend itself and the use of the blend.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/IB2006/000898

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