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Optimum Condition on Overlap of Physical Properties of HIPS Samples

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To find optimum conditions necessary in converting physical properties of any resin into those of others, eleven kinds of HIPS (High-Impact Polystyrene) resins were prepared. First physical properties of eleven samples divided into three groups are analyzed by a torque rheometer (named Plasti-Corder, Model No.: PLD 651) and GPC (Gel Permeation Chromatography), and then optimum conditions on conversion among samples are obtained by calculation from computer simulation so that any sample subjected to each group can show physical properties of other samples in its group. Even though the kind of plasticizer of any sample is different with others in its group, once optimum conditions on conversion among samples are met, it is found that physical properties of any sample are identical or similar to those of others in each group.

Introduction

Though it is almost impossible for the end-to-end distance of individual polymer molecule to be exactly measured or calculated, but the mean value of end-to-end distances of all the molecules in the system can be evaluated by a statistical mechanical method.[1-5] Consider the state of motion of general polymer chains of which the structure of a repeat unit is a carbon-carbon single bond.

For one polymer chain, let the number of C-C segments be N, the length of C-C segments be l, and a mean-square end-to-end distance be $\bar{R}^2$. Then the relation is given as follows:

$$\bar{R}^2 = Nl^2 \left(\frac{1-\cos\theta}{1+\cos\theta} \right) \left(\frac{1+\overline{\cos\phi}}{1-\overline{\cos\phi}} \right) \tag{1}$$

$$b^2 \equiv l^2 \left(\frac{1-\cos\theta}{1+\cos\theta} \right) \tag{2}$$

$$l_o^2 \equiv b^2 \left(\frac{1+\overline{\cos\phi}}{1-\overline{\cos\phi}} \right) \tag{3}$$

where θ is the specific bond angle between two neighbored segments, and ϕ is the angle in which the C_{n+1}th segment rotates freely about the C_nth segment. The quantity $\overline{\cos\phi}$ is the mean value of $\cos\phi$'s. Generally, the value of $\overline{\cos\phi}$ is evaluated as a function of N by computer simulation using Monte Carlo methods.

Let the number of monomers bonded to a polymer molecule be N, and then for polymers repeatedly made up of C-C bonds, the following is given

$$n = 2N. \tag{4}$$

Though the mean value of n is called degree of polymerization, but hereafter let the mean value of n be represented simply as n.

For polystyrene, since θ equals 109.5°, and l is 1.54 Å, once that the values of N and $\overline{\cos\phi}$ are known, then the value of $\bar{R}^2$ can be evaluated by Eq. (1). The quantity l_o defined by Eq. (3) is called a segmental step length or simply a step length.

As the equation representing viscosity of polymers in a melt state, the Debye viscosity equation is given as follows:

$$\zeta = \frac{36\eta M_o}{N_A l_o^2 \rho n} = \frac{36\eta M}{N \bar{R}^2 \rho N_A} \tag{5}$$

where η is viscosity, M_o is a molecular weight of the monomer, and ρ is the density of polymer molecules. The quantity N_A is the Avogadro's number, and N is the number of C-C segments in the backbone chain. The quantity ζ of Eq. (5) is proportional to viscosity of polymers, being called the friction coefficient. A diffusion coefficient D of polymers in a melt state is given.[6-8]

$$D = \frac{1}{135} \left(\frac{\bar{R}^2}{M} \right) \frac{M_c}{M} \frac{\rho RT}{\eta} \tag{6}$$

For polystyrene a characteristic molecular weight M_c is given as 183932.3. In Eq. (6), R is the ideal gas constant, and T is an absolute temperature of the system. Since the diffusion coefficient D is a function of T, every sample has a specific value of D according to the temperature given.

Since the viscosity of a sample is measured in Plasti-Corder, the diffusion coefficient of the sample is subjected to two controlling factors, such as temperature and shear rate (usually represented in the unit sec^{-1} or S^{-1}). Thus the step length and end-to-end distance of polymer chains depend on temperature and shear rate of flowing polymers besides the size of rubber particles, the role of plasticizer for flow, and *etc.*

The computer simulation has been carried out by using Monte Carlo methods so that various factors discussed earlier are considered fully. From these simulation data the values of step length and end-to-end distance which can be substituted into Eq. (5) are obtained.[9-11] The value of M in Eq. (5) is obtained with GPC, which shows readily the values of a weight average molecular weight and a number average molecular weight and the curve of distribution of molecular weight.[12-14] As discussed earlier, since the viscosity of polymers is obtained by Plasti-Corder, the value of a diffusion coefficient can readily be obtained by Eq. (6).

