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(54) Title: BLOCK COPOLYMERS		
(57) Abstract <p>The present invention relates to a stable polymer composition comprising a first polymer and a second polymer, which second polymer is not compatible with the first polymer, and an amount of a copolymer comprising at least one block of a polyalkadiene and at least one block of random poly(aromatic vinyl-acrylonitrile), and in which the ratio of the block copolymer to the total polymer composition is between 1:500 and 1:50. Besides, the invention relates to the use of the above block copolymer as compatibilizer and/or as modifier for the mechanical properties of polymer compositions.</p>		

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Title: **BLOCK COPOLYMERS**

The invention relates to block copolymers comprising at least one polyalkadiene block and at least one (aromatic vinyl-co-acrylonitrile) block, and the use thereof as additive for polymers.

5 Mixtures of polymers can in principle give a wide variety of mechanical properties by adjusting the type and the amount of polymers in mixtures. In particular, mixtures are prepared for the purpose of modifying the impact strength, particularly at lower temperatures, the
10 dimensional stability and the processability.

However, most polymers show no proper miscibility with other polymers, so that no homogeneous product is formed, but a polymer product with many (macroscopic) domains formed by the individual polymers. Such products have no good
15 mechanical properties, in particular not as regards ductility.

Moreover, mixtures of different polymer fractions often occur when reprocessing polymers. In fact, a waste fraction will seldom consist 100% of the same polymer. To yet obtain
20 a product having stable mechanical properties, a homogeneous polymer product must also be realized.

Thus, mixtures of polyethylene, e.g. low density PE, and polyvinyl chloride are inherently brittle. These mixtures are interesting both from the viewpoint of
25 modifying the (mechanical) properties of PVC and for considerations of recycling.

In the prior art a lot of research has been done on block copolymers to be used as compatibilizing agent for mixtures of polymers, in particular homopolymers, which
30 per se do not mix together; and as modifier for specific mechanical properties of polymers. Compatibilizing agents reduce the interfacial tension between the immiscible components, so that the polymer mixture can form a dispersion with much smaller domains. These dispersions
35 often have improved ductility.

In spite of the large number of research studies from the prior art, it is still not completely clear which criteria a copolymer must satisfy so as to act as an effective compatibilizing agent. Besides simple diblock copolymers which, on the basis of theoretical predictions, should have the most effective compatibilizing activity, different more complex copolymers have been proposed. Thus, in the prior art random copolymers, graft copolymers, tapered diblock copolymers and low molecular triblock copolymers have been proposed which have an effectiveness higher than that of the simple diblock copolymers.

For the above-mentioned example of polyethylene and polyvinyl chloride, inter alia graft copolymers of PVC or polymethyl methacrylate grafts on polyethylene polymers have been proposed. Thus, an article by Boutevin et al. in Polymer Bulletin 14 (1985) 25-30 describes that the mechanical properties of a PE/PVC mixture can be optimized by adding at least 5 wt.% of a graft copolymer of polyethylene with methyl methacrylate. Besides, the optimization in properties is qualitatively and quantitatively hardly spectacular.

An article by Hajian et al. in Eur. Polym. J. 20 (1984), 135-138 describes the effect of specific copolymers on mixtures of PE and PVC and of PE and polystyrene. Acceptable results are only obtained if the copolymers are used in amounts above 10%.

Block copolymers of, e.g., polybutadiene (PB) and polystyrene (PS) are used to compatibilize, inter alia, polyethylene/polystyrene and polypropylene/polystyrene mixtures. These block copolymers are usually prepared by anionic techniques. Anionic techniques have a number of evident disadvantages. They require strict polymerization conditions, e.g. very pure monomers, an absolute moisture- and oxygen-free atmosphere and cryogenic temperatures. These conditions are hard to realize on an industrial scale.

Moreover, no random copolymers can be obtained by using anionic techniques.

European patent application 0 418 118 describes copolymers prepared by using iniferters.

In an article in Polym. J. 17 (1985) 97, Otsu and Kuriyama describe a process in which random and alternating
5 copolymer sequences could be prepared by using the iniferter technique.

By the term "iniferter" are designated specific free radical initiators which simultaneously also function as chain transfer agent and as polymer radical terminator.

10 According to the present invention it has now been found that specific block copolymers of polyalkadiene which may or may not be hydrogenated and poly(aromatic vinyl-co-acrylonitrile) form very effective compatibilizers, in particular for mixtures of polyolefins or polyalkadienes, on
15 the one hand, with polystyrene acrylonitrile (SAN) and with homopolymers with which the poly(aromatic vinyl-co-acrylonitrile) properly mixes, such as poly(methyl methacrylates), polycarbonates, polyvinyl chloride and poly(ϵ -caprolactam), on the other hand.

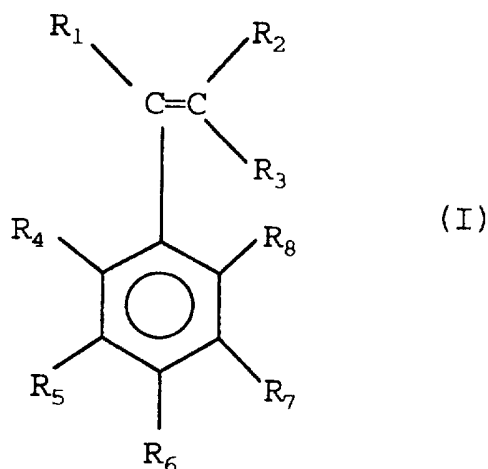
20 These specific block copolymers are copolymers comprising at least one blok of a polyalkadiene and at least one block of random poly(aromatic vinyl-co-acrylonitrile). The compatibilizing properties of these block copolymers are substantially better than those of known copolymers, such as
25 copolymers in which random copolymer blocks are grafted on a polymer chain. In the case of using known compatibilizing agents in amounts of 5-10 wt.% and more, based on the complete composition comprising at least two non-compatible polymers, an amount of about 1 wt.% is sufficient when using
30 the copolymers according to the present invention.

