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CA 2591623 C 2013/05/07

(11)(21) **2 591 623**

(12) **BREVET CANADIEN
CANADIAN PATENT**

(13) **C**

(86) Date de dépôt PCT/PCT Filing Date: 2005/12/31
(87) Date publication PCT/PCT Publication Date: 2006/07/20
(45) Date de délivrance/Issue Date: 2013/05/07
(85) Entrée phase nationale/National Entry: 2007/06/19
(86) N° demande PCT/PCT Application No.: EP 2005/014166
(87) N° publication PCT/PCT Publication No.: 2006/074819
(30) Priorité/Priority: 2005/01/12 (DE10 2005 001 637.5)

(51) Cl.Int./Int.Cl. *C08L 53/02* (2006.01)

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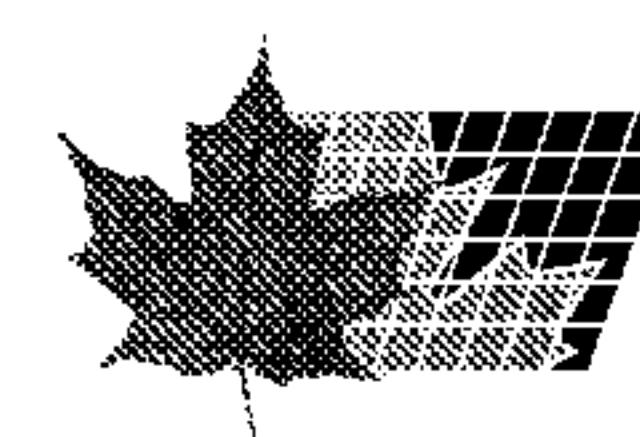
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(54) Titre : MELANGES DE COPOLYMER SEQUENCE DE STYRENE/BUTADIENE POUR FILMS RETRECISSEABLES
(54) Title: STYRENE/BUTADIENE BLOCK COPOLYMER MIXTURES FOR SHRINK FILMS

(57) Abrégé/Abstract:

The invention relates to a mixture, comprising a) 5 to 50 wt. % of a block copolymer (A), with one or more block copolymers (B/S)_A, each made from 65 to 95 wt. % vinylaromatic monomers and 35 to 5 wt. % dienes with a glass transition temperature T_{gA} in the range 40° to 90 °C, b) 95 to 50 wt. % of a block copolymer B, with at least one hard block (S) made from vinylaromatic monomers and one or more copolymer blocks (B/S)_B, each made from 20 to 60 wt. % vinylaromatic monomers and 80 to 40 wt. % dienes and a glass temperature T_{gB} in the range -70° to 0 °C, c) 0 to 45 wt. % of a block copolymer (C) different from (A) and (B), or polystyrol and d) 0 to 6 wt. % of a plastifier and the use thereof for the production of shrink films.



(12) NACH DEM VERTRAG ÜBER DIE INTERNATIONALE ZUSAMMENARBEIT AUF DEM GEBIET DES PATENTWESENS (PCT) VERÖFFENTLICHTE INTERNATIONALE ANMELDUNG

(19) Weltorganisation für geistiges Eigentum
Internationales Büro(43) Internationales Veröffentlichungsdatum
20. Juli 2006 (20.07.2006)

PCT

(10) Internationale Veröffentlichungsnummer
WO 2006/074819 A1(51) Internationale Patentklassifikation:
C08L 53/02 (2006.01)(74) Gemeinsamer Vertreter: BASF Aktiengesellschaft;
67056 Ludwigshafen (DE).

(21) Internationales Aktenzeichen: PCT/EP2005/014166

(81) Bestimmungsstaaten (soweit nicht anders angegeben, für jede verfügbare nationale Schutzrechtsart): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, LY, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(22) Internationales Anmeldedatum:

31. Dezember 2005 (31.12.2005)

(25) Einreichungssprache: Deutsch

(26) Veröffentlichungssprache: Deutsch

(30) Angaben zur Priorität:
10 2005 001 637.5 12. Januar 2005 (12.01.2005) DE

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(84) Bestimmungsstaaten (soweit nicht anders angegeben, für jede verfügbare regionale Schutzrechtsart): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), eurasisches (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), europäisches (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Veröffentlicht:

— mit internationalem Recherchenbericht

Zur Erklärung der Zweibuchstaben-Codes und der anderen Abkürzungen wird auf die Erklärungen ("Guidance Notes on Codes and Abbreviations") am Anfang jeder regulären Ausgabe der PCT-Gazette verwiesen.

