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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: THERMOPLASTIC BLOCK COPOLYESTER ELASTOMER

(57) Abstract: The invention relates to a novel block copolyester elastomer comprising hard segments derived from at least one alkylene glycol and at least one aromatic dicarboxylic acid, and soft segments of a triblock copolymer containing one, optionally hydrogenated, polyalkadiene block and two poly(alkylene oxide) blocks. The novel block copolyester elastomer shows typical elastomeric properties and a very good water vapour permeability, but without the drawback of high water absorption. The invention also relates to a process for the preparation of the triblock copolymer from a polyalkadiene diol and at least one alkylene oxide, and to the use of the triblock copolymer as a soft segment in block copolymer elastomers.

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THERMOPLASTIC BLOCK COPOLYESTER ELASTOMER

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The invention relates to a thermoplastic block copolyester elastomer comprising hard segments composed of units derived from at least one alkylene glycol and at least
10 one aromatic dicarboxylic acid, and soft segments of a triblock copolymer containing one, optionally hydrogenated, polyalkadiene block and two poly(alkylene oxide) blocks, which segments are linked to each other by ester bonds.

The invention also relates to a triblock
15 copolymer, the preparation of the triblock copolymer, its use as a soft segment and the preparation of the thermoplastic block copolyester elastomer.

Thermoplastic block copolyether ester elastomers with hard segments composed of units derived from at least one
20 alkylene glycol and at least one aromatic dicarboxylic acid and with soft segments derived from at least one polyalkylene oxide are known and are described extensively in for instance Chapter 8 of the book entitled "Thermoplastic Elastomers", ed. by G. Holden et al., 2nd ed. (1996) from Hanser Verlag,
25 Munich, Vienna and New York, ISBN 1-56990-205-4.

The known block copolyether esters find application in many areas and offer advantages over other thermoplastic elastomers, e.g. due to better processability as a result of the presence of the rapidly crystallising
30 polyester hard segments.

An important area of application is that of breathable films, i.e. films that are permeable to water vapour, but impermeable to water. Such films find application in sanitary products such as diapers, in surgical protective
35 clothing, in rainproof clothing, in tent cloth and as sheets in roofing and housing constructions. In order to ensure a

good water vapour permeability the film used in these products should be very thin. In order to retain sufficient mechanical strength, such films are mostly applied onto a fabric or a non-woven carrier, for instance a polyester fabric.

5 The water vapour permeability of the film can be influenced in various manners by the chemical composition of the polyether ester block copolymer. A low hard segment : soft segment ratio has a favourable effect on the water vapour permeability. However, the processability of such a material
10 into film is adversely affected. In presently current commercial film materials the aim is to have the lowest possible C:O ratio in the polyether soft segments. This is achieved by applying the highest possible content of units based on polyethylene oxide. However, the drawback then
15 encountered is the high water absorption capacity of the film, which results in swelling and a considerable decline in mechanical properties in case of prolonged contact with water.

 The object of the invention therefore is to provide a material which exhibits improved water vapour
20 permeability, but does not have said restrictions or only to a much lesser extent. This object is achieved with the thermoplastic block copolyester elastomer defined in the first paragraph.

 Another advantage of the block copolyester
25 elastomers according to the invention is that they show surprisingly good mechanical properties, in particular very good elastic properties. It has been observed that for example tension set, i.e. the residual deformation after relaxation of an initially elongated sample is significantly lower than with
30 known a block copolyether ester elastomer with similar length of the polyester hard soft segment.

 Still another advantage of the block copolyester elastomers according to the invention is that they retain much of their mechanical properties at low temperatures, until just

above the glass transition of the polyalkadiene blocks.

The improved mechanical properties are not only of advantage for said applications as breathable films, but also for other applications, like for example boots and
5 bellows, tubes and hoses, sheets, films and fibers.

The alkylene glycol preferably used is a C₂-C₆ alkylene glycol, for instance ethane diol, 1,3-propane diol and 1,4-butane diol. Suitable aromatic dicarboxylic acids are for example terephthalic acid, 1,6-naphthalene dicarboxylic
10 acid, 4,4'-diphenyl dicarboxylic acid and, to a lesser extent, isophthalic acid or mixtures of these dicarboxylic acids. Particularly suitable as hard segment is for instance polybutylene terephthalate, because of its favourable crystallisation behaviour.

15 The polyalkadiene blocks in the soft segments are preferably derived from butadiene or isoprene; but in general C₃-C₈ alkadienes are suitable. The polyalkadienes are preferably, at least partly, hydrogenated. Advantages thereof are better low temperature properties, e.g. a lower glass
20 transition, and better properties at elevated temperatures, e.g. improved thermal-oxidative stability.