More in particular, the invention relates to a polymer composition comprising a first polymer and a second polymer, which second polymer is not compatible with the first
polymer, and an amount of a copolymer comprising at least
35 one block of a polyalkadiene and at least one block of random poly(aromatic vinyl-acrylonitrile), the ratio of the block copolymer to the second polymer ranging between 1:50

and 1:5. In a preferred embodiment the first polymer forms a continuous phase in which the second polymer is dispersed. However, blends, such as 50/50 blends, are also possible.

Any random copolymer block, also referred to in this specification as SAN block, which is present in the block copolymer used according to the present invention, is build up from at least acrylonitrile units and units of an aromatic vinyl compound.

The aromatic vinyl compound to be used can be represented by formula I,



in which R_{1-3} may be independently selected from a hydrogen atom, a C_{1-4} alkyl group or a C_{1-4} alkyl group substituted with an inert group; and in which R_{4-8} may independently represent a hydrogen atom, a halogen atom, a C_{1-4} alkyl group or a C_{1-4} alkyl group substituted with an inert group.

Preferably, however, the aromatic vinyl compound is styrene.

The above random copolymers, which can be used according to the present invention, are miscible with polymers, with which also known block copolymers of acrylonitrile and aromatic vinyl are miscible, such as, e.g., with poly(methyl methacrylate), polycarbonate, polyvinyl chloride, poly(ϵ -caprolactone), and with those known poly(aromatic vinyl-acrylonitrile) block copolymers, such as styrene-co-acrylonitrile copolymers. In the

preferred polymer composition according to the invention these polymers can form both the first polymer phase and the second polymer phase.

If required, the degree of miscibility can be adapted
5 to the ratio of acrylonitrile/aromatic vinyl compound in the SAN blocks.

In a preferred embodiment the polymer composition according to the invention comprises a copolymer in which the polyalkadiene blocks present are based on polybutadiene
10 which may or may not be hydrogenated. However, good results are also obtained by using other polyalkadienes, such as polymers of isoprene, pentadienes which may or may not be conjugated, hexadienes which may or may not be conjugated, etc.

15 These polyalkadiene blocks properly mix with all polymers with which the corresponding homopolymers of the alkadiene monomers also properly mix, in particular with polyalkenes. However, depending on the purpose of adding the copolymer according to the invention, the polyalkadiene can
20 be hydrogenated. When the block copolymer is used as, e.g., compatibilizer in polyalkene-based blends and preferably in polyethylene-based blends, hydrogenated polyalkadiene blocks are used in principle. On the other hand, when the block copolymer is used as modifier for the mechanical properties,
25 in particular as impact modifier, of polymers miscible with SAN, including rubber compositions, it is used in non-hydrogenated form.

Essential for the present invention is that available polymer blocks consisting of acrylonitrile and an aromatic
30 vinyl compound are random polymer blocks. Random polymer blocks turn out to give a much more effective activity than non-random copolymer blocks. The method of preparing this part of the copolymer to be used has to comply with special requirements, and in fact, only free radical polymerization
35 techniques are eligible.

Thus, a polyalkadiene ((random (aromatic vinyl-co-acrylonitrile)-polyalkadiene)_n) block copolymer, in which n

≥ 1 is preferably obtained by thermal copolymerization of an aromatic vinyl compound and acrylonitrile, using polyalkadien-based thermal iniferters as initiators. The iniferters can be obtained in the known manner, e.g. by carrying out end group reactions on, e.g., dihydroxy- and dicarboxy-terminated polyalkadienes.

Suitable copolymers of this type are described in the article Kroeze et al. in *Macromolecules* 28 (1995) 28, the contents of which document are inserted herein by reference.

In the above-described block copolymers all random (acrylonitrile-co-aromatic vinyl) blocks are surrounded on both sides by polyalkadiene blocks. However, this is not necessary. In fact, similar results are found with block copolymers of the (aromatic vinyl-co-acrylonitrile) block poly(alkadiene) block (aromatic vinyl-co-acrylonitrile) type. Such a triblock copolymer can be prepared using macrophotoiniferters. To this end, dichloro-terminated polyalkadiene, which, for instance, can be obtained by converting dihydroxy- or dicarboxy-terminated polyalkadiene with phosphorus pentachloride, is reacted with a dialkyldithiocarbamate, preferably the sodium salt, and most preferably the sodium salt of diethyldithiocarbamate. This iniferter functions as photoinitiator. In the presence of this compound and using UV light, a block copolymer with two random blocks from the monomer mixture can be obtained from a mixture of monomers (acrylonitrile, aromatic vinyl).

Such polymer structures and such a process are not described in the prior art and also form the subject of the present invention. The invention therefore also relates to a triblock copolymer of the (random aromatic vinyl-co-acrylonitrile)-polyalkadiene-(random aromatic vinyl-co-acrylonitrile) type; and to a process for preparing such a triblock copolymer in which a dichloro-terminated polyalkadiene is contacted with a dialkyldithiocarbamate, preferably the sodium salt thereof, to prepare a photoiniferter which is then brought into a mixture

comprising acrylonitrile and aromatic vinyl, which mixture is subjected to a photopolymerization.

The polyalkadiene-poly(random aromatic vinyl-co-acrylonitrile) block copolymers can be hydrogenated in the conventional manner, e.g. with hydrogen, using Raney nickel, nickel on diatomaceous earth, copper chromate, molybdenum sulfide, finely divided platinum on carriers with a small specific surface area etc. Only alkene unsaturations are then hydrogenated and, for instance, not the nitrile function.

The block copolymers which form the gist of the present invention not only have favorable compatibilizing properties with which polymer compositions having improved morphology are obtained, using small amounts of compatibilizing agent, viz. compatibilizing agent/blend 1:500-1:50, more preferably 1:200-1:80, and most preferably 1:100. They also have properties leading to improved mechanical properties and in particular improved impact strength. The advantages in morphology modification and improvement in mechanical properties can be obtained with specific compositions in combination.

