In the rubber composition of the present invention, the block copolymer (A) has two glass transition temperatures separated from each other by 5°C or more, preferably from 10°C or more within a range of -100 to 20°C in measurement with ASTM D3418.

Of the two glass transition temperatures, one is a transition temperature of the polymer block (a-1) and the other one is a transition temperature of the polymer block (a-2~~1~~).

The glass transition temperature of the polymer block (a-1) is preferably from -60 to 20°C, more preferably from -50 to 10°C.

The glass transition temperature of the polymer block (a-2) is preferably from -100°C to -30°C, more preferably from -90 to -40°C.

[0027]

When the glass transition temperature of the polymer block (a-1) is lower than -60°C, the wet skid resistance is remarkably deteriorated. On the other hand, when the glass transition temperature of the polymer block (a-1) exceeds 20°C, the low hysteresis loss property is remarkably deteriorated.

Also, when the glass transition temperature of the polymer block (a-2) is lower than -100°C, the wet skid resistance is remarkably deteriorated. On the other hand, when the glass transition temperature of the polymer block (a-2) exceeds -30°C, the low hysteresis loss property is remarkably deteriorated.

Moreover, when a difference between the glass transition temperature of the polymer block (a-1) and the glass transition temperature of the polymer block (a-2) is less than 5°C, the low hysteresis loss property and the tensile strength are deteriorated.

The glass transition temperatures of the polymer block (a-1) and the polymer block (a-2) can be controlled by changing the ratio of the structural unit of the aromatic vinyl compound in the total structural units of each block and the content of 1,2-vinyl bonds.

[0028]

Moreover, the ratio of the structural unit derived from an aromatic vinyl compound in the total structural units of the polymer block (a-1) is preferably from 20 to 60% by mass, more preferably from 25 to 55% by mass. When the ratio is less than 20% by mass, there is a possibility that the fracture characteristic and the wet skid resistance are remarkably deteriorated.

[0029]

Also, the ratio of the structural unit derived from an aromatic vinyl compound in the total structural units of the polymer block (a-2) is preferably 30% by mass or

polymerization temperature reached 70°C, the reactor was cooled and the temperature in the reactor was maintained at 70°C.

After reaching the polymerization conversion rate 99%, 10 g of a prepolymer solution was sampled from the resulting prepolymer solution as a solution for measuring the molecular weight and micro structure of the polymer block (a-1).

(2) Second Polymerization Step

Then, 12.5 g of styrene and 102.5 g of 1,3-butadiene were added into the reactor at 70°C for a period of 40 minutes. After reaching the polymerization conversion rate 99%, 10 g of 1,3-butadiene was further added into the reactor and polymerization was further conducted for 5 minutes. Thereafter, 10 g of an unmodified polymer solution was sampled from the resulting unmodified polymer solution as a solution for measuring the molecular weight and micro structure.

(3) Polymer Modification Step

Then, a cyclohexane solution containing 4.96 mmol of N,N-bis(triethylsilyl)aminopropylmethyldimethoxysilane (hereinafter referred to as a "compound (1) for functional group introduction") was added as a polymerization terminator into the reactor, followed by reaction for 15 minutes. Subsequently, 2.0 g of 2,6-di-tert-butyl-p-cresol was added to a polymer solution after the reaction. Thereafter, solvent removal was performed by steam stripping with using hot water and then, a drying treatment was performed with a hot roll controlled to 110°C to obtain a block copolymer (A). The block copolymer (A) was referred to as "polymer (A1)".

The following Table 1 shows the bound styrene content, vinyl bond content, glass transition temperature, and weight average molecular weight of each of the polymer block (a-1) and the polymer block (a-2~~1~~) in the resulting polymer (A1) and the bound styrene content, vinyl bond content, and weight average molecular weight of the whole polymer (A1).

[0056]

Synthetic Example 2

(1) First Polymerization Step

Into an autoclave reactor having an internal volume of 5 liters, in which the atmosphere was replaced with nitrogen, 2,750 g of cyclohexane, 2.80 mmol of 2,2-di(tetrahydrofuryl)propane, 125 g of styrene, and 175 g of 1,3-butadiene were charged. After adjusting the temperature in the reactor to 35°C, a cyclohexane solution containing 4.92 mmol of n-butyllithium was added thereto to conduct polymerization. At the time when polymerization temperature reached 70°C, the reactor was cooled

and the temperature in the reactor was maintained at 70°C.

