

STABILIZATION OF A POLYMER

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The present invention relates to the
 stabilization of a polymer by a stable free radical and
 in particular to the use of a stable free radical for
 5 inhibiting the degradation of a polymer by a mechanism
 which does not involve oxygen. This use can be
 implemented when the polymer is in the presence or in
 the absence of oxygen and/or of light.

US Patent 5,322,912 teaches that a stable
 10 free radical can be mixed with styrene at between 100
 and 160°C to decrease the molecular mass and the
 distribution of the molecular mass of the polystyrene
 finally synthesized.

The Journal of Applied Chemistry of the USSR,
 15 vol. 52, No. 9, pp. 1948-1951 (10 March 1980) teaches
 that a piperidinoxy radical can inhibit the oxidation
 of polybutadiene in a high-impact polystyrene at
 between 60 and 160°C.

It has now been found that a stable free
 20 radical can be used to stabilize the molecular mass of
 a polymer, independently of the presence or absence of
 oxygen and/or of light in its environment.

According to one aspect, the present
 invention provides use of a stable free radical for
 25 inhibiting the degradation of a polymer by a mechanism
 which does not involve oxygen.

The heating of a polymer can cause

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modifications of its structure, such as, for example, crosslinking or depolymerization. These reactions can be regarded as undesirable because they can result in a detrimental change or a modification, which is

5 difficult to control, of the structure and of the molecular mass of the polymer and can result in a loss of certain properties. These reactions can take place by a mechanism which involves neither oxygen nor light.

It may be desirable to avoid the crosslinking
10 of a polymer, for example when it is desired to heat it to graft a chemical species on to it. A polymer appears more crosslinked when it is more difficult to dissolve in organic solvents such as aromatic solvents (eg. ethylbenzene and toluene) or aliphatic or alicyclic
15 hydrocarbons (eg. hexane and cyclohexane).

It may be desirable to avoid the depolymerization of a polymer, for example when it has to be converted while hot to produce a material or a component. Indeed, depolymerization is capable of
20 modifying the properties of the final material.

Moreover, if the monomer is toxic, its generation by depolymerization may need to be prevented, for example, if the material is intended for the food industry. Some monomers are very toxic whereas the polymer which
25 derives therefrom is not toxic. For example, styrene and vinyl chloride monomers are toxic whereas polystyrene and poly(vinyl chloride) are not.

Introducing a stable free radical into a composition comprising a polymer makes it possible to avoid the abovementioned difficulties and to limit the depolymerization or crosslinking of this polymer when heated. The nature of the problem, that is to say, the avoidance or inhibition of crosslinking and/or depolymerization, depends on the nature of the polymer and on the temperature to which it is intended to be exposed. Within the context of the present invention, the term polymer encompasses copolymers.

In one embodiment of the present invention the polymer may not comprise a carbon-carbon double bond. In this embodiment the mixture comprising the stable free radical also does not comprise a polymer comprising a carbon-carbon double bond.

Alternatively the polymer to be stabilized may not be a poly(phenylene ether). The mixture comprising the stable free radical may then comprise such a resin.

It is not necessary for a costabilizer, such as one of those mentioned for ingredient (b) in the composition of US Patent 4,123,418 (the contents of which are included by reference), to be present with the stable free radical.

The use according to the invention can be implemented at any pressure, for example, at a pressure of less than 100 bars.

The nature of the problem and the temperature

range within which this problem occurs are listed, in a non-exhaustive way, in the table below according to the nature of the polymer.

POLYMER	PROBLEM	TEMPERATURE RANGE
Vynylaromatic	Depolymerization	180 to 300°C
Polyolefin	Depolymerization and crosslinking	180 to 300°C
Polydiene	Crosslinking	80 to 150°C
Acrylic	Depolymerization	160 to 300°C
Methacrylic	Depolymerization	160 to 300°C

TABLE 1

A vinylaromatic polymer is understood to mean the polymer or copolymer resulting from the polymerization or copolymerization of at least one vinylaromatic monomer. Vinylaromatic monomers are, for example, styrene, styrene substituted on the vinyl group by an alkyl group, such as α -methylstyrene, ortho-vinyltoluene, para-vinyltoluene, ortho-ethylstyrene or 2,4-dimethylstyrene, or styrene substituted on the ring by a halogen, such as for example 2,4-dichlorostyrene, or vinylanthracene.