Thus, the block copolymers in hydrogenated form are very efficient and multifunctional compatibilizing agents for mixtures of polyalkenes with polymers not compatible therewith, such as PVC, PMMA, polycarbonate, poly(ϵ -caprolactone), and styrene-acrylonitrile copolymers (SAN-copolymers).

They form excellent impact modifiers and compatibilizers for polybutene terephthalate/polycarbonate, polyethylene terephthalate/polycarbonate and polyethylene terephthalate/HDPE/polycarbonate mixtures, which mixtures are used to make plastic bottles that can be recycled.

Besides, the block copolymers can be used as impact modifier for polymers, such as PVC, polycarbonate, poly(ϵ -caprolactone), SAN copolymers, PMMA, PET and polybutene terephthalate.

On the other hand, as for composition the block copolymer can be adapted to the polymers or polymer mixtures which have to be improved as regards mechanical properties or morphological properties, e.g. by regulating the length of the alkadiene block, the length of the random block or the composition of the random block.

For a proper compatibility with polyalkenes it is generally required that the polyalkene block has a molecular weight of at least about 2,000, more preferably 3,000 or more.

Saturated polyalkene blocks can be excellently combined with linear polyalkenes, which may form both the first phase and the second phase in the polymer compositions according to the invention. When the copolymers are combined with a fraction of branched polyalkenes, the alkadiene monomer can be adapted thereto. Thus, an excellent compatibilizer on the basis of isoprene is obtained for polypropylene-based blends.

The random acrylonitrile-co-aromatic vinyl fraction usually has a molecular weight of at least 15,000-20,000, preferably more than 25,000.

The acrylonitrile/aromatic vinyl compound ratio can readily be adjusted by varying the ratio in the monomer mixture. A research has shown that the acrylonitrile/aromatic vinyl compound ratio in the random block exceeds that in the starting monomer mixture.

For a system in which polybutadiene-(poly(styrene-co-acrylonitrile)-polybutadiene)_n is used as compatibilizing agent for PE/PVC mixtures, an acrylonitrile content in the random block of about 20 wt.%, based on the weight of that block, turns out to give the best results, both as for mechanical properties and as for morphological properties.

With respect to the amount of compatibilizing agent added to a PE/PVC mixture (10/90) a good effect is already obtained with 0.2 wt.%, based on the weight of the complete composition, which effect is optimal when adding about 1 wt.%.

Finally, the use of the block copolymers according to the invention as emulsifier for the rubber phase in rubber-modified polymers, such as PVC, polycarbonate, poly(ϵ -caprolactone), SAN copolymers, ABS, PMMA, PET and polybutene terephthalate forms the subject of the invention. The emulsifier is then used in an amount of 0.2-2 wt.%, more preferably 0.5-1.25 wt.%, and most preferably about 1 wt.%, based on the weight of the complete mixture. Thus, as for volume the emulsified globules of the rubber phase become 5 times smaller when using about 1% emulsifier.

The present invention will now be explained with reference to the following non-limitative examples.

In these examples tensile strength specimens according to ASTM D1708 are prepared by subjecting mixtures to compression molding at 180 or 190°C. After a preheating time of 4 minutes and degassing of the mixture, this compression molding was carried out for 3 min, and the product was quenched in cold water. The tensile strength was measured in an Instron Tensile Tester at room temperature, using a crosshead speed of 10 mm/min. The results of at least 4 tests per specimen were averaged.

The morphology of the mixtures was studied by means of SEM on cryo-fractured specimens, using a JEOL 6320F Field Emission Scanning Electron Microscope.

Example 1: Preparation of an inifer terpolymer based on dihydroxypolybutadiene (according to steps 1-3 of the scheme)

25.3 g dihydroxy-terminated polybutadiene (Aldrich) was dissolved in 250 ml toluene and dried by azeotropic distillation. After cooling to room temperature 3.35 g PCl_5 were added to the solution. This solution was allowed to stand overnight.

Toluene was removed by vacuum distillation. The polymer was dissolved in chloroform and washed twice with water. This was followed by drying over magnesium sulfate. Then

filtration took place, the solvent was evaporated, and the polymer was dried in vacuum.

20 g of the thus obtained chloro-terminated polybutadiene (molecular weight 3300) was dissolved in a three-necked flask in 50 ml toluene under a nitrogen atmosphere. After adding 5.04 g piperazine the system was subjected overnight to reflux. Then the solution was cooled, filtered and extracted with methanol. The polymer was dried in vacuum.

The amine-terminated polybutadiene (20.3 g) was dissolved in 200 ml toluene under a nitrogen atmosphere. Added were 1 ml triethylamine and 1 ml CS₂, followed by a solution of I₂ in toluene, until the iodine was no longer consumed by the reaction. The mixture was filtered, after which the polymer was precipitated twice from toluene in a large excess of methanol at room temperature.

Thus iniferters were obtained having an average molecular weight of 10400 and an average number of polybutadiene blocks of 2.9.

Example 2: Preparation of an inifer terpolymer based on dicarboxypolybutadiene

Example 1 was repeated starting from dicarboxy-terminated polybutadiene (molecular weight 10200; Scientific Polymer Products Inc.). After the chlorination step no purification took place, but the product was subjected directly to a reaction with an excess of piperazine at -10 to -20°C. The amine-terminated polybutadiene was precipitated in cool methanol (-50°C). The reaction with CS₂ was carried out analogously to Example 1.

Thus iniferters were obtained having an average molecular weight of 26500 and an average number of polybutadiene blocks of 2,5 .

Example 3: Preparation of a segmented block copolymer (according to step 4 of the scheme)

In an ampule an amount of iniferter as prepared in Example 2 was brought under nitrogen atmosphere. Styrene and acrylonitrile were added, after which the ampule was placed in a thermostated oil bath (70°C). After the required
5 polymerization time (95 h) the mixture was precipitated directly in methanol. After a second precipitation from toluene in methanol the obtained block copolymer was filtered off, washed with methanol and dried in vacuum.