After reaching the polymerization conversion rate 99%, 10 g of a prepolymer solution was sampled from the resulting prepolymer solution as a solution for measuring the molecular weight and micro structure of the polymer block (a-1).

(2) Second Polymerization Step

Then, 190 g of 1,3-butadiene was added into the reactor at 70°C over a period of 40 minutes. After reaching the polymerization conversion rate 99%, 10 g of 1,3-butadiene was further added into the reactor and polymerization was further conducted for 5 minutes. Thereafter, 10 g of an unmodified polymer solution was sampled from the resulting unmodified polymer solution as a solution for measuring the molecular weight and micro structure.

(3) Polymer Modification Step

Then, a cyclohexane solution containing 4.96 mmol of N,N-bis(triethylsilyl)aminopropylmethyldimethoxysilane was added as a polymerization terminator into the reactor, followed by reaction for 15 minutes. Subsequently, 2.0 g of 2,6-di-tert-butyl-p-cresol was added to a polymer solution after the reaction. Thereafter, solvent removal was performed by steam stripping with using hot water and then, a drying treatment was performed with a hot roll controlled to 110°C to obtain a block copolymer (A). The block copolymer (A) was referred to as "polymer (A2)".

The following Table 1 shows the bound styrene content, vinyl bond content, glass transition temperature, and weight average molecular weight of each of the polymer block (a-1) and the polymer block (a-2~~1~~) in the resulting polymer (A2) and the bound styrene content, vinyl bond content, and weight average molecular weight of the whole polymer (A2).

[0057]

Synthetic Example 3

(1) First Polymerization Step

Into an autoclave reactor having an internal volume of 5 liters, in which the atmosphere was replaced with nitrogen, 2,750 g of cyclohexane, 2.80 mmol of 2,2-di(tetrahydrofuryl)propane, 75 g of styrene, and 125 g of 1,3-butadiene were charged. After adjusting the temperature in the reactor to 35°C, a cyclohexane solution containing 4.92 mmol of n-butyllithium was added thereto to conduct polymerization. At the time when polymerization temperature reached 70°C, the reactor was cooled and the temperature in the reactor was maintained at 70°C.

After reaching the polymerization conversion rate 99%, 10 g of a prepolymer

solution was sampled from the resulting prepolymer solution as a solution for measuring the molecular weight and micro structure of the polymer block (a-1).

(2) Second Polymerization Step

Then, 50 g of styrene and 240 g of 1,3-butadiene were added into the reactor at 70°C over a period of 40 minutes. After reaching the polymerization conversion rate 99%, 10 g of 1,3-butadiene was further added into the reactor and polymerization was further conducted for 5 minutes. Thereafter, 10 g of an unmodified polymer solution was sampled from the resulting unmodified polymer solution as a solution for measuring the molecular weight and micro structure.

(3) Polymer Modification Step

Then, a cyclohexane solution containing 4.96 mmol of N,N-bis(triethylsilyl)aminopropylmethyldimethoxysilane was added as a polymerization terminator into the reactor, followed by reaction for 15 minutes. Subsequently, 2.0 g of 2,6-di-tert-butyl-p-cresol was added to a polymer solution after the reaction. Thereafter, solvent removal was performed by steam stripping with using hot water and then, a drying treatment was performed with a hot roll controlled to 110°C to obtain a block copolymer (A). The block copolymer (A) was referred to as "polymer (A3)".

The following Table 1 shows the bound styrene content, vinyl bond content, glass transition temperature, and weight average molecular weight of each of the polymer block (a-1) and the polymer block (a-2~~1~~) in the resulting polymer (A3) and the bound styrene content, vinyl bond content, and weight average molecular weight of the whole polymer (A3).

[0058]

Synthetic Example 4

(1) First Polymerization Step

Into an autoclave reactor having an internal volume of 5 liters, in which the atmosphere was replaced with nitrogen, 2,750 g of cyclohexane, 2.80 mmol of 2,2-di(tetrahydrofuryl)propane, 150 g of styrene, and 150 g of 1,3-butadiene were charged. After adjusting the temperature in the reactor adjusted to 35°C, a cyclohexane solution containing 4.92 mmol of n-butyllithium was added thereto to conduct polymerization. At the time when polymerization temperature reached 70°C, the reactor was cooled and the temperature in the reactor was maintained at 70°C.

After reaching the polymerization conversion rate 99%, 10 g of a prepolymer solution was sampled from the resulting prepolymer solution as a solution for measuring the molecular weight and micro structure of the polymer block (a-1).

(2) Second Polymerization Step

Then, 20 g of styrene and 170 g of 1,3-butadiene were added into the reactor at 70°C for a period of 40 minutes. After reaching the polymerization conversion rate 99%, 10 g of 1,3-butadiene was further added into the reactor and polymerization was further conducted for 5 minutes. Thereafter, 10 g of an unmodified polymer solution was sampled from the resulting unmodified polymer solution as a solution for measuring the molecular weight and micro structure.

(3) Polymer Modification Step

Then, a cyclohexane solution containing 4.96 mmol of N,N-bis(triethylsilyl)aminopropylmethyldimethoxysilane was added as a polymerization terminator into the reactor, followed by reaction for 15 minutes. Subsequently, 2.0 g of 2,6-di-tert-butyl-p-cresol was added to a polymer solution after the reaction. Thereafter, solvent removal was performed by steam stripping with using hot water and then, a drying treatment was performed with a hot roll controlled to 110°C to obtain a block copolymer (A). The block copolymer (A) was referred to as "polymer (A4)".

The following Table 1 shows the bound styrene content, vinyl bond content, glass transition temperature, and weight average molecular weight of each of the polymer block (a-1) and the polymer block (a-2~~1~~) in the resulting polymer (A4) and the bound styrene content, vinyl bond content, and weight average molecular weight of the whole polymer (A4).

[0059]

Synthetic Example 5

A block copolymer (A) was obtained in the same manner as in Synthetic Example 2 except that a cyclohexane solution containing 4.96 mmol of 1-(3-triethoxysilylpropyl)-2,2,5,5-tetramethyl-1-aza-2,5-disilacyclopentane (hereinafter referred to as a "compound (2) for functional group introduction") was used instead of the cyclohexane solution containing 4.96 mmol of the compound (1) for functional group introduction. The block copolymer (A) was referred to as "polymer (A5)".

The following Table 1 shows the bound styrene content, vinyl bond content, glass transition temperature, and weight average molecular weight of each of the polymer block (a-1) and the polymer block (a-2~~1~~) in the resulting polymer (A5) and the bound styrene content, vinyl bond content, and weight average molecular weight of the whole polymer (A5).

[0060]

Synthetic Example 6

A block copolymer (A) was obtained in the same manner as in Synthetic Example 2 except that a cyclohexane solution containing 4.96 mmol of 3-(4-trimethylsilyl-1-piperazino)propyltriethoxysilane (hereinafter referred to as a "compound (3) for functional group introduction") was used instead of the cyclohexane solution containing 4.96 mmol of the compound (1) for functional group introduction. The block copolymer (A) was referred to as "polymer (A6)".

The following Table 1 shows the bound styrene content, vinyl bond content, glass transition temperature, and weight average molecular weight of each of the polymer block (a-1) and the polymer block (a-2) in the resulting polymer (A6) and the bound styrene content, vinyl bond content, and weight average molecular weight of the whole polymer (A6).

[0061]

Synthetic Example 7

(1) First Polymerization Step

Into an autoclave reactor having an internal volume of 5 liters, in which the atmosphere was replaced with nitrogen, 2,750 g of cyclohexane, 2.80 mmol of 2,2-di(tetrahydrofuryl)propane, 125 g of styrene, and 175 g of 1,3-butadiene were charged. After adjusting the temperature in the reactor to 35°C, a cyclohexane solution containing 4.92 mmol of n-butyllithium was added thereto to conduct polymerization. At the time when polymerization temperature reached 70°C, the reactor was cooled and the temperature in the reactor was maintained at 70°C.

After reaching the polymerization conversion rate 99%, 10 g of a prepolymer solution was sampled from the resulting prepolymer solution as a solution for measuring the molecular weight and micro structure of the polymer block (a-1).

(2) Second Polymerization Step

Then, 190 g of 1,3-butadiene was added into the reactor at 70°C for a period of 40 minutes. After reaching the polymerization conversion rate 99%, 10 g of 1,3-butadiene was further added into the reactor and polymerization was further conducted for 5 minutes. Thereafter, 10 g of an unmodified polymer solution was sampled from the resulting unmodified polymer solution as a solution for measuring the molecular weight and micro structure.

(3) Polymer Modification Step

Then, a cyclohexane solution containing 4.96 mmol of N,N-bis(triethylsilyl)aminopropylmethyldimethoxysilane was added as a polymerization terminator into the reactor, followed by reaction for 15 minutes.

