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(54) Titre : PROCEDE DE FABRICATION ET UTILISATION DE MATERIAUX RENFORCES AU CHOC CONTENANT DES COPOLYMERES BLOCS OBTENUS PAR POLYMERISATION RADICALEE CONTROLEE EN PRESENCE DE NITROXYDES

(54) Title: METHOD OF PRODUCING AND USING MATERIALS WHICH ARE REINFORCED AGAINST IMPACT AND WHICH CONTAIN BLOCK COPOLYMERS THAT ARE OBTAINED BY MEANS OF CONTROLLED RADICAL POLYMERISATION IN THE PRESENCE OF NITROXIDES

(57) **Abrégé/Abstract:**

The invention relates to the production and use of block copolymers which are obtained by means of controlled radical polymerisation in the presence of nitroxides for the purpose of reinforcing fragile polymer matrices. The invention offers advantages such as (i) simplicity of copolymer synthesis and use and (ii) fine dispersion of the copolymer molecules in the fragile matrix, which ensures both the transparency of the material and high reinforcement against impact. More specifically, the invention relates to the radical synthesis of block copolymers comprising at least three blocks, which include one block having a glass transition temperature of less than 0 °C and a thermoplastic end block having a glass transition temperature of more than 0 °C, thereby guaranteeing compatibility with the fragile matrix to be reinforced against impact.



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(54) Title: METHOD OF PRODUCING AND USING MATERIALS WHICH ARE REINFORCED AGAINST IMPACT AND
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SATION IN THE PRESENCE OF NITROXIDES(54) Titre : PROCEDE DE FABRICATION ET UTILISATION DE MATERIAUX RENFORCES AU CHOC CONTENANT
DES COPOLYMERES BLOCS OBTENUS PAR POLYMERISATION RADICALEIRE CONTROLEE EN PRESENCE DE
NITROXYDES(57) Abstract: The invention relates to the production and use of block copolymers which are obtained by means of controlled
radical polymerisation in the presence of nitroxides for the purpose of reinforcing fragile polymer matrices. The invention offers
advantages such as (i) simplicity of copolymer synthesis and use and (ii) fine dispersion of the copolymer molecules in the fragile
matrix, which ensures both the transparency of the material and high reinforcement against impact. More specifically, the invention
relates to the radical synthesis of block copolymers comprising at least three blocks, which include one block having a glass tran-
sition temperature of less than 0 °C and a thermoplastic end block having a glass transition temperature of more than 0 °C, thereby
guaranteeing compatibility with the fragile matrix to be reinforced against impact.(57) Abrégé : L'invention décrit la mise en oeuvre et l'utilisation de copolymères blocs obtenus par polymérisation radicalaire
contrôlée en présence de nitroxydes dans le but de renforcer des matrices polymères fragiles. Un avantage de l'invention consiste en
la simplicité de synthèse et de mise en oeuvre des copolymères. Un autre avantage de l'invention consiste en la dispersion fine des
molécules de copolymères dans la matrice fragile qui assure à la fois une transparence du matériau et un bon renforcement au choc.
Particulièrement, l'invention décrit la synthèse de copolymères à blocs par voie radicalaire possédant au moins trois blocs dont un
bloc possède une température de transition vitreuse inférieure à 0°C et un bloc terminal thermoplastique de température de transition
vitreuse supérieur à 0°C assurant la compatibilité avec la matrice fragile que l'on souhaite renforcer au choc.

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— avant l'expiration du délai prévu pour la modification des revendications, sera republiée si des modifications sont reçues

En ce qui concerne les codes à deux lettres et autres abréviations, se référer aux "Notes explicatives relatives aux codes et abréviations" figurant au début de chaque numéro ordinaire de la Gazette du PCT.

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**METHOD OF PRODUCING AND USING MATERIALS WHICH ARE
REINFORCED AGAINST IMPACT AND WHICH CONTAIN BLOCK
COPOLYMERS THAT ARE OBTAINED BY MEANS OF CONTROLLED RADICAL
POLYMERIZATION IN THE PRESENCE OF NITROXIDES**

5

The present invention relates to the field of materials reinforced against impacts and particularly to materials which are both transparent and reinforced against impacts and more particularly to materials reinforced against impacts using a block copolymer.

10

The present invention discloses the preparation and the use in brittle thermoplastic polymer matrices of block copolymers obtained by controlled radical polymerization in the presence of stable nitroxides, the materials thus obtained exhibiting improved properties of impact strength.

15

Impact-resistant thermoplastic resins are conventionally obtained by hot blending an impact-reinforcing additive, resulting from the stages of coagulating, dehydrating and drying an elastomer latex, with the particles of the "hard" polymer or thermoplastic resin, which results in what is known as an alloy, from which it is possible to obtain articles shaped by extrusion, injection molding or compression.

20

The Applicant Company has just found a novel class of polymer materials which are both transparent and impact-resistant and a novel way of preparing impact-resistant polymer materials.

25

The first subject matter of the present invention is transparent and impact-resistant polymer materials composed of a brittle matrix (I), representing from 0 to 95% by weight of the total weight of the materials of the invention, in which is dispersed a block copolymer (II) of general formula $B-(A)_n$. Advantageously, the portion of the brittle matrix is between 10 and 85% by weight.

30

The materials of the invention can additionally comprise other impact-reinforcing additives, such as those

35

of the DurastrengthTM or MetablendTM trade mark, and the like.

Generally, the brittle matrix (I) exhibits a glass transition temperature (T_g) of greater than 0°C. The brittle matrix is composed to greater than 50 % by weight at at least one polymer chosen from the group consisting of poly(methyl methacrylate), on polystyrene, on poly(vinylidene fluoride), on polyesters, on polycarbonate, on poly(vinyl chloride), on polyamide, on polyepoxide, on polyethylene or on polyacrylonitrile, or their copolymers. The brittle matrix is preferably a polymethacrylate.

The block copolymers of the invention correspond to the general formula $B-(A)_n$, n being a natural number of greater than two, preferably between 2 and 20 and preferably between 2 and 8;

where B represents a polymer block composed of the sequence of monomer units which can be polymerized by the radical route, the overall T_g of which is less than 0°C. The average molar mass of the block B is greater than 5000 g/mol, preferably greater than 20 000 g/mol and more preferably still greater than 50 000 g/mol.

A is a polymer block composed of a sequence of monomer units which can be polymerized by the radical route, the overall T_g of which is greater than 0°C. The average molar mass of each block A is between 10 000 g/mol and 10^6 g/mol, preferably between 10 000 g/mol and 200 000 g/mol and preferably between 20 000 and 100 000 g/mol.

The relative lengths of the blocks A and B are chosen such that $n \cdot M_n(A) / (n \cdot M_n(A) + M_n(B))$ is between 0.5 and 0.95, preferably between 0.6 and 0.8, and such that $M_n(B)$ is greater than or equal to the mean entanglement length of the block B,

where M_n denotes the number-average molecular mass of the polymer.

According to the invention, the block copolymer (II)

exhibits a polydispersity index of between 1.5 and 3, advantageously of between 1.8 and 2.7 and preferably of between 2.0 and 2.5. On the other hand, the block B exhibits a polydispersity index of less than 2.

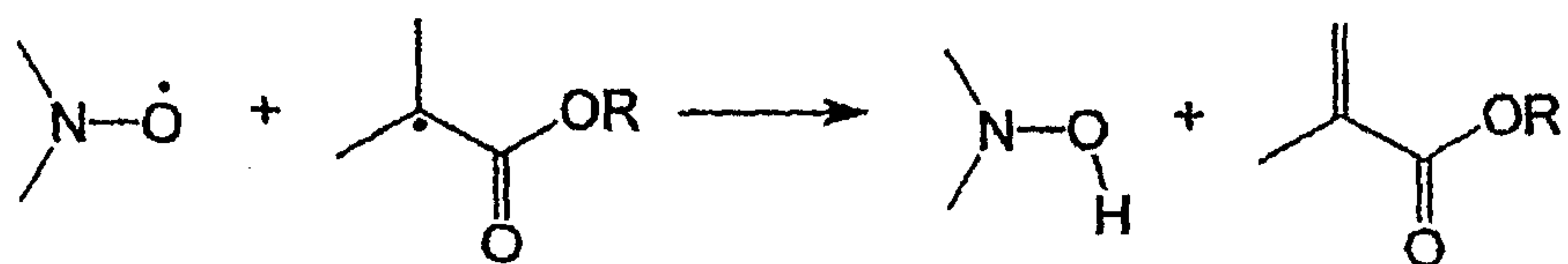
5 Generally, A represents from 50% to 95 % by weight of the total weight of the copolymer (II) and preferably between 60 and 95%.

10 In particular, B is a polyacrylate with a glass transition temperature of less than 0°C; preferably, B will comprise butyl acrylate units. A is a polymer compatible with the matrix to be reinforced. By way of indication, in order to reinforce poly(methyl methacrylate) (PMMA), poly(vinylidene fluoride) (PVDF) or poly(vinyl chloride) (PVC), PMMA will be chosen for A. In order to reinforce
15 polyesters, such as poly(butylene terephthalate) or poly(ethylene terephthalate), or epoxys, A will preferably be chosen from polymethacrylates comprising glycidyl methacrylate or methacrylic acid units and, in order to reinforce polystyrene, PS will preferably be chosen for A.

20 Another subject-matter of the invention is a process for the preparation of the transparent and impact-resistant materials of the invention. This process is based on the "controlled radical polymerization" polymerization technique based on the use of stable nitroxides. The
25 general synthetic scheme is as follows: in a first step, the block B, with a flexible or elastomeric nature, is prepared by polymerization in the presence of a well chosen nitroxide and, in a second step, by using the block B as polymerization initiator, the branches A, with a stiff or
30 thermoplastic nature, are prepared.