Table 1 contains further data of the conducted
10 reactions.

The acrylonitrile content in the obtained polymers was calculated from the nitrogen content which was determined by a known elemental analysis. The nitrogen contents found were corrected for the nitrogen atoms originating from the
15 iniferter. Table 1 shows that the acrylonitrile content in the obtained polymer is higher than in the starting monomer mixture. In fact, acrylonitrile has a higher reactivity in the radical polymerization than styrene.

The average number of alternating blocks in the
20 multiblock copolymers was calculated as follows:

$$N_{pb} = M_{\text{block copolymer}} \cdot x_{pb} / M_{\text{prepolymer}} \quad (1)$$

$$N_{san} = N_{pb} - 1 \quad (2)$$

$$N_{alt} = N_{pb} + N_{san} = 2N_{pb} - 1 \quad (3)$$

in which x_{pb} represents the polybutadiene content of the
25 block copolymer and N_{pb} , N_{san} and N_{alt} respectively the average number of polybutadiene blocks, poly(styrene-acrylonitrile) blocks and alternating blocks. The relation (2) follows from the assumption that no -SH end groups are present in the iniferter, which assumption is supported by
30 the fact that no -SH peaks were found in FTIR spectra. From this it follows that all final polymers begin and end with a polybutadiene block.

Table 1: Characteristics of the multiblock copolymers after copolymerization of styrene and acrylonitrile
35 with the iniferter according to Example 2

Table 1

[M] / [PIN]en ^{1/2}	[PIN]eff (mmol/l)	fAN in monomer feed (mol.%)	FAN in SAN		SAN conversion (%)	10 ⁻⁴ Mn of block copolymer	Nr: alter- nating blocks in copolymers	% SAN in block copolymers	SAN block length x 10 ⁻⁴
			(mol.%)	(wt.%)					
186.1	2.4	12.1	9.4	5.0	21.6	17.7	4,8	82	6,6
161.7	2.4	24.3	33.3	20.3	29.1	21.1	7,2	80	5,5
155.4	2.5	20.9	28.5	16.9	25.4	15.9	6,1	77	4,8
147.9	3.8	10.0	19.5	11.0	20.6	15.5	7,0	74	3,8
131.1	5.0	14.6	23.6	13.7	15.8	7.6	5,4	62	2,5
100.6	7.9	9.7	26.3	15.4	8.7	6.0	6,6	36	0,8

In this table [M] stands for the concentration of monomers (styrene and acrylonitrile); $[PIn]_{eff}$ for the effective concentration of iniferter groups in the polymer iniferter; f_{an} for the fraction of acrylonitrile in the monomer feed; and F_{an} for the fraction of acrylonitrile in the block copolymer.

When the SAN block length is plotted against $[M]/[PIn]_{eff}^{1/2}$, it turns out that there is a linear dependence. This means that by selecting a suitable monomer/iniferter ratio the length of the SAN blocks can be adjusted.

The obtained copolymer was hydrogenated in a three-necked flask provided with a reflux cooler under nitrogen atmosphere. To this end, the copolymer was dissolved in dry toluene (about 1 g polymer on 50 ml toluene). Paratoluenesulfonylhydrazide and tri-n-propylamine were added, both in an amount of 2 mol per mol unsaturated alkene. This system was subjected to reflux for 2 h at 110°C. Then the polymer was isolated by washing with deionized water (2x100 ml) and precipitating in methanol. The recovered polymer was dried in vacuum. Proton-NMR measurements showed a degree of hydrogenation of more than 99%.

Example 4: Preparation of polymer mixtures of PVC and PE

Mixtures of PVC (PVC-LOX; Wavin KLS Hardenberg; NL) and LDPE (Stamylan LD 2100 TN00; DSM Geleen; NL) (90/10) and different amounts of $PB(SAN \text{ block } PB)_n$ block copolymers were prepared by mixing the components for 5 min. at 200°C and at a rotation speed of 75 rpm in a co-rotating twin-screw microextruder. Then the mixture was immediately cooled in coldwater. The mixtures were dried fore at least 1 day in vacuum at 40°C.

Tables 2 and 3 contain data of the different mixture components, while Table 4 shows data and results of the obtained mixtures.

Tabel 2

Code	FAN in SAN		Mn block copoly- mer $\times 10^{-4}$	Average number alter- nating blocks in the copolymer	% SAN in block copoly- mer	PB block length $\times 10^{-4}$	SAN block length $\times 10^{-4}$
	(mol%)	(wt.%)					
EBSAN-5	9.4	5.0	17.7	4.8	82	1.1	6.6
EBSAN-11	19.5	11.0	15.5	7.0	80	1.1	5.5
EBSAN-17	28.5	16.9	15.9	6.1	77	1.1	4.8
EBSAN-20	33.3	20.3	21.1	7.2	74	1.1	3.8

Table 3

Material	Trade name	E _{young} (GPa)	σ _{yield} (MPa)	σ _{break} (MPa)	ε _{yield} (%)	ε _{break} (%)	Toughness (MPa)
Poly(vinyl chloride)	PVC-LOX	1.7	55.0	28.2	6.5	32	13.7
	Lucovyl RB 8010	1.6	54.0	36.7	6.2	37.1	14.9
LDPE	Stamylan LD 1808 A/ LD 2100 TN00	0.1	9.4	11.6	16	450	47.0

