JOURNAL OF MATERIALS SCIENCE 25 (1990) 3368–3374

Chemical modification of silicone elastomers for optics

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Polysiloxanes with Si–H groups were chemically modified using vinyl compounds with phenyl, naphthyl, anthryl, and *n*-perfluorooctyl side groups by platinum catalysis (hydrosilylation). The introduction of aromatic groups increased the refractive index of poly(dimethyl siloxane) ($n = 1.403$) up to $n = 1.70$ depending on the degree of substitution and the kind of aromatic groups. Similarly, the *n*-perfluorooctyl group reduced the refractive index to 1.35. Therefore, the chemical modification enabled us to obtain polysiloxanes with refractive indices between 1.35 and 1.70. The modifications affected the glass-transition temperature of polysiloxanes, and the effects were analysed. The modified polysiloxanes may be of use in fabrication of very flexible optical fibres for purposes such as sensors, image guides, data links and optical fibres for communications over very short distances.

1. Introduction

The development of the use of light in electronics has been remarkable over the last two decades, and the trend is continuing [1, 2]. The importance of opto-electronics is increasing not only in electronics but also in the field of science and technology in our modern society. The key in this development was the discovery of coherent light, i.e. laser light [3]. In optical communications especially, the invention of the optical fibre was most important. It is well known that extraordinary purification of the materials was the main factor in the industrialization of optical fibres [4–7]. For optical communications over long distances,. optical fibres made from quartz are suitable. Additionally, it is reported that fibres of inorganic multicomponent glass are excellent for intermediate-distance communications, together with its good processability. Recently, however, optical fibres for communications over very short distances became in demand [8]: optical fibre networks in a house or in an automobile, data links between or among computers, and image guides, to name a few.

To meet these applications, much more flexible fibres, which are of better processability, must be developed. Along these lines, plastic optical fibres (POFs) have been developed and now a few POFs are commercially available for which polystyrene or poly(methyl methacrylate) have been used [9–11]. Elastomeric materials may be better materials than plastics for meeting the requirements of shorter distance communications. We assume that silicone elastomers are promising materials for these flexible optical fibres in some applications, because even the plastic polymers may not be flexible enough in quite a few cases, for example, a pressure-sensitive sensor [12]. Silicones are already employed as coating materials for optical fibres [13, 14]. However, in our objectives, silicones are to be used as the core material of the optical fibre. There are several reasons why silicones are chosen: first, silicone elastomers are known to be one of the best elastomeric materials, because their glass-transition temperatures are very low; secondly, polysiloxanes are usually much more transparent than any other elastomers. This factor is, of course, most important due to the fact that transparency is a determining factor for reducing the optical loss [1, 5, 10]; thirdly, silicones are already used in the electronic industry because of their superior properties, such as excellent thermal stability, chemical resistance and non-flammability.

As the first step towards the production of elastomeric optical fibres, we investigated the preparation of silicone elastomers with various refractive indices. To achieve this synthesis, the hydrosilylation reaction is employed. This reaction is an addition of a Si–H group to the carbon–carbon double bond. The resultant Si–C bond is very stable compared with Si–O–C bonds which are hydrolysable under certain conditions [15]. The usual product of condensation of silanols contains Si–O–C bonds. Therefore, hydrosilylation is preferred for the synthesis of durable materials.

2. Experimental details

2.1. Materials

As mother polymers, poly(methyl hydrogen siloxane), PS 120, and copolymers of dimethyl siloxane and

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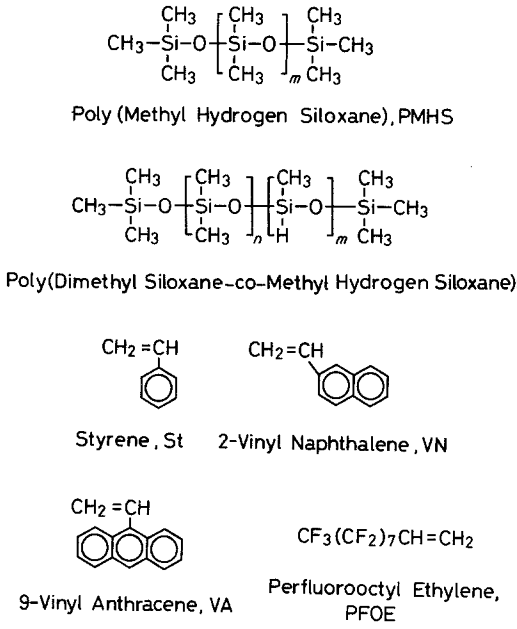