A vinylaromatic copolymer originates from the

copolymerization of at least one vinylaromatic monomer and of at least one monomer chosen from, for example, acrylonitrile, methacrylonitrile, acrylic acid, methacrylic acid, an alkyl ester in which the alkyl group contains from 1 to 4 carbon atoms, an N-alkylmaleimide in which the alkyl group contains from 1 to 4 carbon atoms, or N-phenylmaleimide.

A polyolefin is a polymer or copolymer resulting from the polymerization or copolymerization of at least one olefin.

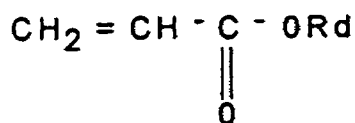
Olefins are, for example, those containing from two to twenty carbon atoms and in particular the α -olefins of this group. Mention may be made, as olefin, of ethylene, propylene, 1-butene, 4-methyl-1-pentene, 1-octene, 1-hexene, 3-methyl-1-pentene, 3-methyl-1-butene, 1-decene or 1-tetradecene or their mixtures. A polyolefin copolymer originates from the copolymerization of at least one olefin and of at least one monomer chosen from, for example, vinyl esters, such as vinyl acetate or vinyl propionate, acrylic acid or acrylic or alkylacrylic esters, such as methyl acrylate or methyl methacrylate.

A polydiene is a polymer or copolymer resulting from the polymerization or copolymerization of at least one diene and in particular a conjugated diene.

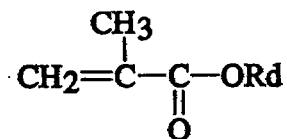
Conjugated dienes preferably comprise from 4 to 8 carbon atoms, such as 1,3-butadiene, isoprene,

2,3-dimethyl-1,3-butadiene or piperylene.

Acrylic and methacrylic polymers are polymers or copolymers resulting from the polymerization or copolymerization respectively of at least one acrylic monomer of formula:



or of at least one methacrylic monomer of formula



in which Rd is chosen from C₁-C₁₈ alkyl radicals, which are linear or branched and primary, secondary or tertiary, C₅-C₁₈ cycloalkyl radicals, (C₁-C₁₈)alkoxy(C₁-C₁₈)alkyl radicals, (C₁-C₁₈)alkylthio(C₁-C₁₈)alkyl radicals, aryl radicals and arylalkyl radicals, these radicals optionally being substituted by at least one halogen atom and/or at least one hydroxyl group after protection of this hydroxyl group, the above alkyl groups being linear or branched. The (meth)acrylic monomer can also be chosen from glycidyl, norbornyl or isobornyl (meth)acrylates or mono- and di(C₁-C₁₈)alkyl(meth)acrylamides.

Examples of useful methacrylates are methyl, ethyl, 2,2,2-trifluoroethyl, n-propyl, isopropyl,

n-butyl, sec-butyl, tert-butyl, n-amyl, i-amyl,
n-hexyl, 2-ethylhexyl, cyclohexyl, octyl, i-octyl,
nonyl, decyl, lauryl, stearyl, phenyl, benzyl,
 β -hydroxyethyl, isobornyl, hydroxypropyl and
5 hydroxybutyl methacrylates. The preferred methacrylic
monomer is methyl methacrylate.

Examples of acrylates of the above formula
are methyl, ethyl, n-propyl, isopropyl, n-butyl,
sec-butyl, tert-butyl, hexyl, 2-ethylhexyl, isooctyl,
10 3,3,5-trimethylhexyl, nonyl, isodecyl, lauryl,
octadecyl, cyclohexyl, phenyl, methoxymethyl,
methoxyethyl, ethoxymethyl and ethoxyethyl acrylates.

The invention can also be applied to mixtures
of polymers, such as mixtures of the polymers mentioned
15 above. Thus, the invention can also be applied to
compositions comprising a vinylaromatic polymer and a
rubber, such as a polydiene. The invention thus can be
applied to high-impact polystyrene, which usually
comprises a polystyrene matrix and rubber nodules, the
20 latter usually comprising polybutadiene. In such a
composition, the stable free radical acts as
stabilizer, acting both against depolymerization of the
polystyrene phase and against crosslinking of the
polybutadiene phase.