 It is known that stable nitroxides can result in the formation of block copolymers by controlled radical polymerization (WO 9624620, WO 2000071501 A1 20001130, EP 1142913 A1 20011010). By virtue of certain families of
35 nitroxides described in the abovementioned patents, block copolymers incorporating units as difficult to control by

the conventional radical route as acrylates are described. In the case of methacrylates, certain limitations well known to a person skilled in the art appear, such as the transfer reaction with the nitroxide (eq. 1), which brings about a premature loss in the control of the polymerizations:



(eq.1)

However, starting from a first block controlled by the nitroxide, it is possible to reinitiate a radical methacrylate polymerization, which will be limited in its living nature but will still result in a block copolymer.

The limitations of the living nature are reflected by a broadening of the polydispersity of the copolymer block, of between 1.5 and 2.5, and the Applicant Company has discovered that this had an effect on the morphology of the block copolymer.

This is because monodisperse block copolymers will experience transitions in morphology for copolymer block compositions which are very specific (cf. G. Holden et al. in "Thermoplastic elastomers", 2nd edition, Carl Hanser Verlag, Munich, Vienna, New York, 1996). For this reason, when the proportion of the thermoplastic block increases, the morphology changes towards a topology where the continuous phase is the thermoplastic phase.

As long as this situation is not reached, the block copolymer cannot be homogeneously blended with a matrix compatible with the thermoplastic block. For this reason, the blend becomes opaque and the mechanical properties thereof are very poor.

As the two-stage synthesis according to any one process for the polymerization (mass, solvent, emulsion, suspension) of copolymer block in the presence of

nitroxides is very simple to carry out, it was essential to find the compositions or the methods of synthesis which result in copolymers which can be compatibilized with thermoplastic matrices. The Applicant Company has
5 discovered that, for compositions comprising between 50% and 95% of thermoplastic phase, preferably between 60% and 85% of thermoplastic phase, the morphology of the copolymers obtained by controlled radical polymerization in the presence of nitroxides was compatible with a good
10 mixture of the copolymer in brittle thermoplastic matrices.

Furthermore, unlike the document JP2000198825 A 20000718, in which the authors claim the use of block copolymers obtained by controlled radical polymerization in the presence of copper salt with a low polydispersity index
15 (PI<1.5), the Applicant Company has found that, by virtue of the controlled radical polymerization in the presence of nitroxide, the polymerization of the thermoplastic block could take place at the same time as the polymerization of the matrix and that it was not necessary to isolate the
20 block copolymer beforehand. Thus, starting from a first block functionalized by nitroxides, it is possible to initiate thermoplastic chains at the same time as other chains are initiated by conventional initiators or by thermal initiation. There are two advantages to this:

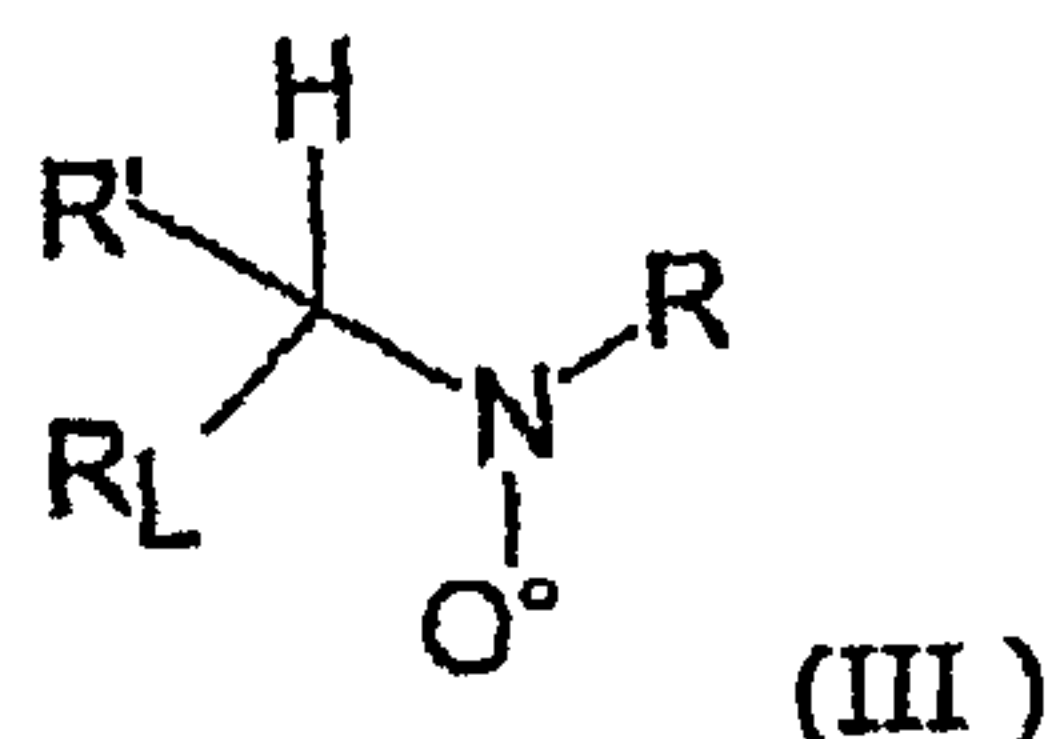
25 1 - If the thermoplastic matrix to be reinforced against impact has the same composition as the thermoplastic block of the copolymer, the reinforced material is obtained directly.

30 2 - If another matrix has to be reinforced, the fact of adding homopolymers to the block copolymer makes it possible to fluidify the copolymer, which, if not, exhibits too excessive a viscosity to be converted by extrusion without undergoing decomposition.

The Applicant Company thus claims a process for the
35 manufacture of block copolymers which are compatible with thermoplastic matrices and the use of these block

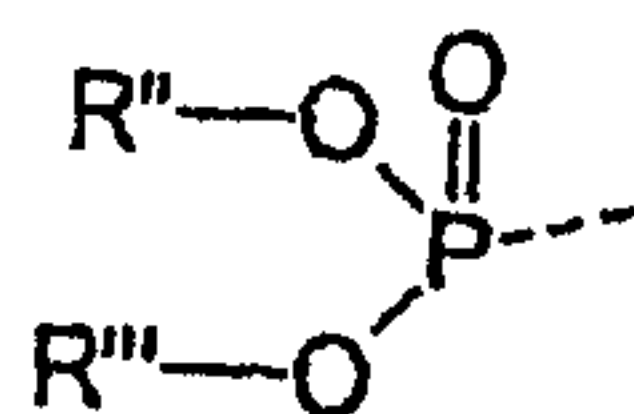
copolymers in the manufacture of these resins which are more resistant to impact.

In particular, the process according to the invention consists of the synthesis of the copolymers in the presence of nitroxides, (III):



- where R' and R, which are identical or different, optionally connected so as to form a ring, are alkyl groups having between 1 and 40 carbon atoms optionally substituted by hydroxyl, alkoxy or amino groups; in particular, R and R' will be tert-butyl groups;

- and where R_L is a monovalent group with a molar mass of greater than 16 g/mol; in particular, R_L will be a phosphorus group and more particularly a phosphonate group of formula:



- where R'' and R''', which are identical or different, optionally connected so as to form a ring, are alkyl groups having between 1 and 40 carbon atoms optionally substituted by hydroxyl, alkoxy or amino groups; in particular R'' and R''' will be ethyl groups.

In particular, the block copolymers are of general formula B-(A)_n, where B represents a polymer block composed of the sequence of monomer units which can be polymerized by the radical route in the presence of nitroxides (III) and for which the overall T_g is less than 0°C. The average molar mass of the block B is between 3000 g/mol and 10⁶ g/mol, preferably between 5000 g/mol and 200 000 g/mol and preferably between 5000 and 100 000 g/mol;

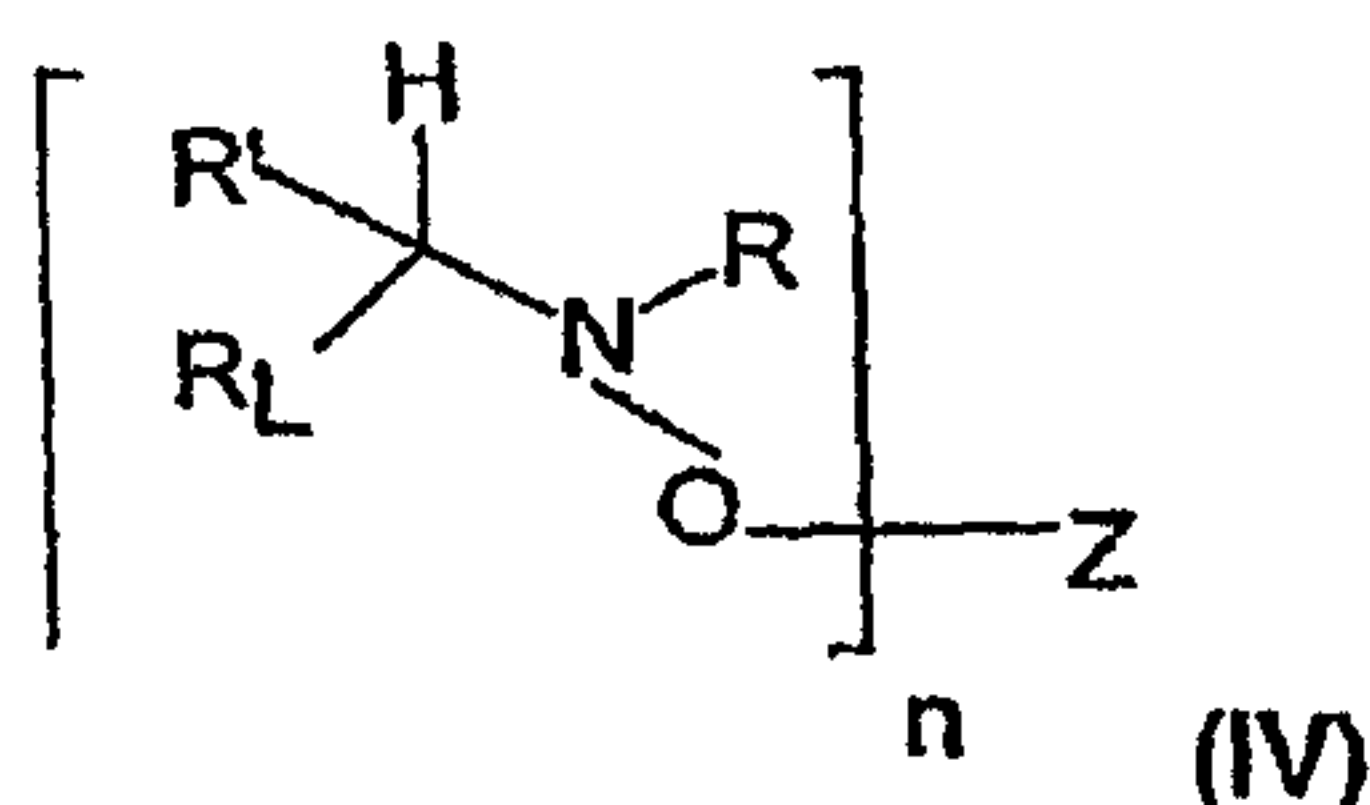
A is a block of the polymer composed of a sequence