Table 4

Compati- bilizer	Compati- bilizer content (%)	Compression molding temp. (°C)	Eyoung (GPa)	σ_{yield} (MPa)	σ_{break} (MPa)	ϵ_{yield} (%)	ϵ_{break} (%)	Toughness (MPa)
-----	-	180	1.5	-	33.1	-	3.8	0.8
EBSAN-17	0.2	180	1.4	44.8	41.5	6.8	7.7	2.5
EBSAN-17	0.5	180	1.5	-	46.3	-	5.7	1.7
EBSAN-17	1.0	180	1.7	46.2	32.1	6.8	12.7	4.5
EBSAN-17	5.0	180	1.4	4.1	32.3	5.7	8.9	2.9
EBSAN-20	0.2	180	1.5	-	43.4	-	6.1	1.5
EBSAN-20	0.5	180	1.3	-	37.1	-	7.4	1.8
EBSAN-20	1.0	180	1.2	-	40.0	-	4.6	1.6
EBSAN-20	5.0	180	1.4	-	30.2	-	3.4	0.7
-----	-	190	1.3	-	40.3	-	5.5	1.5
EBSAN-5	5.0	190	1.2	-	26.4	-	3.0	0.5
EBSAN-5	10.0	190	1.2	-	20.9	-	1.8	0.2
EBSAN-11	5.0	190	1.2	-	32.1	-	5.0	1.1
EBSAN-11	10.0	190	1.2	-	38.2	-	6.3	1.5
EBSAN-17	0.2	190	1.4	44.8	28.8	5.6	11.5	3.7
EBSAN-17	0.5	190	1.5	44.2	35.7	5.0	16.0	5.7
EBSAN-17	1.0	190	1.3	43.3	30.9	6.4	20.7	6.8
EBSAN-17	5.0	190	1.4	44.1	33.7	5.8	22.0	7.8
EBSAN-20	0.2	190	1.4	45.8	28.6	5.9	12.2	4.9
EBSAN-20	1.0	190	1.4	46.8	35.9	5.8	29.1	10.7

Table 4 shows that the compression molding temperature has a considerable effect on the mechanical properties of the mixtures. The beste results are found at a pressing temperature of about 190°C. This difference is possibly to
5 be explained by inferior flow behavior at 180°C.

When the acrylonitrile content in the random block is 5 wt.%, inferior mechanical properties are found; the results for an acrylonitrile content of 11 wt.% give substantially the same properties as when no compatibilizer
10 is added. When using copolymers having acrylonitrile contents of 17 and 20 wt.%, very surprising improvements in properties are found.

These data turn out to correspond to the degree of miscibility of SAN polymers with PVC as described by Kim et
15 al. J. Polym. Sci., Polym. Phys. Edn. 27 (1989) 2211.

Fig. 1 shows the dependence of the toughness of the mixture on the amount of added EBSAN-17 and EBSAN-2. This figure shows that the toughness of the mixture reaches and maintains a constant level when at least about 1 wt.% block
20 copolymer is added.

Fig. 2 shows the "stress-strain" behavior of pure PVC-polymer, a 10/90 LDPE/PVC mixture and a 10/90 LDPE/PVC mixture with EBSAN-20. From this it follows that the mixture with EBSAN-20 shows a behavior comparable to that of pure
25 PVC. Addition of 1% EBSAN-20 gives an increase in the elongation-at-break value by a factor of about with respect to the mixture without EBSAN-20, while the toughness increases by a factor of more than 7.

For all mixtures in which EBSAN-17 or EBSAN-20 was
30 included it was found that no break occurred to the "yield point". This indicates energy dissipation by micromechanical mechanisms, such as "crazing" and "shear yielding", which mechanisms only occur with properly compatibilized dispersions.

This last was confirmed with SEM elektron microscope
35 pictures.

Example 5: 10/90 LDPE/PVC mixtures processed in a Brabender Plasticorder.

Experiments were conducted in a Brabender Plasticorder, in which mixtures were compatibilized with 1% segmented polybutadiene- (SAN block polybutadiene)_n block copolymer under different conditions. More in detail, a mixture of PVC (Lucovyl RB 8010) with LDPE (Stamylan LD 1808 A; DSM Geleen; NL) was prepared in a Brabender Plasticorder at a selected temperature for 5 min. at a rotation speed of 100 rpm. Di-n-octyltin-bis(isooctylthioglycolate) (Irgastab Mok 17A; 2.5 wt.%) was added to the PVC mixture as stabilizer.

Table 5 shows that the results found in the preceding example are confirmed.

Table 5

Compati- bilizer	Compati- bilizer content (%)	Mixing temperature (°C)	E _{young} (GPa)	σ _{yield} (MPa)	σ _{break} (MPa)	ε _{yield} (%)	ε _{break} (%)	Toughness (MPa)
----	0	180	1.3	37.8	29.9	5.9	16.4	5.0
EBSAN-15	1.0	180	1.3	39.0	28.7	6.1	12.7	3.8
EBSAN-11	1.0	180	1.2	36.9	27.8	5.7	13.5	3.7
EBSAN-17	1.0	180	1.3	39.9	33.1	5.9	22.0	7.2
EBSAN-20	1.0	180	1.4	46.4	35.7	6.3	43.6	14.6
---	0	200	1.3	36.2	21.3	5.0	13.4	4.5
EBSAN-17	1.0	200	1.3	39.0	32.5	6.3	24.5	6.2
EBSAN-17	1.0	200	1.2	41.7	34.1	7.2	20.2	6.6

Example 6: Preparation of a polybutadiene-photoiniferter

Dihydroxy-terminated polybutadiene (molecular weight 3300; see Example 1) was dissolved in 150 ml toluene and dried by azeotropic distillation of 50 ml toluene. Then the mixture was cooled to room temperature. 3.53 g phosphorus pentachloride were added, and the mixture was stirred overnight. The polymer solution was poured out in cold methanol (-50°C). The recovered chloro-terminated polybutadiene was dried in vacuum (yield 93%).

The obtained chloro-terminated product was dissolved in a three-necked flask containing 200 ml tetrahydrofuran under nitrogen atmosphere. A twofold excess of sodium diethyldithiocarbamate was added, and this mixture was allowed to reflux overnight. The solution was cooled, filtered and precipitated in cold methanol (-50°C). The polymer was dried in vacuum at 40°C. Elemental analysis showed that 88% of the end groups were converted to diethyldithiocarbamate end groups.

