
Development of the Solution SBRs for High-performance Tires.

Sumitomo Chemical Co., Ltd.
Petrochemicals Research Laboratory
Katsunari INAGAKI
Mayumi HAYASHI
Advanced Polymers Division
Akio IMAI

In the latest decade, synthetic rubbers and fillers for automotive tires have been changed drastically. The tendency to make much of “energy saving (fuel economy)” has come to be more remarkable year by year. In order to satisfy this demand, new silica compound systems have been developed in stead of the conventional CB (carbon black) systems for tire tread. In addition, for the purpose of improving the performances of this silica compound systems, precise polymer designs such as the functionalization are needed. Living anionic polymerization procedure is a very useful method to meet this aim. For example, precise chain-end functionalization and multi-functionalization can be achieved.

In this article, the trend in the field of the silica compound system and the polymer design of solution SBRs are surveyed, including the authors’ study on the new multi-functionalization method.

This paper is translated from R&D Report, “SUMITOMO KAGAKU”, vol. 2004-I.

Introduction

With the recent worldwide trend toward conserving resources and environmental protection and the increasing consciousness about safety during the operation of automobiles, there are increasing demands for higher performance in automobile tires, and there is an increasing acceleration of the force behind this. In all of this, a great amount of attention is being paid to performance for reducing fuel costs, and many improvements and much ingenuity are being brought to everything from the basic structure of tires to various materials, with the tire tread, which is the part in contact with the road, playing a large role. The greatest expectations for this part are for tire polymer makers meaning the providing¹⁾ of polymer materials that improve both the fuel saving properties and the road gripping properties, which are diametrically opposed characteristics.

On the other hand, compound designs for automotive tire treads have been transfigured in the last ten years or so, and what is called “silica compounding,” where silica is used as a reinforcing filler in place of the carbon black (reinforcing

filler) that has been used for a long time has taken over the main position, starting in Europe and spreading worldwide, from the standpoint of fuel saving performance and wet skid performance (brake performance on wet roads).

Although silica seems similar to carbon black in particle form, its surface is covered with silanol groups, and compared with carbon black, its affinity for hydrocarbon based polymers is generally low, and kneading is difficult, so there has been a difficulty in that its reinforcing properties are inferior when used as is.

What has appeared as a solution for this are usable silane coupling agents, and these chemically bond silica particles to polymers for which they have a low affinity, so they are becoming a typical means for collectively achieving high-level physical properties. Be that as it may, kneading control is difficult with silane coupling agents in addition to their structures being specific and expensive, so there is a need to develop a grade of polymers that allow for a reduction in the amount of silane coupling agent used. Recently various studies for obtaining even higher performance have been attempted with the development of a new

grade with a polymer structure designed to be optimal for silica compounding, and with the use of microstructure design and modification techniques, the expectations for new solution SBR polymerizations have increased even more.

In this paper, we will give an overview of the current progress in this field, mainly focusing on polymer synthesis and methods for polymer design, including the development of peripheral technology, while touching on research done by the authors.

Changes in SBR for Tires

Styrene-butadiene copolymer rubber (SBR) is representative of the synthetic rubbers used for tires, and the name generally indicates an emulsion SBR obtained through a redox polymerization of styrene and butadiene in an aqueous solution of an emulsifying agent. Because of technical factors such as their being suited to mass production, the polymer grades having been unified internationally, having superior workability among synthetic rubbers, and exhibiting a high-level grip performance (gripping force on the road in wet conditions) that cannot be obtained with natural rubber, emulsion SBR have a history of being widely used as tire tread polymers.

Conversely, solution SBR is a polymer synthesized in a living anionic polymerization reaction where an organic lithium compound is used as a polymerization initiator in a hydrocarbon solvent,

and it has been said that its inferior processability and strength in the formation stage are its weak points. However, there has subsequently been progress in development and studies that make use of the superior structural design properties of living anionic polymerization reactions, and at present, various new polymer grades where molecular structural elements, such as molecular weight distribution, butadiene microstructure, and chemical modification of the ends of molecular chains (“chain end modification” in the following) are precisely controlled, so the idea of using molecular structural design in the development of tire materials has made it into our thinking. Saeki, et al. express this aspect as “the expansion of design freedom with S-SBR,” as is shown in (Fig. 1).²⁾

As was mentioned at the beginning, it has been said that, among the main properties required for tires that save fuel, fuel savings (low rolling resistance and low heat build up) and grip property on road surface are mutually exclusive, but the research group of Saitoh et al. has made the assumption that both characteristics can be improved if the viscoelasticity of curing rubber members, the temperature (or frequency) dependence of dynamic loss (Tan- δ) in particular, can be controlled.³⁾ The differences in the main frequency ranges where the two properties are expressed are shown schematically in (Fig. 2).

Of these two properties, it has been known for a long time from experience that the grip property depends on control of the glass transition tem-

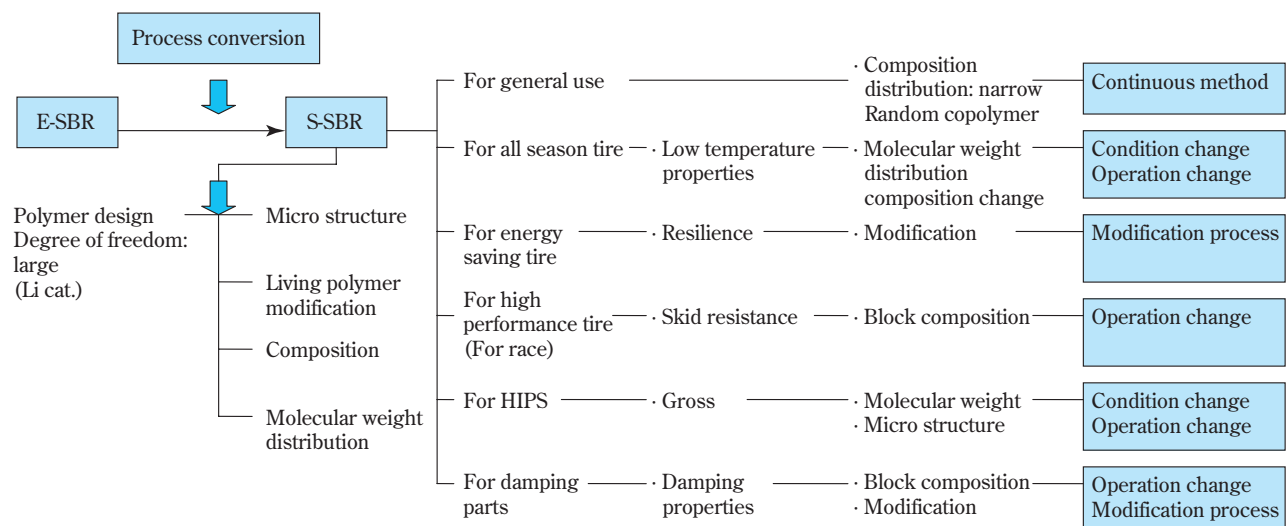


Fig. 1 Expansion of the degree of freedom about the S-SBR designs.

