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Preparation and Properties of Inorganic–Organic Composite Materials Containing $R_3SiO_{1/2}$, SiO_2, and TiO_2 Units

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A new class of inorganic–organic composite materials containing $RMe_2SiO_{1/2}$ (R = vinyl or methyl), SiO_2, and TiO_2 units, namely, organically modified polytitanosiloxane, have been synthesized. The synthetic procedure is as follows: (1) partial hydrolysis of a tetraalkyl titanate in THF at −78 °C; (2) addition of a tetraalkyl silicate and partial hydrolysis under the same conditions: (3) addition of dimethylvinylsilanol and optionally trimethylsilanol and reaction at room temperature; (4) addition of excess water; (5) removal of volatile components. The resulting polytitanosiloxanes are either viscous liquid or solid materials with good solubility in common organic solvents. The polytitanosiloxane can be cured with an SiH-functional polyorganosiloxane and a Pt catalyst via hydrosilylation to form a transparent hard material. While the cured polytitanosiloxane showed remarkable stability toward hydrolysis, uncured material tends to increase their molecular weight upon exposure to moisture.

Introduction

Recently, silicate-based inorganic–organic composite (hybrid) materials prepared by sol–gel processes are gathering attention in both academic and industrial fields.[1-7] These materials are sometimes referred to as ormocers,[8] Ormosils,[9] or Ceramers.[10] Among them, optically transparent materials are of special interest since they have potential in optical applications such as lenses,[11] waveguides,[12] and matrices for functional molecules.[13,14] The inorganic–organic composite materials are expected to reveal the combined properties of inorganic glasses and organic plastics.

Copolymers consisting of triorganosiloxy units ($R_3SiO_{1/2}$, M units, monofunctional) and silicate units (SiO_2, Q units, quadrifunctional) are called MQ resins and have long been commercially produced and utilized in various applications.[15] MQ resin can be considered to be one of the simplest forms of inorganic–organic composites at the molecular level. MQ resins display good solubility in organic solvents and low melting points (even below room temperature for low molecular weight species) despite the existence of inorganic silicate at the resin cores. Another characteristic feature of MQ resins is that the molecular weight can be easily controlled by varying the molar ratio of the M units to the Q units when an alkyl silicate is used as the starting material.[16] Usually, the M/Q ratio can range from ca. 0.3, to give a high polymer, to 4 to give monomeric $(R_3SiO)_4Si$. In addition, it is possible to cross-link MQ resins to form monoliths when appropriate reactive groups are attached to the M units. The use of hydrosilylation reactions as a means of cross-linking between vinyl and silicon hydride groups attached to the resin results in the formation of cured materials without elimination of byproducts:[17]

$$\text{—CH=CH}_2 + \text{HSi—} \rightarrow \text{—CH}_2\text{CH}_2\text{Si—} \quad \text{(cross-link)}$$

This allows one to obtain molded parts with little shrinkage (normally less than 1%), which has been very difficult with the coventional sol–gel processes which produce significant quantities of volatile species. In an attempt to resolve this problem, Ellsworth and Novak reported a very sophisticated technique for attaining minimal shrinkage using special poly(silicic acid esters), but the resulting shrinkage was still as large as 10%.[18]

When the application of MQ resins to specific optical devices such as lenses and waveguides is considered, the low refractive index of MQ resins (normally ca. 1.41) may be a problem because most applications require an index higher than 1.45. Various ways to increase the refractive index of MQ resins have been assessed in our laboratory from which it was concluded that the incorporation of TiO_2 moieties into MQ resins at the molecular level,

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[⊗] Abstract published in *Advance ACS Abstracts*, April 1, 1994.

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namely, synthesis of a new class of polytitanosiloxanes, would be the most effective route. Schmidt and Popall reported the effect of TiO_2 unit concentration on the refractive index of a copolymer of TiO_2 and diphenylsiloxane units.[19]

In this paper we wish to report preparation and properties of polytitanosiloxanes consisting of SiO_2, TiO_2, $H_2C{=}CH(Me_2)SiO_{1/2}$, and $Me_3SiO_{1/2}$ units. Molding of the novel inorganic–organic molecular composite materials via hydrosilylation cure will be demonstrated.

