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(54) Titre : PROCEDE DE FABRICATION ET UTILISATION DE MATERIAUX RENFORCES AU CHOC CONTENANT DES COPOLYMERS BLOCS OBTENUS PAR POLYMERISATION RADICALE 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 POLYMERIZATION IN THE PRESENCE OF NITROXYDES

(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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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.

Abrégé: L'invention décrit la mise en œuvre et l'utilisation de copolymères blocs obtenus par polymérisation radicale 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 œuvre 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 radicale 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 supérieure à 0°C assurant la compatibilité avec la matrice fragile que l'on souhaite renforcer au choc.
— 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.
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

FIELD OF THE INVENTION

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 impact using a block copolymer.

BACKGROUND OF THE INVENTION

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.

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.

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.

SUMMARY OF THE INVENTION

In a first aspect, the present invention concerns 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 composed of a sequence of monomer units polymerized by a radical route in the presence of nitroxides, B having a glass transition temperature of less than 0°C and a polydispersity index of less than 2, and A being a polymer block composed of a sequence of monomer units polymerized by a radical route in the presence of nitroxides, A having a glass transition temperature of greater than 0°C and being of the same nature as or compatible with the matrix, said brittle matrix (I) being present in a proportion of between 1 to 95% of the transparent and impact-resistant polymer material.

In another aspect, the invention concerns a process for the preparation of the transparent and impact-resistant polymer material described above, consisting in:

a) preparing the first block B by mixing the monomer(s) with an alkoxyamine of general formula:

\[
[\begin{array}{c}
R' \\
\text{N}
\end{array} \begin{array}{c}
H \\
\text{O}
\end{array} \begin{array}{c}
R \\
\text{Z}
\end{array} \begin{array}{c}
R_L \\
\text{n}
\end{array}] 
\]

- 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;
- where \( R_L \) is a monovalent group with a molar mass of greater than 16 g/mol;
- where \( Z \) is a polyvalent radical carrying end functional groups of styryl or acryloyl type,

and polymerizing the monomer(s) in the presence of nitroxides at
temperatures ranging from 60 to 250°C, and at pressures ranging from 10 kPa to 8000 kPa;

b) diluting the first block B obtained in step a) in a mixture of monomers intended to form the blocks A in the presence of 0 to 100 molar equivalents of a radical polymerization initiator; polymerizing the mixture at temperatures ranging from 60 to 250°C, such that the conversion of the monomer varies from 10 to 100%; and separating the polymer obtained from the residual monomers by evaporation under vacuum at temperatures ranging up to 250°C;

c) mixing the product obtained in b) and the brittle matrix.

Advantageously, the portion of the brittle matrix is between 10 and 85% by weight.

The materials of the invention can additionally comprise other impact-reinforcing additives, such as those of the Durastrength™ or Metablend™ trade mark, and the like.

**BRIEF DESCRIPTION OF THE FIGURE**

Figure 1 represents a diagram showing the results of the traction-elongation test carried out on polymer materials according to preferred embodiment of the invention. **Key:** (1) Black, V825 (conventional PMMA matrix); (2) Blue, 25% of Flopil 9†; (3) Red, 50% of Flopil 9†; (4) Green, 75% of Flopil 9†; and (5) Pink, 100% of Flopil 9†.

**DETAILED DESCRIPTION OF THE INVENTION**

Generally, the brittle matrix (I) exhibits a glass transition temperature (Tg) 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,

† Trademarks
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 Tg 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 Tg 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*Mn(A)/(n*Mn(A)+Mn(B)) is between 0.5 and 0.95, preferably between 0.6 and 0.8, and such that Mn(B) is greater than or equal to the mean entanglement length of the block B,

where Mn 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.

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

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 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.

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 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 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 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:

\[
\begin{align*}
\text{N-O} & + \text{OR} \quad \rightarrow \quad \text{N-O} + \text{OR} \\
\text{(eq. 1)}
\end{align*}
\]

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 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 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 (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 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:

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.

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 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):

\[
\text{(III)}
\]

- 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:

\[
\text{(IV)}
\]

- 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 \( 10^5 \) 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 \( n^*M_n(A)/(n^*M_n(A)+M_n(B)) \) 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. 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):

\[
\begin{array}{c}
\text{Z} \\
\mid \\
\text{R}_L \quad \text{N} \\
\mid \\
\text{R} \quad \text{O} \\
\mid \\
\text{n} \\
\end{array}
\]

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 Luperox™ or azo compound type, for example AZDN™) 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 Durastrength™ or Metablend™ 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), it is also possible to use the material as an impact-resistant resin without blending.

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:

\[
\begin{align*}
\text{O} & \\
\text{O} & \\
\text{R}_1 & \\
\end{align*}
\]

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:

\[
\begin{align*}
\text{O} & \\
\text{R}_2 & \\
\end{align*}
\]

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.