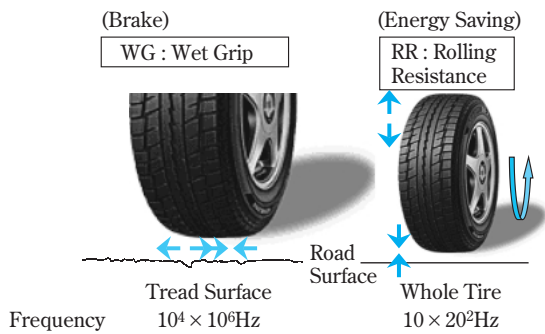


Fig. 2 Wet Grip and Rolling Resistance.

perature of the raw material rubber and polymer,⁴⁾ but on the other hand, the structural factors for polymers that control fuel savings have not been analyzed quantitatively. The authors have shown experimentally that there is a primary correlative relationship between high temperature Tan- δ , which is an index of the fuel saving properties of tire tread rubber and the concentration of long chain end (polymer terminals) per unit volume in tire treads under conditions of identical compounding recipe and cross-linking density^{5a-5e)} and have established a synthesis design technique for SBR solution polymerization that allows for independent control of fuel saving and grip properties. A solution SBR with reduced long chain end concentration developed using the above technique is used widely in automobile tires, but it should be called the “first generation” solution SBR, meaning that it is the first new solution SBR designed for use in tires.

Starting in the latter half of the 1980s, compounds with polar groups have been bonded to SBR long chain polymer terminals and methods for bonding the chain end modified SBR obtained with carbon black as a filler for the purpose of further improving the fuel savings properties have been developed and put into practical use. The authors' studies⁶⁻⁹⁾ have been a part of this, and these chain end modified solution SBR were widely used through the 1990s. There was competition among the various solution SBR makers in Japan, and similar modified terminal SBRs were developed,¹⁰⁾ and the 1990s were the era of “second generation” solution SBR.

Use of Silica Fillers in Tire Tread Compounding

(1) Carbon Black Compounded Rubber

Carbon black has been used as a filler for cured rubber products, starting with tires, for a long time. One reason given for this is the reinforcing effects due to the concerted action of chemical bonding and physical bonding in the interaction of carbon and the polymer.¹¹⁾ With regard to the mechanism for bringing out the reinforcing effects in the kneading process for carbon black compounded rubber, it is known, for example, that the tensile rupture energy increases as more carbon black (HAF) is added to an emulsion SBR.¹²⁾

In this case, the Tan- δ temperature distribution pattern flattens with increases in the amount added, and since the Tan- δ value increases in the high temperature part, tire treads compounded with an excess of carbon have large rolling resistance, and the fuel saving properties are lost.¹³⁾

Various analyses have been done on changing the interaction between carbon and the SBR polymer in the kneading process for carbon black compounded SBR compositions. First, it is presumed that the restriction of polymer molecules by carbon black produces a component with a long stress relaxation time,¹²⁾ and it is thought to be observed as a reduction in the pulse NMR spin-spin relaxation time (T₂).¹³⁾ In addition, it is said that the dispersion structure of carbon black, which forms a network in the compounded composition is destroyed by the kneading energy and Tan- δ increased,¹⁵⁾ and along with the phenomenon of dynamic strain dependency related to the dispersion of a filler, this is known as the “Payne effect.” Furthermore, Fujimoto et al. have gotten a grasp on the progress in uniform distribution and stabilization of higher order rubber-carbon black structures that accompanies progress in the kneading process as changes in the Tan- δ temperature distribution,¹⁶⁾ and the formation of a rubber-carbon black bonded component (bonded rubber, also called “carbon gel” because it is insoluble in solvents¹⁷⁾) is also known.

Therefore, the uniform distribution of carbon black in the compounded rubber is an effective means for reducing the rolling resistance. Furthermore, since the polymer and carbon bonds are formed intentionally, it has been shown that the addition of N,N-bis(2-methyl-2-nitropropyl)-1,6-diaminohexane (trade name: SUMIFINE 1162) lowers Tan- δ in the rolling resistance region.¹⁸⁾

(2) Use of Silica Filler in Compounded Rubber Products

As was described in the previous section, it has been thought that fillers exhibiting little reinforcing effect could not be put to practical use in cured rubber products used under dynamic conditions. For example, since the surface of silica particles is covered with silanol groups, the affinity with polymers is low and sufficient reinforcing properties cannot be obtained, a compound (a so-called silane coupling agent) that chemically bonds to the polymer and silica particles is introduced to compensate for this, and we can finally get a practical level of reinforcement.¹²⁾ In terms of how this relates to tire characteristics, it was discovered in the middle of the 1990s that silica compounded tires achieve a high property balance between both rolling resistance and friction properties on wet road surfaces (**Fig. 3**) when compared with carbon black compounded tires.¹⁸⁾ Therefore, research and development as well as applications development was carried out in various directions presupposing silica compounding, and the developmental concepts have varied widely. We shall only introduce a part of these here, but in terms of their content, we can mention methods related to the silica filler itself, ones specifying silane coupling agents, ones aimed at improving physical properties by combining silica with other specific compounding auxiliaries and specific kneading methods, ones focusing on selection of polymers (structures) suitable for silica compounding and making improvements in polymers (modifications, etc., using various functional groups), and chemical and physical modi-

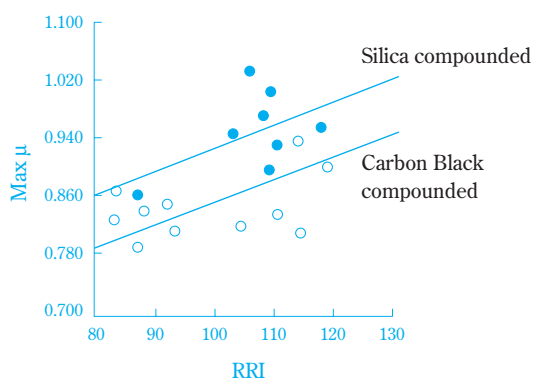


Fig. 3 Max μ (maximum friction coefficient) and RRI (Rolling Resistance Index) on wet asphalt surface.

fications of silica itself.

