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(54) Title: BLOCK COPOLYMERS

(57) Abstract: Block copolymer of the structure Y-X, containing A) from 95 to 99.5% by weight of block Y containing, as monomeric units, al) a mixture composed of al 1) at least one vinylaromatic monomer, and a12) at least one comonomer which is not maleic anhydride, a2) at least one ethylenically unsaturated ester, and B) from 0.5 to 5% by weight of block X composed of styrene and maleic anhydride as monomeric units, where the block X substantially has a strictly alternating structure; where the entirety of components A) and B) gives a total of 100%.

WO 2004/108783 A1

Block copolymers

The present invention relates to block copolymers of the structure Y-X, containing

A) from 95 to 99.5% by weight of block Y containing, as monomeric units,
  a1) a mixture composed of
    a11) at least one vinylaromatic monomer, and
    a12) at least one comonomer which is not maleic anhydride, or
  a2) at least one ethylenically unsaturated ester,

and

B) from 0.5 to 5% by weight of block X composed of styrene and maleic anhydride as monomeric units,

where the block X substantially has a strictly alternating structure and where the entirety of components A) and B) gives a total of 100%. The present invention further relates to block copolymers of this type which are obtainable by means of controlled free-radical polymerization, and also to a process for preparing these block copolymers. The present invention further relates to the use of these block copolymers for preparing thermoplastic molding compositions, and to the thermoplastic molding compositions in which these block copolymers are present. Details can be found in the claims and in the description. The features mentioned above and explained below of the inventive process may, of course, be used within the scope of the invention in combinations other than the particular combination given.

Copolymers which contain maleic anhydride and styrene as monomeric units are known per se.

Japanese Laid-Open Application JP-A2 10101942 describes block copolymers which have a thermoplastic polymer as one block and may contain another block composed of from 0.1 to 99 mol% of a vinylaromatic monomer and from 0 to 99 mol% of a vinyl monomer which may contain acid groups, epoxy groups, and/or anhydride groups. Among these, mention is also made of acrylonitrile-maleic acid-styrene block copolymer. The block copolymers are used to compatibilize a thermoplastic polymer, such as ABS, with an organic filler, such as wood flour.

JP-A2 56041215 has disclosed heat-resistant, and also solvent-resistant and moldable, maleic anhydride-styrene-vinyl cyanide copolymers. By way of example, these are prepared by combined polymerization of two mixtures composed of styrene and maleic

anhydride and differing from one another in their maleic anhydride content. Acrylonitrile is then added once monomer conversion has reached from 30 to 70%.

JP-A2 55116712 moreover gives a two-stage process for preparing terpolymers from acrylonitrile, maleic anhydride, and styrene. A first stage of this process reacts styrene with maleic anhydride. A second stage adds acrylonitrile and polymerizes the mixture.

Copolymers composed of styrene, acrylonitrile, and maleic anhydride are known to have compatibilizing action in blends which comprise polyamide and plastics of ABS type. The result is an improvement in the properties of the blends, in particular a substantial increase in impact strengths.

Blends of this type, for example those in which copolymers composed of styrene, acrylonitrile, and maleic anhydride are used as compatibilizers, have been disclosed in, inter alia, EP-A 202 214, Kudva et al., Polymer 41 (2000) 239 – 258, or from M. Staal et al., Poster Technische Universiteit Eindhoven, January 2003, "Characterization of the Molar Mass Chemical Composition Distribution of Styrene-Acrylonitrile-Maleic Anhydride Terpolymers". They feature good low-temperature impact strengths and processing properties.

It is an object of the present invention to develop novel block copolymers which contain maleic anhydride and styrene. A further object of the present invention is to use novel block copolymers of this type to achieve further improvements in the properties of thermoplastic molding compositions. In particular, emphasis is to be placed on the ability to use controlled structure-formation of the block copolymers to exert a desired effect on the properties of the thermoplastic molding compositions. One aspect of the present invention concerns improvement in the flowability of the molding compositions based on ABS and nylon-6, this property still being unsatisfactory for many applications. The flowability of these molding compositions can generally be improved by reducing the amount of rubber. As an alternative, a low-viscosity polymer may be used to form the matrix. However, these measures are attended by considerable impairment of toughness.

We have found that this object is achieved by way of the block copolymers defined at the outset.

According to the invention, the block copolymers have a two-block structure (Y-X structure). They also include block copolymers having a block Y whose free end groups may have been capped using monomers of which the block X is composed. This means that they may have been capped using styrene and/or maleic anhydride.

However, the structure of the inventive block copolymers is not to have three or more blocks. Particular preference is given to inventive block copolymers which are linear.

The inventive block copolymers may have a broad, or a narrow, molecular weight distribution. One measure of the breadth of the molecular weight distribution is the polydispersity index. This is defined as

PDI = weight-average molecular weight Mw / number-average molecular weight Mn

(where Mw and Mn must, of course, have been measured using the same method of determination, the nature of the method of determination being, however, as desired). Among the preferred block copolymers of this invention are block copolymers with a polydispersity index in the range from 1.1 to 5, in particular from 1.2 to 4. Preference is given to block copolymers whose molar mass (Mw) is in the range from 15 000 to 500 000 g/mol, in particular in the range from 20 000 to 300 000 g/mol. The molecular weight is determined here by means of gel permeation chromatography (GPC) on the basis of a polystyrene standard, using tetrahydrofuran as eluent. The precise experimental conditions can be found in the examples.

According to the invention, the proportion of the block Y is from 95 to 99.5% by weight of the block copolymer A), preferably from 96 to 99% by weight, and that of the block X B) is from 0.5 to 5% by weight, preferably from 1 to 4% by weight.

According to the invention, the block Y may contain, as monomeric units, a mixture a1). The mixture a1) is composed of at least vinylaromatic monomer a11) and of at least one comonomer a12) which is not maleic anhydride. Preference is given to mixtures a1) composed of from 60 to 90% by weight, particularly preferably from 65 to 85% by weight, in particular from 70 to 82% by weight, of component a11) and of from 10 to 40% by weight, particularly preferably from 15 to 35% by weight, in particular from 18 to 30% by weight, of component a12), where the entirety of components a11) and a12) gives a total of 100%.

Component a11) may derive from a vinylaromatic monomer or from a mixture composed of two or more different vinylaromatic monomers. Preferred examples of vinylaromatic monomers are styrene or styrene derivatives, for example C_1-C_8-alkyl-substituted styrenes, such as α-methylstyrene, p-methylstyrene, or vinyltoluene. Styrene is particularly preferably used alone.

Component a12) may derive from one, or from a mixture of two or more, different copolymerizable monomer(s). Particularly suitable comonomers are:

unsaturated nitriles, such as acrylonitrile, methacrylonitrile;
aliphatic esters, such as C_1-C_4-alkyl esters of methacrylic acid or of acrylic acid, e.g. methyl methacrylate, and also the glycidyl esters, glycidyl acrylate and glycidyl methacrylate;
N–substituted maleimides, such as N-methyl-, N-phenyl-, and N-cyclohexylmaleimide;
acids, such as acrylic acid, methacrylic acid; and also dicarboxylic acids, such as maleic acid, fumaric acid, and itaconic acid;
nitrogen-functional monomers, such as dimethylaminoethyl acrylate, diethylaminoethyl acrylate, vinylimidazole, vinylpyrrolidone, vinylcaprolactam, vinylcarbazole, vinylaniline, acrylamide, and methacrylamide;
aromatic and araliphatic esters of (meth)acrylic acid, e.g. phenyl acrylate, phenyl methacrylate, benzyl acrylate, benzyl methacrylate, 2-phenylethyl acrylate, 2-phenylethyl methacrylate, 2-phenoxyethyl acrylate, and 2-phenoxyethyl methacrylate;
unsaturated ethers, such as vinyl methyl ether or vinyl butyl ether.

Preferred comonomers a12) used are acrylonitrile, C_1-C_4-alkyl esters of methacrylic acid or of acrylic acid, or else N-substituted maleimides, or mixtures of these. Particularly preferred comonomers are acrylonitrile, methyl methacrylate, methyl acrylate, and N-phenylmaleimide. In one of the preferred embodiments, these abovementioned comonomers may be used individually. In another preferred embodiment, use may be made of a mixture composed of two of the abovementioned comonomers, e.g. acrylonitrile with methyl methacrylate, or of three, or of all of the abovementioned comonomers. It is particularly preferable to use either acrylonitrile or methyl methacrylate alone. With particular preference, acrylonitrile is used alone.