The poly(alkylene oxide) blocks are by preference derived from one or more alkylene oxides chosen from the group comprising C₂-C₄ alkylene oxides. Most preferred are ethylene
25 oxide and propylene oxide or combinations of these, because of their hydrophilicity/polarity.

The invention also relates to a triblock copolymer containing one, optionally hydrogenated, polyalkadiene block and two poly(alkylene oxide) blocks, characterised in that the
30 poly(alkylene oxide) blocks have a number-averaged molecular weight of less than 5000 g/mol.

In JP-A-62 232493 a triblock copolymer containing one polybutadiene block and two poly(alkylene oxide) blocks is disclosed, but without said selection of molecular weight. In

this accidental anticipation the triblock copolymer is used as a dispersion aid to make coal/water slurry compositions with a high concentration of coal.

The present invention therefore also relates to
5 the use of a triblock copolymer containing one, optionally hydrogenated, polyalkadiene block and two poly(alkylene oxide) blocks as a soft segment for the preparation of block copolymer elastomers. These block copolymers generally are thermoplastic in nature, although some crosslinking may have
10 taken place. Examples of such elastomers are segmented block copolymers comprising hard segments derived from a polycondensation polymer. Suitable polycondensation polymers include for example polyurethanes, polyamides, or polyesters. Especially polyesters are preferred in view of the favourable
15 combination of properties of the resulting block copolyester elastomers.

The invention also relates to a process for the preparation of the triblock copolymer containing one polyalkadiene block and two poly(alkylene oxide) blocks,
20 starting from hydroxy-terminated (optionally hydrogenated) polyalkadiene and at least one alkylene oxide, comprising:

a) reaction of the hydroxy-terminated, optionally hydrogenated, polyalkadiene with an organic compound, whereby the terminal hydroxyl groups are substituted by groups that
25 initiate anionic ring-opening polymerisation, and

b) started by the initiator groups introduced in step a), anionic ring-opening polymerisation of the at least one alkylene oxide on the (hydrogenated) polyalkadiene until a desired poly(alkylene oxide) block length has been obtained.

30 In JP-A-62 232493 preparation of a triblock copolymer containing one polybutadiene block and two poly(alkylene oxide) blocks via addition polymerisation in general is indicated. The anionic ring-opening polymerisation process of the present invention has the advantage that the

block length of the poly(alkylene oxide) can be well controlled.

For the anionic ring-opening polymerisation any suitable initiator group, which can be substituted for the hydroxyl group in the hydroxy-terminated, optionally hydrogenated polyalkadiene, can in principle be used, for instance radical anions, alkali metal hydroxides, alkali metal alkyls, alkali metal aryls, alkali salts of aromatic amines, (carbazole derivatives), or tetraphenyl porphyrine Al-complexes. Anionic ring-opening polymerisation is described extensively for instance in "Comprehensive Polymer Science", Vol. 3, Chapter 32, Pergamon Press, Oxford (1989), pp. 467 ff. and in the contribution from S.S. Pomkowski and A. Dude, Anionic Ring-opening Polymerization, in "Ring-opening polymerization", D.J. Brunelle, ed., Hanser Verlag, Munich (1993) pp. 87. ff.

The length of the blocks in the triblock copolymer can vary within wide limits. Especially for use as soft segment in block copolymer elastomers, this length is preferably chosen such that the polyalkadiene segment shows entanglement, while the poly(alkylene oxide) blocks show no entanglement. The number-averaged molecular weight, M_n , of the hydroxy-terminated polyalkadiene started from is therefore preferably at least 2,000, more preferably at least 3,000 g/mol., The number-averaged molecular weight, M_n , of the poly(alkylene oxide) blocks is preferably less than 5,000, more preferably less than 3,000 and still more preferably less than 2,000 g/mol. A minimum value of M_n of the poly(alkylene oxide) blocks of 500 is preferred to give the triblock copolymer some polar character. The number-averaged molecular weight of the triblock copolymer preferably varies between approx. 4,500 and 13,000 g/mol, more preferably between 5,000 and 10,000 g/mol.

The block copolyester elastomer according to the

invention can subsequently be obtained by a process similar to the process for the preparation of polyether ester block copolymer according to the state of the art, as described for instance in the above-mentioned reference in the book

5 'Thermoplastic Elastomers'.

The process for the preparation of the thermoplastic block copolyester elastomer according to the invention, starting from the triblock copolymer containing one, optionally hydrogenated, polyalkadiene block and two
10 poly(alkylene oxide) blocks, derived from at least one polyalkadiene and at least one alkylene oxide, and at least one alkylene glycol and at least one aromatic dicarboxylic acid or an ester thereof, comprises

a) a transesterification reaction at about 200°C
15 at atmospheric pressure and optionally in the presence of a transesterification catalyst, in which process volatile reaction products are removed by distillation and a low-molecular prepolymerizate is formed, followed by

b) polycondensation at a temperature of about
20 250°C and reduced pressure, in which process volatile compounds are removed until a product having the desired molecular weight is obtained.

The proportions of the starting materials in step a) are chosen such that the desired ratio between hard and
25 soft segments in the end product is obtained. The hard : soft segments weight ratio is normally between 10:90 and 90:10, preferably between 15:85 and 80:20, still more preferably between 20:80 and 50:50.

Any current transesterification and
30 polycondensation catalyst can be used as catalyst, for instance Ti-tetraisoibutoxide. The transesterification and polycondensation reactions are preferably carried out in the presence of a thermal-oxidative stabiliser. Suitable antioxidants are for instance sterically hindered phenolic

compounds such as IRGANOX® 1330 from Ciba.

The invention will now be elucidated with reference to the following example, without however being limited thereto.

5

Chemicals used:

- Hydroxy-terminated hydrogenated polybutadiene KRATON LIQUID® Polymer HPVM-2203, from Shell, Mn = approx. 3600, OH functionality approx. 1.9. Dried by freeze-drying with
10 benzene.
- Ethylene oxide 3.0, Linde $\geq$ 99.90%, dried over CaH₂
- Tetrahydrofuran, water-free (THF)
- 1,4-butane diol
- dimethyl terephthalate
- 15 - potassium naphthalide, obtained by reacting potassium with naphthalene in tetrahydrofuran (0.4 mmol/l)
- titanium tetraisobutoxide Ti(OBu)₄
- IRGANOX® 1330

20 Synthesis of the triblock copolymer

The polymerisation reactions were carried out in a 1- or 3-litre glass autoclave, Büchi make.

The KRATON HPVM-2203, to be referred to in the following shortly as 'polybutadiene diol', was dissolved in
25 water-free THF to an end-group content of approx. 10 mmol/l and supplied in a known quantity to the reactor.

Then, using a syringe, the potassium naphthalide solution was added slowly and with stirring at 30°C until a permanent green coloration persisted, i.e. for at least 45
30 minutes.

Next, the reactor was cooled to 0°C and the required amount of ethylene oxide was supplied to the reactor at a slight underpressure. This resulted in an immediate decoloration of the reaction solution. The solution was heated

to 55°C. The polymerisation was terminated after 4 days through the addition at room temperature of a 1:5 mixture (vol/vol) mixture of methanol and acetic acid. The reactor contents were filtered and concentrated by means of a rotary
5 evaporator. After removal of acetic acid by azeotropic distillation with toluene the crude product was dissolved in chloroform and extracted with distilled water. After drying over water-free sodium sulphate the chloroform is evaporated. The resulting product, as an approximately 10% solution in
10 THF, was precipitated in a 10-fold excess of acetone at -30°C, filtered off and dried for more than one day at 40°C in vacuum.

With quantities of some tens of grams this process already gave yields of 85% of the theoretical value.

15 By means of differential scanning calorimetry (DSC) the transition temperatures, T_{ons} , T_{m} and T_{g} as well as ΔH_{m} of the triblock copolymers obtained were determined. T_{ons} is the onset temperature at which the polyethylene oxide block starts to melt, T_{m} the maximum in the melt transition and T_{g}
20 the glass transition temperature and ΔH_{m} the melt enthalpy. In Table 1 are also given the calculated average length of the polyethylene oxide blocks and the lengths derived from NMR measurements by correlating the integrals on the basis of the signal at $\delta = 0.85$ ppm and the average molecular weight $M_{\text{n}} =$
25 3590 of the polybutadiene diol.

Table 1

No.	Com-pound	M_n (PEO) _{theor.} [g/mol]	M_n (PEO) _{NMR} [g/mol]	T_{Ons} [°C]	T_m [°C]	ΔH_m [J/g]	T_g [°C]
0	PB	[3590]	-	-	-	-	-
I	72/28	4470	4600	46.55	53.67	110.22	-61.94
II	58/42	2340	2510	40.32	44.27	86.15	-63.84
III	54/46	1980	2190	35.17	39.67	79.04	-66.06
IV	50/50	1430	1730	33.47	38.26	71.07	-64.31
V	44/56	1280	1380	29.45	35.93	63.33	-62.15
VI	36/64	990	1000	23.18	29.83	42.42	-60.95
VII	32/68	800	820	14.07	24.43	36.99	-61.17
VIII	26/74	620	610	-2.30	22.69	23.90	-67.63

Synthesis of the copolyester elastomers

The synthesis was carried out via a two-step melt polycondensation in the presence of titanium tetrabutoxide as a transesterification and polycondensation catalyst and
5 Irganox® 1330 as a thermal-oxidative stabilizer. In the first step of the polycondensation the reactor mixture was heated at atmospheric pressure at 190, 210 en 220°C successively, each time for 1 hour, with the methanol forming in the transesterification being distilled off. In the subsequent
10 second step of the polycondensation the temperature was raised to 230-250°C and the excess of butanol was removed under reduced pressure ($2-5 \cdot 10^{-2}$ mbar). After about 2.5 hours the polycondensation was stopped.

Table 2 presents an overview of the synthesised
15 copolyester elastomers. The nomenclature is based on the weight proportion of the PBT and the length of the polyethylene oxide blocks of the triblock copolymer used. The yield was in virtually all cases more than 95% with reference to the theoretical value. The thermal transition points were
20 determined by means of DSC (20°C/min).

Dumb-bell-shaped specimens were made of the various polymers for testing on an Instron 5565 tensile test machine at room temperature.

Table 2

Composition	T _{m1} [°C]	ΔH _{m1} [J/g]	T _{m2} [°C]	ΔH _{m2} [J/g]	T _g [°C]
PBT50-4600	32.2	19.3	209.9	15.1	-64.6
PBT50-2510	30.2	15.5	216.4	16.9	-60.8
PBT50-2190	25.1	11.6	217.6	15.1	-58.7
PBT50-1730	17.2	11.1	217.4	15.6	-59.8
PBT50-2190	19.8	11.3	212.2	18.5	-66.3
PBT40-2510	23.8	20.2	210.2	11.8	-65.7
PBT40-1730	12.5	14.7	208.8	10.1	-65.5
PBT40-1380	6.99	9.62	207.7	9.15	-66.1
PBT30-1380	3.81	11.0	202.5	10.4	-66.5
PBT20-1380	13.5	15.1	184.0	6.29	-60.3
PBT40-1000	3.74	2.35	212.6	10.4	-60.5
PBT30-1000	6.24	3.25	217.8	7.46	-59.9
PBT20-1000	2.81	3.33	192.1	4.11	-60.1
PBT10-1000	8.48	11.2	-	-	-59.9
PBT40-820	-	-	213.8	13.1	-59.9
PBT30-820	-	-	212.4	6.89	-59.7

In the range of 3-4% strain a drawing rate of 0.2
5 mm/s was chosen in order to determine the modulus of
elasticity. Then the rate was increased to 20 mm/s and
measurement was continued until the specimen failed. (Table 3)
(Figure 1)

Table 3

Probe	E[GPa]	σ_R [MPa]	ϵ_R [%]
PBT40-1000	1.27×10^{-2} (5.7×10^{-4})	11.0 (1.3)	370 (99)
PBT30-1000	1.05×10^{-2} (7.3×10^{-4})	10.8 (0.4)	670 (57)
PBT20-1000	7.02×10^{-3} (1.3×10^{-3})	9.32 (0.5)	980 (55)
PBT10-1000	3.94×10^{-3} (1.1×10^{-4})	3.72 (0.3)	450 (58)
PBT40-820	1.87×10^{-2} (3.1×10^{-3})	11.4 (1.2)	400 (50)
PBT30-820	1.31×10^{-2} (1.8×10^{-3})	8.98 (0.4)	490 (37)

5 Figure 1 shows the stress-strain diagrams of some copolyester elastomers: (■) PBT40-1000, (●) PBT30-1000, (▲) PBT20-1000, (▼) PBT10-100.

On sample PBT20-1000 some additional tensile tests were performed. The sample was initially elongated to 500%,
 10 and subsequently the stress was released. The sample was allowed to relax after which an elastic recovery of 397%, i.e. a tension set of 103%, was observed. This points to a significant improvement in elastic properties compared to a known copolyether ester containing polyester hard segments of
 15 similar length.

Further the water absorption (swelling) of a large number of samples was determined by keeping specimens submerged in water for 3 weeks at room temperature and measuring their increase in weight. Figure 2 shows the
 20 dependence of the water absorption, i.e. weight increase in %, of the proportion by weight of the triblock copolymer [%] and the block length of the PEO (g/mol).