Optimization of the silica filler itself has been widely investigated, focusing on BET surface area and DBP oil absorption, and while each has its own characteristics,¹⁹⁾ studies of practical applications seem to be converging on ultra fine silica particles with a primary particle diameter of 20nm. The same is true of silane coupling agents, and they are converging on various derivatives for which bis-(3-triethoxysilyl)-tetrasulfide is representative and various modifications of this, but we would like attention to focus on future innovative developments. **Fig. 4** schematically shows the reaction mechanism for typical silane coupling agents (chemical bonding with polymers and silica).

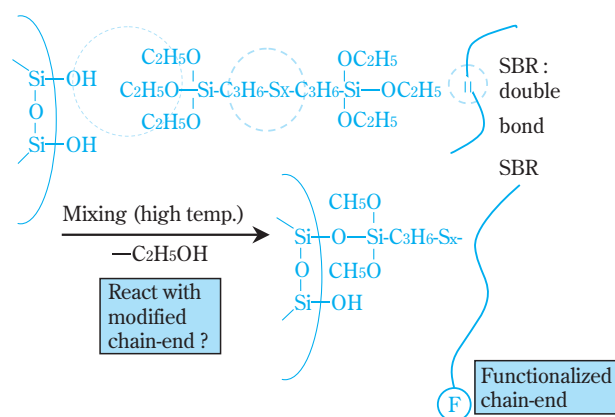


Fig. 4 Chemical reactions between silica and silane-coupling agent.

In addition, as example of compounding auxiliaries, there are organic silicon compounds, of which polysiloxanes containing functional groups are representative, and there are examples showing that the kneading properties of silica and the polymers can be improved for the use of these in silica compounding systems, that is, through the compatibilizer effect of what are called “polymer blends” in attempts to achieve high-level physical properties.²⁰⁾ Specifically, the conclusions are that because the mechanical strength and abrasion resistance are superior and the rolling resistance low with a rapid curing rate, the production efficiency should also be superior (**Tables 1** and **2**).

In a similar test, the method of using a poly(alkylene glycol) oligomer such as polyethylene glycol, which has a high molecular weight, in specific kneading conditions has been proposed,²¹⁾ and it

Table 1

	Example		Comparative Example	
	1	1	2	3
Composition				
(A)				
Kind*1	A1	A1	A1	A1
Amount (wt)	100	100	100	100
Silica	78.5	78.5	78.5	78.5
Amount (wt)				
Silane coupling agent	6.4	6.4	0	0
Amount (wt)				
(D)				
Kind*2	D1	—	D1	—
Amount (wt)	5	0	5	0
Maximum Temperature				
During Kneading (°C)	152	151	153	153
Evaluation				
Tear Strength kgf/cm ²	57	54	46	53
300% Modulus kgf/cm ²	124	121	40	49
Loss on Wearing mg/1000 cycle	370	372	996	564
Tan δ(60°C) Index	100	91	146	111
Vulcanization Velocity t ₉₀ min	16	36	30	35

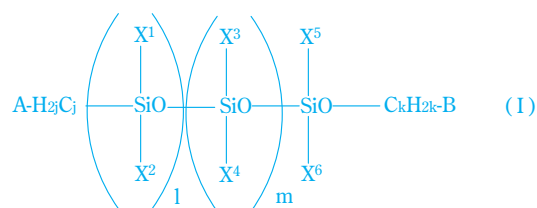
has been shown to have an effect in improving the fuel savings.

(3) Improvements to Silica Fillers

There have been wide ranging developments in attempts at surface processing of the silica itself and hybridization with carbon black. Considering the affinity with non-polar polymers, making the surface of silica hydrophobic is a conventionally known technology, but for example, the use of hexamethyldisilazane to make the silica surface partially hydrophobic makes for an improvement in dispersibility that is not inferior to the conventional.²²⁾ A balance between Tan δ at high temperatures and Tan δ at low temperatures that is equal to or superior to conventional silica systems can be obtained by compounding NR/SBR with a composite filler where silica is precipitated (0.1 to 50%) on the surface of carbon black, and since

Table 2

	Example			
	2	3	4	5
Composition				
(A)				
Kind*1	A2	A2	A2	A2
Amount (wt)	100	100	100	100
Silica	78.5	78.5	78.5	78.5
Amount (wt)				
Silane coupling agent	6.4	6.4	6.4	6.4
Amount (wt)				
(D)				
Kind*2	D1	D1	D1	D1
Amount (wt)	7	5	3	1
Maximum Temperature				
During Kneading (°C)	148	151	150	152
Evaluation				
Tear Strength kgf/cm ²	52	53	54	55
300% Modulus kgf/cm ²	139	143	148	124
Loss on Wearing mg/1000 cycle	335	384	347	395
Tan δ(60°C) Index	94	100	102	101
Vulcanization Velocity t ₉₀ min	18	20	27	27



*1 (A1): a solution polymerized SBR (styrene unit/vinyl unit: 15/45 (wt %/%) ML1+4 125°C = 87) manufactured by adding SiCl₄ as a coupling agent

A2: a solution polymerized SBR (styrene unit/vinyl unit: 29/49 (wt %/%) ML1+4 125°C = 91) manufactured by adding SiCl₄ as a coupling agent

*2: D1: A compound (molecular weight: 611) of formula (1) as defined above, wherein A and B are hydroxyl groups, j, k and m are 0, 1 is 7 and x₁, x₂, x₅ and x₆ are methyl groups.

electric resistance is small compared with conventional silica fillers there are no problems with noise generation in electrical equipment or static electricity and dispersibility during compounding is good (**Table 3, Fig. 5**).²³⁾