Results and Discussion

Preliminary Trial. Typically, simple alkyl silicate-based MQ resins (i.e., no TiO_2 unit) are prepared by the hydrolysis of tetraethyl silicate (TEOS) using a mixture of hexamethyldisiloxane, water, ethanol, and HCl. In this process, the disiloxane is hydrolyzed in the reaction mixture to form silanol species, which then react with the hydrolyzed TEOS to form SiOSi bonds. The resulting MQ resin has a general formula of $(Me_3SiO_{1/2})_x(SiO_2)_y$, and the molecular weight is primarily determined by the x/y ratio. The larger the x/y ratio, the smaller the molecular weight and the more organic the nature of the resin. Residual alkoxysilyl or silanol groups are sometimes observed in the final product, and this is probably the result of insufficient hydrolysis/capping due to the reaction conditions or steric hindrance.

As a preliminary experiment, a mixture of tetrabutyl titanate (TBT) and TEOS was added dropwise into a reaction mixture of hexamethyldisiloxane, water, ethanol, and HCl. The result was that the TBT was hydrolyzed very quickly forming a TiO_2 precipitate, which implied that the capping by the silanol was not successful. Another possibility is that Me_3SiOTi bonds were formed during the early stage of the reaction but were subsequently hydrolyzed. Bradley and Prevedorou-Demas examined the reactivity of $Ti(OSiMe_3)_4$ with water in dioxane at room temperature and reported that it undergoes hydrolysis and subsequent disproportionation to form a soluble polymer.[20] We also observed quick hydrolysis of the $Ti(OSiMe_3)_4$ in THF under neutral conditions. Thus it became apparent that simple hydrolysis in the presence of excess water is not a suitable method for the preparation of the desired polytitanosiloxane.

Philipp and Schmidt reported the use of silica gel loaded with the required amount of water for the hydrolysis of titanium or zirconium alkoxide in the presence of an epoxy-functional alkoxysilane.[21] The idea behind this is that the rate of water release from the silica gel is sufficiently slow, allowing for slow hydrolysis of titanium or zirconium alkoxide and incorporation of the alkoxysiloxane into the resin. We tried this technique in the cohydrolysis of TBT and TEOS and confirmed that precipitation of TiO_2 was prevented, but it was difficult to isolate the resulting polymeric materials from the silica gel after the reaction.

After evaluation of several other possible ways to prevent precipitation of TiO_2, we have found that the procedure illustrated in Scheme 1 produces polytitanosiloxanes without difficulties. The important points in this procedure are (1) addition of a less than stoichiometric amount of water as a solution in tetrahydrofuran (THF) at low temperature (−78 °C), (2) hydrolysis of the titanate first and then the silicate, (3) addition of a separately synthesized silanol species after the partial hydrolysis, and (4) final addition of excess water for maximizing the removal of residual alkoxy groups.

Scheme 1

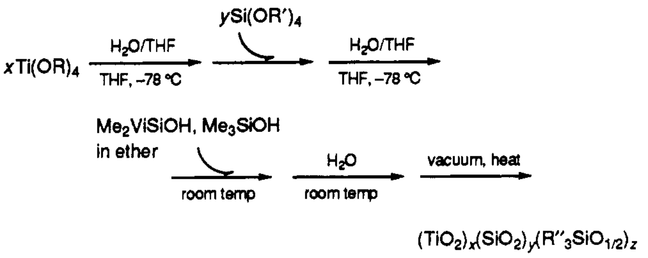

Table 1. Preparation of Polytitanosiloxanes[a]

run	TiO_2 source[b]	SiO_2		H_2O			RMe_2SiOH	
		source[c]	amt	1st[d]	2nd[e]	3rd[f]	R = Vi[g]	R = Me
1	TBT	PTEOS	0.53	0.93	0.90	1.5	4.0	
2	TBT	PTEOS	0.97	1.00	1.5	1.3	2.2	
3	TBT	PTEOS	1.0	0.25	0.24	1.2	2.2	
4	TBT	TMOS	0.23	1.00	1.00	2.6	4.2	2.4
5	TPT	TMOS	0.65	1.00	1.00	2.8	2.5	2.1
6	TBT	TEOS	0.66	1.00	1.00	3.1	4.0	1.9
7	TPT	TMOS	0.70	1.00		2.7	1.7	1.4