Instead of this, the block Y may contain, as monomeric units a2), at least one, e.g. one, or a mixture composed of two or more different, ethylenically unsaturated ester(s). Esters suitable as component a2) are aliphatic, aromatic, or else araliphatic esters, as listed above under a11). Preferred components a2) used are C_1-C_4-alkyl esters of methacrylic acid or of acrylic acid, or a mixture of these. Methyl methacrylate is particularly preferably used.

In one preferred embodiment, the block Y contains a mixture a1) as monomeric units.

According to the invention, the block X is composed of styrene and maleic anhydride as monomeric units. According to the invention, these are substantially strictly alternating. This means that each styrene radical is generally followed by a maleic anhydride radical, but there is no intention to exclude the possibility that two or more, e.g. two or three, radicals of the same type may follow one another. However, this does not mean that further block formation takes place within the block X. For each styrene radical there is therefore generally one maleic anhydride radical present in the block X.

There may, however, be a slight excess of one of the radicals over the other radical, and therefore specifically in the case of short block lengths it is not essential that there be equimolarity in the strict sense. The block X particularly preferably has a purely and strictly alternating structure.

The molecular weight (weight-average Mw) of block X is generally smaller than that of block Y. Block X preferably has a molar mass (weight-average Mw) smaller than 5000 g/mol, preferably smaller than 1500 g/mol, in particular smaller than 1000 g/mol, determined by GPC measurement, using tetrahydrofuran as eluent and polystyrene calibration. The precise experimental conditions can be found in the examples.

In one of the particularly preferred embodiments, the inventive block copolymer contains a block Y composed of styrene and acrylonitrile, the molar mass of which (weight-average Mw) is in the range from 80 000 to 200 000 g/mol, and a block X, the molar mass of which (weight-average Mw) is in the range from 500 to 1500 g/mol.

The block copolymers may be prepared by suitable methods, e.g. by free-radical polymerization. According to the invention, controlled free-radical polymerization is preferably used to prepare the inventive block copolymers. The feature of controlled free-radical polymerization is that, in a free-radical polymerization initiated thermally, by high-energy radiation and/or by way of a mixture of different, initiator(s), concomitant use is made of what is known as a stable free radical which substantially lacks any initiating action, the result being that the free-radical polymerization becomes controllable. The person skilled in the art is aware of methods of controlled free-radical polymerization, e.g from DE-A 19917675, DE-A 19939031, and DE-A 19858103.

The inventive block copolymers may be prepared in bulk, or by means of solution, suspension, microsuspension, emulsion, or miniemulsion polymerization. The process may take place continuously or batchwise. The apparatus used for the polymerization depends on the polymerization process used. Depending on the polymerization process, other suitable additives may be added. In a microsuspension polymerization process, for example, suitable protective colloids may be added for stabilization. These protective colloids are water-soluble polymers which encapsulate the monomer droplets and the polymer particles formed therefrom, and thus prevent their coagulation. In emulsion polymerization processes, suitable emulsifiers are used concomitantly to stabilize the emulsion. These are soap-like auxiliaries which encapsulate the monomer droplets and thus prevent their coalescence. Use may also be made of other additives, such as buffers, solvents, and other polymerization auxiliaries, depending on the nature of the polymerization process. These additives are described individually by way of example in DE-A 19917675. The inventive process

may also be worked as a combined process in which two of the abovementioned polymerization methods are combined with one another. Mention may be made here in particular of bulk/solution, bulk/suspension, and bulk/emulsion, the first-mentioned being used at the start and the last-mentioned being used at the conclusion. The inventive process is preferably carried out in bulk, and continuously. Preferred additives during the preparation of the inventive block copolymers are ethylbenzene, toluene, or other solvents, these permitting control of viscosity.

The selection of the initiator, and the manner of its addition, depends firstly on the nature of the polymerization process and secondly on the nature of the monomers to be polymerized. For example, for emulsion polymerization it is preferable to use initiators which have low solubility in the monomer but have good solubility in water. It is therefore preferable to use peroxosulfates, such as potassium peroxodisulfate, sodium peroxodisulfate, or ammonium peroxodisulfate, or else redox systems, in particular those derived from hydroperoxides, such as cumene hydroperoxide or dicumyl peroxide. In emulsion polymerization processes, or in the other polymerization processes mentioned, it can be advantageous to use a mixture of initiators whose dissociation constants kD differ by a factor of from 10^2 to 10^3. It is particularly preferable here for a first initiator to have a dissociation constant kD of from 10^{-2} to 10^{-3} s^{-1} at 115°C and for a second initiator to have a dissociation constant of about 10^{-5} s^{-1} at 115°C. In this embodiment, it is very particularly preferable to use benzoyl peroxide (BPO) or 2,2′-azobisisobutyronitrile (AIBN) and, as second initiator, dicumyl peroxide (DCPO). 2,2′-Azobisisobutyronitrile (AIBN) is particularly preferably used as initiator to prepare the inventive block copolymers.

Supplementary addition of the initiator(s) may take place, by way of example, immediately prior to the start of the polymerization, or else continuously during the course of the polymerization. In particular in the case of monomers which have a tendency toward uncontrolled polymerization, or polymerize even at low temperature, it is advisable to delay addition of the initiator until the emulsification process is complete, or until the polymerization is about to begin. In particular in the case of polymerization processes with a long polymerization time, it can be advantageous to add the initiator during the polymerization, in the form of a continuous feed or in portions. The duration of the initiator feed here may be different from or the same as the duration of the polymerization. In the case of preparation of the inventive block copolymers in a batch process, the initiator is preferably either used to form an initial charge or in particular is entirely added at the beginning of the polymerization. In the case of continuous operation, the initiator is preferably metered in continuously, in stages, or in compliance with a feed profile, if desired in the presence of a molecular weight regulator.

The amount of initiator is usually from 0.05 to 2% by weight, preferably from 0.07 to 1% by weight, based on the amount of monomers to be polymerized.

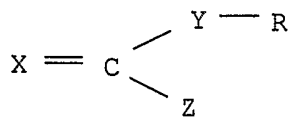
Various methods may be used for the controlled free-radical polymerization. Each method used is a different system for controlled free-radical polymerization, these being known per se to the person skilled in the art and being described by way of example in further detail in DE-A 199 17 675.

By way of example, the method used may be that known as Atom Transfer Radical Polymerization (ATRP) or a related method. Here, the change of oxidation state of a metal, e.g. copper, nickel, or ruthenium, is used to establish an equilibrium between the polymer chain end growing by a free-radical mechanism and an unreactive "sleeping" species. The ATRP method involves reversible homolysis of a covalent, inactive species, followed by monomer insertion and then reversible recombination.

It is also possible to use triazolinyl compounds for controlled re-initiation during controlled free-radical polymerization.

Another possible method for controlled free-radical polymerization uses catalytic chain transfer (CCT). This method uses small amounts of a metal complex, e.g. a cobalt complex, with a high chain-transfer constant, thus establishing defined molecular weights.

It is also possible to use reversible addition fragmentation chain transfer (RAFT) as a method of controlled free-radical polymerization. This method achieves controlled free-radical polymerization monomers in the presence of compounds of the formula below.



X = S, Se
Y = S, Se
R, Z = any desired radicals

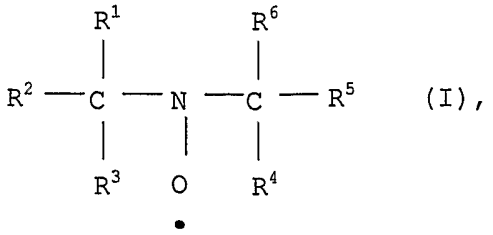
Another method which can be used for the controlled free-radical polymerization of the inventive block copolymers is initiator/transfer/termination (iniferter). This method uses compounds which act as chain initiator, as chain-transfer agent, and as chain terminator.

The stable free-radical polymerization method (SFRP) is particularly preferred for preparing the inventive block copolymers. This polymerization takes place in the

presence of stable free radicals, and the equilibrium between growing polymer chain end and inactive species is utilized to control the polymerization reaction.

Particularly stable free radicals used are stable N-oxyl radicals, and in principle it is possible to use any of the stable N-oxyl radicals.