Table 3

	Surface treated CB1	Surface treated CB2	Surface treated CB3	Surface treated CB4	Surface treated CB5	Surface treated CB6	Surface treated CB7
Type of carbon used		N339(HAF)		N110(SAF)			N550(FEF)
Nitrogen specific surface area of carbon used (m ² /g)		93		142			42
DBP oil adsorption of carbon used (ml/100 g)		119		115			115
Silica content (wt %)	2	22	74	3	25	58	5

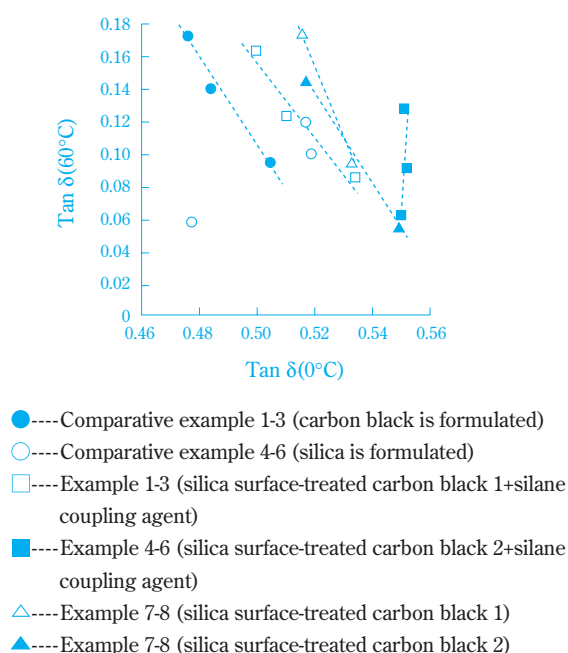


Fig. 5 Temperature Dependency of Tan δ

A carbon/silica hybrid filler called “dual phase filler” has been proposed based on a similar concept, and there are reports that a compound with superior balance in wet gripping, rolling resistance, etc., has been obtained.²⁴⁾ There has been a wide range of developments in attempts to create similar composites, and we would like to give attention to future trends.

Besides this, examples of interesting results can be drawn from the search for fillers other than carbon and silica. For example, it has been shown that by compounding SBR that has a glass transition temperature of -27°C with aluminum hydroxide that has a boehmite crystal structure, it is possible to obtain tread rubber that has good processability equal to that of conventional carbon black compounding, but with performance as good or better than silica compounding (**Tables 4 and 5**).²⁵⁾

Table 4

Kinds of Aluminum Hydroxide	Physical properties				
	Loosed bulk density; g/cm^3	DOP oil absorption; $\text{cm}^3/100\text{ g}$	BET specific surface area; m^2/g	Crystal structure	Crystal size of boehmite (020) plane; nm
Example A aluminum hydroxide A	0.21	121	153	boehmite	12.9
Example B aluminum hydroxide B	0.33	80	208	boehmite	7.3
Comparative aluminum hydroxide C example C	0.94	54	250	boehmite	2.4
Comparative aluminum hydroxide D example D bayerite	0.61	84	110	boehmite	3.0
Comparative aluminum hydroxide E example E	0.20	55	8	gibbsite	—

Moreover, in terms of the problems in silica compounding systems, silica itself is not conductive, so the electrical resistance of tires is high, and the problems of static electricity and electrical noise mentioned earlier still remain. The problems are generally solved to a certain extent through the combined use of carbon black, but various kinds of ingenuity are necessary for compounding systems with silica alone. For example, a cured rubber composition where the electrical resistance value is reduced by adding a compound containing an alkali metal salt or alkali earth metal salt (or an electrically conductive filler where these were supported on the surface of silica), that is one with superior electrical conductivity, has been demonstrated, and it is said to be suitable for tire treads.^{26), 27)}

Otherwise, in terms of peripheral technology, studies are not always intended for use in tires, but it is very interesting that using a sol-gel method, a silica compounded cured rubber was, for example, immersed in an alkoxy silane compound, swollen and hydrolyzed with the effect being not only to increase the reinforcing effect of the silica and polymer, but also to reduce hysteresis loss.²⁸⁾

(4) Development of SBR Suitable for Silica Compounding (from the second generation to the third generation)

It is possible to improve the balance between fuel savings and wet grip performance using a combination of the methods in the previous section, but the performance required for tires is moving to an increasingly higher standard each day, and for further improvements, structural selection of the polymer itself and modified recipes are said to carry great weight.

Table 5

(Parts by weight)	Examples					Comparative examples						
	1	2	3	4	5	1	2	3	4	5	6	
Ingredients												
SBR N. 9520(pure polymer)	1)	70	70	70	70	50	70	70	70	70	70	70
BR 150B	2)	30	30	30	30	50	30	30	30	30	30	30
Carbon black N220	3)	65	65	40	40	65	65	65	85	65	65	65
Aluminum hydroxide A		40		65	65	40						
Aluminum hydroxide B			40									
Aluminum hydroxide C									40			
Aluminum hydroxide D										40		
Aluminum hydroxide E												40
Silica VN3	4)						40					
TESPT	5)				5.2		3.2					
Aromatic oil (incl. oil extended polymer)		40	40	35	40	40	50	35	50	45	45	45
Antioxidant		2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
WAX		2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Stearic acid		2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Zinc oxide		3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0
Sulfur		2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Vulcanization accelerator		1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Evaluation Mooney viscosity		105	106	105	107	105	130	100	100	108	106	104
Abrasion resistance		100	98	98	103	103	94	95	100	74	65	81
Rolling resistance		108	110	113	118	113	106	125	100	108	110	111
Wet grip performance (ABS brakeage)		111	109	112	115	87	116	82	100	105	106	106

1) SBR : styrene content : 35% by weight, 37.5 PHR oil extended rubber, glass transition temperature (T_g): -38°C.