[a] Each figure denotes the molar ratio of the reagent to the titanate. [b] TBT = tetrabutyl titanate, TPT = tetraisopropyl titanate. [c] PTEOS = partially hydrolyzed TEOS, TMOS = tetramethyl silicate, TEOS = tetraethyl silicate. [d] Before addition of silicate. [e] After addition of silicate. [f] After addition of silanol. [g] Vi = vinyl.

Synthesis of Polytitanosiloxanes. Polymers consisting of TiO_2, SiO_2, $Me_2ViSiO_{1/2}$ (Vi: vinyl), and optionally $Me_3SiO_{1/2}$ units were prepared according to the procedure shown in Scheme 1. The $Me_2ViSiO_{1/2}$ unit is essential for cross-linking via hydrosilylation, and the $Me_3SiO_{1/2}$ unit is added to control the cross-link density. Table 1 summarizes the synthesis of the polytitanosiloxanes under various conditions. In all cases, TBT or tetraisopropyl titanate (TPT) was used as the TiO_2 source. As the SiO_2 source, TEOS, partially hydrolyzed TEOS (PTEOS, SiO_2 content: 40 wt %) or tetramethyl silicate (TMOS) was used. The silanol compounds were not isolated before addition but added as diethyl ether solutions because of their tendency toward condensation in the bulk phase.

The products obtained in this study are either viscous liquid or solid materials that are soluble in common organic solvents such as THF, toluene, chloroform, and hexane. The apparent molecular weights, chemical compositions and refractive indexes of some of the polytitanosiloxanes are listed in Table 2. The M_w and M_n values, which can be regarded as a measure of the molecular size, were determined by gel permeation chromatography (GPC) using standard polystyrene samples as references. The chemical compositions were deduced according to the following procedure: (1) The molar ratio of $Me_2ViSiO_{1/2}$/$Me_3SiO_{1/2}$/alkoxy was determined from ^1H NMR data. (2) The molar ratio of $Me_2ViSiO_{1/2}/Me_3SiO_{1/2}/SiO_2$ was determined from ^{29}Si NMR data. (3) The TiO_2 content was deduced from the total Ti content obtained by atomic absorption measurements. The remaining "alkoxy" groups were mostly butoxy or isopropoxy groups depending on the kind of alkyl groups of the starting titanate compounds. Ethoxy or methoxy groups derived from the starting alkyl silicates were also observed, but their contents were fairly low. It is likely that these lower alkoxy groups were

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Table 2. Analytical Results of Polytitanosiloxanes

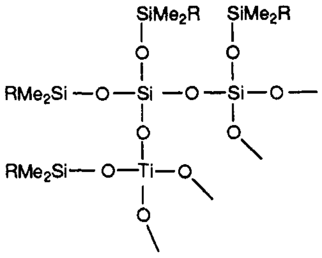
		mol wt[a] ($\times 10^4$)		component (molar ratio)[b]					
run	appearance	M_w	M_n	TiO_2	SiO_2	M^{Vi}	M	RO	refractive index (n_d^{24})
1	solid	0.148	0.119	0.65 (0.65)	0.35 (0.35)	0.52 (1.07)		0.10	
2	solid	973	19.5	0.51 (0.51)	0.49 (0.49)	0.25 (0.64)		0.17	
3	solid	60.7	4.76	0.53 (0.50)	0.47 (0.50)	0.41 (1.03)		0.38	
4	liquid	24.5	1.47	0.67 (0.65)	0.33 (0.35)	0.81 (0.90)	0.50 (0.51)	0.04	1.482
5	liquid	17.3	7.06	0.64 (0.61)	0.36 (0.39)	0.45 (0.84)	0.52 (0.72)	0.03	1.490
6	solid	778	84.0	0.63 (0.60)	0.37 (0.40)	0.52 (1.07)	0.41 (0.51)	0.06	
7	liquid	3.99	2.05	0.60 (0.59)	0.40 (0.41)	0.83 (1.54)	0.60 (1.26)		1.477

[a] Apparent molecular weight relative to polystyrene standards. [b] $M^{Vi} = ViMe_2SiO_{1/2}$, $M = Me_3SiO_{1/2}$, RO alkoxy. Values calculated from the loaded amounts of starting materials are indicated in parentheses.

liberated preferentially as a result of facile alkoxy–alkoxy exchange reactions, thus leading to a higher proportion of higher alkoxy groups in the products.

Each molar ratio listed in Table 2 is presented such that the sum of the molar amounts of SiO_2 and TiO_2 units is unity.

It is strongly suggested from the analytical data as well as the appearance of the bulk materials that the products are homogeneous polytitanosiloxanes without phase-separated domains. The formation of SiOTi bonds was confirmed by IR analysis (around 920 cm^{-1}).[22] The structure of a portion of the product molecule is as follows (R = vinyl or methyl):



The apparent M_n values for the products range from 1190 to 8.4×10^5 implying that the degree of polymerization is in the range ca. 10–6000. For example, if it is assumed that the M_n values obtained by GPC are close to the actual values, the product from run 1 consists of approximately 6 TiO_2 and 3 SiO_2 units/molecule on average, whereas the product from run 6 has 3400 and 2000 units/molecule, respectively. This difference in the molecular size may seem unusual given the fact that ordinary MQ resins can be produced in a more controlled manner. However, this kind of fluctuation is not necessarily abnormal for sol–gel type polymers with three-dimensional structures, especially when an extremely reactive species like a titanate is used. The products also showed relatively wide molecular weight distributions as revealed by the M_w/M_n ratios. Figure 1 shows a representative GPC chromatogram of the product obtained from run 5.

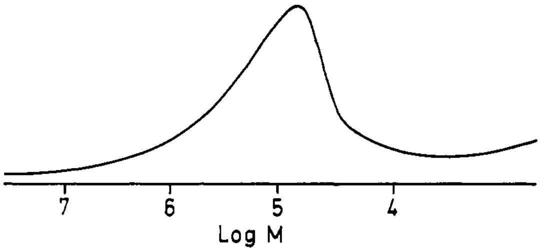


Figure 1. Gel permeation chromatogram of the product from run 5.

The amounts of triorganosiloxy groups present in the products are not as large as the calculated values based upon the amounts of available alkoxy groups after the partial hydrolysis (assuming that 100% of water reacted) and the loaded amounts of silanol species. For example, the amount of dimethylvinylsiloxy groups found in the product from run 6 is 0.56 equiv per titanate/silicate group, whereas the calculated amount is 1.07 equiv. This can be explained on the basis that the silanol species are less reactive than water as a reult of steric hindrance. On the other hand, the observed amount of the trimethylsiloxy groups in the same sample is 0.44 equiv, which is close to the calculated amount of 0.51. This implies that the steric effect of the trimethylsilyl group is less than that of the dimethylvinylsilyl group.

The amount of water added in the final stage of the reaction is important in determining the amount of residual alkoxy groups. According to Table 2, the products from runs 4–7 have considerably less alkoxy groups than those from runs 1–3 owing to the larger amount of added water.

It is important to know whether the triorganosiloxy groups are attached to the SiO_2 or TiO_2 moieties. The R_3SiOSi bond is very stable against hydrolysis under neutral conditions, but the R_3SiOTi bond is, as described earlier, not so stable. While it is not possible with IR analysis to quantify these differences, it appears to be so with ^{29}Si NMR analysis. The ^{29}Si NMR spectrum (R_3SiO unit region) of the product from run 7 is shown in Figure2 as an example. The major resonances centered at ca. −2 ppm and at ca. 9 ppm are assigned to the $Me_2Vi\mathit{Si}OSi$ and $Me_3\mathit{Si}OSi$ silicons, respectively, based on the established literature data.[23] The minor peaks centered at ca. 2 ppm can be confidently assigned to $Me_2Vi\mathit{Si}OTi$ silicons, and those centered at ca. 15 ppm are assignable to the $Me_3\mathit{Si}OTi$ silicons. These assignments are also supported by the absence of peaks centered at ca. 15 ppm for the

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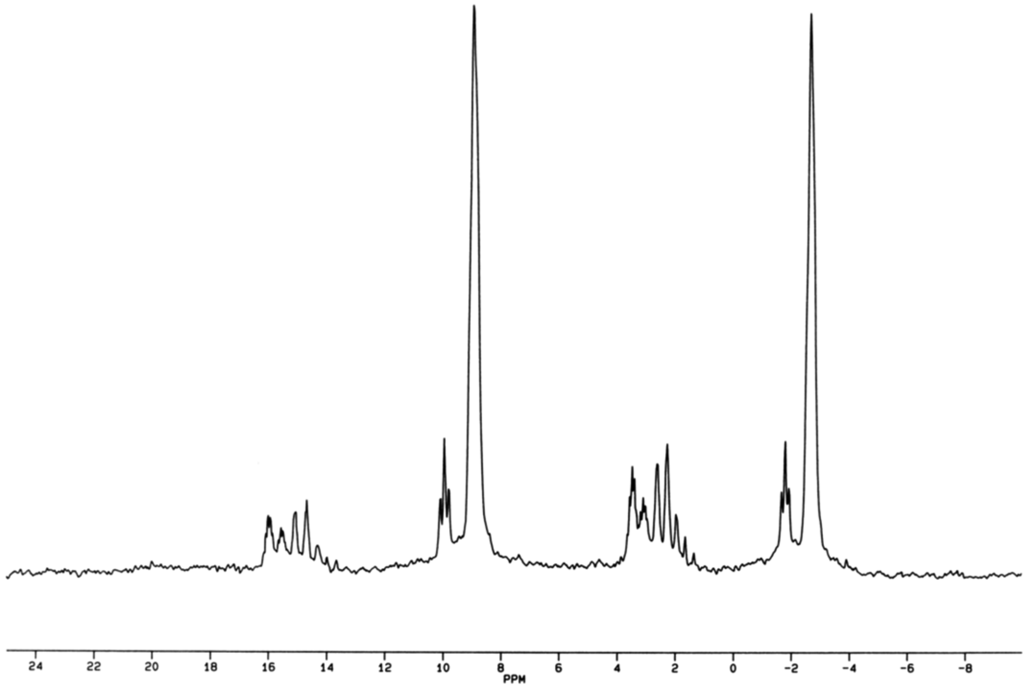

Figure 2. ^{29}Si NMR spectrum (R_3SiO unit region) of the product from run 7.

Table 3. SiOTi/SiOSi Ratios by ^{29}Si NMR

run	$Me_2ViSiOTi/Me_2ViSiOSi$[a]	Me_3SiOTi/Me_3SiOSi
1	0.55	
2	0.13	
3	0.11	
4	1.2	0.44
5	0.48	0.40
6	0.33	0.28
7	0.44	0.37

[a] Vi = vinyl.

products from runs 1–3 which do not contain Me_3SiO units. Table 3 summarizes the ratios of the $R_3\textit{Si}OSi/R_3\textit{Si}OTi$ silicons calculated from the integral ratios of the peaks as assigned above. As expected from the preparation procedure (partial hydrolysis of titanate, then silicate) and the reactivity difference toward water (titanate > silicate), the number of SiOSi bonds generated is generally larger than the number of SiOTi bonds. The large $Me_2ViSiOTi/Me_2ViSiOSi$ value of 1.2 for run 4 can be explained by the small amount of loaded silicate (silicate/titanate = 0.23).

The products are fairly stable against hydrolysis or oxidation when stored as bulk materials. They slowly increase in molecular weight upon storage in the ambient atmosphere with some of the samples becoming insoluble after six months. This process is accelerated when the samples are stored as solutions in THF. Furthermore, when some of the products were mixed with wet THF, precipitation occurred within one day. The molecular weight increase and gelation are considered to be caused by hydrolysis of the R_3SiOTi bonds.

Cross-Linking of Polytitanosiloxane. The product from run 7 was mixed with an SiH-functional MQ resin ($(Me_2HSiO_{1/2})_x(SiO_2)_y$, $x/y = 1.6$, apparent $M_n = 1000$), a platinum catalyst, and a reaction controlling agent (2-methyl-3-butyn-2-ol). Surprisingly, the polytitanosiloxane was freely miscible with the SiH-functional MQ resin despite the fact that both are polymeric materials with significantly different refractive indexes (1.477 vs 1.402). The mixture was freed from air bubbles in vacuum, poured in a mold and then cured at 80 °C. The cured material was slightly yellow-colored, transparent, rigid, and hard but slightly brittle. Figure 3 shows the appearance of the cured sample, the dimensions of which are ca. 13 mm in diameter and 4 mm in thickness. The linear shrinkage upon cure was less than 1.0% (mm/mm). Table 4 lists the properties of the cured sample. The cured samples were found to show remarkable oxidative and moisture stability. No change in appearance was observed either when stored under an ambient atmosphere or when immersed in water for more than 6 months at room temperature.

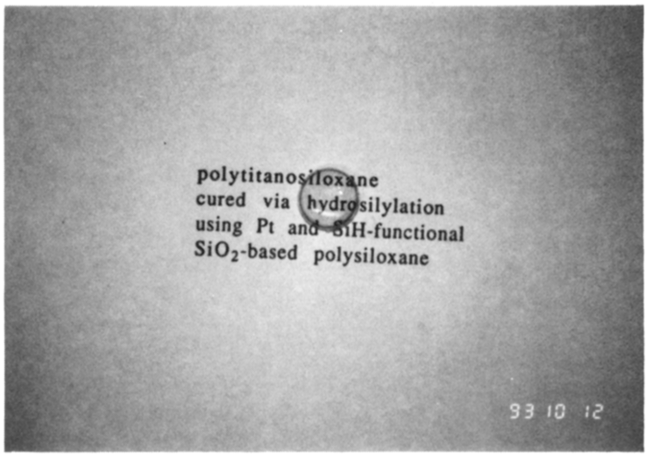

Figure 3. Cross-linked polytitanosiloxane (13-mm diameter).

Table 4. Properties of the Cured Sample

property (unit)	value
flexural modulus (MPa)	820
refractive index	1.4793
Abbe's number[a]	40
RI temp coefficient (°C^{-1})	-2.0×10^{-4}

[a] $(n_d - 1)/(n_F - n_C)$ where n_d, n_F, and n_C denote refractive indexes at d, F, and C lines, respectively.

The refractive index profile of a sample molded into a prism shape is shown in Figure 4. This figure shows the relationship between the intensity of refracted light (vertical axis) and the refraction angle, i.e., refractive index

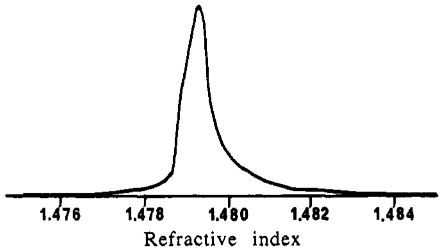

Figure 4. Refractive index profile of a cross-linked polytitanosiloxane sample.

(horizontal axis). The absence of minor peaks with meaningful intensity and the narrowness of the major peak can be regarded as evidence for the good optical homogeneity of the sample.

Experimental Section

General Methods. The preparation of polytitanosiloxanes was carried out using carefully dried glassware under a dry argon atmosphere unless otherwise stated. Silicates (Tama Chemical), titanates (Mitsubishi Gas Chemical), chlorosilanes (Dow Corning Toray Silicone), and other reagents (Wako Chemical) were used as purchased. Tetrahydrofuran (THF) was distilled from a purple solution of THF/Na/benzophenone under nitrogen prior to use.

Analytical gas chromatography (GC) was performed using a Shimadzu GC-14AH gas chromatograph equipped with a DB-5 glass capillary column (J & W Scientific). Gel permeation chromatography (GPC) was carried out with a Shodex system-11 equipped with a series of Shodex KF802 and KF80M columns and a refractometer. Apparent molecular weights, as a measure of the molecular sizes, were calculated by use of polystyrene standards. Infrared spectra were recorded on a Nicolet 740 spectrometer. ^{1}H and ^{29}Si NMR data (300.13 MHz for ^{1}H) were collected using a Bruker ACP300 spectrometer. Al_2O_3 sample tubes (Shigemi Standard & Joint Co. Ltd.,) and a Si-free probe were used in the ^{29}Si NMR measurements. $CDCl_3$ was used as the solvent. Chemical shifts were referenced to $CHCl_3$ (^{1}H, 7.24 ppm) or polydimethylsiloxane (^{29}Si, −21.9 ppm). Chromium acetylacetonate [$Cr(acac)_3$, 0.02 M] was used as the relaxation agent for ^{29}Si NMR measurements. Refractive indexes and Abbe's number were measured by use of a Kalnew KPR-200 precision refractometer. Titanium contents were measured by means of atomic absorption after decomposition of samples by $H_2SO_4/HNO_3/HF$ using a Hitachi Z-8000 spectrometer. Mechanical properties were measured with an Instron 4301 testing instrument.

Synthesis of a Polytitanosiloxane (Run 5 in Table 1 as a Typical Example). Tetraisopropyl titanate (5.69 g, 20.0 mmol) and THF (10 mL) were placed in a three-necked flask, which was then cooled with a solid CO_2–methanol bath. Water (0.358 g, 19.9 mmol) in THF (5 mL) was slowly added to the solution with magnetic stirring. After the addition was completed, the mixture was warmed to room temperature and stirred for 1 h. Tetramethyl silicate (1.97 g, 12.9 mmol) was added to the solution, and the flask was cooled with the solid CO_2–methanol bath. Water (0.363 g, 20.0 mmol) in THF (5 mL) was added dropwise, and the mixture was warmed to room temperature again. After it was stirred for 0.5 h, dimethylvinylsilanol (50 mmol) and trimethylsilanol (42 mmol) in ether were added. After this stirred for 0.5 h at room temperature, water (56 mmol) in THF (15 mmol) was added to the mixture and stirred for 0.5 h. The solvents and volatile materials were evaporated at 120 °C/2 mmHg. A pale yellow liquid was obtained. Yield: 6.13 g (90% based on titanate). ^{1}H NMR ($CDCl_3$, Vi = vinyl) δ = 0.10 (Me_3Si–), 0.17 (Me_2ViSi–), 0.95 (Me_2CHO–), 4.25 ($Me_2C\mathit{H}O$–) and 5.70–6.12 ($Me_2\mathit{Vi}Si$–). ^{29}Si NMR ($CDCl_3$) δ = 15 ($Me_3\mathit{Si}OTi$–), 8.9 ($Me_3\mathit{Si}OSi$–), 2.6 ($Me_2Vi\mathit{Si}OTi$–), −2.7 ($Me_2Vi\mathit{Si}OSi$–), −96 and −107 (SiO_2). IR (cm^{-1}): 3051, 2961, 2901, 1595, 1406, 1254, 1071, 1007, 943, 922, 843, 787. GPC: M_n = 70600, M_w/M_n = 2.45. $n_d(24°)$ = 1.490.

Cross-Linking of Polytitanosiloxane. A toluene solution of tris(tetramethyldivinyldisiloxane)diplatinum(0)[24] (Pt 2.18×10^{-6} mol) and 2-methyl-3-butyn-2-ol (20 μL) were mixed with the product from run 7 (5.04 g, Vi = 21.7 mmol) and then $(Me_2HSiO_{1/2})_x(SiO_2)_y$ (x/y = 1.6, M_n = 1000, 2.66 g, SiH = 21.8 mmol) was added to the mixture. The obtained viscous liquid was poured into a rectangular shape mold and was cured at 80 °C for 1 h. The cured sample was further heated at 150 °C for 2 h. The resulting cured material was a transparent yellow solid.

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