Examples of suitable stable N-oxyl radicals derived from a secondary amine are those of the formula I



(I),

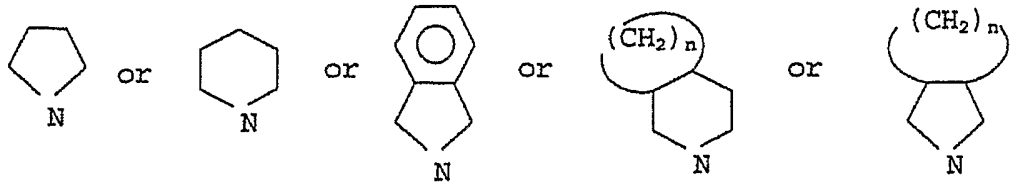
where

R^1,R^2,R^5 and R^6 = identical or different straight- or branched-chain, unsubstituted or substituted alkyl groups, cycloalkyl groups, aralkyl groups, or aryl groups, and

R^3 and R^4 = identical or different straight- or branched-chain, unsubstituted or substituted alkyl groups, or

R^3CNCR^4 = a portion of a cyclic structure which has, where appropriate, another fused saturated or aromatic ring, where the cyclic structure or the aromatic ring may, where appropriate, have substitution.

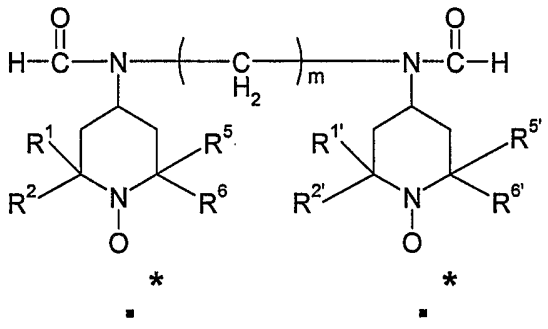
Examples of these are the stable N-oxyl radicals of the formula I where R^1, R^2, R^5 and R^6 are (identical or different) methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, tert-butyl, linear or branched pentyl, phenyl, or substituted groups from among these, and R^3 and R^4 are (identical or different) methyl, ethyl, n-propyl, isopropyl, n-butyl, iso-butyl, tert-butyl, linear or branched pentyl, or substituted groups from among these, or – if R^3CNCR^4 forms a portion of a cyclic structure – the cyclic structure



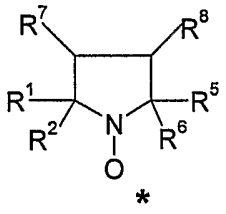
where n is a whole number from 1 to 10 (often from 1 to 6), including substituted cyclic groups of this type. Representative examples which may be mentioned are 2,2,6,6-tetramethyl-1-oxylpiperidine, 2,2,5,5-tetramethyl-1-oxylpyrrolidine, and 4-oxo-2,2,6,6-tetramethyl-1-oxylpiperidine.

The stable N-oxyl radicals may be prepared from the corresponding secondary amines via oxidation, e.g. using hydrogen peroxide. They can generally be prepared as pure substance.

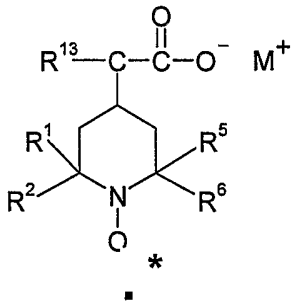
Among the stable N-oxyl radicals are in particular piperidine- or pyrrolidine-N-oxyl compounds and di-N-oxyl compounds of the formulae II to V below:



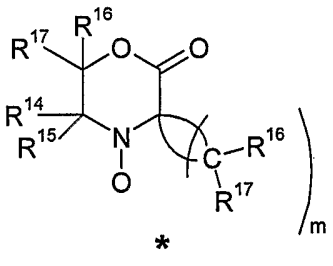
(II),



(III),



(IV),

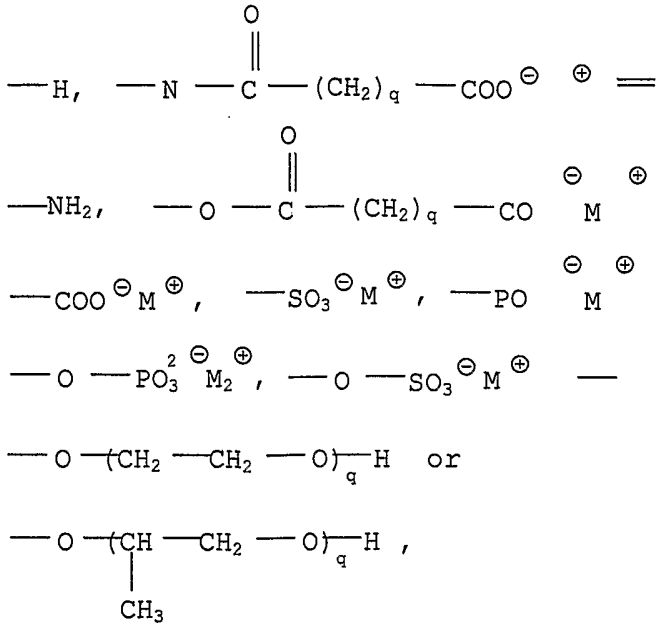


(V),

where

m = 2 - 10,

R^7,R^8,R^9 = independently of one another

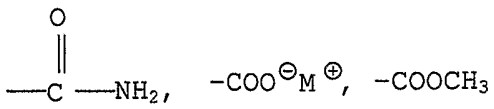


$M^{\oplus}$ = a hydrogen ion or an alkali metal ion (in particular $K^{\oplus}$ or $Na^{\oplus}$),

q = a whole number from 1 to 100,

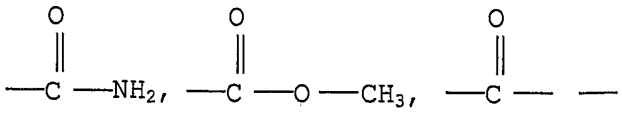
$R^{1'}$,$R^{2'}$,$R^{5'}$,$R^{6'}$ = independently of one another, and independently of R^1, R^2, R^5, R^6, groups corresponding to those for R^1,

R^{10} = -H, C_1-C_4-alkyl, -CH=CH_2, -C_5CH, -CN,

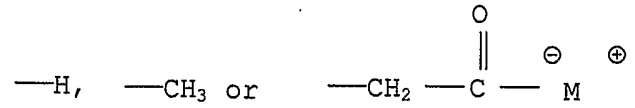


R^{11} = an organic radical which has at least one primary, secondary (e.g. -NR^1) or tertiary amino group (e.g. -NR^1R^2), or has at least one ammonium group -$NR^{13}R^{14}R^{15}X^{\ominus}$, where $X^{\ominus}$ = $F^{\ominus}$, $Cl^{\ominus}$, $Br^{\ominus}$, $HSO_4^{\ominus}$, $SO_4^{2\ominus}$, $H_2PO_4^{\ominus}$, $HPO_4^{2\ominus}$, or $PO_4^{3\ominus}$, and R^{13}, R^{14}, R^{15} are mutually independent organic radicals (e.g. independently of one another, groups corresponding to those for R^1),

R^{12} = independently of R^{11}, groups corresponding to those for R^{11}, or –H, -OH, C_1-C_4-alkyl, -$COO^{\ominus}M^{\oplus}$, -C_5CH,



or hydroxy-substituted C_1-C_4-alkyl (e.g. hydroxyethyl or hydroxypropyl), and

R^{13} = 

R^{14},R^{15} independently of one another, are identical or different straight- or branched-chain, unsubstituted or substituted alkyl groups, or cycloalkyl groups, or unsubstituted or substituted C_6-C_{20}-aryl groups, and

R^{16},R^{17} independently of one another, are hydrogen or groups corresponding to those for R^{14}, R^{15}.

It is preferable that $R^1 = R^2 = R^5 = R^6 = R^{1'} = R^{2'} = R^{5'} = R^{6'} = -CH_3$.

Mention may be made of the following representative examples of stable N-oxyl radicals suitable for the purposes of the invention:
2,2,6,6-tetramethyl-1-oxylpiperidine (TEMPO),
4-oxo-2,2,6,6-tetramethyl-1-oxylpiperidine (4-oxoTEMPO),
2,2,5,5-tetramethyl-1-oxylpyrrolidine,
3-carboxy-2,2,5,5-tetramethyl-1-oxylpyrrolidine,
2,6-diphenyl-2,6-dimethyl-1-oxylpiperidine,
4-hydroxy-2,2,6,6-tetramethyl-1-oxylpiperidine (4-hydroxyTEMPO),
2,5-diphenyl-2,5-dimethyl-1-oxylpyrrolidine, and
di-tert-butyl nitroxide.