Experimental

Plasticizer. The kind of plasticizers used in preparation of HIPS samples is given in Figure 1. Backbones of plastici-
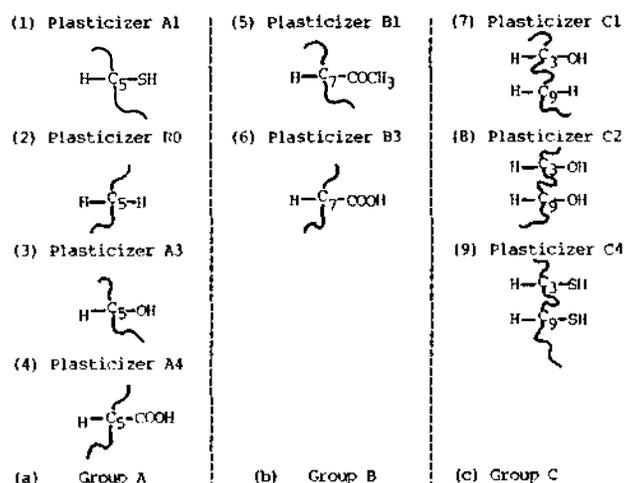
Figure 1. Three groups (A, B, and C) of plasticizer molecules used in the experiment.

zers used in the experiment are all liner hydrocarbons with twenty-two carbon atoms commonly. Every molecule of the plasticizer Al has a S-H substituent in the position of the fifth carbon in place of a hydrogen atom. For the plasticizer A3 the fifth carbon in a backbone chain bonds with a *O-H* group in place of a hydrogen atom. A molecule of the plasticizer R0 is a typical hydrocarbon of twenty-two carbon atoms without any substituent. For the plasticizer A4 the fifth carbon in a backbone chain bonds with a COOH substituent in place of a hydrogen atom. In Figure 1 the position of the carbon atom which is bonded with substituents is represented as a number subscript attached to the captical letter '*C*'. The amount and kind of plasticizers used in all the sample are given in Table 1.

Rubber and other Additives. All the rubber used in the experiment is poly (butadiene) rubber, which is called the 755A. The original state of rubber exists in solid and bulk. After the rubber has been crushed into quite a small particles, these small particles enter the solvent of styrene. The amount of composition of rubber and styrene is also given in Table 1. Additionally 1,000 ppm of internal lubricant $(Zn(OOCC_{17}H_{35})_2)$ and 1,090 ppm of antioxidant (called Irganox 1076) are contained by total weight percent in each HIPS sample.

Preparation of Rubber Solution. All the rubber particles crushed are dissolved in the reactor with all the other additives at 25℃. The time necessary in dissolution takes five hours at 20 rpm of the agitator. When the preparation of the rubber solution has been completed, the size of rubber particles is 2-3 μ in diameter.

Process of Polymerization. The eleven kinds of HIPS samples which are used in this experiment are all polymerized at 145℃ and 28 rpm for five hours. To prevent oxidation of the products, the purge with nitrogen has been carried out during bulk polymerization. The volume of the reactors used takes 3*l*. When polymerization has been completed, the amount of bulk polymer approaches to 80-85%, which being measured by weighing the sample after having evaporated the residual monomer from the sample in the vacuum dry oven at 135℃ for an hour.

The products of the reactor take the form of bulk polymers. After having all been dried in the vacuum dry oven at 135℃ for two hours in order to evaporate residual monomers, the bulk polymers are divided into small blocks (*e.g.*, 2 cm × 3 cm × 2 cm in volume size), and then the blocks has been dried at 25℃ for twenty-four hours. These samples of block form are transformed into small spherical resins (1.0-1.5 cm in diameter) through the electrical crusher. Small spherical resins are transformed into numerous equivalent pellets through the twin extruder. Almost all the measurements of physical properties are carried out by using the HIPS samples of pellet form.

Measurements of Physical Properties. The viscosity of HIPS samples has been measured over the shear rates of 5 to 115 S^{-1} at 220, 230, and 240℃ by using Plasti-Corder. At the given temperature, the HIPS samples of pellet types are packed into the hopper of Plasti-Corder, crushed in the barrel, transformed into melt state with the given rotation of the screw in the barrel, and finally extruded in continuous sheet types through the nozzle. The data processor of Plasti-Corder accumulates automatically all the data, such as torque *vs.* shear rate, viscosity *vs.* shear rate, and shear stress *vs.* shear rate, obtainable on rheology by the program stored in itself during extrusion of samples at the given temperature and rpm's. The values of molecular weight have been measured by GPC (Model No.: Waters 150-C). The values of degree of polymerization are calculated from those of molecular weight.