of monomer units which can be polymerized by the radical route in the presence of nitroxides (III) and for which the overall T_g is greater than 0°C . The average molar mass of each block A is between 10 000 g/mol and 10^6 g/mol, preferably between 10 000 g/mol and 200 000 g/mol and preferably between 20 000 and 100 000 g/mol, where n is a natural number greater than two, preferably of between 2 and 20 and preferably between 2 and 8.

The relative lengths of the blocks A and B are chosen such that $n \cdot \text{Mn}(A) / (n \cdot \text{Mn}(A) + \text{Mn}(B))$ is between 0.5 and 0.95, preferably between 0.6 and 0.8, and such that $\text{Mn}(B)$ is greater than or equal to the mean entanglement length of the block B. The polydispersity of the block copolymer obtained is between 1.5 and 3, preferably between 1.8 and 2.7 and more preferably from 1.9 to 2.5.

The process is characterized in that it consists:

- 1) firstly, in preparing, according to a conventional polymerization recipe, the first block B by mixing the monomer(s) with an alkoxyamine of general formula (IV):



where Z is a polyvalent radical carrying terminal functional groups of styryl or acryloyl type, the other radicals having the same meanings as above,

nitroxide (III) being added to the mixture in a proportion ranging from 0 to 20 mol% with respect to the moles of alkoxyamine functional groups (one alkoxyamine contributes n alkoxyamine functional groups).

The polymerization is carried out at temperatures ranging from 60 to 250°C , preferably from 90 to 160°C , for pressures ranging from 0.100 bar to 80 bar, preferably from 0.5 bar to 10 bar.

The polymerization has to be controlled and the

latter will preferably be halted before 99% conversion, preferably before 90% conversion. The block B thus obtained is either used with the residual monomers or is purified from the monomers by distillation or washing and drying with a solvent which is immiscible with B and miscible with the monomers used.

2) Secondly, the process consists in diluting the first block B obtained in the mixture of monomers intended to form the blocks A. Between 0 and 100 molar equivalents of conventional radical polymerization initiator (of the LuperoxTM or azo compound type, for example AZDNTM) are added to this mixture. The choice of this ratio depends on the viscosity/impact-reinforcing compromise which it is desired to have.

The polymerization is carried out at temperatures ranging from 60 to 250°C, preferably from 90 to 160°C, for pressures ranging from 0.100 bar to 80 bar, preferably from 0.5 bar to 10 bar.

The conversion of the monomer varies from 10 to 100% and the polymer obtained is separated from the residual monomers by evaporation under vacuum at temperatures ranging up to 250°C and preferably 200°C.

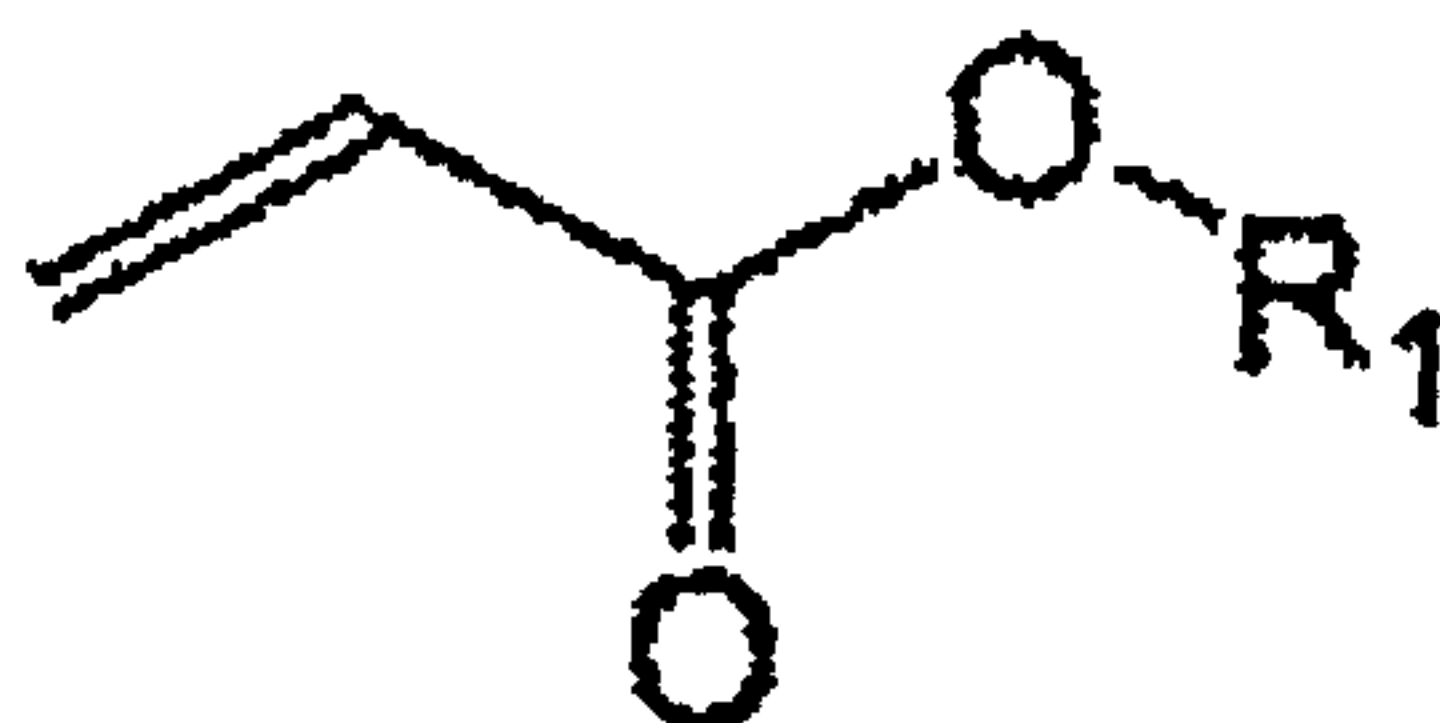
3) Thirdly,

- either the material obtained is extruded in the presence of the brittle matrix which it is desired to see reinforced against impact: mention may in particular be made of PMMA, polyesters of PET or PBT type, polystyrene, PVDF, polyamides, polycarbonates, PVC and the like. This extrusion stage can also involve other additives, in particular impact additives, such as those of the DurastrengthTM or MetablendTM trade mark,
- or else the material obtained is diluted in a mixture of monomers which is itself subsequently polymerized. Mention may be

made, for example, of styrene, MMA, epoxides, mixtures of diols and of diacid, or precursors of polyamides (lactam or mixtures, diamine, diacids),

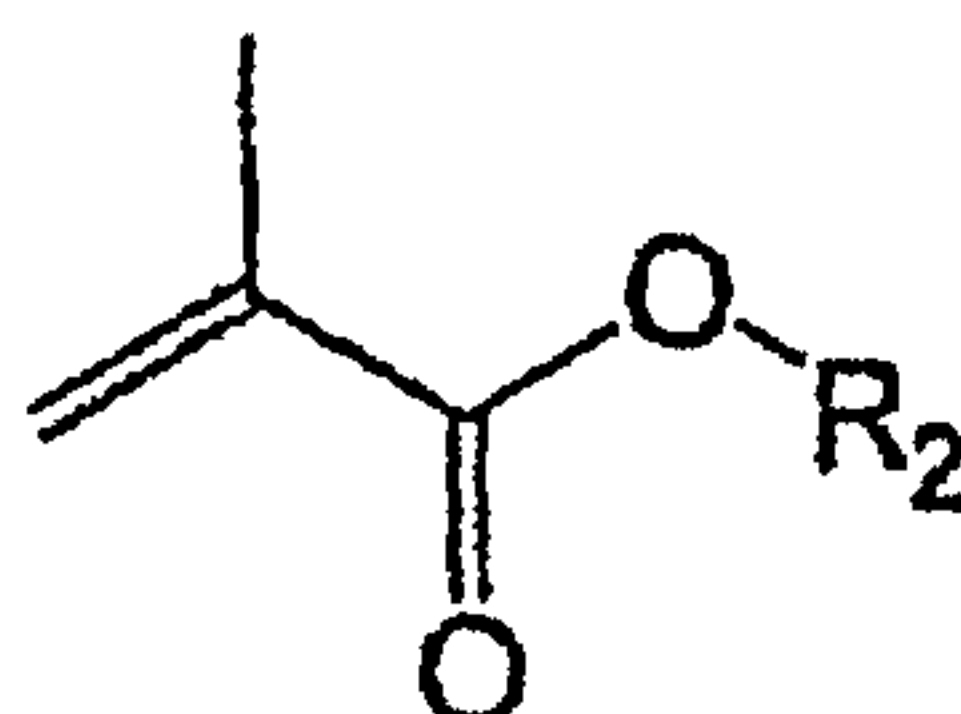
- 5 - it is also possible to use the material as an impact-resistant resin without blending.