25 In another aspect, the invention provides a
process for the development of a composition or of a
material or of a component comprising a polymer
prepared by a polymerization, including

copolymerization, stage, which process comprises a heating stage in the absence of oxygen wherein the stable free radical is introduced so that it is present as a mixture with the polymer at the latest during the heating stage. The process is optionally carried out in the absence of light. The heating stage can be carried out at any temperature at which it is desired to stabilize the polymer. The invention preferably relates to processes in which the heating stage is carried out at a temperature of from 180 to 300°C, more preferably at from 200 to 300°C and more especially from 220 to 300°C.

The presence of the stable free radical may be of advantage when, at the end of the development of a composition comprising a polymer, the composition is subjected to hot devolatilization under vacuum to remove volatile species such as any solvent used during the polymerization or copolymerization and any monomers which have not reacted during the polymerization or copolymerization stage. This devolatilization stage is used in processes for the industrial manufacture of compositions comprising at least one vinylaromatic monomer, such as crystal polystyrene or high-impact polystyrene. For these polymers, this stage is generally carried out at a temperature of from 180 to 300°C.

The stable free radical can be introduced into the polymerization or copolymerization mixture



before or during the polymerization or copolymerization stage which leads to the polymer.

Indeed, by introducing the stable free radical in this way, the stable free radical is present as a mixture with the polymer or copolymer and is thus present during the heating stage which the composition comprising the polymer has to be subjected to after its synthesis.

If it is desired to avoid possible disturbance which the stable free radical can cause to the polymerization or copolymerization, the stable free radical can be introduced after the polymerization or copolymerization and before or at the latest during the heating stage.

The stable free radical can be introduced into the mixture comprising the polymer to be stabilized at a temperature at which the mixture is free from radicals.

The invention is also of advantage when it is desired to convert a composition comprising a polymer within the context of the development of a material. The conversion is generally an extrusion, an injection, a moulding or a blowing (film manufacture). These operations are generally carried out at a temperature above the melting temperature of the polymer and generally in the absence of oxygen.

In the case of the polymers mentioned in Table 1, this conversion is generally carried out at

from 180 to 300°C, except for the polydienes which it is preferable to convert at from 80 to 150°C.

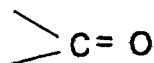
The invention is also of advantage when it is desired to graft, during a heating stage, a species
5 onto a polymer. The reactions of grafting onto a polymer generally require heating the polymer, the chains of which can crosslink or depolymerize under the effect of the heat.

The presence of a stable free radical during
10 this heating stage stabilizes the polymer chains while enabling grafting to take place. The presence of the stable free radical furthermore makes it possible to produce grafts exhibiting more uniform lengths. The reaction of grafting on to the polymer in the presence
15 of the stable free radical can be carried out under the usual conditions for grafting a species on to a polymer, with the stable free radical being added at the latest during the grafting. The invention thus also provides a process for grafting a species onto a
20 polymer comprising a stage of preparing a mixture of a stable free radical, of the polymer and of the species to be grafted. There is also disclosed the use of a stable free radical in the above grafting process. It is not necessary, before mixing, for the polymer to
25 comprise alkoxyamine groups. A free radical initiator can be added to the mixture. The free radical initiator can be chosen from organic peroxides and hydroperoxides, such as dibenzoyl peroxide, tert-butyl

peroxybenzoate or 1,1-bis(tert-butylperoxy)cyclohexane, or azo compounds, such as azobisisobutyronitrile. The free radical initiator can be present in the grafting mixture in the proportion of from 1000 to 10,000 ppm with respect to the sum of the mass of species to be grafted, of the mass of free radical initiator and of the mass of polymer. The presence of a free radical initiator is preferable but is not essential. The mixture is generally heated to from 80 to 200°C. The mixture can be free of solvent.

The invention makes it possible to carry out grafting reactions on to a polymer in the absence of a solvent, even during a stage of conversion of the polymer, while avoiding degradation of the main chains of the polymer.

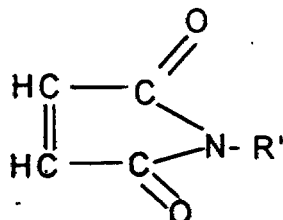
All the polymers mentioned in Table 1 can undergo grafting reactions. The species to be grafted on to a polymer can be chosen from compounds comprising at least one carbon-carbon double bond. These compounds can furthermore comprise a carbonyl



and/or hydroxyl -OH and/or epoxy and/or amino and/or alkoxysilyl group.