The N-oxyl radicals are either known or may be obtained by processes known per se (e.g. US-A 4665185 (e.g. Example 7) or else DE–A 19510184).

It is particularly preferable to use N-oxyl radicals whose enthalpy of bond dissociation with respect to the growing, free-radical chain end is lower than that of TEMPO or of 4-oxoTEMPO. Examples of these are the compounds of the abovementioned formula (X).

Other suitable representative examples are:

Beilstein Registry Number 6926369: ($C_{11}H_{22}N_3O_2$);

Beilstein Registry Number 6498805: (4-amino-2,2,6,6-tetramethyl-1-oxylpiperidine);
Beilstein Registry Number 6800244: ($C_{11}H_{23}N_2O_2$);
Beilstein Registry Number 5730772: (N-methyl-4-amino-2,2,6,6-tetramethyl-1-oxyl-piperidine;
Beilstein Registry Number 5507538: (2,2,6,6-tetramethyl-4-(2-aminoethylamino)-1-oxylpiperidine);
Beilstein Registry Number 4417950: (4-bis(2-hydroxyethyl)amino-2,2,6,6-tetramethyl-1-oxylpiperidine);
Beilstein Registry Number 4396625: ($C_{12}H_{25}N_2O_2$);
Beilstein Registry Number 4139900: (4-amino-2,2,6,6-tetramethyl-4-carboxy-1-oxyl-piperidine);
Beilstein Registry Number 4137088: (4-amino-4-cyano-2,2,6,6-tetramethyl-1-oxyl-piperidine);
Beilstein Registry Number 3942714: ($C_{12}H_{25}N_2O_2$);
Beilstein Registry Number 1468515: (2,2,6,6-tetramethyl-4-hydroxy-4-acetyl-1-oxyl-piperidine);
Beilstein Registry Number 1423410: (2,2,4,6,6-pentamethyl-4-hydroxy-1-oxyl-piperidine);
Beilstein Registry Number 3546230: (4-carboxymethyl-2,2,6,6-tetramethyl-1-oxyl-piperidine);
Beilstein Registry Number 3949026: (4-carboxy-2,2,6,6-tetramethyl-1-oxylpiperidine);
Beilstein Registry Number 4611003: (the mono(1-oxyl-2,2,6,6-tetramethylpiperidin-4-ylamide) of ethylenediaminetetraacetic acid);
Beilstein Registry Number 5592232: ($C_{15}H_{27}N_2O_4$);
Beilstein Registry Number 6205316: (4-carboxymethylene-2,2,6,6-tetramethyl-1-oxyl-piperidine);
Beilstein Registry Number 5961636: ($C_{13}H_{21}N_2O_4$)
Beilstein Registry Number 5080576: (the N-(2,2,6,6-tetramethyl-1-oxylpiperidin-4-yl)monoamide of succinic acid);
Beilstein Registry Number 5051814: (4-(4-hydroxybutanoylamino)-2,2,6,6-tetramethyl-1-oxylpiperidine);
Beilstein Registry Number 1451068: ($C_{11}H_{18}NO_2$);
Beilstein Registry Number 4677496: (2,2,6,6-tetramethyl-4-oximino-1-oxylpiperidine);
Beilstein Registry Number 1451075: ($C_{11}H_{20}NO_2$);
Beilstein Registry Number 1423698: (4-ethyl-4-hydroxy-2,2,6,6-tetramethyl-1-oxyl-piperidine);
Beilstein Registry Number 5509793: (4-ethoxymethyl-4-hydroxy-2,2,6,6-tetramethyl-1-oxylpiperidine);
Beilstein Registry Number 3985130: (2,2,6,6-tetramethyl-1-oxyl-4-piperidylidene)-succinic acid);

Beilstein Registry Number 3960373: ($C_{10}H_{19}N_2O_3$).

According to the invention it is, of course, also possible to use mixtures of stable N-oxyl radicals.

Depending on its solubility behavior, the stable N-oxyl radical may be added either undiluted or dissolved in organic solvents, such as alcohols, e.g. methanol and/or ethanol, or else ethyl acetate and/or dimethylformamide.

For the purposes of the inventive process, the molar ratio between stable N-oxyl radicals and free-radical polymerization initiator is normally from 0.5:1 to 5:1, preferably from 0.8:1 to 4:1. It is particularly preferable for the ratio to be 1.5:1 for preparing the inventive block copolymers.

The polymerization rate can generally be increased in the inventive process by adding organic acids, such as camphorsulfonic acid or p-toluenesulfonic acid (US-A 5,322,912) or by adding dimethyl sulfoxide (US-A 5,412,047) or 2-fluoro-1-methylpyridinium p-toluenesulfonate (Macromolecules 28, 8453 et seq. (1995)) or, respectively, indonylacetic acid to the polymerization mixture. Addition of these polymerization accelerators is not generally required when preparing the inventive block copolymers.

The inventive process is usually carried out at an absolute pressure in the range from atmospheric pressure to 60 bar, preferably up to 45 bar, and at a temperature of from 70 to 170°C, preferably from 80 to 150°C. It is particularly preferable to prepare the block copolymers at a pressure in the range from atmospheric pressure to 5 bar and at a temperature in the range from 60 to 120°C.

According to the invention, the block copolymers may be used to prepare thermoplastic molding compositions. To this end, they may be mixed with one or more other thermoplastic polymers and, if desired, with additives. The block copolymers are particularly preferably mixed with other styrene copolymers.

Very particular preference is given to thermoplastic molding compositions which encompass, as one component C), at least one inventive block copolymer, and as another component D), at least one mix comprising at least one graft copolymer d1) containing a rubber as graft base and a graft derived from an unsaturated monomer, and a matrix polymer d2) and also, as component E), at least one thermoplastic polyamide. The thermoplastic molding compositions may moreover optionally comprise a component F) which is at least one monofunctional anhydride with a molar mass

smaller than 3000 g/mol. The thermoplastic molding compositions may, if desired, also encompass additives as component G).

The proportions of the components C) to I) may vary within wide limits. Preference is given to thermoplastic molding compositions which comprise from 0.1 to 15% by weight, in particular from 0.5 to 10% by weight, of component C)
from 10 to 87.9% by weight, in particular from 15 to 84.45% by weight, of component D)
from 10 to 87.9, in particular from 15 to 84.45% by weight of component E)
from 0 to 2% by weight, in particular from 0.05 to 1.5% by weight, of component F)
from 0 to 60% by weight, in particular from 0 to 50% by weight, of component G),
where the proportions of components C to H give a total of 100%.

Component D)

The mix which is present according to the invention as component D) in the molding compositions encompasses at least one graft copolymer (d1). This may be either one graft copolymer or else a mixture of two or more different graft copolymers.

The graft copolymer contains a rubber as graft base d11). In principle, suitable rubbers here are any of those which have a glass transition temperature of 0°C or below (determined to DIN 53765). The rubbers may be of a very wide variety of type. By way of example, it is possible to use silicone rubbers, olefin rubbers, such as ethylene rubbers, propylene rubbers, ethylene-propylene rubbers, EPDM rubbers, diene rubbers, diene-styrene rubbers, acrylate rubbers, ethylene-vinyl acetate rubbers, or ethylene-butyl acrylate rubbers, or a mixture composed of two or more of these rubbers. Among these preference is given to acrylate rubbers and diene rubbers.

Mixtures composed of diene rubber and acrylate rubber, or of diene rubber and silicone rubber, or of diene rubber and rubber based on ethylene copolymers are preferred.

However, diene rubbers are particularly preferably used alone as d11). Very particular preference is given to diene rubbers which are composed of

δ11) from 50 to 100% by weight of at least one diene having conjugated double bonds, and

δ12) from 0 to 50% by weight of one or more other monoethylenically unsaturated monomers,

where the percentages by weight of δ11) and δ12) give a total of 100.

Dienes δ11) which have conjugated double bonds and which may in particular be used are butadiene, isoprene, and their halogen-substituted derivatives, such as chloroprene. Preference is given to butadiene or isoprene, in particular butadiene.