10 A person skilled in the art knows how to choose his monomers according to the block desired. Mention may be made, among the monomers chosen, pure or as a mixture, of acrylic monomers of general formula:



15 where R^1 is a hydrogen atom or a linear, cyclic or branched alkyl comprising from 1 to 40 carbon atoms which is optionally substituted by a halogen atom or a hydroxyl (-OH), alkoxy, cyano, amino or epoxy group.

 Another family of monomers of choice is composed of methacrylic monomers of general formula:



20 where R_2 has the same meaning as R_1 .

 Another possible monomer is acrylonitrile, styrene derivatives, dienes and generally any monomer carrying a vinyl bond which can be polymerized by the radical route.

25 The materials of the invention can be used in various fields, such as the automobile industry or the construction industry. They make it possible to manufacture impact-resistant shaped articles, in particular sheets, and very particularly sheets of use in forming thermoformed

- 10 -

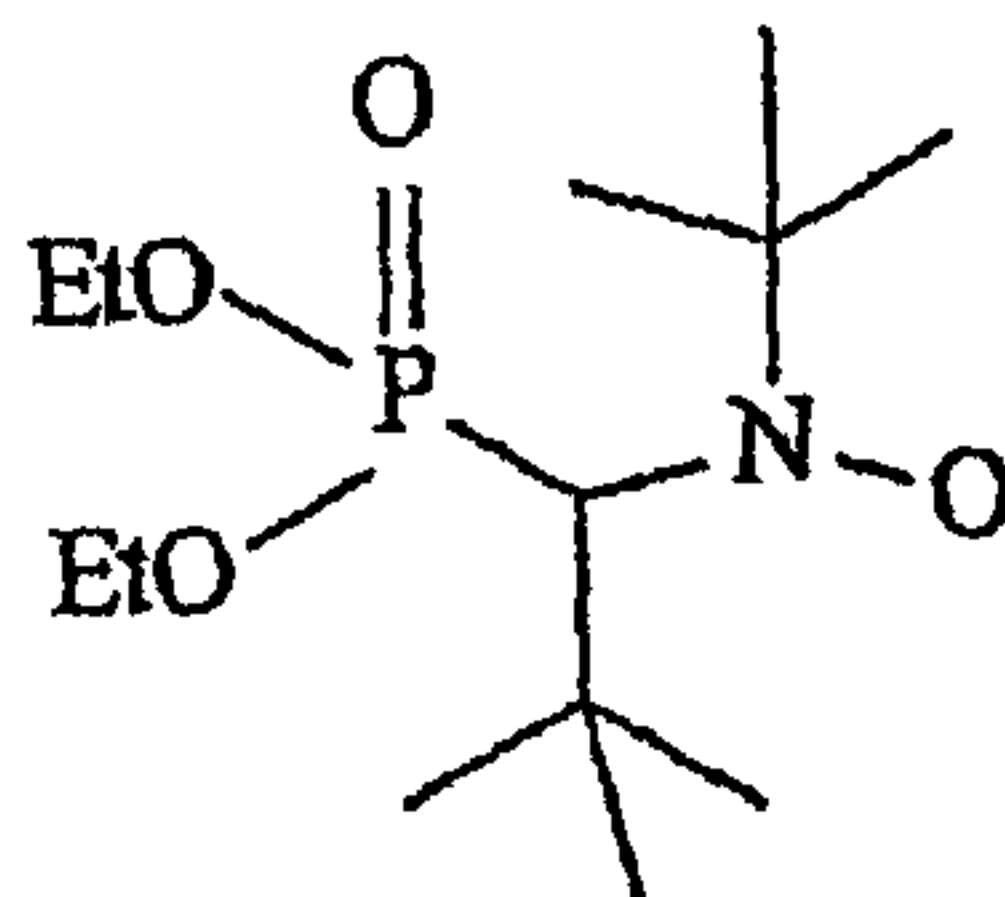
bathroom fittings, such as bath tubs, sinks, shower trays, basins, shower stalls and the like.

These shaped articles exhibit an improved impact strength while retaining good mechanical properties, in particular with regard to flexion (high modulus), that is to say a degree of stiffness.

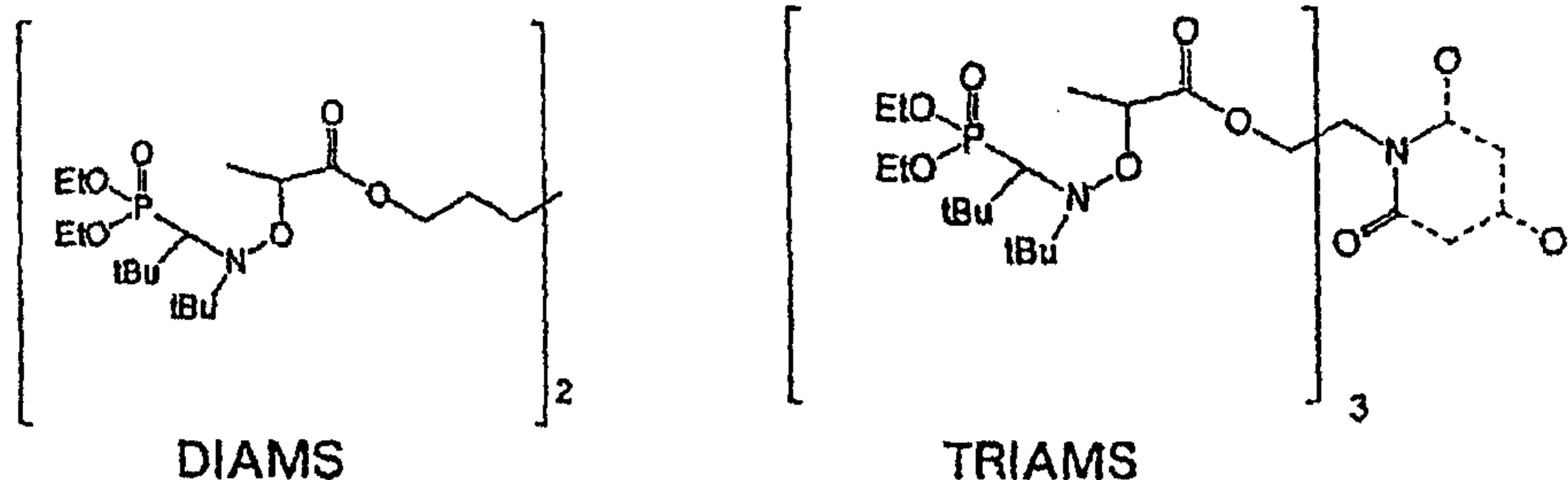
The following examples illustrate the invention without limiting the scope thereof.

Examples:

The stable free radical used in the examples and referenced SG1 corresponds to the following formula:



The alkoxyamines DIAMS and TRIAMS mentioned in the examples correspond to the following formulae:



I. First series: Reinforcement against impacts of a PMMA matrix by a B-(A)_n copolymer with n = 2 or 3

I.1 Preparation of the copolymers:

The general procedure for syntheses and for characterizations is described below.

The syntheses are carried out in two stages in a steel reactor with a working capacity of 9 liters. The starting media are systematically degassed by vacuum/nitrogen cycles before being introduced into the reactor, which is preheated to the reaction temperature.

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The control of the polymerization of butyl acrylate, for example, in the presence of the alkoxyamines 1 or 2 denoted respectively by DIAMS and TRIAMS was optimized at a temperature $T = 115^{\circ}\text{C}$ and in the presence of an excess of free SG1 of 7 mol% per alkoxyamine functional group. Conversion was limited to 50%, so as to retain a good living nature of the PBuA-SG1 macroinitiators obtained, the residual monomer subsequently being removed by a stripping stage (70°C under vacuum for 2 hours).

In a second stage, the di- or trifunctional macroinitiators thus obtained were allowed to reinitiate the polymerization of MMA at 120°C under pressure, so as to prepare triblock and star block copolymers. It is important to note that the conversion of MMA is limited because of disproportionation reactions between the nitroxide and the growing chains. Starting from synthesis No. 2, a rise in temperature in stationary phases between 85 and 120°C was opted for, which made it possible to push back this limit from 20 to 45%.

The operating conditions for the syntheses of the block B functionalized with a stable free radical, SG1, are summarized in table 1 (Tab 1). The operating conditions relating to the preparation of 4 block copolymers, poly(butyl acrylate) for block B and poly(methyl methacrylate) for block A, are summarized in table 2.

I.2 Preparation of the reinforced matrix:

The blends composed of PMMA and of copolymers which reinforce against impacts are prepared by melt extrusion.

I.3 Characterizations

The molar masses and their distribution were determined by steric exclusion chromatography (SEC), by universal calibration using polystyrene standards and the Mark-Houwink coefficients of PBuA for the PBuA-SG1 macroinitiators and of PMMA for the copolymers.