2) BR : polybutadiene rubber BR150B

3) carbon black : Diablock I (N220), BET specific surface area by nitrogen adsorption : 115m²/g

4) silica : VN3

5) silane coupling agent TESPT : Si-69

For example, Choi et al. report that physical properties are improved when NBR is added to silica compounded SBR.²⁹⁾ It is said that NBR has a nitrile group, which is a polar group, and the affinity for silica, which has a hydroxyl group, is good (specifically, Tan-δ at low temperatures (0°C), which is an index of grip performance, is high, and Tan-δ at high temperatures (60°C), which is an index of rolling resistance (fuel savings performance), tends to be low) (Tables 6 and 7). Furthermore, it has become clear that a 1,2 bond in the structure of the BR part of SBR is more suitable to silica compounding than any 1,4 bond.

In addition, in terms of modifications to the polymers themselves studies have developed in a wider range for solution SBR polymerization than for emulsion SBR polymerization systems from the standpoint of the superiority of physical properties in an unmodified state and the variety of methods for synthesis. For example, polymers with quaternary ammonia groups on at least one SBR chain end are superior in terms of having low heat

Table 6 Formulations (phr)

Ingredients	Compound No.							
	S1	S2	S3	S4	C1	C2	C3	C4
SBR1500	100.0	95.0	90.0	85.0	100.0	95.0	90.0	85.0
KNB 35L	0.0	5.0	10.0	15.0	0.0	5.0	10.0	15.0
Z175	50.0	50.0	50.0	50.0	0.0	0.0	0.0	0.0
Si69	3.0	3.0	3.0	3.0	0.0	0.0	0.0	0.0
N330	0.0	0.0	0.0	0.0	50.0	50.0	50.0	50.0
Stearic acid	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
ZnO	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
HPPD	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
WAX	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
TBBS	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4
Sulfur	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2
DPG	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0

SBR 1500 : styrene-butadiene rubber with 23.5% of styrene content ; acrylonitrile-butadiene rubber with 35% acrylonitrile content ; Z175 : silica ; Si69: silane coupling agent, bis-(3-(triethoxysilyl)propyl)tetrasulfide (TESPT); N330 : carbon black ; HPPD : *N*-phenyl-*N'*-(1,3-dimethylbutyl)-*p*-phenylenediamine ; DPG : diphenylguanidine ; TBBS : *N*-*tert*-butyl-2-benzothiazolesulfenamide.

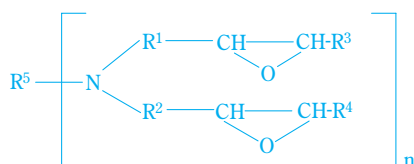
buildup, which is an indicator of rolling resistance, in silica compounding systems.³⁰⁾ It is already

Table 7 Tan δ

Ingredients	Compound No.							
	S1	S2	S3	S4	C1	C2	C3	C4
-20°C	0.378	0.350	0.369	0.377	0.368	0.359	0.374	0.369
0°C	0.182	0.198	0.227	0.229	0.202	0.220	0.235	0.256
10°C	0.159	0.162	0.178	0.176	0.194	0.204	0.212	0.220
50°C	0.122	0.118	0.121	0.120	0.150	0.152	0.160	0.162
60°C	0.118	0.113	0.117	0.114	0.145	0.147	0.155	0.157
70°C	0.114	0.109	0.113	0.110	0.141	0.143	0.151	0.153

known that amine modifiers are effective in improving the physical properties of conventional compounding systems that use carbon black, but this is one example indicating that is also effective for silica compounding.

Furthermore, besides the fact that polymers from reactions of the active chain ends of SBR and multifunctional groups (**Fig. 6**) with two or more epoxy groups are superior in terms of low rolling resistance and wet skid resistance, they have been shown to have superior processability.³¹⁾ Examples of the use of epoxy compounds in conventional carbon compounding systems are already known, but in this case, it is thought to be an example of using epoxy groups to increase the affinity (or strength of chemical bonds) for silica with its higher polarity.

**Fig. 6** Polymer modification agent.

The above is an example of polymer modification using solution SBR polymerization where targeted structural design is easily done, but there has been a proposal for a method of epoxidation treatment (0.5 to 20% of conjugated diene) of the conjugated diene in SBR with a tungstic acid/hydrogen peroxide system in toluene. In this case, it is said that modified polymers that can be applied to white filler systems, such as silica calcium carbonate and magnesium carbonate without the use of silica coupling agents can be obtained.³²⁾ As a result, these polymers are said

to give satisfactory physical properties for both rolling resistance and wet skid properties in tire treads, in addition to having superior rupture strength, impact resilience and abrasion properties.

On the other hand, one of the difficulties mentioned for using living anionic polymerization that uses alkyl lithium catalysts, is the poor selectivity for copolymerization monomers (particularly polar monomers containing functional groups). With regard to this point, there is an example of obtaining a modified polymer suitable for silica compounding through copolymerization of polar monomers, making use of the characteristics in emulsion SBR polymerization. For example, using copolymerization of polar monomers, such as acrylamide and vinyl pyridine in an emulsion polymerization system, it is possible to obtain a modified polymer with superior silica dispersibility that is suitable for low fuel consumption tire materials.³³⁾ However, what we should give attention to here is the point that there is a solution that increases the Mooney viscosity during kneading and storage, as often observed in silica compounds of SBR that include large numbers of polar groups, along with use of a phenol stabilizer that contains sulfur atoms. This is one theme for silica compounding systems, and besides this, gaining the coexistence of fatty acid esters, etc., are also widely studied, but here we will end this description here.

Development of Third Generation Solution SBR

(1) Development of Living Polymerization Synthesis Methods

Up through the preceding section, we have mainly shown structural designs for solution SBR with superior silica dispersibility, suitable as materials for low fuel consumption tires. Various studies are progressing on basic and practical aspects even for living anionic polymerization, which are the basic synthesis technique. The details of the history from the original stages, basic method and polymer chain end modification method are left to a previous report,¹⁾ and here, we will focus on polymerization that can contribute to multifunctional group formation. Basically, since termination reactions for growing terminal ions and polarized compounds are easily provoked in living anionic polymerization reaction systems,^{35), 36)} the

inclusion of polar groups in polymerization initiators themselves has been seen as being difficult. Various devices have been used by several research groups recently, and there have been reports of an example of carrying out copolymerization of styrene and isoprene³⁸⁾ using a reaction adduct of trimethylsilyl group-protective aminostyrene/*s*-BuLi (1:1)³⁷⁾ as an initiator, examples of using alkylolithium compound containing an alkoxy group as an initiator,³⁹⁾⁻⁴²⁾ and examples of using a phenyllithium containing a dimethylamino group,^{43), 44)} etc.