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
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 SGI corresponds to the following formula:

![Chemical Structure](image)

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

```
[\begin{align*}
[Di(\text{EBN})]_2 & \quad \text{DIAMS} \\
[\text{Tri}(\text{EBN})]_3 & \quad \text{TRIAMS}
\end{align*}]
```

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.
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 $T = 115^\circ C$ and in the presence of an excess of free SGI of 7 mol% per alkoxyamine functional group. Conversion was limited to 50%, so as to retain a good living nature of the PBuA-SGI macrorinitiators obtained, the residual monomer subsequently being removed by a stripping stage (70$^\circ C$ under vacuum for 2 hours).

In a second stage, the di- or trifunctional macrorinitiators thus obtained were allowed to reinitiate the polymerization of MMA at 120$^\circ C$ 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$^\circ C$ 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, SGI, 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.
Table 1: Synthesis of PBuA-SGl macroinitiators

<table>
<thead>
<tr>
<th></th>
<th>DIAMS/TRIAMS*</th>
<th>SGL</th>
<th>BuA</th>
<th>Mn (th)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>w (g) C (mol/l)</td>
<td>w (g) C (mol/l)</td>
<td>w (g) C (mol/l)</td>
<td></td>
</tr>
<tr>
<td>PBuAFLOPIL6† (DIAMS)</td>
<td>59.7073 1.49×10⁻²</td>
<td>3.1907 2.09×10⁻³</td>
<td>3600 6.98</td>
<td>60 000</td>
</tr>
<tr>
<td>PBuAFLOPIL7† (DIAMS)</td>
<td>58.0488 1.49×10⁻²</td>
<td>2.7919 2.09×10⁻³</td>
<td>3500 6.98</td>
<td>60 000</td>
</tr>
<tr>
<td>PBuAFLOPIL8† (DIAMS)</td>
<td>54.0488 1.49×10⁻²</td>
<td>2.7919 2.09×10⁻³</td>
<td>3500 6.98</td>
<td>60 000</td>
</tr>
<tr>
<td>PBuAFLOPIL9† (TRIAMS)</td>
<td>69.9200 0.99×10⁻²</td>
<td>2.8716 2.09×10⁻³</td>
<td>3600 6.98</td>
<td>90 000</td>
</tr>
</tbody>
</table>

Table 2: Syntheses of the PBuA-SGl copolymers

<table>
<thead>
<tr>
<th></th>
<th>PBuA-SGl</th>
<th>MMA</th>
<th>Ethylbenzene</th>
<th>Mn (f=1) (PMMA)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>w (g) C (mol/l)</td>
<td>w (g) C (mol/l)</td>
<td>w (g) C (mol/l)</td>
<td></td>
</tr>
<tr>
<td>FLOPIL6†</td>
<td>1800 9.81×10⁻³</td>
<td>6250 7.16</td>
<td>1780 1.92</td>
<td>73 000</td>
</tr>
<tr>
<td>FLOPIL7†</td>
<td>1800 1.29×10⁻³</td>
<td>6420 8.21</td>
<td>830 1.00</td>
<td>64 000</td>
</tr>
<tr>
<td>FLOPIL8†</td>
<td>1100 5.31×10⁻³</td>
<td>6750 8.25</td>
<td>840 0.97</td>
<td>155 200</td>
</tr>
<tr>
<td>FLOPIL9†</td>
<td>1100 3.23×10⁻³</td>
<td>6750 8.25</td>
<td>840 0.97</td>
<td>245 500</td>
</tr>
</tbody>
</table>

I.2 Preparation of the reinforced matrix:
The blends composed of PMMA and of copolymers which reinforce against impacts are prepared by melt extrusion.

† trademarks
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.

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.

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

Table 3: Characteristics of the macroinitiators

<table>
<thead>
<tr>
<th>BuA conversion %</th>
<th>Mn (theoretical g/mol)</th>
<th>Mn (SEC) g/mol</th>
<th>Mw (SEC) g/mol</th>
<th>PI</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBuA-FLOPIL6†</td>
<td>35</td>
<td>21 000</td>
<td>21 000</td>
<td>31 700</td>
</tr>
<tr>
<td>PBuA-FLOPIL7†</td>
<td>50</td>
<td>30 000</td>
<td>17 800</td>
<td>55 400</td>
</tr>
<tr>
<td>PBuA-FLOPIL8†</td>
<td>47</td>
<td>28 200</td>
<td>25 300</td>
<td>35 000</td>
</tr>
<tr>
<td>PBuA-FLOPIL9†</td>
<td>50</td>
<td>45 000</td>
<td>28 000</td>
<td>44 000</td>
</tr>
</tbody>
</table>

† trademarks
Table 4: Characteristics of the copolymers

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

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

II.1 Cast sheet
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 SGL. The copolymer is recovered by evaporation of the volatile components and then dissolution in 8 kg of methyl methacrylate.
The macroinitiator obtained exhibits the following characteristics: 17% by weight of styrene, Mn = 70 000 g/mol, Mw = 142 000 g/mol.