The size of rubber particles can be measured by taking a photograph of the sample with the optical microscope (Model No.: Olympus BH-2) of one thousand magnifications by taking the solution sample a little (*e.g.*, 1-3 g). The solution sample is prepared by solving the HIPS products of pellet form in the styrene solvent so that the concentration of solution reaches thirty weight percent. Transmission electron micrographs show that the inner part of each rubber particle is occluded with polystyrene or styrene monomer molecules. In these experiments, it is exposed that the shape of rubber particles is spherical and that rubber particles are distributed evenly in the HIPS systems.

Table 1. The Composition of Eleven Samples used in the Experiment

Composition	HIPS	PA1	PA2	PA3	PA4	PB1	PB2	PB3	PC1	PC2	PC3	PC4
Plasticizer	(%)	A1	R0	A3	A4	B1	R0	B3	C1	C2	R0	C4
		2.3	2.3	2.3	2.3	4.1	4.1	4.1	3.5	3.5	3.5	3.5
Rubber	(%)	6.5	6.5	6.5	6.5	6.0	6.0	6.0	7.2	7.2	7.2	7.2
Styrene	(%)	91.2	91.2	91.2	91.2	89.9	89.9	89.9	89.3	89.3	89.3	89.3

Table 2. The Physical Properties of Samples in Group A at 220℃ and 55 S⁻¹

HIPS Items	PA1	PA2	PA3	PA4
n	1990	1971	2163	1731
ζ (10^{-7} kg/S)	17.44	16.60	6.66	22.32
η (PaS)	46,000	44,570	44,050	42,990
D (10^{-19} m²/S)	4.59	4.75	10.13	4.72
l_o (10^{-10} m)	2.87	2.91	4.36	2.63

Table 3. The Physical Properties of Samples in Group B at 220℃ and 55 S⁻¹

HIPS Items	PB1	PB2	PB3
n	2308	1942	1702
ζ (10^{-7} kg/S)	4.43	16.19	22.99
η (PaS)	42,750	42,530	41,980
D (10^{-19} m²/S)	13.39	5.17	4.66
l_o (10^{-10} m)	5.10	2.90	2.56
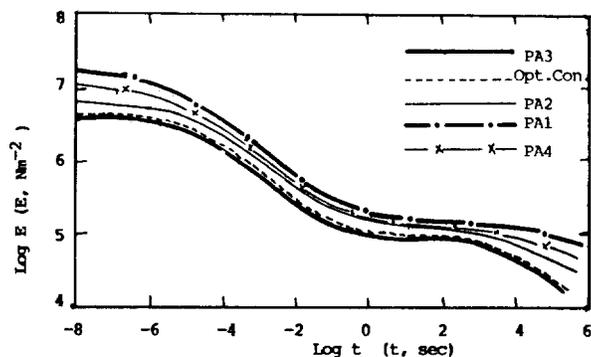
Figure 2. Log-log plots of modulus versus time for Group A (HIPS) at 220℃.
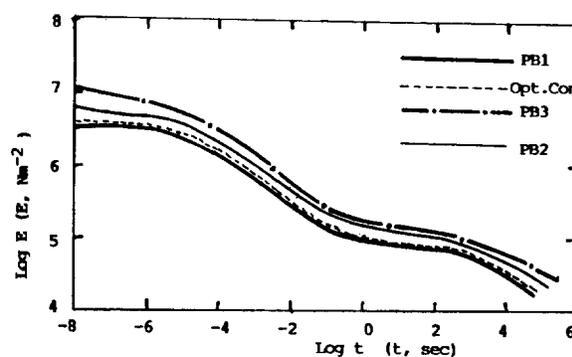
Figure 3. Log-log plots of modulus versus time for Group B (HIPS) at 220℃.

Results and Discussion

The most reliable condition on which physical properties of any sample is transformed into those of another can be called the optimum condition. Generally, two factors controlling optimum conditions are a diffusion coefficient and the distribution of molecular weight.[15-17] When the optimum condition of any sample is met, the values of modulus of two samples, which relate to the optimum condition each other, are nearly similar.[17]

Alternatively, two curves of moduli given as functions of time are almost overlapped, when the elastomer is extended to two times of original length, the external force acting on unit area is conceptually defined the modulus, which has the unit of Nm⁻².