Figure 1 Structures of Si–H and vinyl compounds used in this study.

methyl hydrogen siloxane, PS 123, PS 123.5 and PS 124.5, were used. The designations and molecular weights (MW) of these polysiloxanes are listed in Table I. All the polysiloxanes were purchased from Chisso Co. Ltd. The Si–H group contents were also assayed by the reported titration method using Hg(II) diacetate [16], and found to be in good agreement with those by proton nuclear magnetic resonance (NMR) spectroscopy (Table I). Styrene (St), 9-vinyl anthrathene (VA), and perfluorooctyl ethylene (PFOE) were commercially available and purified by standard methods. 2-vinyl naphthalene (VN) was synthesized and purified according to the literature [17]. The structures of these materials are shown in Fig. 1.

2.2. Hydrosilylation reaction

The reaction shown in Fig. 2 was carried out in chloroform as a reaction medium and using hexachloroplatinic acid ($H_2PtCl_6 \cdot 6H_2O$) as a catalyst (the Spieser catalyst [18]). The degree of reaction was determined by proton NMR spectroscopy: the relative intensity of the Si–H peak at $\delta = 2.0$ p.p.m. to that of the Si–CH_3 peak at 0.0 p.p.m. was measured at intervals, in order to follow the reaction.

2.3. Analysis

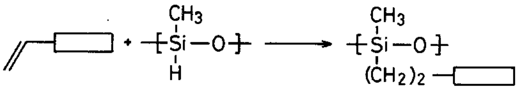


Figure 2 Hydrosilylation of vinyl compound.

The molecular weight was determined using gel-permeation chromatography (GPC) with an HLC 802 UR (Tosoh Co., Japan). The eluent was tetrahydrofuran and the flow rate was 1.0 ml min^{-1}. The GPC is equipped with a dual detector consisting of an ultraviolet (254 nm) photometer and a refractometer, (refractive index, TI). The proton NMR was measured on a Varian T-60 A spectrometer. The glass-transition temperature was determined by DSC 20 from Seiko Instruments Co. Ltd. The temperature increment was 20° C min^{-1}. The refractive index and the Abbe number were measured on a Abbe-type refractometer (Atago Optical Works Co. Ltd.) at 20° C.

3. Results and discussion

3.1. Hydrosilylation reaction

The time courses for the reaction of PMHS and VN in chloroform are shown in Fig. 3. The reaction proceeded rapidly in the initial stage, and tended to level off later. From the results shown in Fig. 3, it is seen that it is necessary to conduct the reaction at higher temperatures to attain a high conversion, for example, above 90%. The kinetic features, i.e. fast reaction in the initial stage and an asymptotic value of the degree of reaction in the final stage, were always observed in the hydrosilylations reported here. Therefore, it is reasonable to assume that there exists a final conversion that is determined by temperature (see Fig. 3) and some other reaction conditions, for example, catalyst concentration. The established hydrosilylation mechanism by the Spieser catalyst is depicted in Fig. 4 [18]. In this mechanism both an olefin and an Si–H compound have to occupy the coordination sites around a platinum atom to form a complex, and the hydrosilylation takes place in the complex. The Si–H compounds were polymeric ones, and olefins were carrying relatively bulky groups in the present study. These steric conditions may have limited the reactions in several ways. The failure of *N*-vinyl carbazole and 1-vinyl pyrene to be hydrosilylated by the platinum catalyst was ascribable to the steric congestion. In our experiments on St, VN, VA and PFOE, the reaction proceeded to ~95% by adjusting the reaction conditions. The degree of hydrosilylation was determined by proton NMR (60 MHz) monitoring of the decreases of Si–H and $CH_2=CH$. Various percentages

TABLE I Polysiloxanes

Designation		MHS content* (mol %)	Molecular weight	
			Labelled	Observed[†]
PMHS[‡]	PS-120	93.9	2270	2200
	PS-123	31.0	–	2200
P(DMS-co-MHS)[§]	PS-123.5	13.3	2000–2500	3200
	PS-124.5	2.4	13300	10200

[‡] Poly(methyl hydrogen siloxane).
[§] From GPC.
* From proton NMR.
[†] Poly(dimethyl siloxane-co-methyl hydrogen siloxane).