(54) Title: STYROL/BUTADIENE BLOCK COPOLYMER MIXTURES FOR SHRINK FILMS

(54) Bezeichnung: STYROL-BUTADIEN-BLOCKCOPOLYMERMISCHUNGEN FÜR SCHRUMPFFFOLIEN

(57) Abstract: The invention relates to a mixture, comprising a) 5 to 50 wt. % of a block copolymer (A), with one or more block copolymers (B/S)_A, each made from 65 to 95 wt. % vinylaromatic monomers and 35 to 5 wt. % dienes with a glass transition temperature T_{gA} in the range 40° to 90 °C, b) 95 to 50 wt. % of a block copolymer B, with at least one hard block (S) made from vinylaromatic monomers and one or more copolymer blocks (B/S)_B, each made from 20 to 60 wt. % vinylaromatic monomers and 80 to 40 wt. % dienes and a glass temperature T_{gB} in the range -70° to 0 °C, c) 0 to 45 wt. % of a block copolymer (C) different from (A) and (B), or polystyrol and d) 0 to 6 wt. % of a plastifier and the use thereof for the production of shrink films.(57) Zusammenfassung: Eine Mischung, die a) 5 bis 50 Gew.-% eines Blockcopolymeren A, welches ein oder mehrere Copolymerblöcke (B/S)_A aus jeweils 65 bis 95 Gew.-% vinylaromatischen Monomeren und 35 bis 5 Gew.-% Dienen und einer Glasübergangstemperatur T_{gA} im Bereich von 40° bis 90°C und b) 95 bis 50 Gew.-% eines Blockcopolymeren B, welches mindestens einen Hartblock S aus vinylaromatischen Monomeren und ein oder mehrere Copolymerblöcke (B/S)_B aus jeweils 20 bis 60 Gew.-% vinylaromatischen Monomeren und 80 bis 40 Gew.-% Dienen und einer Glastemperatur T_{gB} im Bereich von -70° bis 0°C, c) 0 bis 45 Gew.-% eines von A und B verschiedenen Blockcopolymeren C oder Polystyrol und d) 0 bis 6 Gew.-% eines Plastifizierungsmittels enthält, sowie deren Verwendung zur Herstellung von Schrumpffolien.

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STYRENE/BUTADIENE BLOCK COPOLYMER MIXTURES FOR SHRINK FILMS

The invention relates to a mixture which comprises

- a) from 5 to 50% by weight of a block copolymer A which comprises one or more copolymer blocks $(B/S)_A$ each composed of from 65 to 95% by weight of vinylaromatic monomers and from 35 to 5% by weight of dienes and of a glass transition temperature Tg_A in the range from 40° to 90°C,
- b) from 95 to 50% by weight of a block copolymer B which comprises at least one hard block S composed of vinylaromatic monomers and comprises one or more copolymer blocks $(B/S)_B$ each composed of from 20 to 60% by weight of vinylaromatic monomers and from 80 to 40% by weight of dienes and of a glass transition temperature Tg_B in the range from -70° to 0°C,
- c) from 0 to 45% by weight of polystyrene or of a block copolymer C other than A and B, and
- d) from 0 to 6% by weight of a plasticizer,

and its use for production of shrink films.