The species to be grafted can thus be a vinylaromatic monomer as already defined, a (meth)acrylic monomer as already defined, acrylonitrile, a vinyl ester, such as vinyl acetate or

vinyl propionate, maleic anhydride, an unsubstituted maleimide monomer or an N-substituted maleimide monomer of formula



in which R' is an alkyl, arylalkyl, aryl or
 5 alkylaryl radical having from 1 to 12 carbon atoms,
 such as N-ethylmaleimide, N-isopropylmaleimide,
 N-n-butylmaleimide, N-isobutylmaleimide,
 N-tert-butylmaleimide, N-n-octylmaleimide,
 N-cyclohexylmaleimide, N-benzylmaleimide and
 10 N-phenylmaleimide, or N-cyclohexylmaleimide.

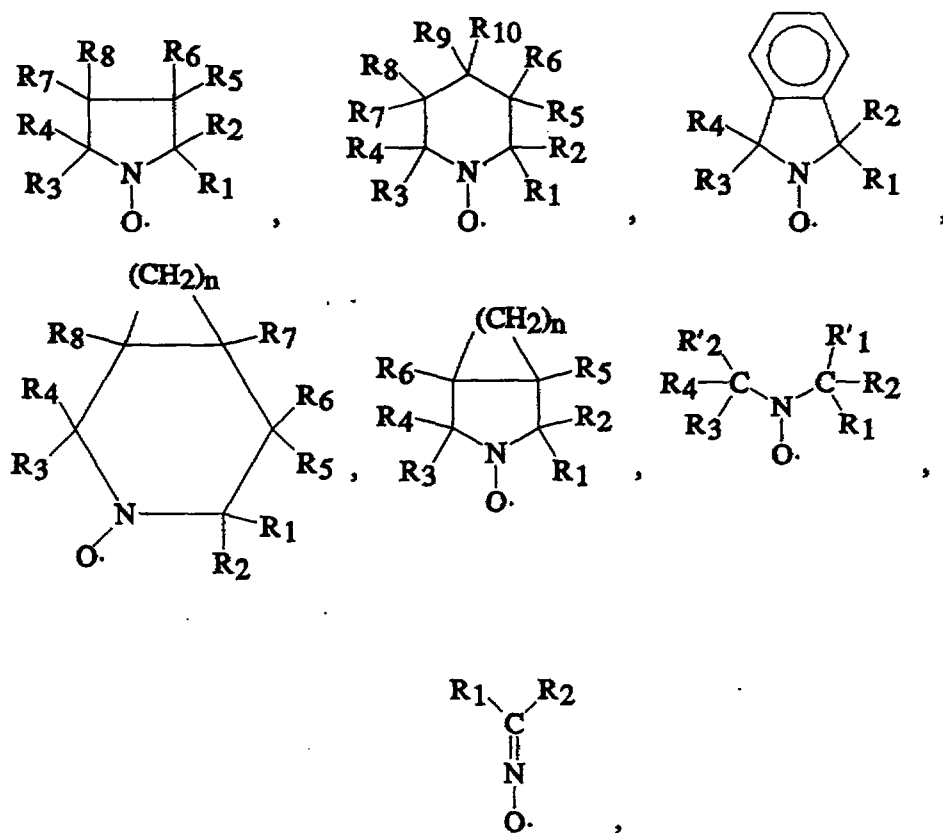
The species to be grafted on to a polymer can
 also be chosen from sulphides and disulphides, such as
 thiocarboxylic acids such as mercaptoacetic acid
 (HOOC-CH₂-SH), mercaptopropionic acid (HOOC-CH₂-CH₂-SH)
 15 or dithiodipropionic acid (HOOC-CH₂CH₂-S-S-CH₂CH₂-COOH).