Example 7: Preparation of a polybutadiene-photoiniferter

Dicarboxy-terminated polybutadiene (molecular weight 10200; see Example 2) was converted to the corresponding dihydroxy-terminated polybutadiene, using a 100% molar excess of lithium aluminium hydride. Then Example 6 was repeated analogously.

Example 8: Preparation of a SAN-PB-SAN triblock copolymer

In a PYREX flask an amount of the photoiniferter according to Example 6 or 7 was brought under a nitrogen atmosphere. Acrylonitrile and styrene were added. While stirring with a magnet stirrer, the photoiniferter was dissolved. The flask was kept at a distance of 2 cm from an UV lamp (365 nm), and the mixture was subjected to photopolymerization at room temperature.

The reaction mixture was dissolved in tetrahydrofuran and precipitated in methanol at room temperature. After a precipitation of tetrahydrofuran in hexane to remove non-

reacted polybutadiene, the obtained triblock copolymers were filtered and dried in vacuum.

Characteristics of the obtained triblock copolymers are shown in Table 6.

Table 6

Characteristics of the photo copolymerisations of styrene/acrylonitrile with MI-3300

[MI]eff (mmol/l) a	FAN in monomer feed (mol.%)	FAN in SAN		Consumption MI-3300 (wt.%)	Con- version SAN (wt.%)	Wt.% SAN in block copolymer	Mn block copolymer (10 ⁴ g/mol)		SAN- block length (10 ³ g/mol)
		(mol.%) b	(wt.%) b				theoretical ^c	CPC	
36.3	30.7	33.3	20.3	n.d.	n.d.	92.2	4.2	3.9	15.5
37.9	24.0	29.0	17.2	n.d.	n.d.	89.5	3.2	3.7	12.0
38.8	18.3	24.2	14.0	79.7	77.8	89.1	3.0	3.2	11.0
50.7	22.5	31.5	19.0	85.5	47.0	73.2	1.3	2.0	8.2
58.7	21.4	29.9	18.0	63.6	55.0	78.6	1.6	1.9	7.7
91.9	24.8	32.9	20.0	69.2	41.8	62.3	0.9	1.2	4.2
108.3	21.6	34.3	21.0	73.2	41.9	57.1	0.8	1.2	4.2
101.7	26.0	44.4	28.9	78.4	37.3	55.5	0.8	1.1	4.5

a) effective concentration of iniferter groups in MI-3300.

b) calculated from %N in block copolymer as determined by elemental analysis, corrected for %N from iniferter groups.

c) calculated from block copolymer composition determined with ¹H NMR.

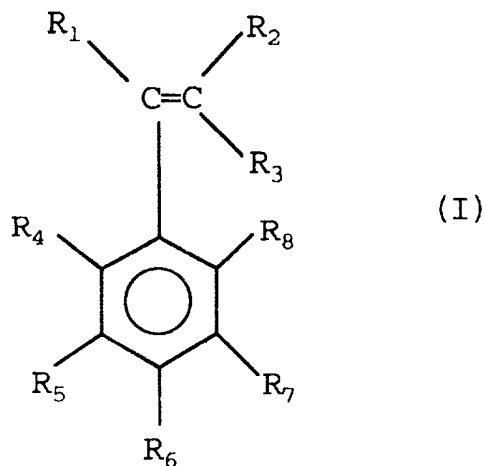
CLAIMS

1. A stable polymer composition comprising a first polymer and a second polymer, which second polymer is not compatible with the first polymer, and an amount of a copolymer comprising at least one block of a polyalkadiene and at
5 least one block of random poly(aromatic vinyl-acrylonitrile), and in which the ratio of the block copolymer to the total polymer composition is between 1:500 and 1:50.

2. A polymer composition according to claim 1, wherein the
10 first polymer forms a continuous phase with the second polymer dispersed therein.

3. A polymer composition according to claim 1 or 2, wherein the aromatic vinyl compound is represented by formula I,

15



in which R_{1-3} may be independently selected from a hydrogen atom, a C_{1-4} alkyl group or a C_{1-4} alkyl group substituted
20 with an inert group; and in which R_{4-8} may independently represent a hydrogen atom, a halogen atom, a C_{1-4} alkyl group or a C_{1-4} alkyl group substituted with an inert group.

4. A polymer composition according to any of claims 1-3, wherein the aromatic vinyl compound is styrene.

5. A polymer composition according to any of the preceding claims, wherein polyalkadiene is polybutadiene which may or may not be hydrogenated.
6. A polymer composition according to any of the preceding
5 claims, wherein the block copolymer is polyalkadiene-
((random (aromatic vinyl-co-acrylonitrile)-polyalkadiene)_n)
block copolymer, wherein $n \geq 1$.
7. A polymer composition according to any of the preceding
10 claims, wherein the first polymer and the second polymer are
polyethylene and polyvinyl chloride or polyvinyl chloride
and polyethylene.
8. A polymer composition according to any of the preceding
15 claims, wherein the ratio of the block copolymer to the
first and the second polymer is between 1:200 and 1:80 and
is most preferably about 1:100.
9. A triblock copolymer of the (random aromatic vinyl-co-
acrylonitrile)-polyalkadiene-(random aromatic vinyl-co-
acrylonitrile) type.
10. A process for preparing a triblock copolymer according
20 to claim 9, wherein a dichloro-terminated polyalkadiene is
contacted with a dialkyldithiocarbamate to prepare a
photoiniferter which is then brought into a mixture
comprising acrylonitrile and aromatic vinyl, which mixture
is subjected to a photopolymerization.
- 25 11. The use of the block copolymer as defined in claim 1 as
impact modifier in polymer compositions.