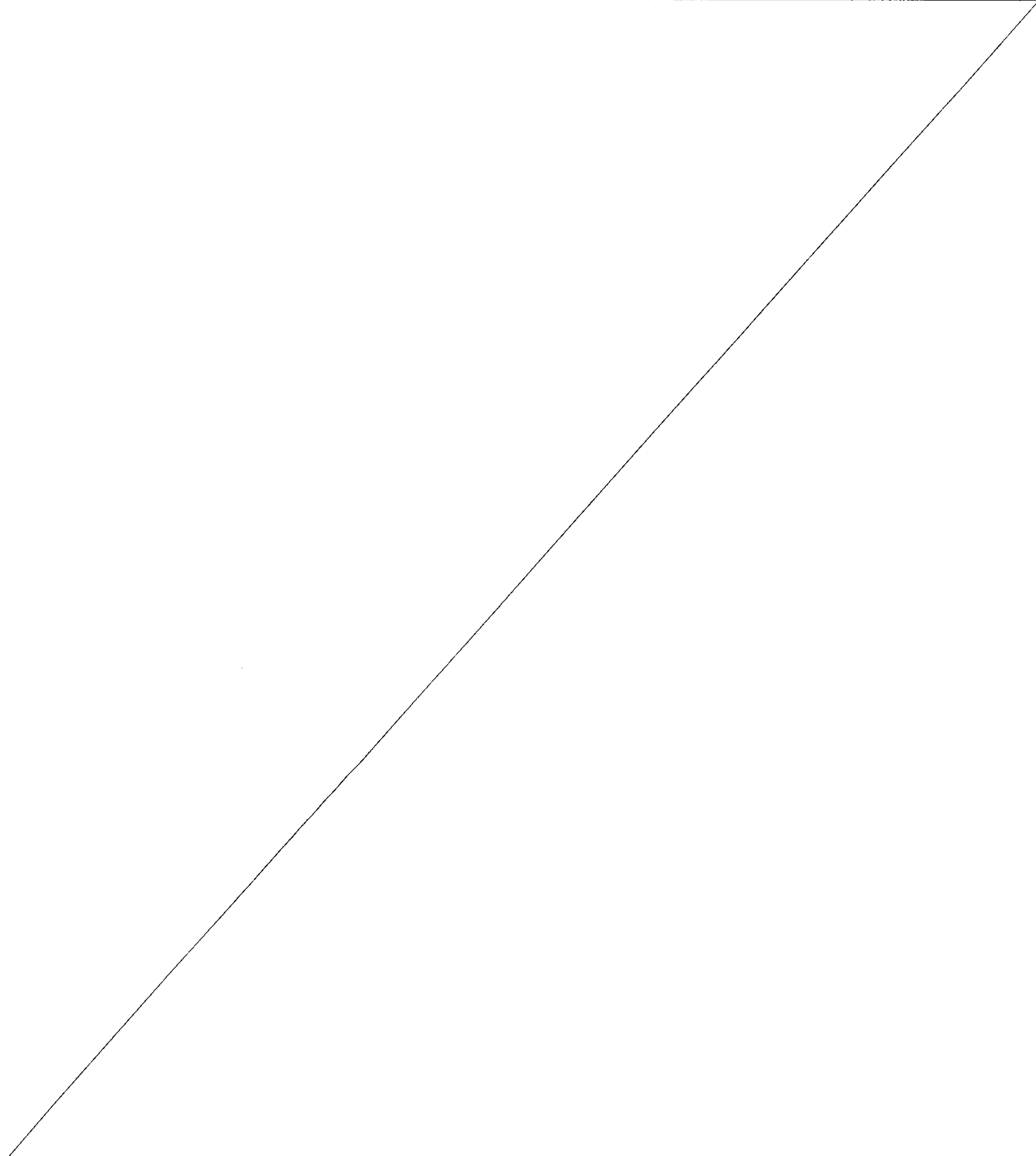
The use of styrene-butadiene block copolymers as heat-shrinkable films has been disclosed by way of example in EP-A 058 952 or EP-A 436 225. The films are stretched to over 500% by heating at from 60 to 100°C, and the stretched state is set after cooling to room temperature. After processing to give pods, these can be printed and by way of example placed over a bottle and reshrunk in a heat tunnel at from about 70 to 90°C, whereupon the film clings to the bottle.

Shrink films are intended to shrink almost to their initial dimensions when applied under hot conditions, but at the same time are intended to have high storage stability, meaning that they are intended to exhibit no shrinkage at temperatures around 20-30°C. Furthermore, they are intended not only to have high transparency but also to have high stiffness and strength.