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The composition of the copolymers in PBuA and PMMA was determined by proton NMR. The results obtained are given in table 3 (Tab 3) as regards the block B and in table 4 (Tab 4) as regards the copolymers.

5 The mechanical properties were evaluated by the well-known traction-elongation test. The results are illustrated by figure No. 1.

10 **II. Second series: In situ preparation of a PMMA reinforced against impacts by the polymerization of a methyl methacrylate/macroinitiator based on butyl acrylate and on styrene mixture (syrup), either by the "cast sheet" technique or continuously**

II.1 Cast sheet

15 Stage 1:

Preparation of butyl acrylate/styrene (83/17) copolymer by polymerizing by up to 69% a mixture comprising 7.2 kg of butyl acrylate, 800 g of styrene, 51 g of TRIAMS and 1.5 g of free SG1. The copolymer is recovered by evaporation of the volatile components and then dissolution in 8 kg of methyl methacrylate.

20 The macroinitiator obtained exhibits the following characteristics: 17% by weight of styrene, $M_n = 70\,000$ g/mol, $M_w = 142\,000$ g/mol.

25 Stage 2:

The formulation of the methyl methacrylate syrup employed is as follows:

30 A variable concentration of macroinitiator obtained according to stage 1: either 2% or 5% or 7.5% or 10% or 20% by weight of the total weight of the mixture.

550 ppm of Luperox 331-80M.

0.2% by weight of the total weight of the mixture of maleic anhydride.

35 21 ppm of γ -terpinene.

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The sheets are introduced into an oven and are heated at 90°C for approximately 16 hours and, in postpolymerization, at 125°C for 2 hours.

5 These examples show (see table 5, Tab 5) that the incorporation of a block copolymer in a PMMA matrix of cast sheet type contributes a significant reinforcement against impact which is greater than the best current commercial reference.

10 They also illustrate the fact that the block copolymers obtained by virtue of the chemistry of the nitroxides of the invention can be introduced in situ during the polymerization of the matrix.

II.2 Continuous polymerization

15 Use is made in this example of an arrangement composed of two reactors in cascade. One is maintained at -40°C and is used to feed the second with polymerization syrup. The second reactor is the polymerization reactor proper. The polymerization temperature is greater than
20 160°C. The monomer syrup is introduced into the polymerization reactor with a flow rate of 8 kg/h. As soon as a level of solid of the order of 60% is obtained, the polymerization medium is pumped continuously to a degassing extruder at a temperature of 230°C. The material is
25 granulated after cooling in a water vat.

The monomer syrup used is as follows (as proportion by weight):

30 Poly(butyl acrylate); it is the copolymer Flopil 9 described above: 15%.

Ethyl acrylate: 0.6%.

Di(tert-dodecyl) disulfide: 100 ppm.

Dodecyl mercaptan: 0.34%.

Luperox 531: 180 ppm.

35 The maximum polymerization temperature achieved is 178°C. The granules obtained have the final composition:

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82.5% PMMA

17.3% acrylate (butyl and ethyl)

0.2% residual MMA.

Mn = 30 000 g/mol (PMMA standard)

5 Mw = 85 000 g/mol (PMMA standard)

10 The measurements of the yield stress of a standard PMMA, of a PMMA reinforced against impacts and of the material prepared according to the invention, carried out by compressive tests on cylindrical test specimens according to Standard ISO 604, made it possible to derive the following values:

Standard PMMA (MC31): 130 MPa

15 PMMA reinforced against impacts (commercial product: M17T): 98 MPa

Reinforced PMMA according to the invention: 96 MPa.

The comparison of these results shows that the product according to the invention has a ductile behavior equivalent to a standard impact grade of PMMA.

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CLAIMS

1. A transparent and impact-resistant polymer material composed of a brittle matrix (I) having a glass transition temperature of greater than 0°C in which is dispersed a block copolymer (II) of general formula B-(A)_n, n being between 2 and 20, with a polydispersity of between 1.5 and 3, B being a polymer block with a flexible nature with a glass transition temperature of less than 0°C and with a polydispersity index of less than 2 and A being a polymer block with a stiff nature with a glass transition temperature of greater than 0°C, A being of the same nature as or compatible with the matrix.

2. The material as claimed in claim 1, characterized in that the block copolymer has a polydispersity of between 1.8 and 2.7 and preferably of between 2 and 2.5.

3. The material as claimed in either of claims 1 and 2, characterized in that the proportion of brittle matrix is between 0 and 95%.

4. The material as claimed in claim 3, characterized in that the proportion of brittle matrix is preferably between 10 and 85%.

5. The material as claimed in one of claims 1 to 4, characterized in that the brittle matrix is composed to greater than 50% by weight of at least one polymer chosen from the group consisting of poly(methyl methacrylate), polystyrene, poly(vinylidene fluoride), polyesters, polycarbonate, poly(vinyl chloride), polyamide, polyepoxides, polyethylene, polyacrylonitrile and their copolymers.

6. The material as claimed in one of claims 1 to 5, characterized in that A represents from 50 to 95% by weight of the total weight of the block copolymer (II).

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7. The material as claimed in claim 6, characterized in that A represents from 60 to 90% by weight of the total weight of the block copolymer (II).

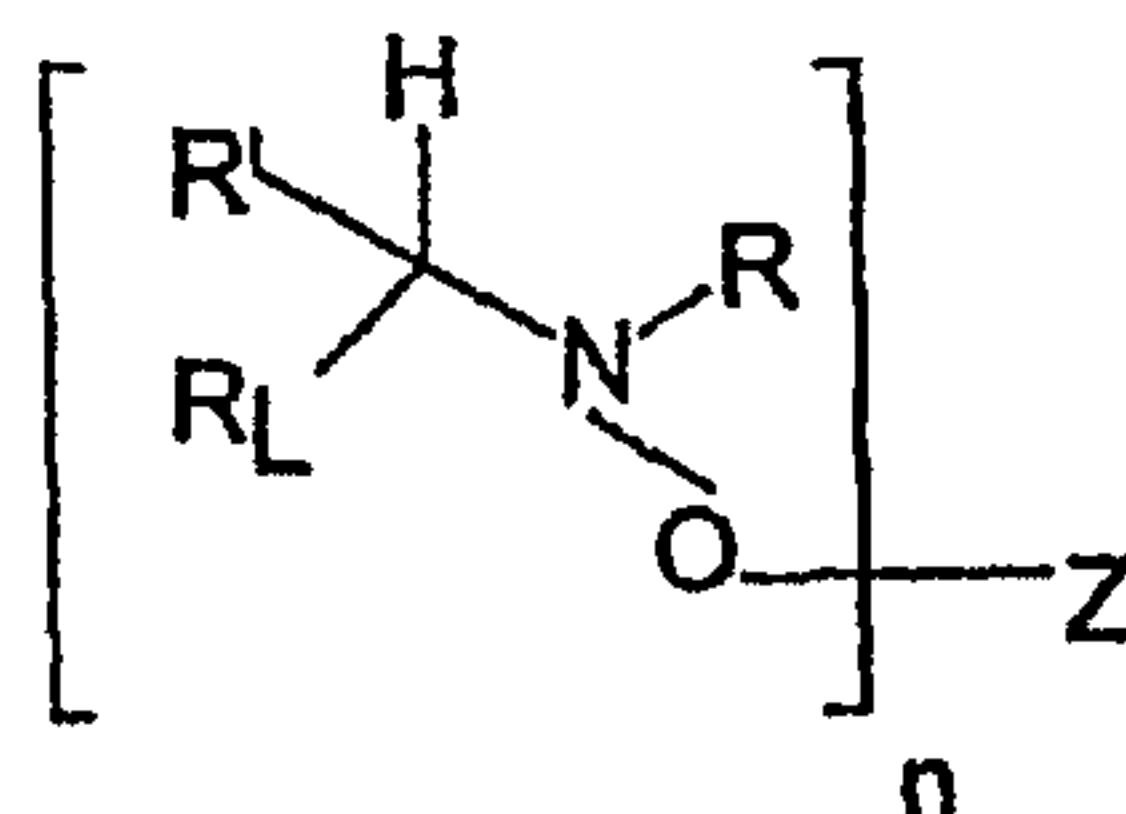
5 8. The material as claimed in one of the preceding claims, characterized in that B is a polyacrylate with a glass transition temperature of less than 0°C.

9. The material as claimed in one of the preceding claims, characterized in that A is a polymethacrylate with a glass transition temperature of greater than 0°C.

10 10. The material as claimed in one of the preceding claims, characterized in that the block B exhibits an average mass of greater than 5000 g/mol, preferably of greater than 20 000 and more preferably still of greater than 50 000 g/mol.

15 11. A process for the preparation of the material of claims 1 to 10, consisting

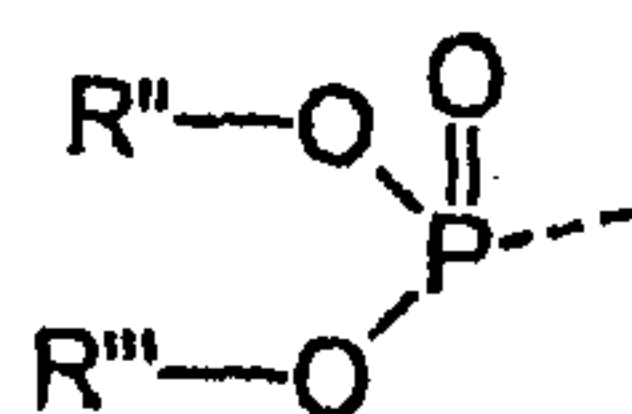
1 - Firstly, in preparing, according to a conventional polymerization recipe, the first block B by mixing the monomer(s) with an alkoxyamine of
20 general formula:



- where R' and R, which are identical or different, optionally connected so as to form a ring, are alkyl groups having between 1 and 40 carbon atoms optionally
25 substituted by hydroxyl, alkoxy or amino groups; in particular, R and R' will be tert-butyl groups;

- and where R_L is a monovalent group with a molar mass of greater than 16 g/mol; in particular, R_L will be a phosphorus group and more particularly a phosphonate
30 group of formula:

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- where R'' and R''', which are identical or different, optionally connected so as to form a ring, are alkyl groups having between 1 and 40 carbon atoms optionally substituted by hydroxyl, alkoxy or amino groups; in particular R'' and R''' will be ethyl groups,

where Z is a polyvalent radical carrying end functional groups of styryl or acryloyl type, the other radicals having the same meanings as above.