† trademarks
Stage 2:
The formulation of the methyl methacrylate syrup employed is as follows:

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. 21 ppm of γ-terpinene.

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. 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. 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.

† trademark
13c

Table 5

A. RESULTS OBTAINED:

<table>
<thead>
<tr>
<th>Amount of PBA</th>
<th>Appearance</th>
<th>Haze</th>
<th>Residual MMA</th>
<th>Resilience* (in kJ.m⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2%</td>
<td>+++</td>
<td>1.18</td>
<td>3.65%</td>
<td>1.35±0.06</td>
</tr>
<tr>
<td>5%</td>
<td>+++</td>
<td>1.59</td>
<td>3.32%</td>
<td>1.78±0.16</td>
</tr>
<tr>
<td>7.5%</td>
<td>+++</td>
<td>2.43</td>
<td>3.87%</td>
<td>2.81±0.18</td>
</tr>
<tr>
<td>10%</td>
<td>+++</td>
<td>3.52</td>
<td>3.45%</td>
<td>3.62±0.25</td>
</tr>
<tr>
<td>20%</td>
<td>+++</td>
<td>5.94</td>
<td>2.38%</td>
<td>6.23±0.25</td>
</tr>
</tbody>
</table>

+++: 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.

II.2 Continuous polymerization

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 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 granulated after cooling in a water vat.

The monomer syrup used is as follows (as proportion by weight):
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\textsuperscript{†} 531: 180 ppm.
The maximum polymerization temperature achieved is 178°C. The granules obtained have the final composition:

\textsuperscript{†} trademark
82.5% PMMA
17.3% acrylate (butyl and ethyl)
0.2% residual MMA.

Mn = 30 000 g/mol (PMMA standard)
Mw = 85 000 g/mol (PMMA standard)

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
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.
WHAT IS CLAIMED IS:

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 composed of a sequence of monomer units polymerized by a radical route in the presence of nitroxides, B having a glass transition temperature of less than 0°C and a polydispersity index of less than 2, and A being a polymer block composed of a sequence of monomer units polymerized by a radical route in the presence of nitroxides, A having a glass transition temperature of greater than 0°C and being of the same nature as or compatible with the matrix, said brittle matrix (I) being present in a proportion of between 1 to 95% of the transparent and impact-resistant polymer material.

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

3. The material as claimed in claim 1 or 2, characterized in that the proportion of the brittle matrix is between 10 and 85%.

4. The material as claimed in any one of claims 1 to 3, 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.
5. The material as claimed in any one of claims 1 to 4, characterized in that A represents from 50 to 95% by weight of the total weight of the block copolymer (II).

6. The material as claimed in claim 5, characterized in that A represents from 60 to 90% by weight of the total weight of the block copolymer (II).

7. The material as claimed in any one of claims 1 to 6, characterized in that B is a polyacrylate with a glass transition temperature of less than 0°C.

8. The material as claimed in any one of claims 1 to 7, characterized in that A is a polymethacrylate with a glass transition temperature of greater than 0°C.

9. The material as claimed in any one of claims 1 to 8, characterized in that the block B exhibits an average mass of greater than 5000 g/mol.

10. A process for the preparation of the material according to any one of claims 1 to 9, consisting in:
    a) preparing the first block B by mixing the monomer(s) with an alkoxyamine of general formula:

\[
\begin{array}{c}
\text{R'} \\
\text{R}_{\text{L}} \\
\text{H} \\
\text{N} \\
\text{R} \\
\text{O} \\
\text{Z} \\
\end{array}
\]

\[n\]
- 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;
- where R_L is a monovalent group with a molar mass of greater than 16 g/mol;
- where Z is a polyvalent radical carrying end functional groups of styryl or acryloyl type,

and polymerizing the monomer(s) in the presence of nitroxides at temperatures ranging from 60 to 250°C, and at pressures ranging from 10 kPa to 8000 kPa;

b) diluting the first block B obtained in step a) in a mixture of monomers intended to form the blocks A in the presence of 0 to 100 molar equivalents of a radical polymerization initiator; polymerizing the mixture at temperatures ranging from 60 to 250°C, such that the conversion of the monomer varies from 10 to 100%; and separating the polymer obtained from the residual monomers by evaporation under vacuum at temperatures ranging up to 250°C; and
c) mixing the product obtained in b) and the brittle matrix.

11. The process of claim 10, characterized in that R and R' are tert-butyl groups.

12. The process of claim 10 or 11, characterized in that R_L is a phosphorus groups.

13. The process of claim 12, characterized in that R_L is 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.

14. The process of claim 13, characterized in that \( R' \) and \( R'' \) are ethyl groups.

15. The process as claimed in claim 10, characterized in that the alkoxyamine used corresponds to the following formula:

16. The process as claimed in claim 10, characterized in that the alkoxyamine used corresponds to the following formula:
traction, \(v = 2 \text{ mm/min}\)

stress (MPa)

strain (%)

Figure 1