1a

EP-A 852240 describes styrene-butadiene block copolymers which after orientation in hot conditions, are claimed to have reduced level of spontaneous shrinkage at 30°C.

It was an object of the invention to find styrene-butadiene block copolymers which can be processed to give storage-stable, heat-shrinkable films with high shrinkage



capability and high stiffness/strength. A further intention was that the films should have high transparency, even after stretching and shrinking.

Accordingly, the abovementioned mixture composed of block polymers has been

5 found.

The mixture preferably comprises from 20 to 40% by weight of the block copolymer A, from 80 to 60% by weight of the block copolymer B, and from 0 to 20% by weight of polystyrene or of a block copolymer C other than A and B. Besides the block 10 copolymers A, B and, if appropriate, C, the mixture may also comprise relatively small amounts of other thermoplastic polymers and from 1 to 6% by weight of conventional auxiliaries, such as plasticizers. Plasticizers which may be used are from 0 to 6% by weight, preferably from 2 to 4% by weight, of a homogeneously miscible oil or oil mixture, in particular white oil or dioctyl adipate, or a mixture of these. Particularly good 15 shrink values are obtained when the white oil content of the mixture is from 2.5 to 3.5% by weight, based on the mixture.

Block copolymer A:

20 The mixture comprises from 5 to 50% by weight of a block copolymer A which comprises one or more copolymer blocks $(B/S)_A$ each composed of from 65 to 95% by weight of vinylaromatic monomers and of from 35 to 5% by weight of dienes and with a glass transition temperature T_{g_A} in the range from 40° to 90°C.

25 The glass transition temperature of the copolymer block $(B/S)_A$ is preferably in the range from 50 to 70°C. The glass transition temperature is affected by the comonomer constitution and can be determined via differential scanning calorimetry (DSC) or differential thermal analysis (DTA), or calculated from the Fox equation. The copolymer block $(B/S)_A$ is preferably composed of from 80 to 90% by weight of styrene and from 30 10 to 20% by weight of butadiene.

Preference is given to block copolymers A which comprise one or more copolymer blocks $(B/S)_A$ composed of vinylaromatic monomers and of dienes with random distribution. By way of example, these may be obtained via anionic polymerization 35 using alkyllithium compounds in the presence of randomizers, such as tetrahydrofuran or potassium salts. It is preferable to use potassium salts with a ratio of anionic initiator to potassium salt in the range from 25:1 to 60:1. This can simultaneously achieve a low proportion of 1,2 linkages of the butadiene units.

40 The proportion of 1,2 linkages of the butadiene units is preferably in the range from 8 to 15%, based on the entirety of the 1,2, 1,4-cis, and 1,4-trans linkages.

It is particularly preferable that the block copolymer A is composed of a single copolymer block $(B/S)_A$ or has linear structures, such as $S-(B/S)_A$ or $S-(B/S)_A-S$, where in each case S is a hard block composed of vinylaromatic monomers. Preference is likewise given to star polymers $[(B/S)_A]_n$ having n star branches, these being obtainable

5 via coupling using an n-functional coupling agent or via initiation using an n-functional initiator. An example of a suitable coupling agent is epoxidized vegetable oil, such as epoxidized linseed or soybean oil. In this instance the product is stars having from 3 to 5 branches. Star block copolymers $[S-(B/S)_A]_n$ are likewise preferred.

10 However, random polymers $(B/S)_A$ can also be prepared via free-radical polymerization.

The weight-average molar mass M_w of the copolymer block $(B/S)_A$ is generally in the range from 50 000 to 400 000 g/mol, preferably in the range from 60 000 to

15 200 000 g/mol, particularly preferably in the range from 100 000 to 160 000 g/mol. For the structures, such as $S-(B/S)_A$ or $S-(B/S)_A-S$, the weight-average molar mass M_w for each block S is preferably in the range from 15 000 to 45 000 g/mol. The blocks S are preferably composed of styrene units. Control of the molecular weight of the anionically prepared polymers takes place by way of the ratio of amount of monomer to amount of 20 initiator. However, initiator can also be added repeatedly after monomer feed has taken place, the result then being bi- or multimodal distribution. For polymers prepared by a free-radical route, M_w is adjusted by way of the polymerization temperature and/or addition of regulators.