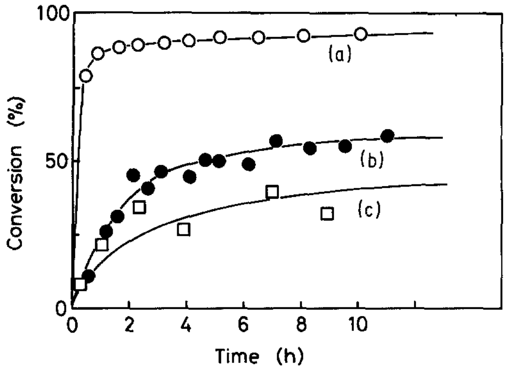


Figure 3 Reaction time courses for PMHS and VN in chloroform: (a) 80° C, (b) 70°C, (c) 60°C; [Si-H] = [VN] = 0.60 mol l^{-1}, [Pt] = 80 μmol l^{-1}.

of reaction were achieved by choosing polysiloxanes (Table I) and adjusting the reaction conditions.

Proton NMR spectra of PS 120, VN, and an example of the reaction products are displayed in Fig. 5, in which the assignments of peaks are included. The spectrum of the reaction product enabled us to determine the relative ratio of α and β structures in the polymer (see Fig. 6 for α and β structures of attached VN units to polysiloxane). The limiting values of α and β ratio, i.e. the ratio at the stage where the reaction reached the asymptotic state, are shown in Table II. VA and PFOE are so bulky that α addition was not possible. In case of smaller St and VN, α and β additions were concomitant with the less regular structures. These results may also be due to the steric hindrance in the complex: α addition is more difficult than β addition (see Fig. 4).

Fig. 7 shows GPC results on VN-grafted PMHS whose MHS units content was 68 mol %. RI and ultraviolet (UV) responses are in good agreement, and the height ratio of UV and RI responses at each count approximately gives a constant value [19]. The RI detector responds to all species passing through the detector, but UV detects only the species that have an absorbance at 254 nm, i.e. usually those carrying aromatic rings. In the present sample, naphthyl groups show absorption in the UV region. The ratio, UV/RI, is a measure of the concentration of naphthyl groups per unit amount of sample. In other words, the ratio is proportional to the number of naphthyl groups per monomeric siloxane unit. The constant value of this ratio in Fig. 7 means that the ratio does not depend on the sample molecular weight. Therefore, the initial molecular weight distribution of PMHS probably did not influence the reactivity of Si–H towards VN, hence the constant ratio was obtained.

TABLE II α structure/β structure ratio

Substituent	Substitution (%)	α/β
St	95	0.80
VN	90	0.75
VA	90	0.05
PFOE	86	0.05

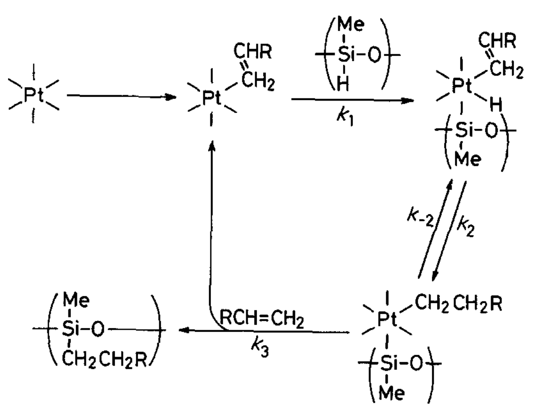


Figure 4 Mechanism of hydrosilylation of olefin by a platinum catalyst.

3.2. Glass-transition temperature of polysiloxanes

Fig. 8 shows differential scanning calorimetry (DSC) traces of PMHS- and VN-grafted PMHSs. The glass-transition temperature (T_g) was determined as indicated in the figure. These values of T_g were plotted as a function of the weight per cent of the attached units, in Fig. 9. The higher the degree of modification, the higher is T_g, irrespective of the kind of substituent. However, an increase of PFOE or VA forms a sigmoidal curve, i.e. there exists a region where T_g increases excessively with increase of substituent. That region is situated at ~ 10 mol % for either substituent. The two substituents are very bulky and a 10 mol % presence is enough to hinder the microbrownian motion of siloxane chains resulting in the shift of T_g to higher temperatures. The modified polysiloxanes can be regarded as a copolymer, though they were synthesized by a polymer reaction, i.e. hydrosilylation using polymeric hydrosilyl reagents.