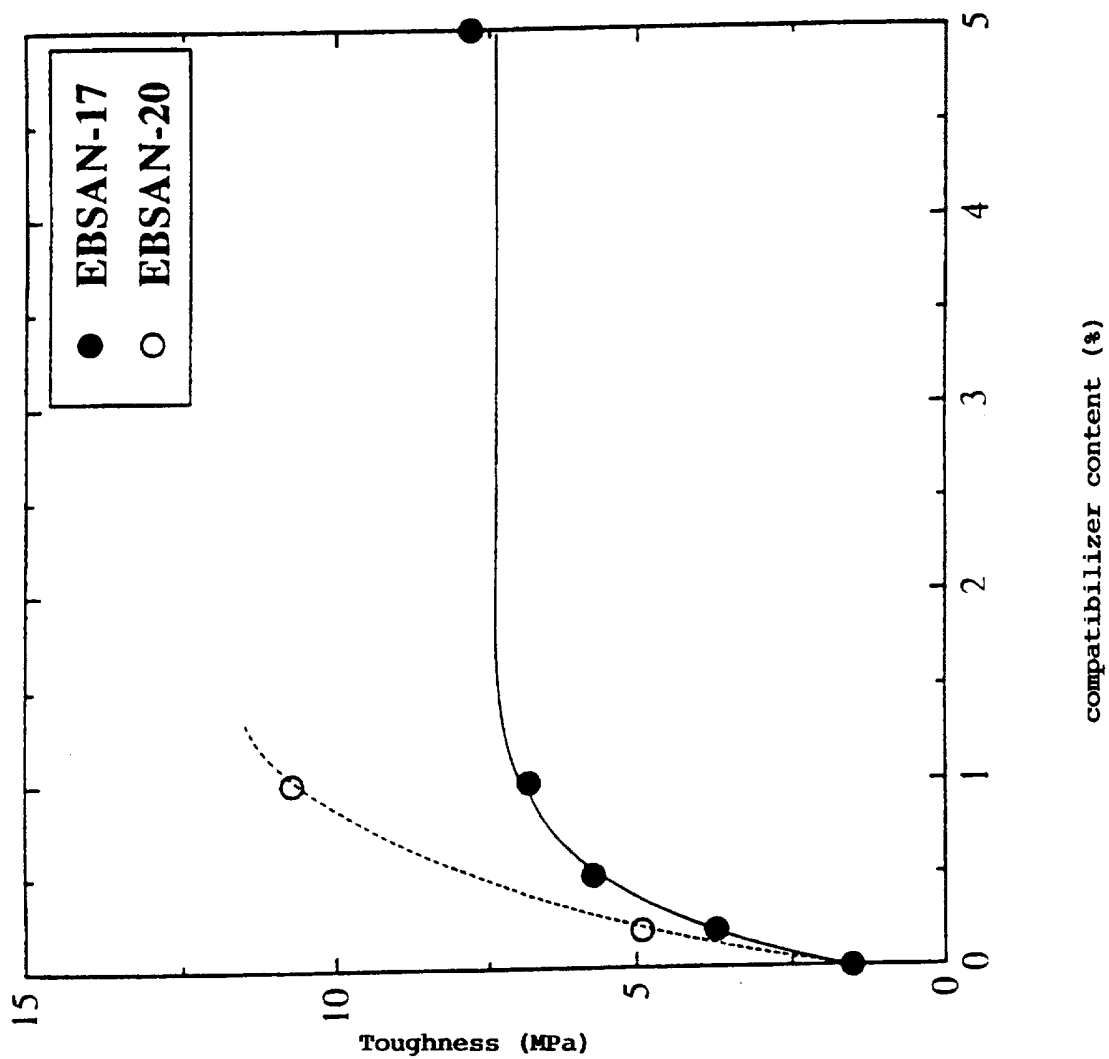
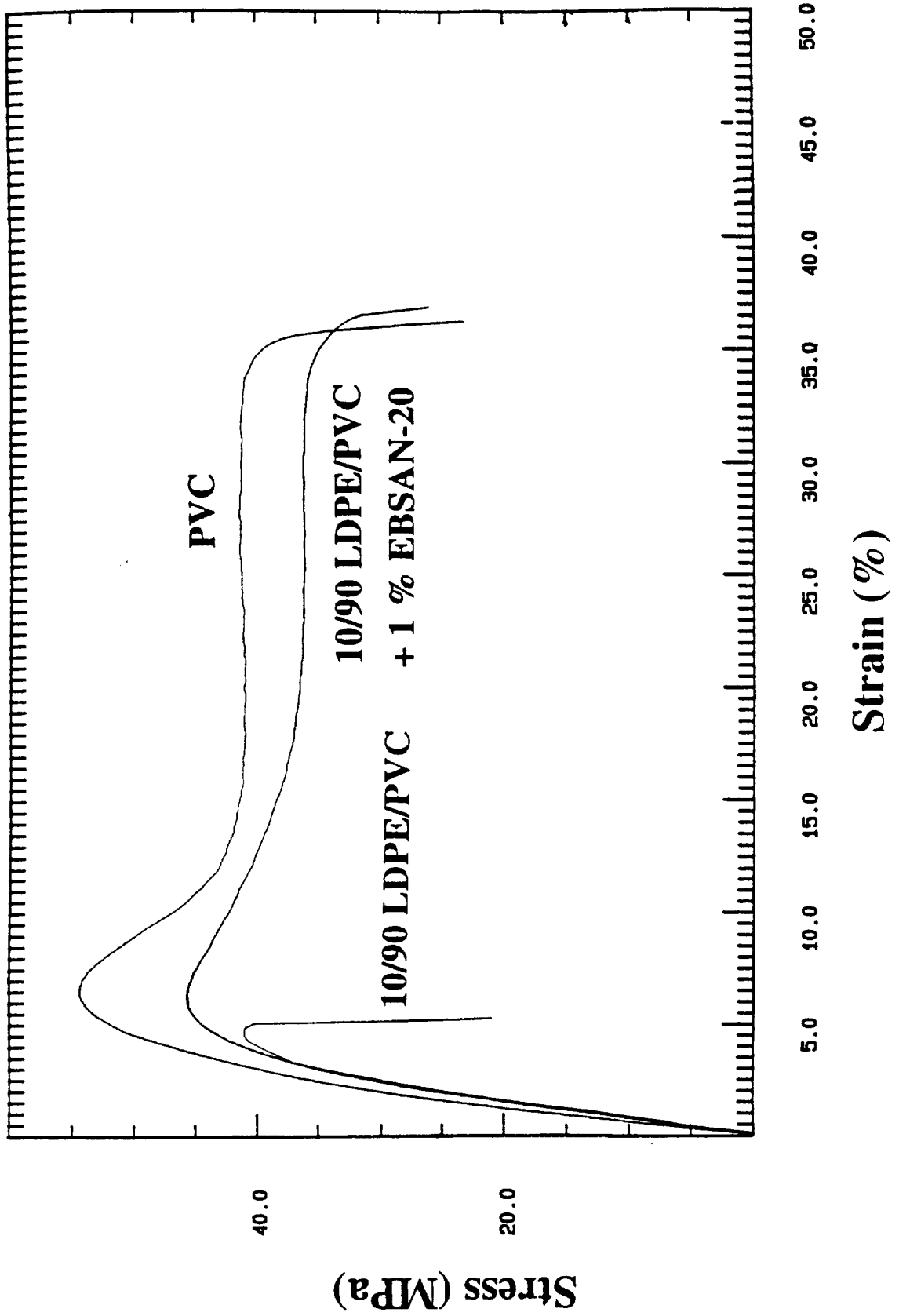
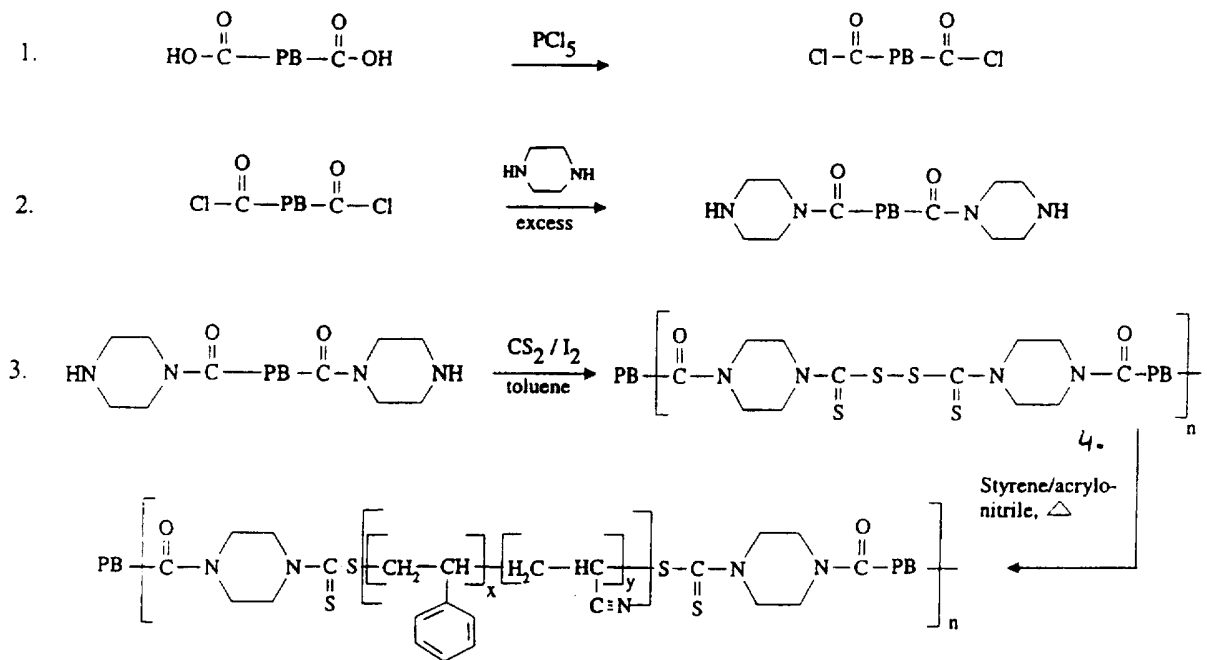