25 Block copolymer B

The inventive mixture comprises, as block copolymer B, from 95 to 50% by weight of a block copolymer B which comprises at least one hard block S composed of vinylaromatic monomers and comprises one or more copolymers blocks $(B/S)_B$ each 30 composed of from 20 to 60% by weight of vinylaromatic monomers and of from 80 to 40% by weight of dienes and of a glass transition temperature Tg_B in the range from -70° to 0°C, preferably in the range from -65°C to -20°C.

Particularly suitable block copolymers B are rigid block copolymers which are 35 composed of from 60 to 90% by weight of vinylaromatic monomers and of from 10 to 40% by weight of diene, based on the entire block copolymer, and are mainly composed of hard blocks S comprising vinylaromatic monomers, in particular styrene, and of soft-blocks B or B/S comprising dienes, such as butadiene and isoprene. Block copolymers with from 70 to 80% by weight of styrene and from 20 to 30% by weight of 40 diene are particularly preferred.

The copolymer blocks $(B/S)_B$ of the block copolymer B preferably have random distribution of the vinylaromatic monomers and dienes.

Preferred block copolymers B have a star-shaped structure having at least two terminal
5 hard blocks S_1 and S_2 with different molecular weight composed of vinylaromatic monomers, the proportion of the entirety of the hard blocks S being at least 40% by weight, based on the entire block copolymer B. Linear structures, such as $(B/S)_B-S_2$ or $S_1-(B/S)_B-S_2$, are also possible. The number-average molar mass M_n of the terminal blocks S_1 is preferably in the range from 5000 to 30 000 g/mol, and the number-
10 average molar mass M_n of S_2 is preferably in the range from 35 000 to 150 000 g/mol.

Preference is given to polymodal styrene-butadiene block copolymers having terminal styrene blocks, for example those described in DE-A 25 50 227 or EP-A 0 654 488.

15 Particular preference is given to block copolymers B having at least two hard blocks S_1 and S_2 composed of vinylaromatic monomers and having at least one random soft block $(B/S)_B$ situated between these and composed of vinylaromatic monomers and of dienes, the proportion of the hard blocks being above 40% by weight, based on the entire block copolymer, and the 1,2-vinyl content in the soft block B/S being below
20 20%, such as those described in WO 00/58380.

The inventive mixtures are highly transparent and are particularly suitable for production of shrink films. They are stable in storage and exhibit no significant shrinkage at from 40°C to 50°C. In the range from 90 to 100°C, the degree of
25 shrinkage is high, and this permits flexible matching to process conditions, and also permits encapsulation of very bulbous shapes.

Examples:

30 Block copolymer A

To prepare the linear styrene-butadiene block copolymers A2 to A10 having B/S structure, cyclohexane was used as initial charge and was titrated to the end point at 60°C with sec-butyllithium (BuLi), in each case using 1.6 ml, and was then treated with
35 the amounts mentioned in Table 1 of sec-butyllithium for initiation and potassium tert-
amyl alcoholate (PTA) as randomizer, and the mixture was cooled to 40°C. The
polymerization was carried out in two portions. In each case, half of the amounts of
40 styrene and butadiene stated in Table 1 were added simultaneously, and the maximum
temperature was restricted to 75°C via countercooling. The living polymer chains were
then terminated via addition of isopropanol, the mixture was acidified with CO₂/water,
and a stabilizer solution was added. Cyclohexane was evaporated in a vacuum drying
cabinet.

To prepare the linear styrene-butadiene block copolymer A1 having the structure S-(B/S)-S, the monomers were added in three portions, and in each case prior to and after the joint styrene-butadiene additions for polymerization of the middle (S/B) block 5 here, 400 g of styrene were added and polymerized to completion to form the terminal styrene blocks. The procedure was otherwise as for preparation of the block copolymers A2 to A10, corresponding to the data in Table 1.