The stable free radical is not to be confused
 with free radicals whose lifetime is fleeting (a few
 milliseconds), such as the free radicals resulting from
 the usual polymerization initiators such as peroxides,
 20 hydroperoxides and initiators of azo type. Free
 radicals which are polymerization initiators have a
 tendency to accelerate polymerization. By contrast,
 stable free radicals generally tend to slow down

polymerization. It may generally be said that a free radical is stable within the meaning of the present invention if it is not a polymerization initiator and if, under the conditions of use of the present

5 invention, the mean lifetime of the radical is at least five minutes. During this mean lifetime, the stable free radical continually alternates between the radical state and the state of being a group bonded via a covalent bond to a polymer chain. It is preferable for
10 the stable free radical to exhibit good stability throughout the duration of its use within the context of the present invention. Generally, the stable free radical can be isolated in the radical state at room temperature.

15 Stable free radicals include compounds acting as radical polymerization inhibitors, the stable nitroxide radicals, which comprise the $=N-O\cdot$ group, such as the radicals represented by the following formulae:



in which each of R_1 , R_2 , R_3 , R_4 , R'_1 and R'_2 , which can be identical or different, represents a halogen atom, such as chlorine, bromine or iodine, a saturated or unsaturated, linear, branched or cyclic hydrocarbon group, such as an alkyl or phenyl radical, or an ester group $-\text{COOR}$ or an alkoxy group $-\text{OR}$, or a phosphonate group $-\text{PO}(\text{OR})_2$, or a polymer chain which can be, for example, a poly(methyl methacrylate) chain, a polybutadiene chain, a polyolefin chain, such as a polyethylene or polypropylene chain, but which is preferably a polystyrene chain, and in which each of R_5 , R_6 , R_7 , R_8 , R_9 and R_{10} , which can be identical or

different, can be chosen from the groups R_1 , R_2 , R_3 , R_4 , R'_1 and R'_2 above, or can represent a hydrogen atom, a hydroxyl group, or an acid group such as $-\text{COOH}$ or $-\text{PO}(\text{OH})_2$ or $-\text{SO}_3\text{H}$. The stable free radical preferably
5 does not comprise an unsaturation, such as a carbon-carbon double bond, because it is not necessary for it to become attached to a species of the medium via such an unsaturation.

In particular, the stable free radical can be
10 2,2,5,5-tetramethyl-1-pyrrolidinyloxy, marketed under the tradename Proxyl, or 2,2,6,6-tetramethyl-1-piperidinyloxy, generally marketed under the name Tempo.

The stable free radical is preferably present
15 in the mixture comprising the polymer to be stabilized in a proportion of from 0.05 to 0.5 % by weight with respect to the sum of the mass of polymer to be stabilized and of the mass of stable free radical.

The invention is further illustrated by way
20 of example, in the following Examples

Example 1 (comparative)

50 g of crystal polystyrene of trademark
Lacqrene 1340 marketed by the Company Elf Atochem S.A.,
in the form of granules which contain 160 ppm of
25 styrene, are introduced into a 120 cm³ mixing vessel
after having brought the vessel to 250°C under a
nitrogen atmosphere, the said vessel, which is equipped
with a cylindrical rotor with a volume of 51 cm³ which

rotates at 20 revolutions per minute, being of Rheomix 600 trademark and marketed by the Company Haake. The polymer melts and then itself takes the temperature of 250°C in two minutes. The point following the two
5 minutes is defined as the starting point of the test (time zero).

Regular withdrawals of the molten polymer are then made in order to analyse the styrene content of the polymer. Each sample withdrawn is rapidly cooled
10 below the softening temperature (approximately 100°C) and then, after returning to room temperature, the styrene is quantitatively determined by gas phase chromatography. To do this, the sample is first of all dissolved in dichloromethane, the polymer is then
15 precipitated with methanol and the styrene remaining in solution in the dichloromethane is quantitatively determined by gas phase chromatography using propylbenzene as internal standard. The development with time of the styrene content due to
20 depolymerization of the polystyrene is shown in Table 2.

Example 2

The procedure is as in Example 1, except that, at "time zero", 0.05 g of 2,2,6,6-tetramethyl-
25 1-piperidinyloxy (Tempo) is introduced, i.e. approximately 0.1 % of Tempo with respect to the polystyrene + Tempo mass.

The results are collated in Table 2.

Example 3

The procedure is as in Example 1, except that, at "time zero", 0.15 g of 2,2,6,6-tetramethyl-1-piperidinyloxy (Tempo) is introduced, i.e.

5 approximately 0.3 % of Tempo with respect to the polystyrene + Tempo mass.