If let the original length of elastomer be L_o, the extended length be ΔL, and the stress of elastomer be σ_t, then the Young modulus E is given as follows:

$$\sigma_t = E \left(\frac{\Delta L}{L}\right)_t \tag{7}$$

$$\sigma_t = E \gamma_t \tag{8}$$

$$\sigma_t = \left(\frac{\Delta L}{L}\right)_t. \tag{9}$$

E is the function of time t, and its equation according to typical molecular dynamics is given[4]

$$E(t) = \frac{C}{N} kT(3 - \frac{1}{V} \frac{dv}{d\gamma}) \int_o^p \text{EXP}(-2t_p/\tau_R)dp \tag{10}$$

$$\tau_R = \frac{\zeta N^2 b^2}{3\pi^2 kT} \tag{11}$$

where C is the characteristic constant given to the system,

Figure 4. Log-log plots of modulus versus time for Group C (HIPS) at 220℃.

γ is strain, V is the volume of elastomer, and τ_R is the Rouse relaxation time. Since the glass state can be regarded as a stationary state of melt state, the stress-strain data from Instron (the name of apparatus measuring elasticity) are required to find the value of dV/dγ in Eq. (10).

In Table 2, physical properties of four samples subjected to Group A are given at 220℃ and 55 S⁻¹. In Figure 2, log-log plots of modulus versus time for Group A are given at 220℃. Figures 2 to 4 are obtained by calculating Eq. (10) with aid of the computer integratioin programs. For example, consider the process which physical properties of sample PA2 transforms into those of sample PA3. When the optimum condition for this case is met, the resultant curve of sample PA2 transfers to the curve made up of broken lines, and are superposed the curve of sample PA3.

In Tables 3 to 10, the physical properties of all the samples in each group are given according to the given temperatures

Table 4. The Physical Properties of Samples in Group C at 220℃ and 55 S^{-1}

HIPS Items	PC1	PC2	PC3	PC4
n	2260	2115	1808	1692
ζ (10^{-7} kg/S)	4.99	10.20	20.35	24.16
η (PaS)	45,570	44,980	43,480	42,430
D (10^{-19} m^2/S)	12.38	6.92	4.74	4.56
l_o (10^{-10} m)	5.01	3.60	2.71	2.54

Table 5. The Physical Properties of Samples in Group A at 230℃ and 75 S^{-1}

HIPS Items	PA1	PA2	PA3	PA4
n	1990	1971	2163	1731
ζ (10^{-8} kg/S)	18.24	17.38	7.12	2.35
η (PaS)	49,800	48,610	48,210	47,400
D (10^{-19} m^2/S)	4.48	4.79	9.70	4.59
l_o (10^{-10} m)	2.92	2.97	4.41	2.69

Table 6. The Physical Properties of Samples in Group B at 230℃ and 75 S^{-1}

HIPS Items	PB1	PB2	PB3
n	2308	1942	1702
ζ (10^{-8} kg/S)	4.70	16.76	24.00
η (PaS)	46,610	46,200	45,800
D (10^{-19} m^2/S)	12.93	5.11	4.65
l_o (10^{-10} m)	5.17	2.97	2.64

Table 7. The Physical Properties of Samples in Group C at 230℃ and 75 S^{-1}

HIPS Items	PC1	PC2	PC3	PC4
n	2260	2115	1808	1692
ζ (10^{-8} kg/S)	5.29	10.75	21.11	25.74
η (PaS)	49,410	49,010	47,800	47,000
D (10^{-19} m^2/S)	11.97	6.72	4.69	4.39
l_o (10^{-10} m)	5.07	3.66	2.79	2.59

Table 8. The Physical Properties of Samples in Group A at 240℃ and 95 S^{-1}

HIPS Items	PA1	PA2	PA3	PA4
n	1990	1971	2163	1731
ζ (10^{-8} kg/S)	18.68	17.74	7.43	24.07
η (PaS)	54,900	53,720	53,320	52,540
D (10^{-19} m^2/S)	4.46	4.78	9.48	4.57
l_o (10^{-10} m)	3.03	3.09	4.54	2.80

Table 9. The Physical Properties of Samples in Group B at 240℃ and 95 S^{-1}

HIPS Items	PB1	PB2	PB3
n	2308	1942	1702
ζ (10^{-8} kg/S)	4.96	17.33	24.21
η (PaS)	51,750	51,350	50,500
D (10^{-19} m^2/S)	12.48	5.05	4.70
l_o (10^{-10} m)	5.30	3.08	2.76

Table 10. The Physical Properties of Samples in Group C at 240℃ and 95 S^{-1}

HIPS Items	PC1	PC2	PC3	PC4
n	2260	2115	1808	1692
ζ (10^{-8} kg/S)	5.57	11.13	21.35	25.90
η (PaS)	54,510	54,110	52,940	52,150
D (10^{-19} m^2/S)	11.60	6.62	4.73	4.49
l_o (10^{-10} m)	5.19	3.78	2.92	2.72

and shear rates. In Figures 3 and 4, log-log plots of modulus versus time for Group B and for Group C, respectively are given at 220℃. In these Figures, commonly, the broken lines represent the curves meeting the corresponding optimum conditins.

For the given HIPS sample the values of physical properties should be calculated at three sets of temperature and shear rate at least in order to obtain the optimum condition satisfied in the overall temperature region.

Thus, for samples belonging to each group, the values of physical properties are given in Tables 2 to 10 after having been calculated according to three sets of temperature and shear rate. In Table 11, there are shown the values of physical properties of three samples corresponding to the optimum conditions in the given experimental conditions. Then in Table 2, there are shown the values of physical properties corresponding to the optimum conditions which are calculated from the data of Tables 2 to 11 and satisfied in the overall temperature region.

Additionally speaking, in Table 11, when samples PA2, PB 2, and PC3 reach the optimum conditions on conversion into physical properties of samples PA3, PB1, and PC4, respectively, physical properties which samples PA2, PB2, and PC3 have are shown at the given temperatures and shear rates. And in Table 12, when physical properties of samples PA2, PB2, and PC3 convert into those of samples PA3, PB1, and PC4, respectively, optimum conditions which are satisfied over all the reliable region of temperature are given. In Figures 2 to 4, when the optimum conditions on conversion of Table 11 are satisfied, the corresponding optimum curves are plotted with the broken lines.

All the experiments carried out are those in which the plasticizers similar in shape and structure are used in the preparation of the HIPS samples. From optical and electron micrographs and the data of physical properties, there can be obtained the information on the structure of HIPS resins

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Table 11. The Optimum Conditions of Three Samples at the Temperature Given

HIPS	Tem.	Item	n	ζ (10^{-8} kg/S)	η (PaS)	D (10^{-19} m^2/S)	l_o (10^{-10} m)
PA 2	55	S^{-1} 220℃	2012	7.73	44,320	10.13	4.21
	75	S^{-1} 230℃	2001	8.32	48,380	9.70	4.25
	95	S^{-1} 240℃	1994	8.75	53,580	9.48	4.37
PB 2	55	S^{-1} 220℃	2005	5.89	42,660	13.39	4.74
	75	S^{-1} 230℃	1985	6.35	46,490	12.93	4.79
	95	S^{-1} 240℃	1966	6.83	51,470	12.48	4.88
PC 3	55	S^{-1} 220℃	1809	21.22	43,050	4.56	2.64
	75	S^{-1} 230℃	1783	23.18	47,390	4.39	2.67
	95	S^{-1} 240℃	1751	24.18	52,630	4.45	2.78

Table 12. The Optimum Conditions Over all the Reliable Region of Temperature

HIPS Physical Property	n	$\overline{Mw}$	$(\overline{R^2})^{1/2}$ (nm)	l_o(10^{-10} m)
PA 2	2005	208,500	13.75	3.07
PB 2	1991	207,100	13.52	3.03
PC 3	1769	184,000	11.40	2.71

in melt state.

In the HIPS systems, the mean end-to-end distance of polystyrene molecule corresponds to one eightieth to one hundredth times the mean diameter of rubber particles. Supposing that a polystyrene molecule extends fully in the linear form, the end-to-end distance of the polystyrene molecule reaches a quarter to one fifth times the mean diameter of rubber particles.

For the HIPS resins belonging to Group A, the HIPS sample comprising the plasticizer A has the high value of degree of polymerization and the large value of the diffusion coefficient. For the HIPS resins belonging to Group B, the HIPS sample comprising the plasticizer B1 has the high value of degree of polymerization and the large value of the diffusion coefficient, and for those belonging to Group C, the HIPS sample comprising the plasticizer B1 has the high value of degree of polymerization and the large value of the diffusion coefficient.