Starting materials, structure, and molecular weights of block copolymers A1 to A10 are 10 given in Table 1.

Table 1: Structure and properties of block copolymers A1 to A10

	Structure	Tg [°C]	Cyclo-hexane [ml]	sec-BuLi 1.4 M [ml]	PTA 0.1175 M [ml]	Styrene [g]	Butadiene [g]	Isopropanol [ml]	Mn (GPC)	Mw (GPC)
A1	S-S/B-S	50	4786	8.79	3.02	400 (S) 664 (S/B) 400 (S)	136 (SB)	1.41	122 000	146 000
A2	S/B	70	4786	19.05	6.55	1440	160	3.06	63 000	71 000
A3	S/B	70	2991	7.14	2.53	900	100	1.15	97 000	108 000
A4	S/B	70	2991	5.1	1.81	900	100	0.82	130 000	149 000
A5	S/B	70	2991	4.46	1.58	900	100	0.72	154 000	163 000
A6	S/B	60	2991	7.14	2.53	870	130	1.15	111 000	122 000
A7	S/B	50	2991	7.14	2.53	792	171	1.15	130 000	141 000
A8	S/B	60	2991	11.9	4.73	870	130	1.91	59 000	64 000
A9	S/B	60	2991	5.95	2.36	870	130	0.96	119 000	131 000
A10	S/B	60	2991	5.1	1.81	870	130	0.82	143 000	155 000

Block copolymer B:

A star-shaped block copolymer B1 (26% by weight of butadiene, 74% by weight of styrene) having random copolymer blocks B/S was prepared via sequential anionic

5 polymerization of styrene and butadiene, followed by coupling using epoxidized linseed oil as in Example 15 of WO 00/58380.

The block copolymer mixtures B2 were prepared in accordance with the data in Table 2 via sequential anionic polymerization using double initiator feed (sec-butyllithium BuLi)

10 in stage 1 or 2 at solids content of about 30% by weight in cyclohexane at temperatures in the range from 50 to 80°C. Once the polymerization had ended, isopropanol was used for termination and CO₂/water for acidification. The polymerization was carried out in the presence of potassium tert-amyl alcoholate (PTA) at a molar lithium/potassium ratio of 38/1, in order to obtain a random S/B copolymer

15 block. The block copolymers were freed from solvent in a 16 mm vented extruder.

The resultant block copolymer mixtures comprise block copolymers having random copolymer blocks of the structure (I) S₁-(B/S)_a-(B/S)_b-S₂ with number-average molar mass of about 150 000 g/mol and having the structure (II) (B/S)_a-(B/S)_b-S₃ with a

20 number-average molar mass of about 75 000 g/mol in a molar ratio (I)/(II) corresponding to the initiator ratio I₁/I₂.

Table 2:

Stage	Feed	2
1	sec-BuLi [mol]	25.65
	Styrene [kg]	1950
	PTA [mol]	1.012
2a	sec-BuLi [mol]	12.82
	Butadiene/styrene [kg]	565/785
2b	Butadiene/styrene [kg]	685/415
3	Styrene	600
	I ₁ /I ₂	2/1

25

Component C

Standard polystyrene PS 158 K with M_w of 270 000 and M_n of 103 000 from BASF Aktiengesellschaft was used as component C.

30

Component D

Medicinal white oil with viscosity of 70 centistokes at 40°C was used as component D1, and dioctyl adipate (Plastomoll DOA from BASF Aktiengesellschaft) was used as component D2.

5 Mixtures M1 - M22

Each of the block copolymer mixtures was prepared in an extruder via melting of the parts by weight stated in Table 5 of the block copolymers A1 - A10 and B1 and, respectively, B2 (for M12), and also of components C (polystyrene PS 158 K) and D (white oil, and also dioctyl adipate in the case of mixtures M9 - M11), and were then pressed to give films.

Comparative experiments c1 to c6

15 Each of the mixtures was prepared in an extruder via melting of the parts by weight stated in Table 5 of block copolymers B1 and, respectively B2 (for c5), and also of components C and D, and were then pressed to give films. They comprise no block copolymers A.