(2) Multifunctional Solution SBR

The introduction of polar functional groups to polymer chain terminals is achieved by reacting living polymer anions with high nucleophilic properties with a electrophilic terminal modifier. Recently, the standards required for improvement in fuel saving properties are ones that cannot be achieved through the general introduction of polar functional groups to polymer chain terminals. There is a trend toward increasing the number of functional groups introduced to polymer chains by introducing functional groups to the polymerization initiation terminals and carrying out terminal modification on both ends of polymer chains by using a lithium reagent with functional groups as described in the previous section as a polymerization initiator. Ideally, if various multifunctional polymers could be synthesized by selecting and designing the kind and number of functional groups, the positions for introduction (length between functional groups), etc. (**Fig. 7**), we can assume that silica dispersibility would be improved and a high degree of fuel savings achieved, so there are great expectations for the possibilities in the performance of these.^{45), 46)} However, in the field of polymer synthesis, it has conventionally been extremely difficult to introduce specific number of functional groups to specific sites, and even looking at the few reports of examples, most of them have required vexatious synthesis procedures.⁴⁷⁾⁻⁵⁰⁾ In order to overcome this problem, the authors have introduced multiple functional groups not only to polymer chain terminals, but also to multiple positions, including intra-chain positions, and have been able to make progress in the development of a method for synthesizing a new mul-

tifunctional polymer and finding multiple types of reaction paths for the synthesis of a new multifunctional polymer. As a result, this has opened up the possibilities for the realization and providing of order made' polymers. A simple synthetic method for a multifunctional polymer using a 1,1-diphenylethylene (DPE) compound will be discussed in the following as an example. Moreover, the Society of Rubber Industry, Japan awarded this research the outstanding performance award for the 16th Elastomer Meeting (part for presentations by young researchers).⁵¹⁾

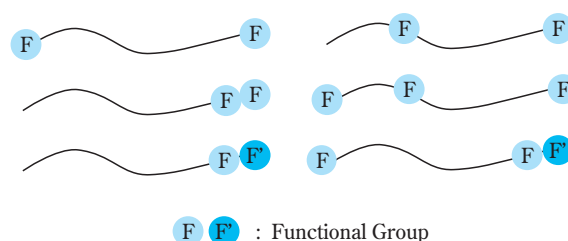
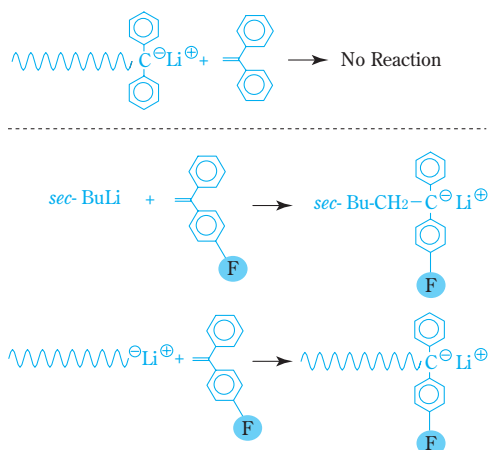


Fig. 7 Various Multi-Functional Polymers

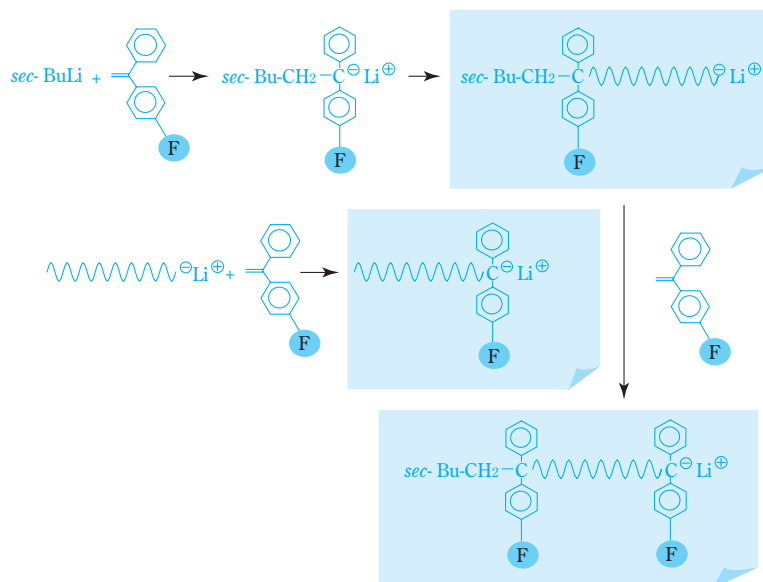
(3) Development of Multifunctional Polymer Using DPE Derivatives

It is known that the 1,1-diphenylethylene (DPE) compound, which was used as a key compound for designing synthesis reaction paths, does not have homopolymerization properties due to steric and electric effects, that is, it reacts 1:1 quantitatively with low molecular weight molecules and polymer carbanions, creating a new DPE type anion at the same time as the bonds. For example, Prof. Quirk of Akron University has developed various multifunctional polymers using this unique property.⁵²⁾ Specifically, polymerization is carried out using an initiator synthesized from a DPE derivative with functional groups and an alkylolithium such as *sec*-BuLi, and a polymer having functional groups at polymerization initiation terminals is synthesized, with functional groups introduced at the polymerization growth terminals of the polymer through a reaction of the living anionic polymer with the DPE derivative that has functional groups. Furthermore, it is possible to introduce functional groups to both chain terminals in the polymer through the joint use of both methods (**Scheme 1**) (**Scheme 2**).⁵³⁾