The polymerization is carried out at temperatures ranging from 60 to 250°C, preferably from 90 to 160°C, for pressures ranging from 0.100 bar to 80 bar, preferably from 0.5 bar to 10 bar.

2 - Secondly, in diluting the first block B obtained in the mixture of monomers intended to form the blocks A. Between 0 and 100 molar equivalents of conventional radical polymerization initiator (of the LuperoxTM or azo compound type, for example AZDNTM) are added to this mixture. The choice of this ratio depends on the viscosity/impact-reinforcing compromise which it is desired to have.

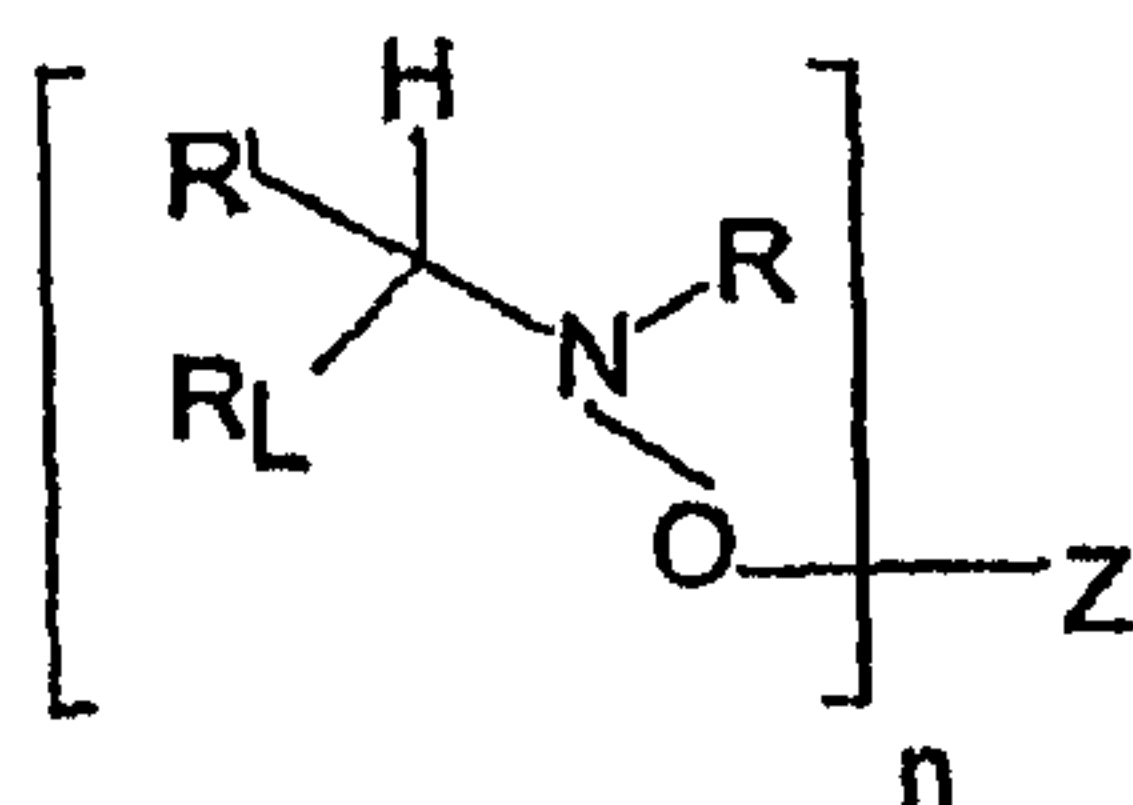
The polymerization is carried out at temperatures ranging from 60 to 250°C, preferably from 90 to 160°C, for pressures ranging from 0.100 bar to 80 bar, preferably from 0.5 bar to 10 bar.

The conversion of the monomer varies from 10 to 100% and the polymer obtained is separated from the residual monomers by evaporation under vacuum at temperatures ranging up to 250°C and preferably 200°C.

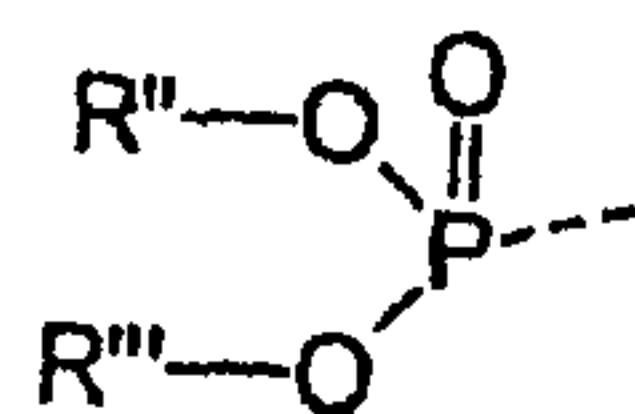
12. A process for the preparation of the material of claims 1 to 10, consisting

1 - Firstly, in preparing, according to a conventional polymerization recipe, the first block B by mixing the monomer(s) with an alkoxyamine of general formula:

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- where R' and R, which are identical or different, optionally connected so as to form a ring, are alkyl groups having between 1 and 40 carbon atoms optionally substituted by hydroxyl, alkoxy or amino groups; in particular, R and R' will be tert-butyl groups;
- and where R_L is a monovalent group with a molar mass of greater than 16 g/mol; in particular, R_L will be a phosphorus group and more particularly a phosphonate group of formula:



- where R'' and R''', which are identical or different, optionally connected so as to form a ring, are alkyl groups having between 1 and 40 carbon atoms optionally substituted by hydroxyl, alkoxy or amino groups; in particular R'' and R''' will be ethyl groups,

where Z is a polyvalent radical carrying end functional groups of type, the other radicals having the same meanings as above.

The polymerization is carried out at temperatures ranging from 60 to 250°C, preferably from 90 to 160°C, for pressures ranging from 0.100 bar to 80 bar, preferably from 0.5 bar to 10 bar.

2 - Secondly, in diluting the first block B obtained in the mixture of monomers intended to form the blocks A. Between 0 and 100 molar equivalents of conventional radical polymerization initiator (of the LuperoxTM or azo compound type, for example AZDNTM) are added to this mixture. The choice of this ratio depends on the viscosity/impact-reinforcing compromise which it is

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desired to have.

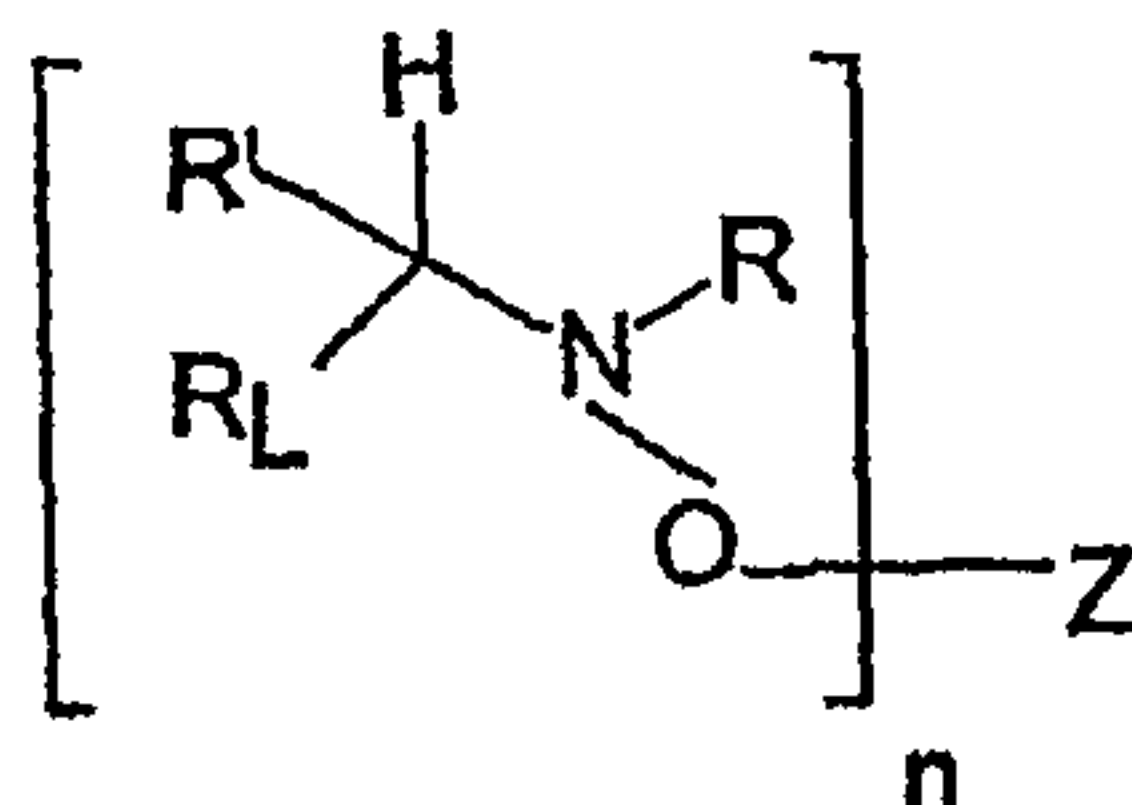
The polymerization is carried out at temperatures ranging from 60 to 250°C, preferably from 90 to 160°C, for pressures ranging from 0.100 bar to 80 bar, preferably from 0.5 bar to 10 bar.