20 Values for mechanical properties, such as modulus of elasticity, tensile stress, and tensile strain, were determined to ISO 527 and are stated in Table 3.

25 The films were cut into strips of length 8 cm and width 1 cm, and stretched in a tensile machine at 80°C almost to the tensile strain at break determined in the preliminary experiment, and were cooled to 23°C in the stretched state. The shrink values were determined as in Table 4 after 10 sec in a waterbath at 90°C. Complete shrink curves were also determined as in Table 6. For this, the film was stretched using a uniform degree of stretching of 4.5 (3.5 in the case of c5), and shrinkage S was then determined at 10 degree intervals.

30

Table 3:

Mixture	Modulus of elasticity [N/mm ²]	Tensile stress [N/mm ²] at			Tensile strain [%] at		
		YS	TSmax	TSB	YS	TSmax	TSB
M1	774	14.1	25.3	25.3	4.8	325	325
M2	802	17.6	23.4	25.3	4.3	271	272

YS = yield stress; TSmax = maximum tensile stress; TSB = tensile stress at break

Table 4:

Mixture	Degree of stretching		Shrinkage (at 90°C)	
	Max.	After shrinkage	Max	For degree of stretching = 4.5
M3	6.1	2.1	65	58
M4	5.3	2.1	60	57
M5	5.0	2.2	55	54
M6	5.3	2.1	61	60
M7	5.9	2.7	55	50

Table 5: Constitution of mixtures and their shrink performance

Mixture	Block copolymer	Parts of A	Parts of B1	Parts of B2	Parts of C	Parts of D1	Parts of D2	Parts of (40°C)	Parts of (50°C)	Parts of (60°C)	Parts of (70°C)	Parts of (80°C)	Parts of (90°C)	Parts of (100°C)
M1	A1	29.25	67.71		3.04		1%	1%	6%	18%	39%	59%	59%	70%
M2	A2	29.25	67.71		3.04		0%	0%	3%	16%	36%	56%	65%	65%
M3	A3	29.25	67.71		3.04		0%	0%	2%	11%	34%	58%	68%	68%
M4	A4	29.25	67.71		3.04		0%	0%	2%	14%	36%	57%	68%	68%
M5	A5	29.25	67.71		3.04		0%	1%	7%	20%	37%	54%	66%	66%
M6	A6	29.25	67.71		3.04		0%	0%	4%	19%	41%	60%	69%	69%
M7	A7	29.25	67.71		3.04		0%	1%	8%	19%	34%	50%	60%	60%
M8	A6	30	68.45		1.55		0%	0%	5%	21%	41%	59%	68%	68%
M9	A6	29.25	67.71		1.54	1.5	0%	0%	4%	19%	41%	59%	68%	68%
M10	A6	29	67.47		1.53	2	0%	0%	3%	18%	41%	59%	69%	69%
M11	A6	28.75	67.22		1.53	2.5	0%	1%	5%	19%	41%	58%	65%	65%
M12	A6	29.25		67.71	3.04		0%	1%	7%	22%	45%	59%	66%	66%
M13	A2	27	61.60		9.48	3.27	1%	1%	2%	11%	31%	54%	67%	67%
M14	A2	24	54.76		18.96	3.49	1%	0%	2%	10%	30%	50%	65%	65%
M15	A2	21	47.91		28.44	3.70	0%	0%	2%	10%	24%	45%	63%	63%
M16	A2	18	41.07		37.92	3.92	2%	1%	3%	9%	20%	40%	61%	61%
M17	A8/A9 (1:2)	29	67.96		3.04		0%	1%	5%	20%	39%	56%	57%	65%
M18	A8/A9 (1:1)	29	67.96		3.04		0%	1%	5%	18%	38%	57%	65%	65%