The authors have succeeded with molecular



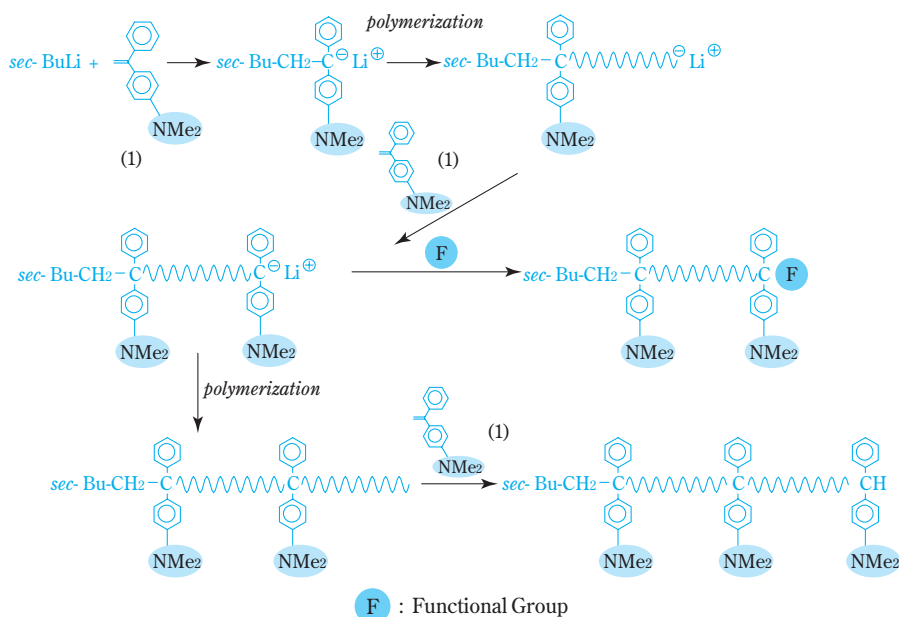
Scheme 1 Reactions of Anionic Species with DPE Derivatives



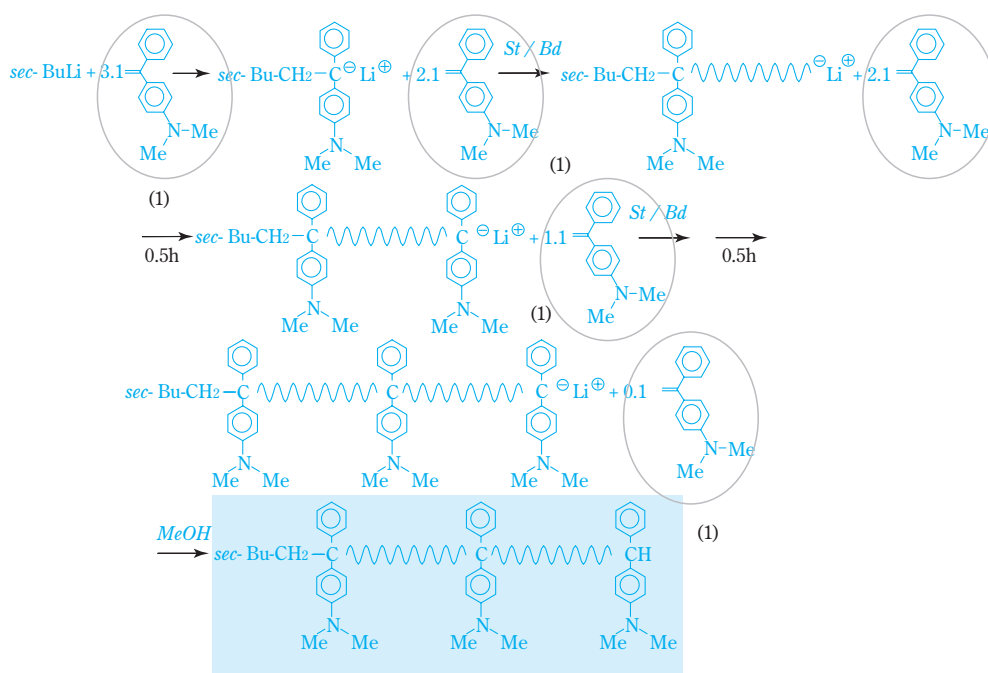
Scheme 2 Synthesis of End-Modified Polymers by Using DPE Derivatives

designs for various multifunctional polymers by the route shown in (**Scheme 3**) using 1-(4-dimethylaminophenyl)-1-phenylethylene (**1**) of a DPE derivative with one dimethylamino group. First, a polymer with dimethylamino groups at the initiation terminals and termination terminals of the polymer is obtained using a 1:1 reaction of (**1**) with alkyl-lithium and a living anionic polymer, and dimethylamino groups can be also introduced to both the initiation terminal and termination terminal. In addition, after the reaction of (**1**) with the polymer

chain terminals, two or more functional groups can be introduced to the polymer chain terminals when another modifying agent reacts with the newly produced DPE type anion.⁵⁴⁾ Furthermore, dimethylamino groups can be also introduced to the polymer chains by initiation of polymerization using the newly formed DPE type anions.⁵⁴⁾ In other words, it was possible to synthesize a multifunctional polymer with amino groups in three positions, the chain terminals and intra-chain sites.⁵⁵⁾



Scheme 3 Synthesis of Multi-Functionalized Polymers



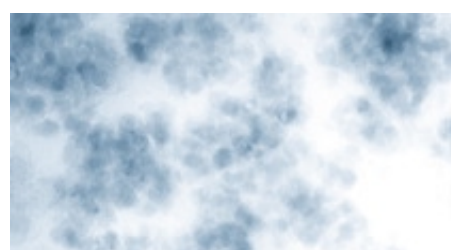
Scheme 4 One-Step Method for Synthesis of Multi-Functional Polymers

Furthermore, it subsequently became clear that even though (1) is used as a polymerization initiator by a reaction with a carbanion and as a terminal functionalizing agent, the reactivity is extremely low compared with styrene and butadiene, so it can exist stably in a system where both monomers are present without reacting with the carbanion. Therefore, it is possible to achieve a one-step synthesis of a multifunctional SBR with dimethylamino groups at the specific positions of both chain terminals and intra-chain sites where the primary structure is controlled by adjusting the amount of (1) used during the synthesis of the initiator, as is shown in **(Scheme 4)**. (Scheme 4) shows an example where three equivalents of (1) have been used.

(4) Third Generation SBR Solution Polymerization

The preceding section described one example of a synthetic method for multifunctional SBRs, but the authors have discovered production methods for several types of new solution SBRs, including other synthetic methods we have been studying. By selecting and optimizing production methods among these that are suited to industrialization, we are developing new solution SBRs that make it possible to respond to the demands for both environmental protection and assurance of safety. As

is shown in **(Fig. 8)**, these new SBRs are improved to high levels that exceed the standards of conventional modified terminal SBRs for both fuel saving properties and road gripping force in particular through improvements in the dispersibility with silica. Since these are designed using a new method that introduces functional groups to the specific locations where they are necessary, and we think they are worthy of being called “third generation solution SBRs.”