The results are collated in Table 2.

Example 4 (comparative)

The procedure is as in Example 1, except that
10 50 g of poly(methyl methacrylate) of Altuglas trademark, 2773 grade, containing 2100 ppm of methyl methacrylate (MMA), are charged and except that the procedure for quantitatively determining the MMA is as follows: each sample is dissolved in acetone and the
15 solution thus obtained is then analysed by gas phase chromatography.

The development of the MMA content as a function of time is given in Table 3.

Example 5

20 The procedure is as in Example 4, except that, at "time zero", 0.15 g of Tempo is introduced. The results are collated in Table 3.

Table 2

	Example No.	Tempo content (weight %)	Time (min)							
			0	10	15	20	30	40	50	60
Styrene content (ppm)	1	0	160	270	449	477	548	693	730	758
	2	0.1	160	187	198	204	296	390		
	3	0.3	160	174	184		223	235	268	277

5

Table 3

	Example No.	Tempo content (weight %)	Time (min)			
			0	5	10	15
MMA content (ppm)	4	0	2100	2630	3900	5400
	5	0.3	2100	2150	2900	3600

Example 6 (comparative)

10

281 g of a styrene-butadiene diblock

copolymer (of Europrène 1205 trademark) containing 25 % by weight of units resulting from styrene and having a weight-average molecular mass of 147,000, in the form of a solution containing 1125 g of ethylbenzene, and

15 then 17.9 g of mercaptopropionic acid, are introduced, under a nitrogen atmosphere at 20°C, into a 3-litre reactor equipped with a ribbon agitator and a temperature control. The whole mixture is brought to

92°C with stirring at 200 revolutions per minute and under a pressure of 2 bars of nitrogen. 6 g of a 10 % by weight solution of benzoyl peroxide in toluene are then added and 3 g of the same solution are then added one hour later. The reactor is kept stirring at this temperature for a further 3 hours, is then cooled and a copolymer carrying mercaptopropionic acid grafts (2.8 % by weight of grafts, measured by infrared) is recovered by evaporation at 100°C under vacuum. This copolymer appears crosslinked because it is insoluble in toluene and cyclohexane.

Example 7

The procedure is as in Example 6, except that 0.44 g of Tempo is added to the reactor before heating the latter and except that the temperature is 125°C. The copolymer recovered contains 2.4 % by weight of grafts derived from mercaptopropionic acid. It is entirely soluble in toluene, which indicates that the polymer has suffered very little degradation by crosslinking although the temperature was greater than that in Example 6.

Example 8

The procedure is as in Example 7, except that the 17.9 g of mercaptopropionic acid are replaced by 17.9 g of methacrylic acid. The final copolymer contains 0.7 % by weight of grafts and is soluble in toluene.

Example 9

50 g of a styrene-butadiene diblock copolymer (Europrène 1205) are introduced into the mixing vessel described in Example 1, which vessel has been rendered inert with nitrogen and heated to 150°C. The mixing rate is 32 revolutions per minute and will be maintained at this value during the grafting. A preparation containing 0.07 g of Tempo, 1.5 g of mercaptopropionic acid and 0.16 g of benzoyl peroxide is then introduced. The whole mixture is kept at 150°C with stirring for 30 minutes and then cooled.

A polymer containing 0.45 % by weight of grafts was thus obtained which is entirely soluble in ethylbenzene, toluene or hexane.

CLAIMS

1. Use of a stable free radical for inhibiting the degradation of a polymer by a mechanism which does not involve oxygen.
- 5 2. Use according to Claim 1, which is carried out in the absence of oxygen.
3. Use according to Claim 1 or 2, which is carried out in the absence of light.
4. Use according to any one of Claims 1 to
10 3, wherein the mechanism is a depolymerization.
5. Use according to any one of Claims 1 to 3, wherein the mechanism is a crosslinking.
6. Use according to any one of Claims 1 to 3 and 5, wherein the polymer is a polydiene.
- 15 7. Use according to Claim 6, wherein the polymer is a polybutadiene.
8. Use according to Claim 6 or 7, which is carried out at a temperature of from 80 to 150°C.
9. Use according to any one of Claims 1 to
20 5, wherein the mixture comprising the stable free radical does not comprise a polymer comprising a carbon-carbon double bond.
10. Use according to any one of Claims 1 to 4 and 9, wherein the polymer is a vinylaromatic
25 polymer.
11. Use according to any one of Claims 1 to 4 and 9, wherein the polymer is an olefinic polymer.
12. Use according to Claim 10 or 11, which





is carried out at a temperature of from 180 to 300°C.

13. Use according to any one of Claims 1 to 4 and 9, wherein the polymer is an acrylic or methacrylic polymer.

5 14. Use according to Claim 13, which is carried out at a temperature of from 160 to 300°C.

15 15. Use according to any one of Claims 1 to 14, wherein the mixture comprising the stable free radical does not comprise a poly(phenylene ether) polymer.

16. Use according to any one of Claims 1 to 15, wherein the stable free radical comprises an =N-O· group.

15 17. Use according to any one of Claims 1 to 16, wherein the stable free radical does not comprise a carbon-carbon double bond.

18. Use according to Claim 17, wherein the stable free radical does not comprise an unsaturation via which it could be grafted onto a species of the mixture.

19. Use according to any one of Claims 1 to 18, wherein the stable free radical is present in a proportion of 0.05 to 0.5 % by weight with respect to the sum of the mass of polymer to be stabilized and of the mass of stable free radical.

20. Use according to any one of Claims 1 to 19, which takes place at a pressure of less than 100 bars.





21. Process for the development of a composition or of a material or of a component comprising a polymer prepared by a polymerization stage, which process comprises a heating stage in the
5 absence of oxygen, wherein a stable free radical is introduced so that it is present as a mixture with the polymer at the latest during the heating stage.

22. Process according to Claim 21, wherein the heating stage is carried out in the absence of
10 light.

23. Process according to Claim 21 or 22, wherein the mixture comprising the stable free radical does not comprise a polymer comprising a carbon-carbon double bond during the heating stage.

15 24. Process according to any one of Claims 21 to 23, wherein the mixture comprising the stable free radical does not comprise a poly(phenylene ether) polymer during the heating stage.

25 25. Process according to any one of Claims 21 to 24, wherein the polymer is a vinylaromatic polymer.

26. Process according to any one of Claims 21 to 24, wherein the polymer is an olefinic polymer.

27. Process according to any one of Claims
25 21 to 24, wherein the polymer is an acrylic or methacrylic polymer.

28. Process according to any one of Claims 21 to 27, wherein the stable free radical is added





after the preparation by polymerization of the polymer.

29. Process according to any one of Claims 21 to 28, wherein the heating stage is carried out at a temperature of from 180 to 300°C.

5 30. Process according to Claim 29, wherein the temperature is from 200 to 300°C.

31. Process according to Claim 30, wherein the temperature is from 220 to 300°C.

10 32. Process according to any one of Claims 21 to 31, wherein the heating stage is carried out at a pressure of less than 100 bars.

15 33. Process for grafting a species onto a polymer which comprises producing a mixture of a stable free radical, of the polymer and of the species to be grafted.

34. Process according to Claim 33, wherein the polymer does not comprise an alkoxyamine group.

20 35. Process according to Claim 33 or 34, wherein the mixture is heated at a temperature of from 80 to 200°C.

36. Process according to any one of Claims 33 to 35, wherein the mixture is free from solvent.

25 37. Process according to any one of Claims 21 to 36, wherein the stable free radical comprises an =N-O· group.

38. Process according to any one of Claims 21 to 37, wherein the stable free radical does not comprise a carbon-carbon double bond.





39. Process according to Claim 38, wherein the stable free radical does not comprise an unsaturation via which it could be grafted onto a species of the mixture.

5 40. Process according to any one of Claims 21 to 39, wherein the stable free radical is present in a proportion of from 0.05 to 0.5 % by weight with respect to the sum of the mass of polymer to be stabilized and of the mass of stable free radical.

10 41. Process according to any one of Claims 21 to 39, wherein a free radical initiator is added to the mixture.

42. Use according to Claim 1 substantially as described in any one of Examples 2, 3, 5 and 7 to 9.

15 43. Process according to Claim 21 substantially as described in any one of Examples 2, 3, 5 and 7 to 9.

44. Composition, material or component whenever prepared by a process as claimed in any one of
20 Claims 21 to 41 and 43.