Examples of the other monoethylenically unsaturated monomers δ12) which may be present in the diene rubber with concomitant reduction in the amount of the monomers δ11) are:

vinylaromatic monomers, preferably styrene or styrene derivatives, for example C_1-C_8-alkyl-substituted styrenes, such as α-methylstyrene, p-methylstyrene, vinyltoluene;

unsaturated nitriles, such as acrylonitrile, methacrylonitrile;

aliphatic esters, such as C_1-C_4-alkyl esters of methacrylic acid or of acrylic acid, e.g. methyl methacrylate, and also the glycidyl esters, glycidyl acrylate and glycidyl methacrylate;

N-substituted maleimides, such as N-methyl-, N-phenyl-, and N-cyclohexylmaleimide; acids, such as acrylic acid, methacrylic acid; and also dicarboxylic acids, such as maleic acid, fumaric acid, and itaconic acid and their anhydrides such as maleic anhydride; nitrogen-functional monomers, such as dimethylaminoethyl acrylate, diethylaminoethyl acrylate, vinylimidazole, vinylpyrrolidone, vinylcaprolactam, vinylcarbazole, vinylaniline, acrylamide, and methacrylamide;

aromatic and araliphatic esters of (meth)acrylic acid, e.g. phenyl acrylate, phenyl methacrylate, benzyl acrylate, benzyl methacrylate, 2-phenylethyl acrylate, 2-phenylethyl methacrylate, 2-phenoxyethyl acrylate, and 2-phenoxyethyl methacrylate; unsaturated ethers, such as vinyl methyl ether or vinyl butyl ether.

It is also possible, of course, to use a mixture of two or more of these monomers.

Preferred monomers δ12) are styrene, acrylonitrile, methyl methacrylate, glycidyl acrylate, glycidyl methacrylate, or butyl acrylate.

The preparation of the rubbers is known to the person skilled in the art or may take place using methods known to the person skilled in the art. For example, the diene rubbers may be prepared in a first step in which they are not produced in particle form, examples of methods here being solution polymerization or gas-phase polymerization,

the polymers then being dispersed in the aqueous phase in a second step (secondary emulsification). For the preparation of the rubbers, preference is given to heterogeneous polymerization processes which form particles. This dispersion polymerization may be conducted, by way of example, in a manner known per se by the emulsion polymerization, inverse emulsion polymerization, miniemulsion polymerization, microemulsion polymerization, or microsuspension polymerization method, using a feed process, continuously, or using a batch process. The rubbers may also be prepared in the presence of a fine-particle latex which forms an initial charge (known as the "seed latex" polymerization method). By way of example, suitable seed latices are composed of polybutadiene or polystyrene. In principle, it is possible to use the rubbers as graft base after their preparation. However, prior to the grafting they may also first be agglomerated through agglomeration processes to give larger particles.

Agglomeration processes are known to the person skilled in the art. Methods known to the person skilled in the art may also be used to undertake the agglomeration process. For example, use may be made of physical methods, such as freeze agglomeration or pressure agglomeration processes. However, it is also possible to use chemical methods to agglomerate the primary particles. Among the latter are the addition of inorganic or organic acids. The agglomeration is preferably undertaken by means of an agglomeration polymer in the absence or presence of an electrolyte, such as an inorganic hydroxide. By way of example, agglomeration polymers which may be mentioned are polyethylene oxide polymers or polyvinyl alcohols. Among suitable agglomeration polymers are copolymers of C_1-C_{12}-alkyl acrylates or of C_1-C_{12}-alkyl methacrylates and of polar comonomers, such as acrylamide, methacrylamide, ethacrylamide, n-butylacrylamide, or maleamide.

The rubbers preferably have particle sizes (ponderal median d_{50}) in the range from 100 to 2500 nm. The particle size distribution is preferably almost or completely monomodal, or almost or completely bimodal.

The graft copolymers d1) contain a graft d12) based on an unsaturated monomer, and this means that the graft may also have been prepared from two or more unsaturated monomers. In principle, a very wide variety of unsaturated compounds may be used for grafting to the rubber. Appropriate compounds and methods are known per se to the person skilled in the art. Preference is given to a graft d12) containing

δ21) from 50 to 100% by weight, preferably from 60 to 100% by weight, and particularly preferably from 65 to 100% by weight, of a vinylaromatic monomer,

δ22) from 0 to 50% by weight, preferably from 0 to 40% by weight, and particularly preferably from 0 to 35% by weight, of acrylonitrile or methacrylonitrile or a mixture of these,

δ23) from 0 to 40% by weight, preferably from 0 to 30% by weight, and particularly preferably from 0 to 20% by weight, of one or more other monoethylenically unsaturated monomers,

where the proportions of components δ21) to δ23) give a total of 100% by weight.

Vinylaromatic monomers which may be used are the vinylaromatic compounds mentioned under δ12), or a mixture composed of two or more of these, in particular styrene or α-methylstyrene. Other monoethylenically unsaturated monomers are the aliphatic, aromatic, and araliphatic esters, acids, nitrogen-functional monomers, and unsaturated ethers listed under δ12), and mixtures of these monomers.

The graft d12) may be prepared in one or more steps of a process. The monomers here δ21), δ22), and δ23), may be added individually or in a mixture with one another. The monomer ratio of the mixture may be constant over time or be graduated. Combinations of these procedures are also possible.

By way of example, styrene may first be polymerized alone onto the graft base d11), followed by a mixture of styrene and acrylonitrile.

By way of example, preferred grafts d12) are composed of styrene and/or of α-methylstyrene, and of one or more of the other monomers mentioned under δ22) and δ23). Preference is given to methyl methacrylate, N-phenylmaleimide, maleic anhydride, and acrylonitrile, methyl methacrylate and acrylonitrile being particularly preferred.

Preferred grafts d12) derive from:

d12–1: styrene
d12–2: styrene and acrylonitrile,
d12–3: α-methylstyrene and acrylonitrile,
d12–4: styrene and methyl methacrylate.

The proportion of styrene or α-methylstyrene, or the proportion of the entirety of styrene and α-methylstyrene, is particularly preferably at least 40% by weight, based on d12).

Other suitable graft polymers are those with two or more "soft" and "hard" stages, especially if the particles are relatively large.

Preference is given to graft polymers d1) which (based on d1)) comprise

d11) from 30 to 95% by weight, preferably from 40 to 90% by weight, in particular from 40 to 85% by weight, of graft base (i.e. rubber), and

d12) from 5 to 70% by weight, preferably from 10 to 60% by weight, in particular from 15 to 60% by weight, of a graft.

Grafting is generally carried out in emulsion. Suitable process measures are known to the person skilled in the art. If ungrafted polymers composed of the monomers d12) are produced, these amounts, which are generally less than 10% by weight of d1), are counted with the weight of component d2).

Component d2) comprises a matrix polymer, which may also mean a mixture of two or more different matrix polymers. The selection of the molecular structure of the matrix polymer d2) is preferably such that the matrix polymer is compatible with the graft. The monomers d12) therefore preferably correspond to those of the matrix polymer d2). However, the matrix polymers preferably contain no functional groups which can react with the end groups of the polyamides.

By way of example, suitable matrix polymers d2) are amorphous polymers, for example SAN (styrene-acrylonitrile) polymers, AMSAN (α-methylstyrene-acrylonitrile) polymers, SNPMIMA (styrene-maleimide-maleic anhydride) polymers, SANMA (styrene-maleic acid (anhydride)-acrylonitrile) polymers, or SMA (styrene-maleic anhydride).

Component d2) is preferably a copolymer composed of

d21) from 60 to 100% by weight, preferably from 65 to 80% by weight, of units of a vinylaromatic monomer, preferably of styrene, of a substituted styrene, or of a (meth)acrylic ester, or of a mixture of these, in particular of styrene or of α-methylstyrene, or of a mixture of these,

d22) from 0 to 40% by weight, preferably from 20 to 35% by weight, of units of an ethylenically unsaturated monomer, preferably of acrylonitrile or of methacrylonitrile or of methyl methacrylate, in particular of acrylonitrile.

In one embodiment of the invention, the matrix polymer is composed of from 60 to 99% by weight of vinylaromatic monomers and from 1 to 40% by weight of at least one of the other stated monomers.

In one embodiment of the invention, the d2) used comprises a copolymer of styrene and/or α-methylstyrene with acrylonitrile. The acrylonitrile content in these copolymers is from 0 to 40% by weight, preferably from 20 to 35% by weight, based on the total weight of d2).

The molar masses (weight-average Mw) are generally in the range from 50 000 to 500 000 g/mol, preferably in the range from 70 000 to 450 000 g/mol.

The matrix polymers d2) are known per se or may be prepared by methods known to the person skilled in the art.

The ratio of component d1) to component d2) may vary within a wide range. The mixes D) mostly comprise from 20 to 85% by weight, preferably from 25 to 80% by weight, of d1) and from 15 to 80% by weight, preferably from 20 to 75% by weight, of d2), where the proportions by weight of d1) and d2) give a total of 100.

Component E)

In principle, any of the thermoplastic polyamides may be used as component E). Components E) are not only those which comprise one polyamide but also those which are composed of two or more different polyamides. The mixing ratio in which the different polyamides may be present can be freely selected. Component E) preferably encompasses only one polyamide.

The polyamides present as component E) in the molding compositions encompass semicrystalline and amorphous resins with a molar mass (weight-average) of at least 2500 g/mol (determined by gel permeation chromatography (GPC) using hexafluoroisopropanol as eluent and polymethyl methacrylate as standard), these generally being termed nylon. These polyamides have been widely described. Their preparation is known, and they may be prepared by methods known per se.

By way of example, the polyamides E) may be prepared via condensation of a saturated or aromatic dicarboxylic acid having from 4 to 12 carbon atoms with a saturated or aromatic diamine which has up to 14 carbon atoms, or via condensation of ω–aminocarboxylic acids or polyaddition of corresponding lactams.

Merely by way of example, mention may be made here of suberic acid, azelaic acid, or sebacic acid as representatives of aliphatic dicarboxylic acids, 1,4-butanediamine, 1,5-pentanediamine, 1,6-hexanediamine, or piperazine as representatives of the diamines, and caprolactam, caprylolactam, enantholactam, laurolactam and ω-aminoundecanoic acid as representatives of lactams and aminocarboxylic acids.

Aromatic dicarboxylic acids generally have from 8 to 16 carbon atoms. By way of example, suitable aromatic dicarboxylic acids are substituted terephthalic and isophthalic acids, for example 3-tert-butylisophthalic acid, polynuclear dicarboxylic acids, e.g. diphenyl-4,4'- and -3,3'-dicarboxylic acid, diphenylmethane-4,4'- and -3,3'-dicarboxylic acid, diphenyl sulfone 4,4'- and 3,3'-dicarboxylic acid, naphthalene-1,4- or -2,6-dicarboxylic acid, and phenoxyterephthalic acid.

Other monomers which may be used are cyclic diamines, and among these preferably bis(4-aminocyclohexyl)methane, bis(4-amino-3-methylcyclohexyl)methane, bis(4-aminocyclohexyl)-2,2-propane, or bis(4-amino-3-methylcyclohexyl)-2,2-propane. Other cyclic diamines which may be mentioned are 1,3- or 1,4-cyclohexanediamine or isophoronediamine. Use may also be made of m-xylylenediamine.

Examples of polyamides which derive from saturated dicarboxylic acids and from diamines are:

polytetramethyleneadipamide (nylon-4,6), polyhexamethyleneadipamide (nylon-6,6), polyhexamethyleneazelamide (nylon-6,9), polyhexamethylenesebacamide (nylon-6,10), polyhexamethylenedodecanediamide (nylon 6,12).

Examples of polyamides obtained by ring-opening of lactams are polycaprolactam (nylon-6), polylaurolactam, and poly-11-aminoundecanoic acid.

It is also possible to use polyamides which have been prepared by copolycondensing two or more of the abovementioned dicarboxylic acids or two or more of the abovementioned diamines, or else by copolycondensing two or more of the abovementioned polymers. Examples of these are copolymers of adipic acid, isophthalic acid, or terephthalic acid and hexamethylenediamine, or copolymers of caprolactam, terephthalic acid, and hexamethylenediamine. These semiaromatic copolyamides generally contain from 40 to 90% by weight of units which derive from terephthalic acid and from hexamethylenediamine. A small proportion of the terephthalic acid, preferably not more than 10% by weight of the entirety of aromatic dicarboxylic acids used, may be replaced by isophthalic acid or other aromatic dicarboxylic acids, preferably those where the carboxy groups are in para position.

Semiaromatic copolyamides may also encompass units which derive from the abovementioned cyclic diamines.

Semiaromatic copolyamides which have proved advantageous for many applications are those having from 50 to 80% by weight, in particular from 60 to 75% by weight, of units which derive from terephthalic acid and hexamethylenediamine and from 20 to 50% by weight, preferably from 25 to 40% by weight, of units which derive from ε-caprolactam.

Among the particularly preferred semiaromatic copolyamides are those substantially composed of

e1) from 30 to 44 mol%, preferably from 32 to 40 mol%, and in particular from 32 to 38 mol%, of units which derive from terephthalic acid,

e2) from 6 to 20 mol%, preferably from 10 to 18 mol%, and in particular from 12 to 18 mol%, of units which derive from isophthalic acid,

e3) from 43 to 49.5 mol%, preferably from 46 to 48.5 mol%, and in particular from 46.3 to 48.2 mol%, of units which derive from hexamethylenediamine,

e4) from 0.5 to 7 mol%, preferably from 1.5 to 4 mol%, and in particular from 1.8 to 3.7 mol%, of units which derive from aliphatic cyclic diamines having from 6 to 30 carbon atoms, preferably from 13 to 29 carbon atoms, and in particular from 13 to 17 carbon atoms,

e5) from 0 to 4 mol% of polyamide-forming monomers other than e1) to e4),

where the molar percentages of components e1) to e5) together give 100%.

It is preferable for the diamine units e3) and e4) to be reacted in approximately equimolar amounts with the dicarboxylic acid units e1) and e2).

By way of example, the polyamide-forming monomers e5) may derive from dicarboxylic acids having from 4 to 16 carbon atoms and from aliphatic diamines having from 4 to 16 carbon atoms, or else from aminocarboxylic acids, or, respectively, corresponding lactams having from 7 to 12 carbon atoms. Examples of these have been mentioned above.

The melting points of these semiaromatic copolyamides are generally in the range from 280 to 340°C, preferably from 290 to 330°C, this melting point generally being associated with a high glass transition temperature, generally more than 120°C, in particular more than 130°C (in the dry state).

Among the semiaromatic copolyamides which encompass components e1) to e5), preference is given to the use of those whose degree of cystallinity is above 30%, preferably above 35%, and in particular above 40%.

The degree of crystallinity is a measure of the content of crystalline fragments in the copolyamide and is determined by X-ray diffraction or indirectly via use of DSC to measure ΔH_{cryst}. X-ray diffraction can give an absolute measurement of the degree of crystallinity. For this, a ratio is calculated between the intensity of the peaks and the amorphous halo (see D.I. Bower, "An Introduction to Polymer Physics", Cambridge University Press, 2002, pp. 118-120).

If specimens with known degree of crystallinity X_c are available it is possible to produce a correlation between X_c and ΔH_{cryst}.

Preferred semiaromatic copolyamides are those whose content of triamine units, in particular units of dihexamethylenetriamine, is below 0.5% by weight. Particular preference is given to those semiaromatic polyamides whose triamine contents are 0.3% by weight or lower.

Either linear or branched polyamides or star-shaped polyamides may be used as component E). Preference is given to linear polyamides whose melting point determined by DSC measurement (e.g. D.T. Bower, abovementioned publication, p. 30) is above 180°C.

Preferred polyamides E) are polyhexamethyleneadipamide, polyhexamethylenesebacamide, and polycaprolactam, and also nylon-6/6T and nylon-6,6/6T, and also polyamides which contain cyclic diamines as comonomers. The viscosity number of the polyamides, determined on a 0.5% strength by weight solution in 96% strength sulfuric acid at 23°C to DIN 53727 is generally from 80 to 400 ml/g, corresponding to a molar mass (number average) of from about 7000 to 45 000 g/mol. Preference is given to the use of polyamides whose viscosity number is from 80 to 300 ml/g, in particular from 100 to 280 ml/g.

Preference is given to polyamides which have one amino end group per chain.

Component F)

Another component which may be used concomitantly is a low-molecular-weight compound which has only one dicarboxylic anhydride group. However, it is also possible to use two or more of these compounds as component F). Besides the dicarboxylic anhydride group, other functional groups which can react with the end groups of the polyamides E) may be present in these compounds. Examples of suitable compounds F) are C_4-C_{10}-alkanedicarboxylic anhydrides, such as succinic anhydride, glutaric anhydride, adipic anhydride. Use may also be made of cycloaliphatic dicarboxylic anhydrides, such as 1,2-cyclohexanedicarboxylic anhydride. However, it is also possible to use dicarboxylic anhydrides which are ethylenically unsaturated or aromatic compounds, examples being maleic anhydride, phthalic anhydride, or trimellitic anhydride.

The proportion of component F) is generally from 0 to 2% by weight, preferably from 0.05 to 1.5% by weight, based on the total weight of components A to G.

Component G)

The molding compositions may comprise additives. The proportion of these is generally from 0 to 60% by weight, preferably from 0 to 50% by weight, based on the total weight of components A to G.

By way of example, these may be particulate mineral fillers. Suitable fillers among these are amorphous silica, carbonates, such as magnesium carbonate or chalk, powdered quartz, mica, a very wide variety of silicates, such as clays, muscovite, biotite, suzoite, tin maletite, tac, chlorite, phlogopite, feldspar, calcium silicates, such as wollastonite, or kaolin, particularly calcined kaolin.

One particularly preferred embodiment uses particulate fillers in which at least 95% by weight, preferably at least 98% by weight, of the particles have a diameter (largest dimension), determined on the finished product, of less than 45 µm, preferably less than 40 µm, and an „aspect ratio" preferably within the range from 1 to 25, preferably in the range from 2 to 20, determined on the finished product, which is generally an injection molding. One way of determining the particle diameters here is to take electron micrographs of thin layers of the polymer mixture and to utilize at least 25 filler particles, preferably at least 50 filler particles, for the evaluation. The particle diameters may also be determined by sedimentation analysis in Transactions of ASAE, p. 491 (1983). A sieving analysis method may also be used to measure the proportion by

weight of fillers which is less than 40 μm. The aspect ratio is the ratio of particle diameter to thickness (largest dimension to smallest dimension).

Particularly preferred particulate fillers are talc, kaolin, such as calcined kaolin, wollastonite, and mixtures composed of two of these fillers, or of all of them. Particularly preferred among these is talc with a proportion of at least 95% by weight of particles with diameters of less than 40 μm and with an aspect ratio of from 1.5 to 25, in each case determined on the finished product. Kaolin preferably has a proportion and at least 95% by weight of particles with a diameter of less than 20 μm and an aspects ratio of from 1.2 to 20, in each case determined on the finished product. The amounts which may be used of these fillers are from 0 to 60% by weight, preferably up to 50% by weight, based on the total weight of A to F.

Fibrous fillers, such as carbon fibers, potassium titanate whiskers, aramid fibers, or preferably glass fibers, may also be used as component G), where at least 50% by weight of the fibrous fillers (glass fibers) have a length greater than 50 nm. The (glass) fibers used may preferably have a diameter of up to 25 μm, particularly preferably from 5 to 15 μm. At least 70% by weight of the glass fibers preferably have a length greater than 60 μm. The average length of the glass fibers in the finished molding is particularly preferably from 0.08 to 0.5 mm. The length of the glass fibers is based on a finished molding, for example one obtained by injection molding. The glass fibers may have the appropriate length before they are added to the molding compositions, or else they may be in the form of continuous-filament fibers (rovings) when they are added. The amounts generally used of these fibers are from 0 to 60% by weight, preferably up to 50% by weight, based on the total weight of A to F.

Phosphorus-containing flame retardants may also be used as component G). Examples are tris(2,6-dimethylphenyl) phosphate, triphenyl phosphate, tricresyl phosphate, diphenyl 2-ethylcresyl phosphate, diphenyl cresyl phosphate, tris(isopropylphenyl) phosphate, and also bis(phenyl) 4-phenyl phosphate, phenyl bis(4-phenylphenyl) phosphate, tris(4-phenylphenyl) phosphate, bis(phenyl) benzylphenyl phosphate, phenyl bis(benzylphenyl) phosphate, tris(benzylphenyl) phosphate, bisphenyl [1-phenylethyl]phenyl phosphate, phenyl bis[(1-methyl-1-phenylethyl)phenyl] phosphate, and phenyl bis[4-(1-phenylethyl)-2,6-dimethylphenyl] phosphate. They may also be used in a mixture with triphenylphosphine oxide or tris(2,6-dimethylphenyl)phosphine oxide.

Preferred flame retardants moreover are resorcinol diphosphate, bisphenol A diphenyl phosphate and correspondingly higher oligomers, hydroquinone diphosphate and correspondingly higher oligomers.

The amounts generally used of the flame retardants are from 0 to 30% by weight, preferably from 0 to 25% by weight. The preferred amounts used of flame retardants, if they are present, are from 0.4 to 7% by weight. The amounts given are in each case based on the total weight of A to G.

Examples of other additives are processing aids, stabilizers and oxidation retarders, agents to inhibit decomposition caused by heat or by ultraviolet light, lubricants, mold-release agents, dyes, pigments and plasticizers. Their proportion is generally from 0 to 45% by weight, preferably from 0 to 20% by weight, in particular from 0 (if present, from 0.2) to 10% by weight based on the total weight of A to G.

Pigments and dyes are generally present in amounts of from 0 to 4% by weight, preferably from 0 to 3.5% by weight and in particular from 0 (if present, from 0.5) to 3% by weight, based on the total weight of A to G.

The pigments for pigmenting thermoplastics are well known. A first preferred group of pigments is that of white pigments, such as zinc oxide, zinc sulfide, white lead, ($2\ PbCO_3.Pb(OH)_2$), lithopones, antimony white and titanium dioxide. Of the two most commonly found crystalline forms of titanium dioxide (rutile and anatase) it is in particular the rutile form which is used for white coloration of the molding compositions of the invention.

Black pigments which may be used according to the invention are iron oxide black (Fe_3O_4), spinel black ($Cu(Cr, Fe)_2O_4$), manganese black (a mixture of manganese dioxide, silicon oxide and iron oxide), cobalt black and antimony black, and also particularly preferably carbon black, mostly used in the form of furnace black or gas black.

According to the invention, it is, of course, also possible to achieve particular shades by using inorganic choromatic color pigments. It may moreover be advantageous to use the aforementioned pigments/dyes in mixture, for example carbon black with copper phthalocyanines, since the dispersion of color in the thermoplastic generally becomes easier.

Examples of oxidation retarders and heat stabilizers which may be added to the thermoplastic materials according to the invention are halides of metals of group I of

the Periodic Table, e.g. sodium halides and lithium halides, where appropriate in combination with copper(I) halides, e.g. with chlorides, bromides and iodides. The halides, in particular of copper, may also contain electron-rich p-ligands. Examples of copper complexes of this type are Cu halide complexes with, for example, triphenylphosphine. It is also possible to use zinc fluoride and zinc chloride. Use may also be made of sterically hindered phenols, hydroquinones, substituted representatives of this group, secondary aromatic amines, HALS, where appropriate in combination with phosphorus-containing acids and, respectively, salts of these, and mixtures of these compounds, preferably in concentrations up to 1% by weight, based on the total weight of A to G.

Examples of UV stabilizers are various substituted resorcinols, salicylates, benzotriazoles and benzophenones, which are usually used in amounts of up to 2% by weight based on the total weight and A to G.

Lubricants and mold-release agents, generally used in amounts of up to 1% by weight, based on the total weight of A to F, are stearic acid, stearyl alcohol, alkyl stearates and stearamides, and also esters of pentaerythritol with long-chain fatty acids. It is also possible to use salts of calcium, zinc or aluminium of the steric acid and dialkyl ketones, e.g. distearyl ketone. Use may moreover be made of ethylene oxide-propylene oxide copolymers as lubricants and mold-release agents.

The thermoplastic molding compositions of the invention are prepared by processes known per se, by mixing the components A) to G). It may be advantageous to premix individual components. It is also possible, but less desirable for the components to be mixed in solution, with removal of the solvents.

Any of the known methods may be used to mix the, for example dry, components. They are preferably mixed at temperatures of from 200 to 320°C by extruding, kneading, or rolling the components together, the components having previously, where appropriate, been isolated from the solution obtained during the polymerization or from the aqueous dispersion.

The inventive thermoplastic molding compositions may be processed by the known methods of thermoplastics processing, for example by extrusion, injection molding, calendering, blow molding, or sintering.

The inventive molding compositions may be used to produce films, fibers, moldings, or foams. They may also particularly preferably be processed to give parts of housings or of chassis, or to give entire housings. However, they are also used as bodywork parts

in the automotive sector and may in particular be used to produce large-surface-area automotive parts.

Examples

The GPC measurements were made on a GPC system composed of a Waters 510 pump and a Waters RI 410 detector (at 254 nm), Spectra Series UV 100. The column combination used was: 5 PSS SDV linear M styrene-divinylbenzene gel columns (each 300 x 8 mm) from the company PSS GmbH, these being temperature-controlled to 35°C. THF was used as mobile phase with a flow rate of 1.2 ml/min.

The viscosity number of the polyamides was determined to DIN 53 727 on 0.5% strength by weight solutions in 96% by weight sulfuric acid at 23°C.

The heat resistance of the specimens was determined by means of the Vicat softening point. The Vicat softening point was determined to DIN 53 460, using a force of 49.05 N and a temperature rise of 50 K per hour, on standard small specimens.

The notched impact strength of the products was determined on ISO specimens to ISO 179 1eA.

The flowability was determined to ISO 1133 at 240°C with a load of 5 kg. In the case of molding compositions comprising nylon-6,6 (PA 6,6), the flowabilities were instead determined at 275 °C with a load of 5 kg, because PA 6,6 has higher melting points.

Component CI

SAN-b-S/MA block copolymer with a viscosity number of 81 ml/g. The block copolymer was prepared as follows by controlled free-radical polymerization: 4.9 g of maleic anhydride and 1035 g of styrene were polymerized using 4.22 g of a mixture composed of 4-hydroxy-2,2,6,6-tetramethyl-1-oxylpiperidine (HO-TEMPO) and of 2,2'-azobisisobutyronitrile, at 80°C until the solids content was 1.9% by weight. 338.4 g of acrylonitrile were added to the cooled reaction mixture and polymerization was carried out at 80°C. The block copolymer was then isolated by precipitation. The maleic anhydride content was 1.1% by weight, and the ratio of the block X to the block Y was 97.7 : 2.3.

Component CII

SAN-b-S/MA block copolymer with a viscosity number of 78 ml/g. The block copolymer was prepared as follows by controlled free-radical polymerization: 12.25 g of maleic anhydride and 1027 g of styrene were polymerized using 4.22 g of a mixture composed of 4-hydroxy-2,2,6,6-tetramethyl-1-oxylpiperidine and of 2,2'-azobisisobutyronitrile, at 80°C until the solids content was 1.3% by weight. 337.9 g of acrylonitrile were added to the cooled reaction mixture and polymerization was carried out at 80°C. The block copolymer was then isolated by precipitation. The maleic anhydride content was 2.3% by weight, and the ratio of the block X to the block Y was 97.7 : 2.3.

Component C1 comp
Styrene-acrylonitrile-maleic anhydride terpolymer with substantially random structure, having 75% by weight of styrene, 24% by weight of acrylonitrile, and 1% by weight of maleic anhydride, and a viscosity number of 80 ml/g.

Component C2 comp
Styrene-acrylonitrile-maleic anhydride terpolymer with substantially random structure, having 75% by weight of styrene, 23% by weight of acrylonitrile, and 2% by weight of maleic anhydride, and a viscosity number of 80 ml/g.

Component D1I
Graft rubber having 62% by weight of polybutadiene as graft base and 38% by weight of a graft composed of 75% by weight of styrene and 25% by weight of acrylonitrile. Median particle size about 400 nm.

Component D2I
Styrene-acrylonitrile copolymer having 75% by weight of styrene and 25% by weight of acrylonitrile and a viscosity number of 80 ml/g (determined in DMF solution at 0.5% strength by weight at 25°C).

Component EI
Nylon-6 obtained from ε-caprolactam and having a viscosity number of 150 ml/g.

Component EII
Nylon-6,6 obtained from hexamethylenediamine and adipic acid and having a viscosity number of 150 ml/g.

Component GI
Chopped glass fiber with polyurethane size, fiber diameter 10 µm.

Component GII

Talc with an aspect ratio of 5 : 1

Preparation

The components were mixed in the weight ratios stated below, and then processed in a twin-screw extruder at a melt temperature of from 240 to 280°C. The melt was passed through a water bath and pelletized.

Table 1

Components	comp 1	2	comp 3	4	5	comp 6	7	comp 8	9
CI	-	4.2	-	-	-	-	4.2	-	3.3
CII	-	-	-	4.2	4.2	-	-	-	-
C1 comp	4.2	-	-	-	-	4.2	-	3.3	-
C2 comp	-	-	4.2	-	-	-	-	-	-
D1I	35.3	35.3	35.3	35.3	35.5	35.5	35.3	28.1	28.1
D1II	19.5	19.5	19.5	19.5	19.5	19.5	19.5	15.5	15.5
EI	41	41	41	41	41	-	-	33.1	33.1
EII	-	-	-	-	-	41	41	-	-
GI	-	-	-	-	-	-	-	20	20
GII	-	-	-	-	0.1	-	-	-	-
Vicat B [°C]	106	106	106	105	106	112	112	117	118
MVI** [ml/10']	5.5	9.7	4.0	8.5	9.2	8.7***	12.3	3.3	6.1
ak, RT [kJ/m^2]	55	56	41	49	54	7	25	7	9

*comp: for comparison

** at 240°C with a load of 5 kg

*** at 275°C with a load of 5 kg

The inventive molding compositions have improved flowability, and also greater toughness.

We claim:

1. A block copolymer of the structure Y-X, containing

A) from 95 to 99.5% by weight of block Y containing, as monomeric units,
a1) a mixture composed of
a11) at least one vinylaromatic monomer, and
a12) at least one comonomer which is not maleic anhydride, or
a2) at least one ethylenically unsaturated ester,
and

B) from 0.5 to 5% by weight of block X composed of styrene and maleic anhydride as monomeric units, where the block X substantially has a strictly alternating structure;

where the entirety of components A) and B) gives a total of 100%.

2. A block copolymer as claimed in claim 1, in which block Y contains styrene and acrylonitrile as monomeric units.

3. A block copolymer as claimed in claim 1 or 2, which has a polydispersity index PDI, equal to weight-average molecular weight Mw/number-average molecular weight Mn of from 1.1 to 5.

4. A block copolymer as claimed in any of claims 1 to 3, obtainable via controlled free-radical polymerization.

5. A process for preparing block copolymers as claimed in any of claims 1 to 3, which comprises undertaking the polymerization under controlled free-radical conditions.

6. A process as claimed in claim 5, wherein the block X is prepared in a first step and the block Y is prepared in a second step.

7. The use of the block copolymers as claimed in any of claims 1 to 4, or prepared as claimed in claim 5 or 6, for producing thermoplastic molding compositions.

8. A thermoplastic molding composition comprising at least one block copolymer c) as claimed in any of claims 1 to 4, or prepared as claimed in claim 5 or 6.

9. A thermoplastic molding composition as claimed in claim 8 comprising

C) at least one block copolymer as claimed in any of claims 1 to 4, or prepared as claimed in claim 5 or 6,

D) a mix comprising

d1) at least one graft copolymer containing a rubber as graft base and a graft derived from an unsaturated monomer, and

d2) a matrix polymer, and also

E) at least one thermoplastic polyamide.

10. The use of the thermoplastic molding compositions as claimed in claim 8 or 9 for producing films, fibers, moldings, or foams.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP2004/006037

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08F293/00 C08L77/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08F C08L

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

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DATABASE WPI Section Ch, Week 198123 Derwent Publications Ltd., London, GB; Class A14, AN 1981-41014D XP002291531 & JP 56 041215 A (MITSUBISHI MONSANTO KK) 17 April 1981 (1981-04-17) cited in the application abstract	1-10
A	WO 97/49742 A (TEN BRINKE GERRIT ; KROEZE ERIK (NL); UNIV GRONINGEN (NL); HADZIIOANNO) 31 December 1997 (1997-12-31) claims; example 3	1-10

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

[X] Patent family members are listed in annex.

° Special categories of cited documents :

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

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Date of the actual completion of the international search	Date of mailing of the international search report
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Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Wirth, M

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP2004/006037

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	D BENOIT, C HAWKER ET AL.: "One-step formation of functionalised Block copolymers" MACROMOLECULES, vol. 33, 2000, pages 1505-1507, XP002291586 the whole document	1-10

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/EP2004/006037

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WO 9749742 A	31-12-1997	NL 1003422 C2	07-01-1998
		AU 3193797 A	14-01-1998
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