(A) Standard SBR



(B) New Functionalized SBR

Fig. 8 Silica Dispersion by TEM (X 200,000)

Conclusion

In this article, we have discussed the trends in the synthesis of solution SBRs, which are raw materials, polymer structure design and peripheral technology as they have progressed in response to aspects where there are increasing standards for the properties required for automobile tires. Even more effort is now coming to bear on the “old but new problem” of simultaneous improvement in fuel saving and wet grip properties, and this is a response to the societal demand for saving resources and protecting the global environment while simultaneously assuring safety in the operation of automobiles. However, it is a fact that there is still room for improvement in solution SBRs for use as tire raw materials when we think in terms of the entire process from the production stage for SBR polymers to tire compounding and molding, and further to the operation of automobiles and after use. The authors would like to make further progress in developmental studies based on our awareness of our attempting to contribute something to the solution of these problems from the standpoint of polymer synthesis and design.

References

- 1) Imai A, Yamamoto K, Sumitomo Kagaku 1990-I 28-40(1990)
- 2) Saeki Y, Kagaku Keizai vol. 5, 58-69(1997) Table 2 (translate to English)
- 3) Saito, Y, International Kautshucktagung (Stuttgart) (1985)
- 4) Engel, E.F., Gummi. Asbest Kunststoffe, 26(5), 362 (1973)
- 5) a) Imai, A., Takao, H., IRC85 KYOTO Full Texts 17D07 (1985);
b) Imai, A., US-Japan Polymer Symposium (1985);
c) Furukawa J, “Kobunshi Bussei” P.139 (1985)
d) Furukawa J, “Tategaki-no Kobunshi Riron” P.21(1988)
e) JP06-865B2
- 6) JP2625875
- 7) JP 2625876
- 8) JP 2625877
- 9) JP 2625878
- 10) Nagata N, Nippon Gomu Kyokaishi 62(10), 630-640 (1984)
- 11) Fujimoto K, *ibid.* 37, 602 (1965)
- 12) Harwood, J.A.C., Rubber. Chem. Technol., 43, 687, (1970)
- 13) Kaido H, Nippon Gomu Kyokaishi 71, 571-577(1998)
- 14) Radoc, J.R.M., Tai C.C., J. Appl. Polym. Sci., 6, 518, (1962)
- 15) Payne, R.E., Whittaker, R.E., Rubber Chem. Technol., 44, 440, (1971)
- 16) Fujimoto K et al., Nippon Gomu Kyokaishi 58, 658 (1985)
- 17) Urabe N, Polymer Digest 41(5), 91 (1989)
- 18) Doi A, *ibid.* 71(9), 588-594 (1998)
- 19) European Patent: 501227
- 20) JP08-302070, United States Patent: 6087424
- 21) JP09-3245
- 22) JP08-176462
- 23) JP08-277347, United States Patent: 5679728
- 24) P. Zhang, M-J Wang, Y. Kutsovsky, S. Laube, K. Mahmud ACS meeting Rubber Division Cleveland, Ohio, October 16-19 2001 Paper No.94
- 25) JP2001-181447, United States Patent: 20010023271
- 26) JP10-237222
- 27) JP10-237223
- 28) JP11-335493
- 29) Sung-Seen choi, Journal of Applied Polymer Science 79, 1127-1133(2001)
- 30) JP09-227628
- 31) United States Patent: 20030199669
- 32) JP09-241429
- 33) JP11-106562
- 34) JP2001-155381
- 35) Kagaku Sosets No.18, pp37-54 (1993)
- 36) Daigakuin Kobunshi Kagaku (1997)
- 37) Dickstein, W. H., Lillya, C. P. Macromolecules 22, 3885 (1989)
- 38) A. Hirao, M. Hayashi Acta Polym. 50, 219 (1999)
- 39) Gauthier, M., Tichagwa, L., Downney, J. S., Gao, S. Macromolecules 29, 519 (1996)
- 40) Bucsi, A., Forcada, J., Gibanel, S., Heroguez, V., Fontaille, M., Gnanou, Y. Macromolecules 31, 2087 (1998)
- 41) R-Lurbert, L., Schappacher, M., Deffieux, A. Macromolecules 27, 6318, (1994)
- 42) Deffieux, A., Schappacher, M., R-Lurbert, L.,

- Macromol., Symp. 95, 103, (1995)
- 43) Antonietti, N., Heyne, J., Sillescu, H. Makromol.Chem., 192, 3021 (1991)
- 44) Ishizu, K., Kitano, H., Ono, T., Uchida, S. Polymer 40, 3229, (1999)
- 45) Hayashi, M. Mabe, S., Inagaki, K., Nakatsuji, Y., Imai, A. Polymer Preprints 43(2), 1083 (2002)
- 46) Hayashi, M. Macromol Symposia in press
- 47) Hayashi, M., Loykulant, S., Hirao, A., Nakahama, S. Macromolecules 31(7), 2057 (1998)
- 48) Hayashi, M., Hirao, A. Macromol. Chem. Phys. 202, 1717 (2001)
- 49) Hayashi, M., Hirao, A. Kobunshi Ronbunshu 57(12), 781 (2000)
- 50) Hayashi, M., Hirao, A., Macromol. Chem. Phys. 202, 1717, (2001)
- 51) Hashimoto Y, Nippon Gomu Kyokaishi 77(1), 40 (2004)
- 52) Quirk, R. P., Zhu, L-F. British Polymer Journal 23, 47 (1990)
- 53) Hsieh, H. L., Quirk, R. P., Anionic Polymerization: Principles and Practical Applications, Marcel Dekker, New York (1996)
- 54) JP2003-231713
- 55) JP2003-292529

PROFILE


Katsunari INAGAKI

Sumitomo Chemical Co., Ltd.
Petrochemicals Research Laboratory
Research Associate



Akio IMAI

Sumitomo Chemical Co., Ltd.
General Manage, Advanced Polymers Division



Mayumi HAYASHI

Sumitomo Chemical Co., Ltd.
Petrochemicals Research Laboratory
Ph. D.