Block copolymer Mixture	Parts of A	Parts of B1	Parts of B2	Parts of C	Parts of S (40°C)	Parts of S (50°C)	Parts of S (60°C)	Parts of S (70°C)	Parts of S (80°C)	Parts of S (90°C)	Parts of S (100°C)
A8/A9 (2:1)	29	67.96	.	3.04	0%	0%	4%	16%	37%	57%	66%
M19	29	67.96	.	3.04	0%	1%	9%	24%	42%	61%	68%
M20	29	67.96	.	3.04	0%	1%	8%	21%	41%	61%	68%
A8/A10 (1:2)	29	67.96	.	3.04	0%	1%	7%	20%	39%	55%	63%
M21	29	67.96	.	3.04	0%	1%	12%	26%	41%	55%	66%
A8/A10 (1:1)	29	67.96	.	3.04	0%	1%	7%	20%	39%	55%	63%
M22	29	67.96	.	3.04	0%	1%	13%	25%	39%	54%	65%
C1	29	67.96	.	3.04	0%	1%	18%	30%	48%	65%	72%
C2	29	67.96	.	3.04	0%	1%	25%	37%	54%	65%	72%
C3	29	67.96	.	3.04	0%	1%	32%	44%	62%	72%	78%
C4	29	67.96	.	3.04	0%	1%	38%	50%	68%	78%	82%
C5	29	67.96	.	3.04	0%	1%	44%	56%	74%	84%	88%
C6	29	67.96	.	3.04	0%	1%	50%	62%	80%	90%	94%

WHAT IS CLAIMED IS:

1. A mixture comprising:
 - a) from 5 to 50% by weight of a block copolymer A which comprises one or more copolymer blocks $(B/S)_A$ each composed of from 65 to 95% by weight of vinylaromatic monomers and from 35 to 5% by weight of dienes and of a glass transition temperature Tg_A in the range from 40° to 90°C,
 - b) from 95 to 50% by weight of a block copolymer B which comprises at least one hard block S composed of vinylaromatic monomers and comprises one or more copolymer blocks $(B/S)_B$ each composed of from 20 to 60% by weight of vinylaromatic monomers and from 80 to 40% by weight of dienes and of a glass transition temperature Tg_B in the range from -70° to 0°C,
 - c) from 0 to 45% by weight of polystyrene or of a block copolymer C other than A and B, and
 - d) from 0 to 6% by weight of a plasticizer.
2. The mixture according to claim 1, which comprises:
 - a) from 20 to 40% by weight of the block copolymer A,
 - b) from 80 to 60% by weight of the block copolymer B, and
 - c) from 0 to 20% by weight of polystyrene or of a block copolymer C other than A and B.
3. The mixture according to claim 1 or 2, wherein the copolymer block $(B/S)_A$ of the block copolymer A has a number-average molar mass M_n in the range from 50 000 to 150 000 g/mol.

4. The mixture according to any one of claims 1 to 3, wherein the copolymer block $(B/S)_A$ of the block copolymer A has a glass transition temperature in the range from 50° to 70°C.

5. The mixture according to any one of claims 1 to 4, wherein the block copolymer A is composed of one copolymer block $(B/S)_A$.

6. The mixture according to any one of claims 1 to 4, wherein the block copolymer A has the structure $S-(B/S)_A-S$, where S is a hard block composed of vinylaromatic monomers.

7. The mixture according to any one of claims 1 to 6, wherein the copolymer blocks $(B/S)_A$ and $(B/S)_B$ of the block copolymers A and B have random distribution of the vinylaromatic monomers and dienes.

8. The mixture according to any one of claims 1 to 7, wherein the block copolymer B has a star-shaped structure having at least two terminal hard blocks S_1 and S_2 with different molecular weight composed of vinylaromatic monomers, and the proportion of the entirety of the hard blocks S is at least 40% by weight, based on the entire star-shaped block copolymer B.

9. The mixture according to claim 8, wherein the star-shaped block copolymer B has terminal blocks S_1 with a number-average molar mass M_n in the range from 5000 to 30 000 g/mol and S_2 with a number-average molar mass M_n in the range from 35 000 to 150 000 g/mol.

10. The use of the mixture according to any one of claims 1 to 9 for production of shrink films.

11. A shrink film, produced from a mixture according to any one of claims 1 to 9.