The conversion of the monomer varies from 10 to 100% and the polymer obtained is separated from the residual monomers by evaporation under vacuum at temperatures ranging up to 250°C and preferably 200°C.

3 - Thirdly, in mixing, according to known techniques, the product obtained in 2 and the brittle matrix which it is desired to see reinforced against impact, such as PMMA, polyesters of PET or PBT type, polystyrene, PVDF, polyamides, polycarbonates or PVC, optionally in the presence of other additives, in particular impact additives, such as those of the Durastrength™ or Metablend™ trade mark.

13. A process for the preparation of the material of claims 1 to 10, consisting

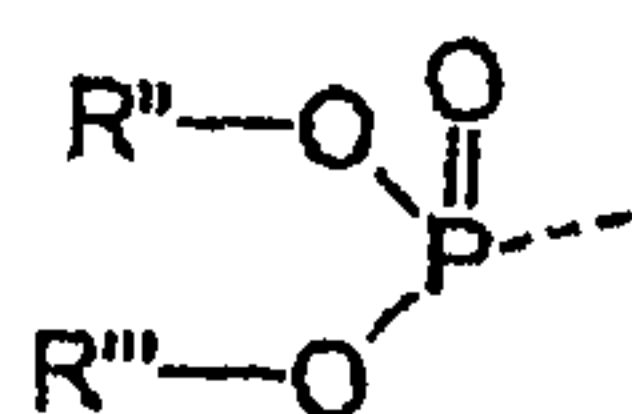
1 - Firstly, in preparing, according to a conventional polymerization recipe, the first block B by mixing the monomer(s) with an alkoxyamine of general formula:



- where R' and R, which are identical or different, optionally connected so as to form a ring, are alkyl groups having between 1 and 40 carbon atoms optionally substituted by hydroxyl, alkoxy or amino groups; in particular, R and R' will be tert-butyl groups;

- and where R_L is a monovalent group with a molar mass of greater than 16 g/mol; in particular, R_L will be a phosphorus group and more particularly a phosphonate group of formula:

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- where R'' and R''', which are identical or different, optionally connected so as to form a ring, are alkyl groups having between 1 and 40 carbon atoms optionally substituted by hydroxyl, alkoxy or amino groups; in particular R'' and R''' will be ethyl groups, where Z is a polyvalent radical carrying end functional groups of type, the other radicals having the same meanings as above.

The polymerization is carried out at temperatures ranging from 60 to 250°C, preferably from 90 to 160°C, for pressures ranging from 0.100 bar to 80 bar, preferably from 0.5 bar to 10 bar.

2 - Secondly, in diluting the first block B obtained in the mixture of monomers intended to form the blocks A. Between 0 and 100 molar equivalents of conventional radical polymerization initiator (of the LuperoxTM or azo compound type, for example AZDNTM) are added to this mixture. The choice of this ratio depends on the viscosity/impact-reinforcing compromise which it is desired to have.

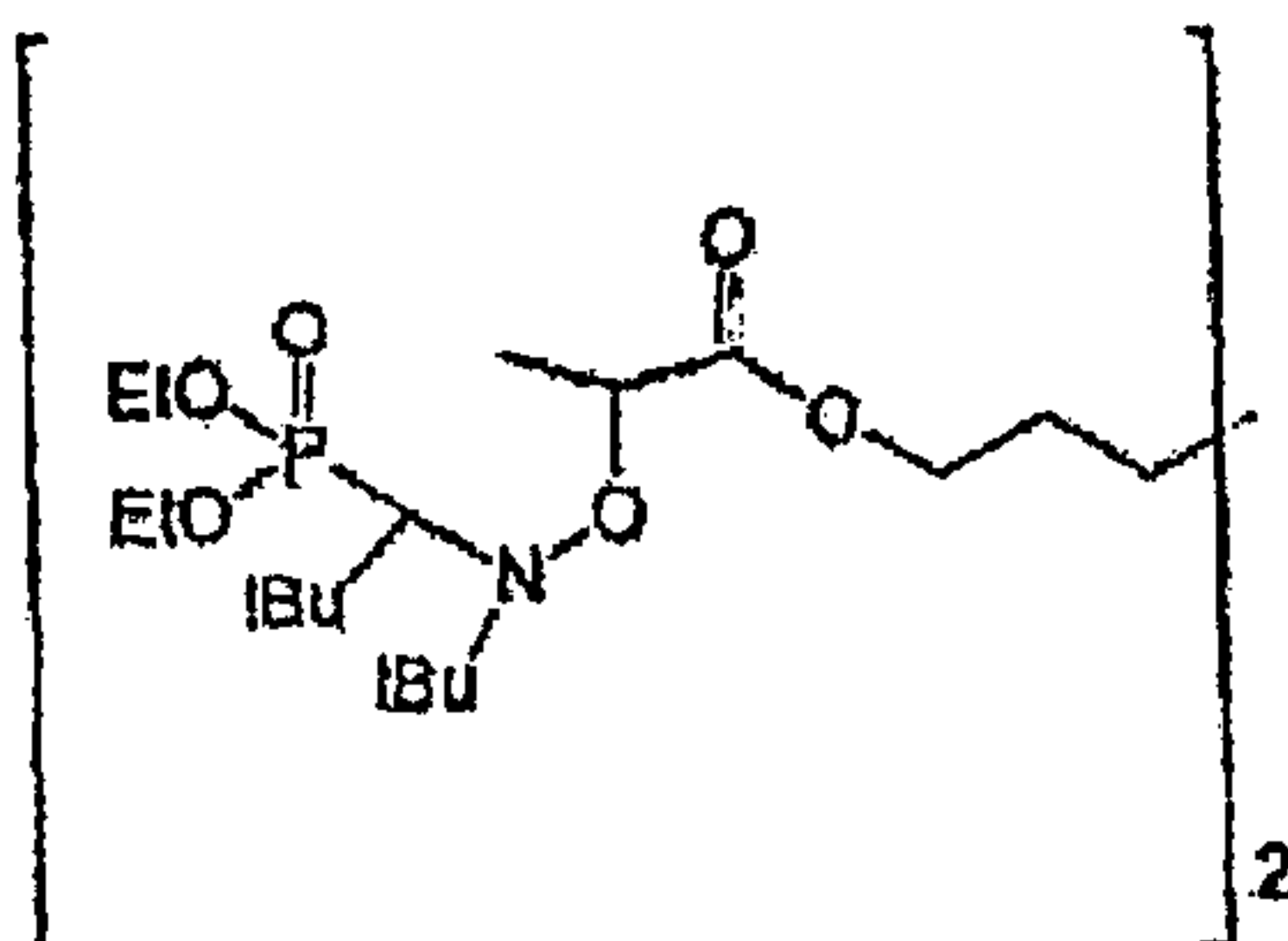
The polymerization is carried out at temperatures ranging from 60 to 250°C, preferably from 90 to 160°C, for pressures ranging from 0.100 bar to 80 bar, preferably from 0.5 bar to 10 bar.

The conversion of the monomer varies from 10 to 100% and the polymer obtained is separated from the residual monomers by evaporation under vacuum at temperatures ranging up to 250°C and preferably 200°C.

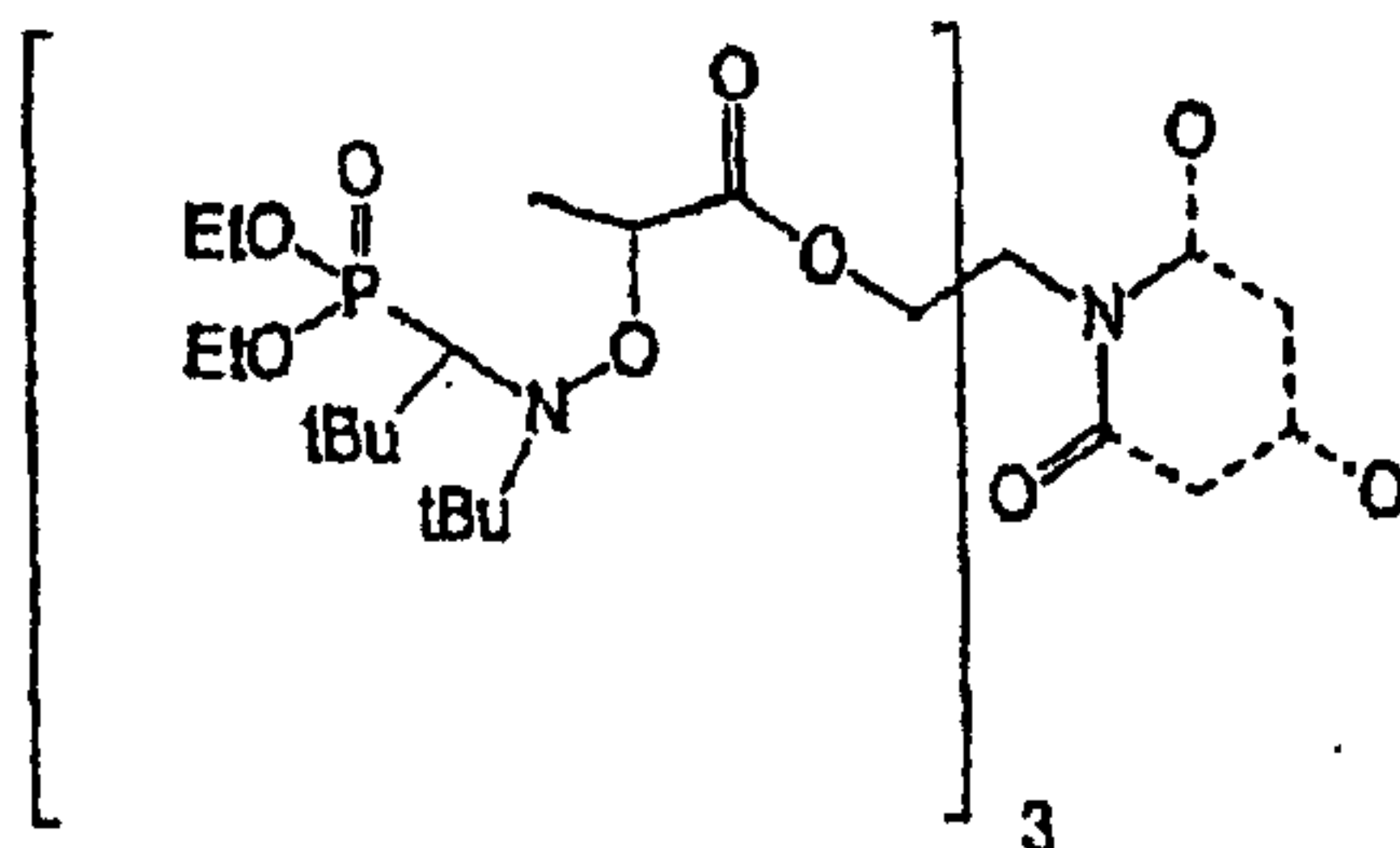
3 - Thirdly, in diluting the product obtained in 2 in a mixture of monomers chosen from styrene, MMA, epoxides, mixtures of diols and of diacid, or precursors of polyamides (lactam or mixtures, diamine, diacids), and in polymerizing the combination as described in 2.