Fig. 1



SCHEME



INTERNATIONAL SEARCH REPORT

International Application No
PCT/NL 97/00352

<p>A. CLASSIFICATION OF SUBJECT MATTER IPC 6 C08F293/00 C08L53/02</p>		
<p>According to International Patent Classification (IPC) or to both national classification and IPC</p>		
<p>B. FIELDS SEARCHED</p>		
<p>Minimum documentation searched (classification system followed by classification symbols) IPC 6 C08F C08L</p>		
<p>Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched</p>		
<p>Electronic data base consulted during the international search (name of data base and, where practical, search terms used)</p>		
<p>C. DOCUMENTS CONSIDERED TO BE RELEVANT</p>		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>MACROMOLECULES, vol. 28, no. 19, 11 September 1995, US, pages 2650-2656, XP000527662 E. KROEZE ET AL.: "Synthesis of segmented (PB(PS-block-PB)_n and (PB(SAN-block-PB)_n block copolymers via polymeric thermal iniferters" cited in the application see the whole document</p>	9-11
X	<p>US 4 169 115 A (L. TUNG ET AL.) 25 September 1979 see examples 3,4</p>	9-11
<p>--- -/--</p>		
<p><input checked="" type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex.</p>		
<p>* Special categories of cited documents :</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"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</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p>		
<p>Date of the actual completion of the international search</p> <p>7 August 1997</p>		<p>Date of mailing of the international search report</p> <p>03.09.97</p>
<p>Name and mailing address of the ISA</p> <p>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</p>		<p>Authorized officer</p> <p>Glikman, J-F</p>

INTERNATIONAL SEARCH REPORT

International Application No
PCT/NL 97/00352

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE "CHEMICAL ABSTRACTS" (HOST: STN); Abstract 119: 226 682, Columbus, OH,US; & JP-A-05 117 341(ASAHI CHEM. Ind., Jap.) 14 Mei 1993 XP002024798 see the whole document ---	9-11
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