From the results it appears that the copolyester elastomers in the tensile test show the typical behaviour of a
 25 thermoplastic elastomer. There is a clear separation between the different phases in the copolyester, as a result of which

the water vapour migration in the polyethylene oxide phase is promoted. The water absorption of the novel copolyester elastomer is low in spite of a high content of high-molecular polyethylene oxide in the segments.

C L A I M S

- 5 1. A thermoplastic block copolyester elastomer comprising
hard segments composed of units derived from at least
one alkylene glycol and at least one aromatic
dicarboxylic acid, and soft segments of a triblock
10 copolymer containing one, optionally hydrogenated,
polyalkadiene block and two poly(alkylene oxide) blocks.
2. A triblock copolymer containing one, optionally
hydrogenated, polyalkadiene block and two poly(alkylene
oxide) blocks, characterised in that the poly(alkylene
oxide) blocks have a number-averaged molecular weight of
15 less than 5000 g/mol.
3. A process for the preparation of a triblock copolymer
containing one, optionally hydrogenated, polyalkadiene
block and two poly(alkylene oxide) blocks, starting from
hydroxy-terminated, optionally hydrogenated,
20 polyalkadiene and at least one alkylene oxide,
comprising
- a) reaction of the hydroxy-terminated polyalkadiene with
a compound, whereby the terminal hydroxyl groups are
substituted by groups that initiate anionic ring-opening
25 polymerisation of alkylene oxides, and
- b) started by the initiator groups introduced in step
a), anionic ring-opening polymerisation of the at least
one alkylene oxide on the polyalkadiene until a desired
poly(alkylene oxide) block length has been obtained.
- 30 4. Use of a triblock copolymer containing one, optionally
hydrogenated, polyalkadiene block and two poly(alkylene
oxide) blocks as a soft segment for the preparation of
block copolymer elastomers.
5. A block copolymer elastomer comprising hard segments

derived from a polycondensation polymer and soft segments of a triblock copolymer containing one, optionally hydrogenated, polyalkadiene block and two poly(alkylene oxide) blocks.

- 5 6. The block copolymer elastomer according to claim 5, characterised in that the polycondensation polymer is chosen from the group consisting of polyurethanes, polyamides, and polyesters.
7. The thermoplastic block copolyester elastomer according
10 to claim 1, characterised in that the hard segments consist of polybutylene terephthalate.
8. The thermoplastic block copolymer elastomer according to claim 1 or 7, characterised in that the polyalkadiene block is derived from butadiene or isoprene.
- 15 9. The thermoplastic block copolyester elastomer according to any one of claims 1, 7-8, characterised in that the poly(alkylene oxide) blocks are derived from one or more alkylene oxides from the group consisting of ethylene oxide, propylene oxide and tetramethylene oxide.
- 20 10. The thermoplastic block copolyester elastomer according to any one of claims 1, 7-9, characterised in that the soft : hard segments weight ratio lies between 90:10 and 20:80.
11. The thermoplastic block copolyester elastomer according
25 to any one of claims 1, 7-10, characterised in that the number-averaged molecular weight of the poly(alkylene oxide) blocks lies between 500 and 5,000 g/mol.
12. The thermoplastic block copolyester elastomer according to any one of claims 1, 7-11, characterised in that the
30 number-averaged molecular weight of the polyalkadiene block is at least 2,000 g/mol.
13. A process for the preparation of the thermoplastic block copolyester elastomer according to claim 1, comprising a) a transesterification reaction at about 200°C at

atmospheric pressure and optionally in the presence of a transesterification catalyst, in which process volatile reaction products are removed by distillation and a low-molecular prepolymerizate is formed,

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followed by

- b) polycondensation at a temperature of about 250°C and strongly reduced pressure, in which process volatile compounds are removed until a product having the desired molecular weight is obtained.

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INTERNATIONAL SEARCH REPORT

Intern 1al Application No

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A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08G63/672 C08G63/00 C08G65/26 C08G18/69 C08G18/62
C08G69/40

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08G

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

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	PATENT ABSTRACTS OF JAPAN vol. 013, no. 105 (C-575), 13 March 1989 (1989-03-13) & JP 63 278926 A (SUNSTAR GIKEN KK), 16 November 1988 (1988-11-16) abstract ---	2,4-6
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Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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Date of the actual completion of the international search

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Date of mailing of the international search report

03/11/2000

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INTERNATIONAL SEARCH REPORT

International Application No

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Information on patent family members

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