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14. The process as claimed in one of claims 11 to 13, characterized in that the alkoxyamine used corresponds to the following formula:



5 15 The process as claimed in one of claims 11 to 13, characterized in that the alkoxyamine used corresponds to the following formula:



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ANNEXES

Table 1: Synthesis of PBuA-SG1 macroinitiators

	DIAMS/TRIAMS*		SG1		BuA		Mn (th)
	w (g)	C (mol/l)	w (g)	C (mol/l)	w (g)	C (mol/l)	
PBuAFLOPIL6 (DIAMS)	59.7073	1.49×10^{-2}	3.1907	2.09×10^{-3}	3600	6.98	60 000
PBuAFLOPIL7 (DIAMS)	58.0488	1.49×10^{-2}	2.7919	2.09×10^{-3}	3500	6.98	60 000
PBuAFLOPIL8 (DIAMS)	54.0488	1.49×10^{-2}	2.7919	2.09×10^{-3}	3500	6.98	60 000
PBuAFLOPIL9 (TRIAMS)	69.9200	0.99×10^{-2}	2.8716	2.09×10^{-3}	3600	6.98	90 000

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Table 2: Syntheses of the PBuA-SG1 copolymers

	PBuA-SG1		MMA		Ethylbenzene		Mn (f=1) (PMMA)
	w (g)	C (mol/l)	w (g)	C (mol/l)	w (g)	C (mol/l)	
FLOPIL6	1800	9.81×10^{-3}	6250	7.16	1780 (20%)	1.92	73 000
FLOPIL7	1800	1.29×10^{-3}	6420	8.21	830 (10%)	1.00	64 000
FLOPIL8	1100	5.31×10^{-3}	6750	8.25	840 (10%)	0.97	155 200
FLOPIL9	1100	3.23×10^{-3}	6750	8.25	840 (10%)	0.97	245 500

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Table 3: Characteristics of the macroinitiators

	BuA conversion n %	Mn (theoretical) (g/mol)	Mn (SEC) (g/mol)	Mw (SEC) (g/mol)	PI
PBuA- FLOPIL6	35	21 000	21 000	31 700	1.50
PBuA- FLOPIL7	50	30 000	17 800	55 400	3.11
PBuA- FLOPIL8	47	28 200	25 300	35 000	1.38
PBuA- FLOPIL9	50	45 000	28 000	44 000	1.57

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Table 4: Characteristics of the copolymers

	MMA conversion %	Mn (th) (g/mol)	Mn (SEC) (g/mol)	Mw (SEC) (g/mol)	PI	%PMMA by weight
FLOPIL 6	20	35 600	44 900	124 200	2.70	68
FLOPIL 7	35	40 000	77 400	170 760	2.20	70
FLOPIL 8	44	93 600	100 200	240 600	2.40	80
FLOPIL 9	40	138 200	87 230	245 900	2.8	77

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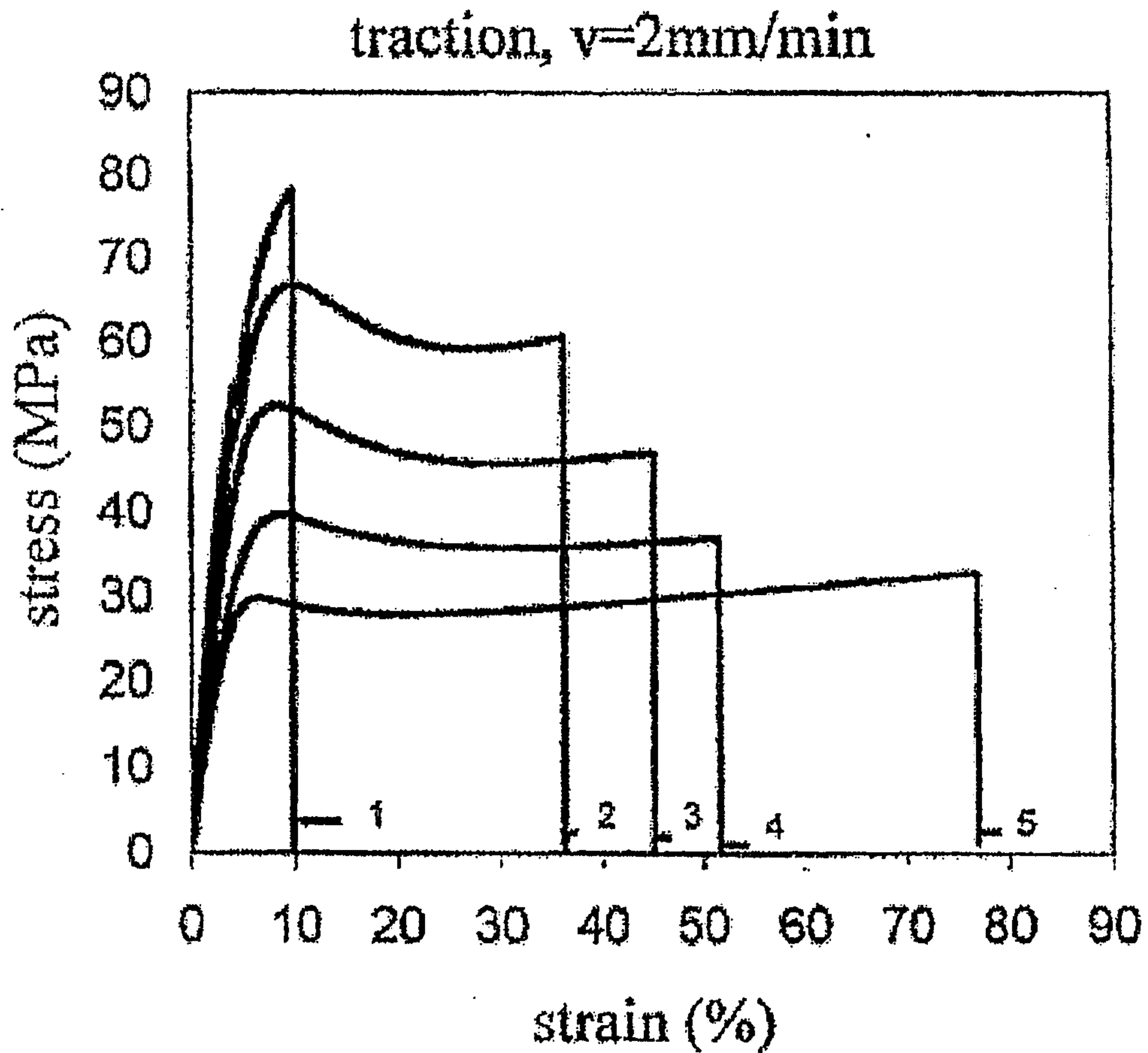


Figure 1 : Traction-elongation test

Key:

- 5
- (1) Black, V825 (conventional PMMA matrix)
 - (2) Blue, 25% of Flopil 9
 - (3) Red, 50% of Flopil 9
 - (4) Green, 75% of Flopil 9
 - (5) Pink, 100% of Flopil 9

Table 5

A. RESULTS OBTAINED:

Amount of PBuA	Appearance	Haze	Residual MMA	Resilience* (in kJ.m ²)
2%	+++	1.18	3.65%	1.35±0.06
5%	+++	1.59	3.32%	1.78±0.16
7.5%	+++	2.43	3.87%	2.81±0.18
10%	+++	3.52	3.45%	3.62±0.25
20%	+++	5.94	2.38%	6.23±0.25

+++ : No bloom, no bubbles, translucent, glossy, smooth.

* : The impact results were produced on notched test specimens with a non-instrument-controlled Charpy device and a 1 joule hammer and at a velocity of 2.9 m.s⁻¹.

For reference, the resilience of an unreinforced cast sheet and that of a cast sheet of commercial impact grade were measured, which have values of 1.35±0.03 kJ.mol⁻¹ and 1.59±0.03 kJ.mol⁻¹ respectively.

Figure 2: