(54) TRANSPARENT POLYMER MIXTURES HAVING
HIGH IMPACT STRENGTH

(71)   We, BASF AKTIENGESELLSHAFT, a German Joint Stock Company of 6700 Ludwigshafen, Federal Republic of Germany, do hereby declare the invention, for which we 5 pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to mixtures of 10 a polystyrene and a thermoplastic star-shaped block copolymer of a monovinyl-aromatic compound and a conjugated diene, which mixtures exhibit good transparency and high impact strength.

15   Polystyrene is a hard thermoplastics material distinguished, in particular, by its transparency. However, its brittleness and low impact strength are disadvantages in numerous applications.

20   It is known to improve the mechanical properties of polystyrene, especially its impact strength, by modification with rubbery materials, either by mixing the rubber with the polystyrene or by polymerizing styrene in the 25 presence of the rubber. The rubbery materials used to improve the impact strength are, in particular, homopolymers and copolymers of conjugated dienes, e.g. polymers of butadiene or isoprene. Particularly advantageous 30 products, in respect of their mechanical properties, are obtained by employing elastomeric block copolymers of styrene and a conjugated diene. These comprise a predominant proportion of the conjugated 35 diene and a minor proportion of styrene and may have a linear or star-shaped branched structure.

However, when rubbery materials are incorporated into polystyrene, the transparency 40 of the latter is destroyed, so that the styrene polymers of improved impact strength, thus obtained, are unsuitable for many applications,

for example in the packaging sector.

It has also been disclosed that styrene polymers having high impact strength and good 45 mechanical properties may be obtained by manufacturing non-elastomeric block copolymers of styrene and a conjugated diene, comprising a predominant proportion of the former and a lesser proportion of the latter. 50 For example, German Laid-Open Application DOS 1,959,922 discloses branched block copolymers having a star-shaped structure, comprising a predominant proportion of styrene and a lesser proportion of a conjugated 55 diene, which exhibit, at one end the same time, good impact strength, clarity, good processability and extreme stability. These branched block copolymers are obtained by coupling styrene-diene two-block copolymers in which 60 the terminal polystyrene blocks are of varying lengths. It is true that these products exhibit a pattern of properties which is satisfactory in many respects and are both impact-resistant and transparent; however, because of the 65 involved process of manufacture they are comparatively expensive.

The present invention seeks to improve the mechanical properties of polystyrene, whilst retaining its transparency, by an economical 70 method which in particular gives products having good impact strength which are, at the same time, substantially glass-clear and readily processable.

We have found that good results can be 75 achieved, according to the invention, by blending polystyrene with a non-elastomeric, star-shaped block copolymer of a monovinyl-aromatic compound and a conjugated diene, the non-elastomeric star-shaped block 80 copolymer having a specific structure.

Accordingly, the present invention provides a mixture comprising essentially

A) from 10 to 70 per cent by weight of a

polystyrene and

B) from 90 to 30 per cent by weight of a thermoplastic, non-elastomeric, star-shaped block copolymer of from 60 to 95 per cent by weight of a monovinyl-aromatic compound and from 40 to 5 per cent by weight of a conjugate diene of 4 to 8 carbon atoms, which block copolymer possesses at least two types, of different average composition, of copolymer blocks which form the branches, in which mixture at least 50 per cent by weight of the total monovinylaromatic compound present as copolymerized units in the star-shaped block copolymer are present as blocks in the terminal polymer segment of one or more of the copolymer blocks of the branches.

Though polystyrene and non-elastomeric, star-shaped block copolymers comprising a predominant proportion of a monovinyl-aromatic compound and a minor proportion of a conjugated diene are inherently transparent products, it is extremely surprising that the transparency is retained on blending the two components in accordance with the present invention, since the refractive indices of the two components are distinctly different and the known blends of polystyrene with branches block copolymers, having an elastomeric character, of a monovinyl-aromatic compound and a conjugated diene give significantly turbid or even opaque products. It is to be assumed that the transparency of the mixtures according to the invention is due to compatibility of the two components, and such compatibility is extremely rarely observed in polymer mixtures.

The polystyrene to be employed as component A of the mixtures according to the invention may be manufactured in the conventional manner by mass polymerization, solution polymerization or aqueous dispersion polymerization of styrene. Preferably, a polystyrene obtained by mass polymerization or solution polymerization is employed; this material is conventional amorphous polystyrene. The viscosity-average molecular weight of the polystyrene is in general from 50,000 to 1,000,000, preferably from 100,000 to 500,000. The mixtures contain from 10 to 70 per cent by weight of polystyrene, based on the sum of the components A and B.

Component B of the mixtures according to the invention, employed in amounts of from 90 to 30 per cent by weight, based on the sum of A and B, is a non-elastomeric, star-shaped (i.e. branched) copolymer comprising a predominant proportion of a monovinyl-aromatic compound and a minor proportion of a conjugated diene of 4 to 8 carbon atoms.

Examples of monovinyl-aromatic compounds which may be used to synthesize the star-shaped block copolymers are styrene, styrenes with alkyl side-chains, e.g. α-methyl-styrene, and nuclear-substituted styrenes, e.g. vinyltoluene or ethylvinylbenzene. The monovinyl-aromatic compounds may be employed individually or as mixtures with one another. However, the use of styrene alone is preferred. Examples of conjugated dienes which may be employed, individually or as mixtures with one another, for the manufacture of the branched block copolymers are butadiene, isoprene and 2, 3-dimethyl-butadiene. Butadiene and isoprene give particularly advantageous results and, of the two, butadiene is preferred.

The star-shaped block copolymers of the mixtures according to the invention contain a total of from 60 to 95 per cent by weight, especially from 70 to 90 per cent by weight, of the monovinyl-aromatic compound and from 40 to 5 per cent by weight, preferably from 30 to 10 per cent by weight, of the conjugated diene, in each case based on total monomers employed, as copolymerized units. The molecular weight of the star-shaped block copolymers is usually from 100,000 to 1,000,000 and preferably from 150,000 to 500,000. These data relate to the weight-average molecular weight, determined by viscosity measurements on an 0.5 per cent strength by weight toluene solution at 25°C.

The star-shaped block copolymers to be employed according to the invention have branches consisting of copolymer blocks in which the monovinyl-aromatic compound and the conjugated diene units are present as blocks, forming individual polymer segments. These copolymer blocks, themselves of block structure, which form the branches, are chemically coupled to one another by means of a coupling agent. The star-shaped block copolymers have at least 3, in general from 3 to 10, and preferably 3 or 4, such branches, and these branches must comprise at least two types of copolymer blocks of different average composition. Furthermore, at least 50 per cent by weight, preferably at least 60 per cent by weight, of all the monovinyl-aromatic compound present as copolymerized units in the star-shaped block copolymer must be contained in the terminal homopolymer segment of one or more of the copolymer blocks of the branches.

The preferred component B of the mixtures of the invention is a star-shaped block copolymer, the most probable average structure of which is represented by one of the general formulae (I), (II) or (III) below:

(I) $(A-B)_k$-X,

(II) $(A^1\text{-}B^1 \rightarrow A^2)_n$-X-$(A^2 AB^1)_m$,

(III) $(A^3\text{-}A^4\text{-}B^2 \rightarrow A^5)_n$-X-$(A^5 \leftarrow B^2\text{-}A^4)_m$.

In these general formulae (I) - (III), A and A^1-A^5 are non-elastomeric polymer segments of the monovinyl-aromatic compound, of which the polymer segments A in the polymer (I) has a polymodal, preferably bimodal, molecular weight distribution, whilst the individual polymer segments A^1-A^5 in the polymers (II) and (III) each have a unimodal molecular weight distribution, B, B^1 and B^2 are elastomeric polymer segments based on the

conjugated diene, X is a radical of a polyfunctional coupling agent by means of which the copolymer blocks forming the branches are chemically coupled to one
5　another, k is an integer not less than 3, in general from 3 to 10 and preferably 3 or 4, and m and n are numbers, m being equal to or greater than n and the sum of m and n being at least 3, in general an integer from 3 to 10 and
10　preferably 3 or 4.

The symbol $\to$ in the general formulae (II) and (III) means that the transition between the polymer segments concerned is gradual rather than sharp.

15　Star-shaped block copolymers of the general formula $(A\text{-}B)_k\text{-}X$ (I) have already been disclosed in German Laid-Open Application DOS 1,959,922. In these, the non-elastomeric polymer segment A is, in particular, a homo-
20　polystyrene segment. The molecular weight and polymodality depend primarily on the intended application of the end product. As explained in more detail below, the molecular weight is decided by the amount of initiator
25　employed per mole of monomer in the manufacturing process; the polymodality depends on the number of times that initiator is added during the polymerization and is preferably 2 or 3 and especially 2. The elastomeric polymer
30　segment B based on the conjugated dienes is preferably a homopolydiene segment, especially a homopolybutadiene or a homopolyisoprene segment. It may however also contain small amounts, of up to about 30 per cent by weight,
35　preferably of less than 20 per cent by weight, based on polymer segment B, of other copolymerizable monomers, especially of styrene, as copolymerized units.

In the star-shaped block copolymers which
40　have the most probable average structure of the general formula (II)

$$(A^1\text{-}B^1\to A^2)_n\text{-}X\text{-}(A^2\leftarrow B^1)_m$$
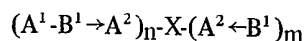
the non-elastomeric polymer segment A^1 ad-
45　vantageously contains, as copolymerized units, from 50 to 80 per cent by weight, preferably from 60 to 78 per cent by weight, of the total monovinyl-aromatic compound employed for the manufacture of the branched block copoly-
50　mer, and is, in particular, a homopolystyrene segment. Its molecular weight depends primarily on the application envisaged for the end product and is preferably from 50,000 to 250,000. The elastomeric polymer segment
55　B^1 is a copolymer block comprising essentially the conjugated diene and a minor proportion of monovinyl-aromatic compound, the distribution of the monomers being subsstantially random. The proportion of the monovinyl-aromatic
60　compound in the polymer segment B^1 is in general less than about 30 per cent by weight and especially less than about 20 per cent by weight, based on the amount of monovinyl-aromatic compound of the branched block
65　copolymer not in the form of units of the

polymer segment A^1. The transition between the polymer segments A^1 and B^1 is sharp, whilst the transition between the polymer segments B^1 and A^2 is gradual in the sense that the proportion of the monovinyl-aromatic　70 compound in the polymer segment B^1 increases progressively in the direction of the polymer segment A^2 and the proportion of the conjugated diene accordingly decreases progressively. The non-elastomeric polymer segments　75 A^2 are, like the polymer segment A^1, preferably homopolystyrene segments. The molecular weight of the polymer blocks $(B^1\to A^2)$ is preferably from 10,000 to 100,000.