For the samples belonging to each Group, it seems that these consistent behaviors are caused by the following two facts. The one is the fact that each plasticizer forces the flow of the melt system to increase so that it allows the monomers to approach easily to polymer radicals, then forces the mean length of polystyrene molecular chains to increase. The other is the fact that the excellent affinity with polystyrene molecules forces the diffusion velocity of polystyrene molecules to increase.

For the optimum conditions of each sample given in Table 11, the degree of polymerization necessary in the optimum conditions decreases with the increment of temperature and shear rate, but the rate of diffusion shows a tendency to decrease on account of the increment of the step length.

Conclusion

As discussed earlier, two factors controlling optimum conditions are a diffusion coefficient and the distribution of molecular weight. Experimentally to control the distribution of molecular weight, the number of rotation per minute should be controlled. As studied fully, the region of 20 to 30 rpm is proper in finding the optimum condition of samples.

In case that the composition of two samples are similar to each other, flow properties of two samples can be controlled to become quite similar or identical. Such control can be attained by finding the optimum condition between two samples.[17]

If apparent flow tendency of two samples is very similar, and the physical properties of two samples are controlled so that the diffusion coefficient and the distribution of molecular weight become nearly similar, then it is observed that two modulus curve of samples are closely superimposed, and general physical properties, such as hardness, impact strength, tensile strength, gloss, flexure strength, flexure modulus, melt flow index, and *etc.*, are very alike[5,18,19]

Application of optimum conditions to various polymers will give a greater of information is studying physical properties of polymers.

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Thermal and Photochemical Reactions of Benzosilacyclobutenes with Alcohols. Intermediacy of o-Silaquinone Methide in the Photochemical Reactions

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Benzosilacyclobutenes were prepared from the reactions of 1,1-dichlorobenzosilacyclobutene with Grignard reagents or t-butyllithium. In the thermal reactions with alcohols, benzosilacyclobutenes underwent both benzyl-silicon and aryl-silicon bond rupture to yield (dialkyl)alkoxy-o-tolylsilanes and (dialkyl)alkoxybenzylsilanes, respectively. The photochemical reactions, however, produced only the former products *via* o-silaquinone methides.

Introduction

Benzo-condensed four-membered ring systems are of special theoretical and synthetic interest because of their valence isomerization between the strained benzenoid form (1) and the o-quinoidal form (2).
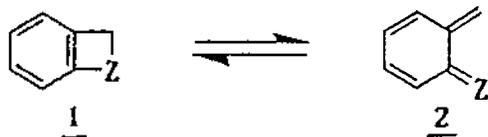
Benzocyclobutenes (1, $Z=CR_2$)[1], benzazetines (1, $Z=NR$)[2], and benzothiete (1, $Z=S$)[3] are well documented.

A benzosilacyclobutene (1, $R=SiPh_2$) has been prepared in 1964[4] as the first example of metallabenzocyclobutenes.[5] However, reports on benzosilacyclobutenes are quite rare.[6] This may be due to the lack of general synthetic routes to benzosilacyclobutenes. When we began our work, only three benzosilacyclobutenes had been prepared.[4,6a,8]

We have succeeded in the development of rather general route to various 1,1-disubstituted benzosilacyclobutenes *via*

the reaction of 1,1-dichlorobenzosilacyclobutene (5) with Grignard reagents or t-BuLi. This easy access renewed the interest to continue our studies on the chemistry of benzosilacyclobutenes.

Here we report the synthesis of benzosilacyclobutenes and their thermal and photochemical reactions with alcohols.[7] We wish to find that these reactions proceed *via* the intermediate formation of o-silaquinone methide (2, $Z=SiR_2$) by the opening of the four-membered ring.[8]

Results and Discussion

Synthesis of Benzosilacyclobutenes. 1,1-Dimethyl- and 1,1-diphenyl-2,3-benzo-1-silacyclo-2-butenes (**6a** and **6b**) have been prepared previously from the reaction of o-bromobenzylbromide with magnesium and subsequently with dichlorodimethylsilane or dichlorodiphenylsilane. The yields were moderate (27-36%).[4,6a] Recently, **6a** was also synthesized from the reaction of 1-magnesabenzocyclobutene with dichlorodimethylsilane in THF.[5] However, these methods have limitations for the general synthetic routes of benzosilacyclobutenes because dialkyldichlorosilanes (except dichlorodimeth-