(4) Onium Salt Formation Step

After adding a cyclohexane solution containing 3.71 mmol of silicon tetrachloride to a polymer solution after the reaction and mixed for 5 minutes, 2.0 g of 2,6-di-tert-butyl-p-cresol was further added tehreto. Thereafter, solvent removal was performed by steam stripping with using hot water and then, a drying treatment was performed with a hot roll controlled to 110°C to obtain a block copolymer (A). The block copolymer (A) was referred to as "polymer (A7)".

The following Table 1 shows the bound styrene content, vinyl bond content, glass transition temperature, and weight average molecular weight of each of the polymer block (a-1) and the polymer block (a-2~~1~~) in the resulting polymer (A7) and the bound styrene content, vinyl bond content, and weight average molecular weight of the whole polymer (A7).

[0062]

Synthetic Example 8

A block copolymer (A) was obtained in the same manner as in Synthetic Example 7 except that a cyclohexane solution containing 4.96 mmol of 1-(3-triethoxysilylpropyl)-2,2,5,5-tetramethyl-1-aza-2,5-disilacyclopentane was used instead of the cyclohexane solution containing 4.96 mmol of N,N-bis(triethylsilyl)aminopropylmethyldimethoxysilane. The block copolymer (A) was referred to as "polymer (A8)". The following Table 1 shows the bound styrene content, vinyl bond content, glass transition temperature, and weight average molecular weight of each of the polymer block (a-1) and the polymer block (a-2~~1~~) in the resulting polymer (A8) and the bound styrene content, vinyl bond content, and weight average molecular weight of the whole polymer (A8).

[0063]

Synthetic Example 9

(1) First Polymerization Step

Into an autoclave reactor having an internal volume of 5 liters, in which the atmosphere was replaced with nitrogen, 2,750 g of cyclohexane, 2.46 mmol of 2,2-di(tetrahydrofuryl)propane, 200 g of styrene, and 200 g of 1,3-butadiene were charged. After adjusting the temperature in the reactor to 35°C, a cyclohexane solution containing 4.92 mmol of n-butyllithium was added thereto to conduct polymerization. At the time when polymerization temperature reached 70°C, the reactor was cooled and the temperature in the reactor was maintained at 70°C.

After reaching the polymerization conversion rate 99%, 10 g of a prepolymer solution was sampled from the resulting prepolymer solution as a solution for measuring the molecular weight and micro structure of the polymer block (a-1).

(2) Second Polymerization Step

Then, 100 g of 1,3-butadiene was added into the reactor at 70°C for a period of 40 minutes. After reaching the polymerization conversion rate 99%, 10 g of 1,3-butadiene was further added into the reactor and polymerization was further conducted for 5 minutes. Thereafter, 10 g of an unmodified polymer solution was sampled from the resulting unmodified polymer solution as a solution for measuring the molecular weight and micro structure.

(3) Polymer Modification Step

Then, a cyclohexane solution containing 4.96 mmol of N,N-bis(triethylsilyl)aminopropylmethyldimethoxysilane was added as a polymerization terminator into the reactor, followed by reaction for 15 minutes. Subsequently, 2.0 g of 2,6-di-tert-butyl-p-cresol was added to a polymer solution after the reaction. Thereafter, solvent removal was performed by steam stripping with using hot water and then, a drying treatment was performed with a hot roll controlled to 110°C to obtain a block copolymer (A). The block copolymer (A) was referred to as "polymer (A9)".

The following Table 1 shows the bound styrene content, vinyl bond content, glass transition temperature, and weight average molecular weight of each of the polymer block (a-1) and the polymer block (a-2~~1~~) in the resulting polymer (A9) and the bound styrene content, vinyl bond content, and weight average molecular weight of the whole polymer (A9).

[0064]

Comparative Synthetic Example 1

(1) Polymerization Step

Into an autoclave reactor having an internal volume of 5 liters, in which the atmosphere was replaced with nitrogen, 2,750 g of cyclohexane, 2.80 mmol of 2,2-di(tetrahydrofuryl)propane, 125 g of styrene, and 365 g of 1,3-butadiene were charged. After adjusting the temperature in the reactor to 10°C, a cyclohexane solution containing 4.92 mmol of n-butyllithium was added thereto to conduct polymerization. Polymerization was carried out under an adiabatic condition, and maximum temperature reached 85°C.

After reaching the polymerization conversion rate 99%, 10 g of 1,3-butadiene was added into the reactor and polymerization was further conducted for 5 minutes. Thereafter, 10 g of an unmodified polymer solution was sampled from the resulting unmodified polymer solution as a solution for measuring the molecular weight and micro structure.