In the star-shaped block copolymers which　80 have most probable average structure of the general formula (III)

$$(A^3\text{-}A^4\text{-}B^2\to A^5)_n\text{-}X\text{-}(A^5\to B^2\text{-}A^4)_m$$
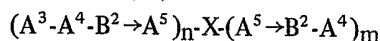
the non-elastomeric polymer segment A^3 ad-　85 vantageously contains, as copolymerized units, from 50 to 80 per cent by weight, preferably from 60 to 75 per cent by weight, of the total monovinyl-aromatic compound employed for the manufacture of the star-shaped block　90 copolymer, and is, in particular, a homopolystyrene segment. Its molecular weight is preferably from 50,000 to 250,000. The polymer segments A^4 correspond to the polymer segments A^3 except that they have a　95 lower molecular weight, usually from 5,000 to 50,000. They contain, as copolymerized units, from 1 to 30 per cent by weight, preferably from 5 to 25 per cent by weight, of the total monovinyl-aromatic compound, but the sum　100 of the monovinyl-aromatic compound copolymerized in the polymer segments A^3 and A^4 should not exceed 90 per cent by weight of the total amount of monovinyl-aromatic compound employed for the　105 manufacture of the star-shaped block copolymers. The elastomeric polymer segment B^2 is a copolymer block comprising essentially the conjugated diene with a minor proportion of monovinyl-aromatic compound, the　110 distribution of the monomers being substantially random. The proportion of the monovinyl-aromatic compound in the polymer segment B^2 is in general less than about 30 per cent by weight, based on the amount of　115 monovinyl-aromatic compound not present as units in the polymer segments A^3 and A^4. The transition between the polymer segments A^4 and B^2 is sharp, whilst the transition between the polymer segments B^2 and A^5 is gradual.　120 The non-elastomeric polymer segments A^5 are, like the polymer segments A^3 and A^4, preferably homopolystyrene segments. The molecular weight of the polymer blocks $(A^3\text{-}A^4\text{-}B^2\to A^5)$ is preferably from 100,000 to　125 500,000 whilst that of the polymer blocks $(A^4\text{-}B^2\to A^5)$ is from 10,000 to 100,000.

According to a preferred embodiment of the invention, non-elastomeric, star-shaped block copolymers in which the content of olefinic　130

double bonds has been reduced by selective
hydrogenation to less than 5%, preferably less
than 2%, are employed as the component B.
Where selectively hydrogenated derivatives of
5   star-shaped block copolymers of the general
formula (I), in which the polymer segment B,
prior to hydrogenation, is a polybutadiene
segment, are employed, it is necessary to ensure
that this polybutadiene segment has a 1, 2-vinyl
10   content of from 10 to 50 per cent by weight
and that after hydrogenation the polymer
segment B has a crystallinity of less than 5%,
preferably of less than 2%, if products having
the desired properties are to be obtained. The
15   crystallinity of the hydrogenated polymer
segments B may be determined by differential
calorimetry using a Perkin-Elmer DSC
calorimeter.

The special composition, and the structure,
20   of the star-shaped block copolymers depend on,
and are determined by, the conditions chosen
for the polymerization of the monomers. In
general, the non-elastomeric, star-shaped block
copolymers suitable for use as component B
25   in the mixtures of the invention are
manufactured by successive polymerization of
the monomers in solution in the presence
of a monolithium-hydrocarbon as the initiator,
with stepwise addition of monomer and
30   initiator and subsequent coupling of the
resulting living linear block copolymers with a
polyfunctional reactive compound as the
coupling agent.

The initiators used are the conventional
35   mono-lithium-hydrocarbons of the general
formula RLi, where R is an aliphatic, cyclo-
aliphatic, aromatic or mixed aliphatic-aromatic
hydrocarbon radical. The latter may be of 1 to
about 12 carbon atoms. The following may
40   be mentioned as examples of suitable lithium-
hydrocarbon initiators: methyl-lithium, ethyl-
lithium, n-, sec.- and tert.-butyl-lithium,
isopropyl-lithium, cyclohexyl-lithium, phenyl-
lithium and p-tolyl-lithium. The use of
45   monolithium-alkyl compounds, where alkyl is
of 2 to 6 carbon atoms, is preferred, n-butyl-
lithium and sec.-butyl-lithium being particularly
preferred.

The polymerization of the monomers is
50   carried out in solution in an inert organic
hydrocarbon solvent. Suitable hydrocarbon
solvents are aliphatic, cycloaliphatic or
aromatic hydrocarbons which are liquid under
the reaction conditions and which are
55   preferably of 4 to 12 carbon atoms. Examples
of suitable solvents are isobutane, n-pentane,
iso-octane, cyclopentane, cyclohexane, cyclo-
heptane, benzene, toluene, the xylenes, and the
like. Mixtures of these solvents may also be
60   employed. Furthermore, the polymerization
can be carried out in the presence of small
amounts, in general from 10^{-3} to 5 per cent
by weight, based on the total solvent, of ethers,
e.g. tetrahydrofuran, dimethoxyethane and
65   anisole, thereby influencing, in the con-

ventional manner, the rate of polymerization,
the configuration of the diene polymer
segments and the random transition between
the segments B^1 and A^2, or B^2 and A^5, in the
products of the general formula (II) and (III),   70
respectively. The concentration of the
monomers in the reaction solution is not
critical and can be so chosen that any desired
apparatus can be used for the polymerization.
In general, the polymerization is carried out in   75
a solution of from 10 to 30 per cent strength
in the inert solvents.

The polymerization is carried out under the
conventional conditions for anionic poly-
merization with lithium-organic compounds,   80
for example in an inert gas atmosphere, with
exclusion of air and moisture. The poly-
merization temperature may be from 0 to
120°C and is preferably kept at from 40 to
80°C.   85

The polyfunctional coupling agent used for
the coupling reaction carried out after the
polymerization should be at least trifunctional,
i.e. it should be capable of reacting with at
least three of the active, linear block copolymer   90
chains formed, at their terminal lithium-carbon
bonds, to form a chemical bond, so that a
single, coupled and accordingly branched
block copolymer is formed. The coupling of
lithium-terminated living polymers with poly-   95
functional coupling agents is known in the art
and is disclosed, for example in British Patent
985,614. Examples of suitable coupling agents
for the manufacture of the star-shaped block
copolymers to be employed according to the   100
invention are polyepoxides, e.g. epoxidized
linseed oil, polyisocyanates, e.g. benzo-1,2,
4-triiso-cyanate, polyketones, e.g. 1,3,6-hexane-
trione or 1,4,9,10-anthracenetetrone, poly-
anhydrides, e.g. pyromellitic dianhydride, or   105
polyhalides. Dicarboxylic acid esters, e.g.
diethyl adipate or the like, may also be used as
coupling agents. A further preferred group of
coupling agents comprises the silicon halides,
especially silicon tetrachloride, silicon tetra-   110
bromide, trichloroethylsilane and 1,2,-bis-
(methyldichlorosilite)-ethane. Polyvinyl-
aromatics, especially divinylbenzene, may
also be used as coupling agents, as disclosed,
for example, in U.S. Patent 3,280,084. In   115
that case, a few divinylbenzene units undergo
addition with crosslinking, to form a branching
center, by means of which the preformed
polymer blocks are bonded to one another.

The nature of the polyfunctional coupling   120
agent employed is not critical, provided it
does not significantly impair the desired
properties of the end product. The use of a
trifunctional or tetrafunctional coupling agent
of the type described, or of divinylbenzene, is   125
preferred. In general, the polyfunctional
coupling agent is added to the reaction solution
in amounts equivalent to the total amount of
the living polymer blocks, i.e. equivalent to
the number of the active lithium-carbon bonds   130

in the previously formed linear copolymer blocks. The reaction of the living, linear block copolymers with the coupling agent is preferably carried out under the same reaction conditions as the preceding polymerization of the monomers.

Advantageously, the non-elastomeric, star-shaped block copolymers to be employed in the mixtures of the invention are manufactured as follows: in a first process stage, a substantial part of the total amount of monovinyl-aromatic compound, in general from 50 to 80 per cent by weight and in particular from 60 to 75 per cent by weight of the total amount of monovinyl-aromatic compound employed for the manufacture of the star-shaped block copolymers, is polymerized by means of a relatively small amount of the monolithium-hydrocarbon initiator until the monovinyl-aromatic compound employed has been completely converted. The amount of initiator employed in the first process stage depends above all on the desired molecular weight of the polymer and is in general from 0.1 to 5 mmoles per mole of the monovinyl-aromatic compounds employed in this first process stage. Preferably, the polymerization in the first process stage is carried out with from 0.4 to 2.5 mmoles of initiator per mole of the monovinyl-aromatic compounds employed in this stage. This gives a solution of non-elastomeric, living polymers of the monovinyl-aromatic compound, with active terminal lithium-carbon bonds, to which further monomers can add. In a second process stage, the remaining monomers are added, all at one or in several successive stages, to the above reaction solution, after addition of a further amount of initiator, which should be as great or greater than the original amounts of initiator employed in the first process stage of the polymerization. Preferably, the amount of fresh initiator added in the second process stage is from 1 to 15 times, and expecially from 1 to 10 times, the amount of initiator originally employed. It is particularly advantageous if this factor is from 1 to 5, especially if tri-functional or tetrafunctional coupling agents are employed in the subsequent coupling reaction. Preferably, the initiator used is the same as in the first process stage. It is advantageous to introduce the additional fresh initiator into the reaction solution before adding the remaining monomers.

The composition and structure of the resulting block copolymers can be decided, and varied, by varying the manner in which the remaining monomers, i.e. both the remaining portion of the monovinyl-aromatic compound and the conjugated diene, are added to the reaction solution produced in the first process stage. For example, the remaining portion of the monovinyl-aromatic compound and the conjugated diene can be added in a single stage, as a mixture; they can however also be added in several successive stages, for example by separately adding first the remaining portion of the monovinyl-aromatic compound and then the conjugated diene, or first a further partial amount of the monovinyl-aromatic compound and then a mixture of the remaining portion of the monovinyl-aromatic compound and the conjugated diene. After each fresh addition of monomers in the second process stage, the polymerization is taken to complete conversion of the added monomers before adding further monomer or before ultimately adding the coupling agent. If appropriate, further additional amounts of initiator may also be employed repeatedly in the second process stage.

To produce star-shaped block copolymers of the general formula (I) $(A-B)_k-X$ which have a polymodal distribution in the non-elastomeric polymer segments A formed from the monovinyl-aromatic compounds, the procedure followed is, for example, first to add the remaining monovinyl-aromatic compound, i.e. from 20 to 50 per cent by weight, preferably from 25 to 40 per cent by weight, of the total monovinyl-aromatic compound employed for the manufacture of the branched block copolymer, in one or more portions to the reaction solution manufactured in the first process stage, each addition of a portion of the monovinyl-aromatic compound being accompanied by the addition of a further amount of initiator which is as great or greater than the original amount of initiator employed in the first process stage of the polymerization. Though it is possible to add the remaining portion of the monovinyl-aromatic compound in as many portions ds desired to the reaction solution in the course of the second process stage, it is preferred to add the remaining monovinyl-aromatic compound to the poly-merization solution in 1 or 2 portions in the course of the said process stage, the addition in one portion having proved particularly advantageous. The monovinyl-aromatic compounds added in the second process stage undergo addition at the active, lithium-terminated chain ends of the previously formed polymers and also form new chains of living polymers whenever fresh initiator is also added. Accordingly, after complete polymerization of the remaining monovinyl-aromatic compound, the solution obtained contains polymers of the monovinyl-aromatic compound with different average chain lengths, i.e. the non-elastomeric polymer segments A formed from the monovinyl-aromatic compounds have a poly-modal distribution, with the polymodality of the polymer segments A corresponding to the total number of additions of initiator and monomer. Thereafter, in a second step, the total amount of the conjugated diene is added and polymerized to complete conversion. In the course thereof, the conjugated diene undergoes addition at the active, lithium-

terminated chain ends of the previously formed polymodal, non-elastomeric polymer segments A to form the elastomeric polymer segments B, so that the reaction solution contains the copolymer blocks (A-B) which form the branches and which possess an active reactive lithium-carbon bond at the free end of the elastomeric diene polymer segment B; these blocks are subsequently coupled.

To manufacture star-shaped block copolymers of the general formula (II)

$$(A^1\text{-}B^1 \to A^2)_n\text{-}X\text{-}(A^2 \leftarrow B^1)_m$$

the procedure followed in the second process stage of the polymerization is to add, to the fully polymerized reaction solution from the first process stage, first an additional amount of initiator and then a mixture of the remaining monovinyl-aromatic compound and the total amount of the conjugated diene, and to polymerize the mixture. In the course thereof, the monomers added in the second process stage undergo addition at the active, living chain ends of the previously formed polymer segments A^1, and also form new chains of living polymers, as a result of the fresh initiator added. Because of the different copolymerization parameters, the conjugated dienes polymerize substantially more rapidly than the monovinyl-aromatic compounds so that, after addition of the monomer mixture in the second process stage, it is first predominantly the conjugated dienes which undergo polymerization, and only occasionally are units of the monovinyl-aromatic compounds copolymerized. Only toward the end of the diene polymerization, i.e. when almost all the conjugated diene has polymerized, does the polymerization of the monovinyl-aromatic compounds commence to a significant degree, so that the predominant proportion - as a rule more than 70 per cent by weight, and in most cases more than 80 per cent by weight - of the monovinyl-aromatic compounds contained in the monomer mixture only polymerizes after the conjugated dienes have been consumed. Accordingly, in this case, the second process stage first results in the formation of the elastomeric polymer segment B^1, based on the conjugated diene, this segment being a copolymer segment mainly comprising the conjugated diene, with small amounts of the monovinyl-aromatic compound, after which the non-elastomeric polymer segment A^2 is formed, which is made up of the monovinyl-aromatic compound only. Since the proportion of the monovinyl-aromatic compound progressively increases toward the end of the polymer segment B^1 and the proportion of the conjugated diene accordingly progressively decreases, the transition between the polymer segments B^1 and A^2 thus formed is not sharp and instead occurs gradually; this is therefore also frequently described as a blurred transition between the segments. After complete polymerization of the monomer mixture in the second process stage, the reaction solution thus contains a mixture of the linear block copolymers of the type $(A^1\text{-}B^1 \to A^2)$ and $(B^1 \to A^2)$, with active reactive lithium-carbon bonds in each case at the free end of the polymer segments A^2, from which block copolymers the branches are formed. The ratio of the two types of block copolymers in the reaction solution corresponds to the initiator ratio in the first and second process stages. The mixture of these two types of block copolymers is then coupled, by adding a polyfunctional reactive compound, to act as the coupling agent, to the reaction solution.

To manufacture star-shaped block copolymers of the general formula (III) $(A^3\text{-}A^4\text{-}B^2 \to A^5)_n\text{-}X\text{-}(A^5 \leftarrow B^2\text{-}A^4)_m$ the procedure followed in the second process stage of the polymerization is to add, to the completely polymerized reaction solution from the first process stage, first a further amount of initiator and then a further 1 - 30 per cent by weight, preferably 5 - 25 per cent by weight, of the total amount of the monovinyl-aromatic compounds used overall for the manufacture of the branched block copolymers. The sum of the amount of monovinyl-aromatic compound employed in the first and second process stage should however be at most 90 per cent by weight of the total amount of the monovinyl-aromatic compound which is employed for the manufacture of the branched block copolymers. The monovinyl-aromatic compounds added undergo addition at the active, lithium-terminated chain ends of the polymer segments A^3, formed beforehand in the first process stage, so as now to form the polymer segments A^4, and also form new chains of living polymers of the monovinyl-aromatic compound as a result of the fresh initiator added. After complete polymerization of the monovinyl-aromatic compound initially added in the second process stage, the solution obtained thus contains living polymers of the monovinyl-aromatic compound with two different average chain lengths, namely, on the one hand, active living polymer segments of type $(A^3\text{-}A^4)$, which have been formed by addition of the monovinyl-aromatic compound, first added in the second process stage, onto the active living polymer segments A^3 formed beforehand in the first process stage, and, on the other hand, active living polymer segments of type A^4, which have been formed by polymerization of the monovinyl-aromatic compound, first added in the the second process stage, with the fresh initiator initially introduced. The ratio in which these two types of non-elastomeric polymer segments based on the monovinyl-aromatic compounds are present in the reaction solution accordingly corresponds to the initiator ratio of the first and second process stages. Both types of polymer

segments, $(A^3\text{-}A^4)$ and A^4, have active, reactive lithium-carbon bonds, capable of undergoing addition of further monomers, at one chain end. A monomer mixture of the remaining monovinyl-aromatic compound and the total amount of the conjugated diene is then added to this reaction solution and polymerized until the monomers are virtually completely converted. As described above, the polymerization of the monomer mixture comprising the remaining monovinyl-aromatic compound and the conjugated diene results, because of the different copolymerization parameters of the monomers, first in the formation of the elastomeric polymer segment B^2 based on the conjugated diene, which segment is a copolymer comprising mainly the conjugated diene with small amounts of the monovinyl-aromatic compound, and thereafter in a non-elastomeric polymer segment A^5 which comprises only the monovinyl-aromatic compounds. Since the monovinyl-aromatic compound is thus copolymerized to a progressively greater degree toward the end of the polymer segment B^2 and the proportion of the conjugated diene accordingly progressively decreases, the transition between the polymer segments B^2 and A^5 which are formed is not sharp but gradual. After complete polymerization of the monomer mixture comprising the remaining monovinyl-aromatic compound and the conjugated diene, the reaction solution contains a mixture of the linear block copolymers of type $(A^3\text{-}A^4\text{-}B^2 \rightarrow A^5)$ and $(A^4\text{-}B^2 \rightarrow A^5)$, having active, reactive lithium-carbon bonds in each case at the free end of the polymer segments A^5, which block copolymers form the branches and are subsequently coupled to produce the star-shaped block copolymer.

The star-shaped block copolymers obtained may be isolated from the reaction solution in the conventional manner, for example by precipitating the polymer from the reaction solution and filtering off.

Following the coupling reaction and advantageously prior to isolating the reaction product from the reaction solution, the olefinic double bonds of the star-shaped block copolymers obtained may be subjected to selective hydrogenation. The latter may be carried out in the conventional manner, using molecular hydrogen and catalysts based on metals, or salts of metals, of group 8 of the periodic table, as described, for example, in U.S. Patent 3,113,986, German Published Application DAS 1,222,260, German Laid-Open Application DOS 2,013,263 or U.S. Patent 3,700,633. According to these publications, the selective hydrogenation of the olefinic double bonds of the star-shaped block copolymer is preferably carried out in a homogeneous phase, using catalysts based on salts, especially carboxylates, enolates or alkoxides, of

nickel, cobalt or iron, which have been reduced with metal-alkyls, especially aluminum-alkyls, at hydrogen pressures of from 1 to 100 bars and at from 25 to 150°C. The selective hydrogenation is advantageously continued until the content of olefinic double bonds in the branched block copolymer has been reduced to less than 5% and preferably less than 2%. This residual content may be determined by a Wijs titration or by analysis by IR spectroscopy. Most desirably, the hydrogenation is continued until the olefinic double bonds have been reduced virtually completely. Preferably, the hydrogenation is carried out under conditions such that the aromatic double bonds of the branched block copolymer are not attacked at the same time.

Components A and B of a mixture within the invention can be homogeneously mixed with one another in the conventional manner using known methods, for example by mixing in the melt, using suitable mixing equipment, e.g. kneaders, internal mixers or extruders. The mixture may in addition contain the conventional additives for polystyrene, e.g. antistatic agents, stabilizers and the like.

Mixtures within the invention exhibit good transparency and clarity, like polystyrene itself. The proportion of light scattered on passage through a film or sheet serves as a measure of the transparency and clarity. Compared to polystyrene, mixtures within the invention exhibit substantially improved mechanical properties, and in particular improved impact strength and notched impact strength. Compared to the non-elastomeric, star-shaped branched block copolymers disclosed in German Laid-Open Application DOS 1,959,922, mixtures within the invention are cheaper without entailing a significant decrease in impact strength and notched impact strength, even if the proportion of polystyrene is relatively high. The mixtures may be processed easily by conventional methods used for thermoplastics, e.g. extrusion, deep-drawing or injection molding, and are above all suitable for the manufacture of shaped articles, e.g. thick and thin films, sheets and the like, and packaging materials.

The Examples which follow illustrate the invention. Unless stated otherwise, parts and percentages are by weight. Either the intrinsic viscosity, measured in an 0.5 per cent strength solution in toluene at 25°C, is recorded as a measure of the molecular weight, or the viscometrically determined weight-average molecular weight is quoted directly. The impact strength a_n and notched impact strength a_k where determined by the method of DIN 53,453, on injection-molded specimens. The transparency was assessed visually, using a 500μ thick film. In all the Examples, component A of the mixture was a mass-polymerized polystyrene having a molecular weight of about 200,000 (intrinsic viscosity

85 cm^3/g), with an impact strength a_n of 4.4 kJ/m^2 and a notched impact strength a_k of 0.61 kJ/m^2.

EXAMPLE 1

Component B employed was a star-shaped block copolymer of the type of the general formula (II), with an average (most probable) structure

[polystyrene-poly(butadiene/styrene)→ polystyrene]$_2$-Si-[polystyrene←poly(styrene/butadiene)]$_2$

The overall proportion of styrene in the block copolymer was 73% and the proportion of butadiene was 27%. The terminal free polystyrene segment contained 76% of the total styrene employed, as copolymerized units, and had an intrinsic viscosity of 37.1 (cm^3/g). The intrinsic viscosity of the star-shaped block copolymer was 90 (cm^3/g). The star-shaped block copolymer was manufactured by successive polymerization of styrene and of a mixture of butadiene and styrene, using n-butyl-lithium as the catalyst, in toluene as the solvent, the initiator being added stepwise and the product then being coupled with silicon tetrachloride.

The polystyrene (component A) and the star-shaped block copolymer (component B) where mixed homogeneously in the ratio of 1:2 in the melt, using an extruder. The mixture had an impact strength a_n of 16.3 kJ/m^2 and a notched impact strength a_k of 2.63 kJ/m^2. A film produced from this mixture was transparent.

EXAMPLE 2

Component B employed was a star-shaped block copolymer of the type of the general formula (I), with an average (most probable) structure

(polystyrene I - polybutadiene)$_2$-Si-(polybutadiene-polystyrene II)$_2$

The proportion of styrene in the total block copolymer was 75% and the proportion of butadiene was 25%. The polystyrene I segment had an mean molecular weight of 65,000, whilst that of the polystyrene II segment was 10,000. The star-shaped block copolymer had been manufactured by successive polymerization of styrene and butadiene with n-butyl-lithium as the catalyst, the initiator being added in two equal portions in the course of the polymerization of the styrene. Coupling was effected by means of silicon tetrachloride.

A mixture produced from the polystyrene (component A) and the star-shaped block copolymer (component B) in the ratio of A:B = 1:2 had an impact strength a_n of 16.3 kJ/m^2 and a notched impact strength a_k of 2.63 kJ/m^2. A film produced from the mixture was transparent.

EXAMPLE 3

Component B employed was a star-shaped block copolymer of styrene and butadiene of the type of the general formula (I), the olefinic double bonds of the copolymer having been selectively hydrogenated. The star-shaped block copolymer was manufactured as follows:

2.7 kg of cyclohexane and 525 g of styrene were titrated with sec.-butyl-lithium in a 6 1 pressure kettle under an inert gas atmosphere, with exclusion of moisture, and were then polymerized with 0.33 g of sec.-butyl-lithium for 30 minutes. The temperature was initially 54°C. 0.22 kg of cyclohexane, 0.9 g of sec.-butyl-lithium and 225 g of styrene were added to the active reaction solution at 71°C and polymerization was carried out for one hour; 10 g of tetrahydrofuran and 250 g of butadiene were then polymerized onto the product in the course of one hour at about 74°C. Finally, coupling was carried out with 10 ml of Epoxol 9-5 (as marketed by Swift Chemical Corp. "Epoxol" is a Registered Trade Mark) in 150 ml of toluene. The intrinsic viscosity was 91.9 [cm^3/g]. The olefinic double bonds of the resulting star-shaped block copolymer were then selectively hydrogenated, using a Ni hydrogenation catalyst, until the residual content of the olefinic double bonds in a block copolymer was less than 1%.

Three mixtures, with different ratios of the two components, were then produced from the polystyrene (component A) and the selectively hydrogenated star-shaped block copolymer (component B). The properties of these mixtures are summarized in the Table below. All the mixtures have transparent films.

TABLE

Mixing ratio A:B	1:2	1:1	2:1
Impact strength a_n (kJ/m^2)	14.1	12.0	11.2
Notched impact strength a_k (kJ/m^2)	1.53	1.36	0.91

WHAT WE CLAIM IS:—

1. A mixture which essentially comprises A) from 10 to 70 per cent by weight of a polystyrene and B) from 90 to 30 per cent by weight of a thermoplastic, non-elastomeric, star-shaped block copolymer of from 60 to 95% by weight of a monovinyl-aromatic compound and from 40 to 5% by weight of a conjugated diene of 4 to 8 carbon atoms, which block copolymer possesses at least two types, of different average composition, of copolymer blocks which form the branches, in which mixture at least 50% by weight of the total monovinyl-aromatic compound present as copolymerized units in the star-shaped block copolymer are present as blocks, in the terminal polymer segment of one or more of the copolymer blocks of the branches.

2. A mixture as claimed in claim 1 which contains, as component B, a non-elastomeric, star-shaped block copolymer, whereof the olefinic double bonds have been reduced to a

residual proportion of less than 5% by selective hydrogenation, and whereof the selectively hydrogenated segments have a crystallinity of less than 5%.

3. A mixture as claimed in claim 1 or 2, in which the star-shaped block copolymer comprises from 70 to 90% by weight of a monovinyl-aromatic compound and from 30 to 10% by weight of a conjugated diene of 4 to 8 carbon atoms, and at least 60% by weight of the total copolymerized monovinyl-aromatic compound in the star-shaped block copolymer is contained in the terminal polymer segment of one or more of the copolymer blocks of the branches.

4. A mixture as claimed in any of claims 1 to 3, in which the star-shaped block copolymer has a viscosity-average molecular weight of from 100,000 to 1,000,000.

5. A mixture as claimed in any of claims 1 to 4, in which a star-shaped block copolymer comprising styrene and butadiene is employed.

6. A mixture as claimed in any of claims 1 to 5, in which a star-shaped block copolymer of the general formula $(A\text{-}B)_k\text{-}X$ is employed, where A is a polymer segment comprising the monovinyl-aromatic compound and having a polymodal molecular weight distribution, B is an elastomeric polymer segment based on a conjugated diene, k is an integer not less than 3 and X is the radical of a polyfunctional coupling agent, by means of which the copolymer blocks (A-B) which form the branches are coupled chemically to one another.

7. A mixture as claimed in any of claims 1 to 5, in which a star-shaped block copolymer of the general formula $(A^1\text{-}B^1 \rightarrow A^2)_n\text{-}X\text{-}(A^2 \leftarrow B^1)_m$ is employed, where A^1 and A^2 are non-elastomeric polymer segments of the monovinyl-aromatic compound, and A^1 contains from 50 to 80% by weight of the total monovinyl-aromatic compound, B^1 is an elastomeric polymer segment based on the conjugated diene, the transition between the polymer segments A^1 and B^1 being sharp whilst the transition between B^1 and A^2 is gradual, X is a radical of a polyfunctional coupling agent by means of which the copolymer blocks $(A^2\text{-}B^1 \rightarrow A^2)$ and $(B^1 \rightarrow A^2)$, which form the branches, are chemically coupled to one another at the polymer segments A^2, and m and n are numbers, m being greater than or equal to n and the sum of m and n being an integer not less than 3.

8. A mixture as claimed in any of claims 1 to 5, in which a star-shaped block copolymer of the general formula $(A^3\text{-}A^4\text{-}B^2 \rightarrow A^5)_n\text{-}X\text{-}(A^5 \leftarrow B\text{-}A^4)_m$ is employed, where A^3, A^4 and A^5 are non-elastomeric polymer segments of the monovinyl-aromatic compound, and A^3 contains from 50 to 80% by weight, and A^4 from 1 to 30% by weight, of the total monovinyl-aromatic compound, but A^3 and A^4 together do not contain more than 90% by weight of the total monovinyl-aromatic compound, B^2 is an elastomeric polymer segment based on the conjugated diene, the transition between the polymer segments A^4 and B^2 being sharp whilst the transition between B^2 and A^5 is gradual, X is the radical of a polyfunctional coupling agent by means of which the copolymer blocks $(A^3\text{-}A^4\text{-}B^2 \rightarrow A^5)$ and $(A^4\text{-}B^1 \rightarrow A^5)$, which form the branches, are chemically coupled to one another at the polymer segments A^5, and m and n are numbers, m being greater than or equal to n and the sum of m and n being an integer not less than 3.

9. A mixture as claimed in claim 1 and substantially as hereinbefore described or illustrated in any of the foregoing Examples.

10. Moldings and packaging materials made from a mixture as claimed in any of claims 1 to 9.