There are several equations describing the relation between T_g of the copolymer and its composition, namely the Gordon–Taylor [20] and Wood [21] equation,

$$W_1(T_g - T_{g_1}) + kW_2(T_g - T_{g_2}) = 0 \quad (1)$$

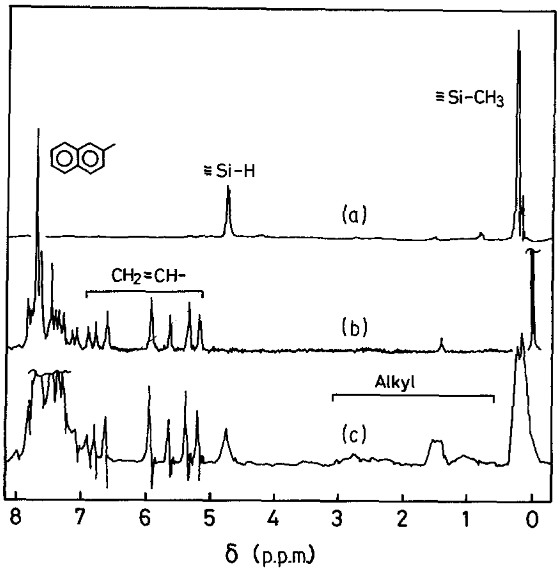


Figure 5 Proton NMR spectra: (a) PMHS, (b) VN, (c) VN-grafted polysiloxane reacted at 80° C for 5 h.

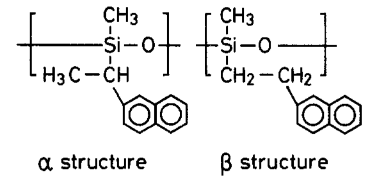


Figure 6 Alpha and beta structures of the VN group attached to an Si-H unit.

or

$$T_g = kW_2(T_{g_2} - T_g)/W_1 + T_{g_1} \qquad (2)$$

Fox's [22] equation,

$$1/T_g = W_1/T_{g_1} + W_2/T_{g_2} \qquad (3)$$

and DiMarzio and Gibbs' [23] equation

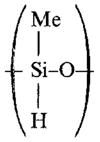
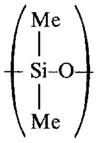
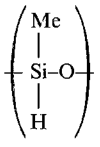
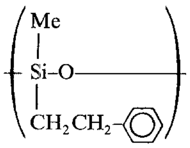
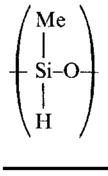
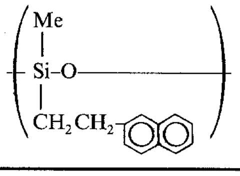
$$T_g = m_1T_{g_1} + m_2T_{g_2} \qquad (4)$$

where W_i is a weight fraction of monomer unit i, T_{g_i} is the glass transition temperature of the homopolymer i, T_g that of the copolymer, k is a constant in the Gordon–Taylor–Wood equation, m_i is a molar fraction of monomer unit i.

We examined all these equations, and found that the Gordon–Taylor–Wood equation gave the best fit from which the constant values of k were determined, these are listed in Table III. In this table, T_{g_1} is the glass transition temperature of PMHS and T_{g_2} is that of the homopolymer the monomer-unit structures of which are shown in the table. The values of T_{g_2} were calculated by extraporation of the experimental results. Note that the structures of St- and VN-grafted units are shown, but in fact β form is also present (see Table II). The more bulky the substituent, the higher was T_g. The variation of constant k also seems to show the same trend. It is noticeable that the k of SBR, which is a copolymer of styrene and 1, 3-butadiene is 0.437 [21] while the styrene-grafted PMHS has a k value of 1.03 as shown in Table III.

Introduction of phenyl groups has more influence on polysiloxane main chains than on polybutadiene main chains. Considering that the k value for methyl group introduction was 0.20, which is much smaller than 0.437 for SBR and 1.03 for St-grafted PMHS, we can assume the values shown in Table III are very reasonable, and the sequence distributions of the grafted St units on the modified polysiloxanes may be random. In the derivations of the equations shown above, random distributions of monomer units have been assumed. In fact, the monomer sequence distributions in SBR was found to be random [24].

TABLE III k value of the Gordon–Taylor–Wood equation

Structure of copolymer content		T_g	T_g	k
1	2	(K)	(K)	
		132	144	0.20
		132	237	1.03
		132	263	1.90

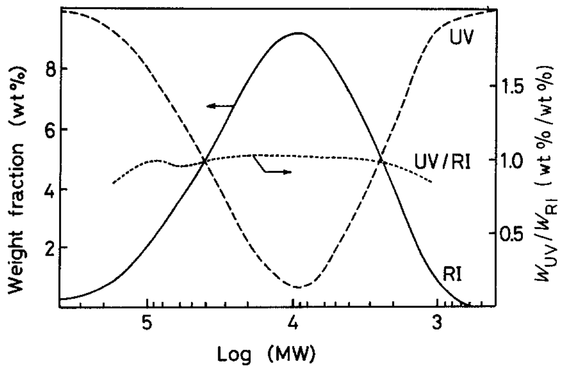


Figure 7 GPC traces of VN-grafted polysiloxanes. For UV/RI see the text.

3.3. Refractive index and the Abbe number of polysiloxanes

As discussed in the previous section, our products are actually copolymers consisting of the modified siloxane units and the remaining methyl-hydrogen siloxane or dimethyl-siloxane units. The refractive index (n) of a random copolymer is usually expressed as [25, 26]

$$n = n_1V_1 + n_2V_2 \qquad (5)$$

$$= (n_2 - n_1)V_2 + n_1 \qquad (6)$$

where n_i is a refractive index of component i and V_i is a volume fraction of component i. In order to use Equation 5 or 6, we must estimate molar volumes. We carried out the evaluation using van der Waals radii and bond lengths [27]. Take atom A, whose van der

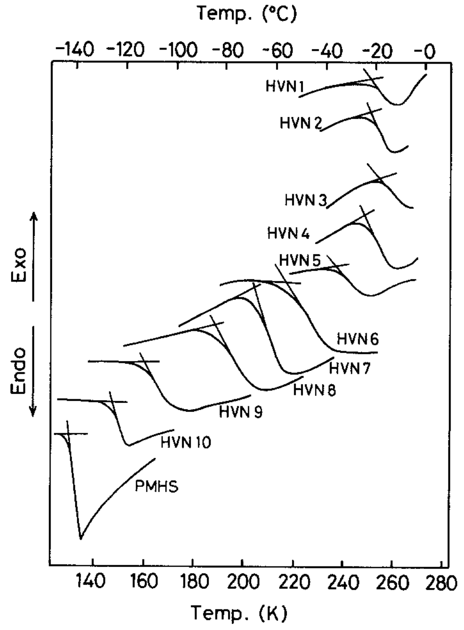


Figure 8 DSC traces of VN-grafted polysiloxanes: the decrease in the numerals following HVN corresponds to the increase in VN-grafted units.

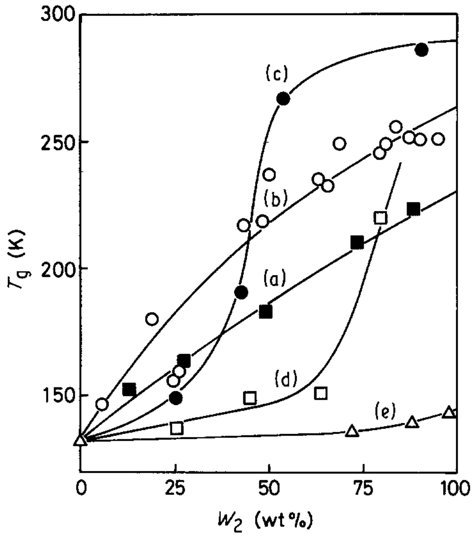


Figure 9 Relationship between T_g of chemically modified polysiloxanes and their composition: (a) St, (b) VN, (c) VA, (d) PFOE, (e) P(DMS-co-MHS). For W_2 see the text.

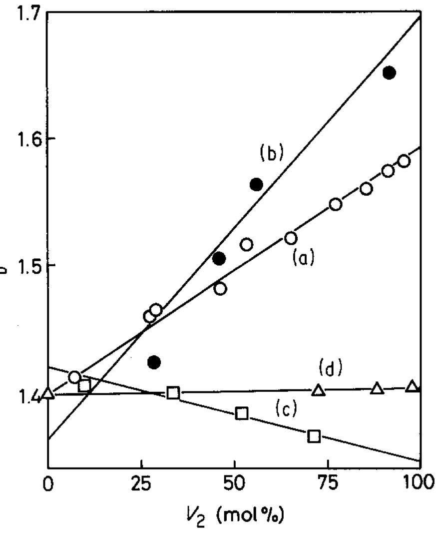


Figure 10 Relationship between refractive index (n) of chemically modified polysiloxanes and their composition: (a) VN, (b) VA, (c) PFOE, (d) P(DMS-co-MHS). For V_2 see the text.

Waals radius is R, and which is bonded to atom A_i, whose van der Waals radius is R_i. When the bond distance is assumed to be d_i ($i = 1, 2, 3, \ldots i$), the volume occupied by atom A is expressed by

$$\delta V(\mathrm{A}) = 4\pi R^3/4 - \sum \pi h_i^2(3R - h_i)/3 \quad (7)$$

$$h_i = R - (R^2 + d_i^2 - R_i^2)/2d_i \quad (8)$$

The molar volume, V, is given by

$$V = N \sum \delta V(\mathrm{A}_j)/K \quad (9)$$

where N is Avogadro's number, K is the filling constant, and the value of 0.681 is used for amorphous polymers. The molecule is assumed to consist of atoms A_j ($j = 1, 2, \ldots j$). Note that for polymers a repeating monomer unit is considered to be a molecule in the above discussion. From Equation 9

$$V(\mathrm{cm}^3) = 10^{-3}(1/1.131) \sum \delta V(\mathrm{A}_j)\,(\mathrm{nm}^3) \quad (10)$$

The molar volumes for the polysiloxanes were calculated from these equations using the parameters collected in Tables IV and V. The molar volumes are shown in Table VI, which were obtained for monomer units in the present polymers.

The experimentally determined values of n are plotted in Fig. 10 against the volume fraction of the copolymers. Good correlations are observed between n and V_2 as claimed by Equation 6. Fig. 10 clearly indicates that the introduction of aromatic groups increased the refractive index and that of fluorine induced the reverse change. These variations are in accord with those described in the literature [25]. The Lorentz–Lorentz equation gives the relation between n and polarizability, p, of the molecule

$$(n^2 - 1)/(n^2 + 2) = 4\pi Np/3 \quad (11)$$

where N is the number of molecules in a unit volume. Aromatic rings contribute to increase the polarizability. From our results, the contribution of one benzene ring to increase the refractive index of polysiloxane was estimated to be 0.098 in the case of VN and 0.092 in the case of VA. Hence it can be concluded that the increment about 0.1 is expected by the introduction of one aromatic ring onto polysiloxanes. The decrease in n in the presence of fluorine is due to its very large atomic volume.

TABLE IV The van der Waals radii

	C	H	O	Si	F
Radius (nm)	0.180	0.117	0.136	0.260	0.150

Because the polarizability in Equation 11 is dependent on the wavelength, we must consider the frequency dependence of n. To describe the wavelength (λ) dependency of n, the Abbe number has been very conveniently used [26]. The Abbe number (ν) is defined as

$$\nu = (n_\mathrm{D} - 1)/(n_\mathrm{F} - n_\mathrm{C}) \quad (12)$$

where n_D, n_F, and n_C are values of n at $\lambda = 589$, 486 and 656 nm, respectively. Combining Equations 5 and 12, we can obtain the following equation

$$(n_\mathrm{D} - 1)/\nu = (n_\mathrm{D1} - 1)\, V_1/\nu_1 + (n_\mathrm{D2} - 1)\, V_2/\nu_2 \quad (13)$$

This equation gives us the relationship of the Abbe number and the composition of the copolymers. Here we propose that the term in Equation 12, i.e. $(n - 1)/\nu$, is called the dispersion index. This index is assumed to be a parameter representing the

TABLE V The bond distance

	C–C	C=C	C–ϕ*	C–H	C–Si	C–F	Si–H	Si–O
Bond distance (nm)	0.154	0.140	0.148	0.108	0.190	0.134	0.148	0.151

*Aromatic ring.

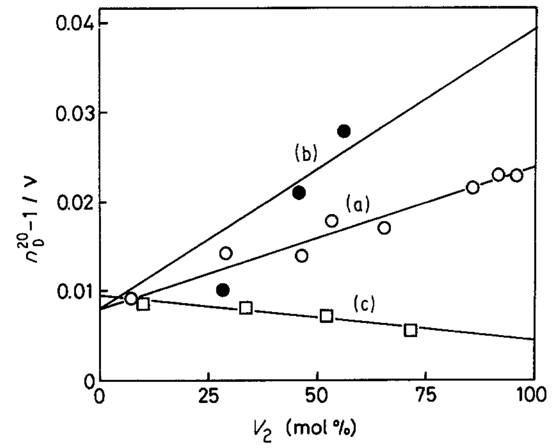


Figure 11 Plot of Equation 13: (a) VN, (b) VA, (c) PFOE; see text.

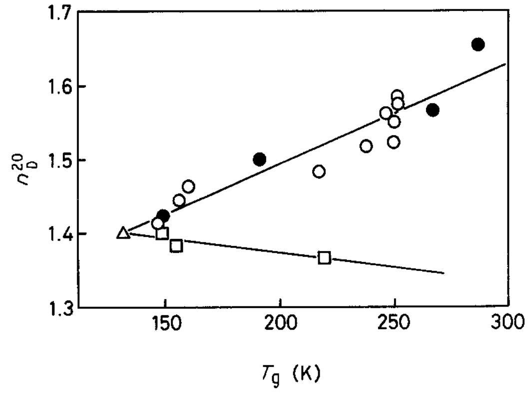


Figure 12 Relationship between refractive index (n) of chemically modified polysiloxanes and their T_gs. (○) VN, (●) VA, (□) PFOE.

wavelength dispersion of n. The plots according to Equation 13 are shown in Fig. 11. Although the points of VA-grafted polymers gave a different line, the other data seem to satisfy Equation 13. The linearities shown in Figs 10 and 11 again suggest that the chemically modified polysiloxanes obtained here are random copolymers and their thermal and optical properties are predicted at least qualitatively by the statistical copolymer theory.

In Fig. 12, the refractive indexes of the polysiloxanes are plotted against their T_gs. The introduction of aromatic substituents increases n, whilst the introduction of fluorine decreases n. Thus we can control the refractive index of polysiloxanes by a suitable chemical modification. However, in either case, i.e. an increase or decrease of n, T_g is shifted to higher temperatures. The higher the T_g, the less elastomeric is the polymer. Some compromise may be necessary between the required optical properties and elastomeric properties.

To demonstrate the range of refractive index and the Abbe number reported in this paper, the results are shown in Fig. 13 in the form n plotted against ν. This figure includes the data for many other polymers [28] and the optical ranges of inorganic optical glasses [29] for comparison [30]. The polysiloxanes prepared in the present study cover the refractive index range between 1.36 and 1.69, which is quite a wide range when we consider the variety of polymers shown in Fig. 13. The other feature easily recognized is the concave curvature which the present experimental points form in Fig. 13. This curve shows that the larger is n, the smaller is ν. Because a small ν means wide wavelength dispersion, the introduction of aromatic groups did increase the refractive index, but it necessarily induced polydispersities. This observation seems to be inevitable if n is augmented by an increase in polarizability. This tendency is also witnessed from the data on organic polymers in general, in Fig. 13. In the case of an inorganic glass, not only the refractive index but also the Abbe number can be controlled by incorporating various compounds, for example, GeO or P_2O_5 to increase and $B_{20}O_3$ or SiF_4 to decrease n of SiO_2 glass. It may be very important to develop polymers with high refractive indices and large Abbe numbers.

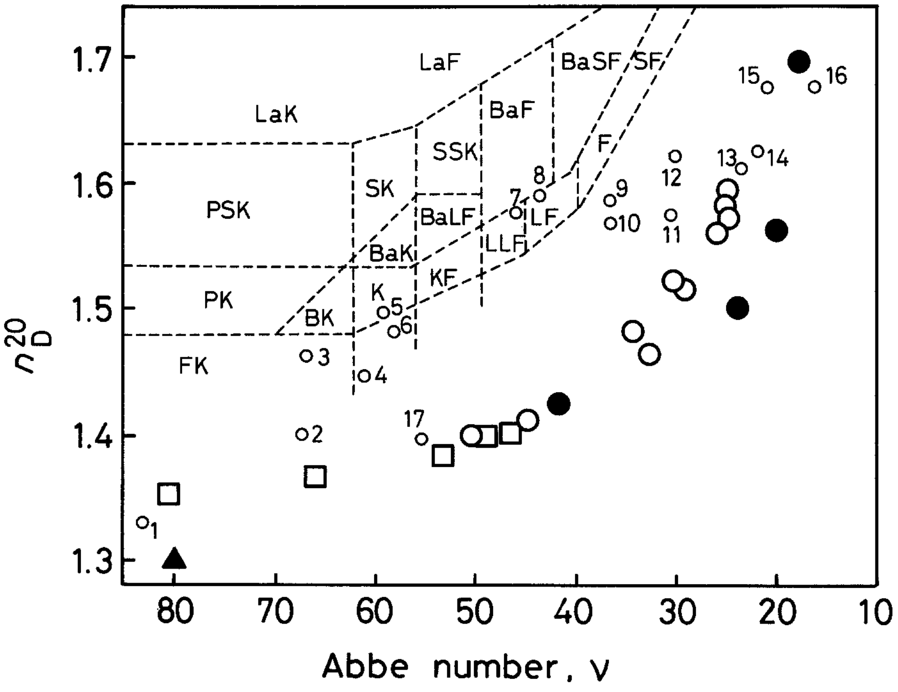


Figure 13 Refractive index (n) plotted against the Abbe number for chemically modified polysiloxanes. (○) VN, (●) VA, (□) PFOE. The numbered small circles represent for various polymers: (1) poly(tetrafluoroethylene-co-hexafluoropropylene), (2) poly(trifluoroethyl methacrylate), (3) poly(isobutyl methacrylate), (4) polymethyl acrylate, (5) diethyleneglycol bisarylcarbonate, (6) polymethyl methacrylate, (7) poly (α-bromomethyl acrylate), (8) poly(2,3-dibromopropyl methacrylate), (9) diaryl phthalate, (10) poly(phenyl methacrylate), (11) poly(vinyl benzoate), (12) polystyrene, (13) poly(pentachlorophenyl methacrylate), (14) poly(*o*-chlorostyrene), (15) poly(vinyl naphthalene), (16) poly(vinyl carbazole), (17) poly(dimethyl siloxane). The areas shown by dotted lines are covered by various inorganic optical glasses.

TABLE VI The molar volume of siloxanes

	DMS[a]	MHS[b]	MNS[c]	MAS[d]	MFS[e]
V ($cm^3 mol^{-1}$)	78.09	67.41	262.19	326.58	330.40

(a) Dimethyl siloxane unit
(b) Methyl hydrogen siloxane unit
(c) Methyl naphtylethyl siloxane unit
(d) Methyl anthrylethyl siloxane unit
(e) Methyl n-perfluorooctylethyl siloxane unit

4. Conclusion

Polysiloxanes with Si–H groups were subjected to a chemical modification to obtain the polysiloxane of a specified refractive index. For this purpose, hydrosilylations of various vinyl compounds were carried out using polymeric hydrosilylation agents, i.e. poly(methyl hydrogen siloxane) or poly(dimethyl siloxane-co-methyl hydrogen siloxane)s. By introducing phenyl, naphthyl, anthryl, or 2-*n*-perfluorooctyethyl groups, a refractive index between 1.35 and 1.70 was realized. This range is comparable to the range covered by many different polymers. The resultant polysiloxanes are expected to be of use when preparing flexible optical fibres. However, the Abbe number also varies between 20 and 80. It was found difficult to prepare polysiloxane having a high refractive index with a large Abbe number, i.e. the synthesis of polysiloxane of high refractivity whose wavelength dependence is very low, remains to be achieved.

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Received 9 May
and accepted 12 September 1989.